

Synthesis and Characterization of Novel *N*-Substituted Polyaniline by Triton X-100

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ABSTRACT

A new *N*-substituted polyaniline is synthesized by insertion of a polyether chain in the form of Triton X-100 onto the polyaniline backbone. In the preparation method, firstly the emeraldine base polyaniline was reacted with NaH to produce the *N*-anionic doped polyaniline and then contacted with chlorinated Triton X-100. The prepared *N*-substituted polyaniline was characterized by UV-vis, FTIR, ¹H NMR spectroscopy techniques and elemental analysis. The physical properties of synthesized polymer such as electrical conductivity, thermal and electroactivity properties were also studied. The prepared polymer has good solubility in common organic solvents such as THF and chloroform.

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Key Words:

polyaniline;
N-substituted polyaniline;
functionalized polyaniline;
triton X-100.

INTRODUCTION

Polyaniline is an important conjugated conducting polymer because of its good stability [1]. Recently, it has aroused great scientific and industrial interest due to its technological applications in electrical device [2].

Polyaniline emeraldine form is

obtained as a dark powder, which is difficult to process due to lack of solubility. This is a result of the stiffness of polymer backbone and the hydrogen bonding between adjacent polymeric chains. Another reason that limits its industrial application is

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being unstable at melt processing temperature.

Recently, many researches have been devoted to enhance the solubility of polyaniline in common solvents. Several ring- and *N*-substituted polyanilines, soluble in common organic solvents, have been prepared directly from polymerization of the corresponding aniline monomers [3,4]. Incorporation of the side groups into polyaniline has enhanced its solubility and processability, and it has changed its properties. Another approach toward soluble polyaniline is copolymerization of aniline with a suitable substituted aniline to produce copolymers. The obtained copolymers have improved its solubility in organic solvents [5,6]. Utilizing a functionalized acid e.g., dodecyl benzenesulphonic acid or 10-camphorsulphonic acid, to protonate the base form of polyaniline improved the processability of the resulting polyaniline [7]. In this paper, the chemical synthesis of a new *N*-substituted polyaniline is described. The structure and properties of this derivative are also investigated.

EXPERIMENTAL

Materials

Aniline from Merck was purified by double distillation under vacuum before use. Ammonium persulphate was used without purification. Sodium hydride (NaH), Triton X-100 ($C_{34}H_{62}O_{11}$, $\bar{M}_W = 646.87 \text{ g mol}^{-1}$), thionyl chloride and dimethylsulphoxide (DMSO) were purchased from Merck. DMSO was totally dried by double distillation and Triton X-100 was dried by sodium sulphate before use. Thionyl chloride was contacted with linseed oil and refluxed about 2 h and then it was distilled before use.

Preparation of Polyaniline

Polyaniline was prepared by oxidative polymerization of aniline in 1.7 M aqueous HCl using ammonium persulphate as oxidant (1:1 mol ratio) at 0-5 C for 2 h. Polyaniline as a green-black powder was formed and it was filtered, washed several times with THF and finally a colourless filtrate was obtained. The collected green-black polyaniline salts were added into ammonia solution (1.7 M) and stirred for 2 h. The undoped polyaniline was filtered and then it was washed several times with water. The resulted powder of polyaniline was placed for 12 h at 60 C in oven to be dried. Then for completing the dryness it was placed under vacuum.

Preparation of Chlorinated Triton X-100

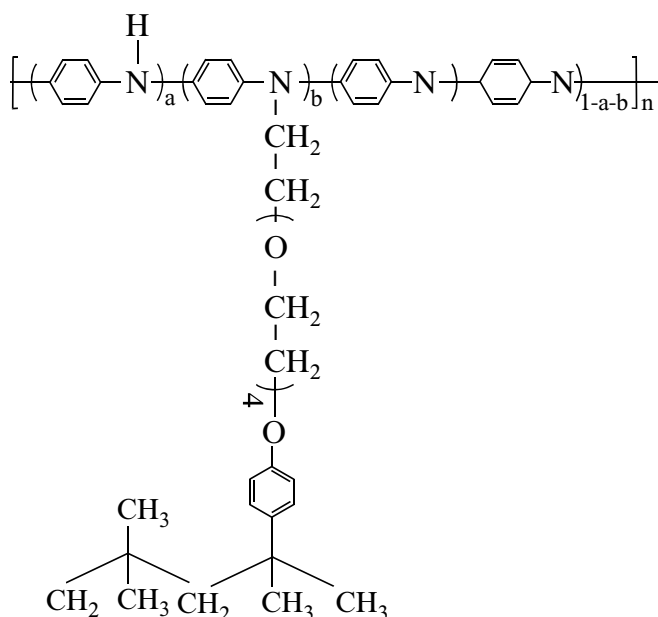
Pure SOCl_2 (22.4 mL, 0.31 mol) was added dropwise into the stirred dried Triton X-100 (19 mL, 0.03 mol) at room temperature (10:1 mol ratio). The addition was performed in half an hour. Then, the reaction temperature was increased and the mixture was refluxed for 6 h. The yellow colour solution was obtained. For separation of the excess thionyl chloride, 50 mL toluene was added to the solution and allowed it to be distilled under vacuum. This process was repeated three times with three portions of 50 mL toluene. At the final stage, the viscous solution was concentrated with rotary. The obtained light brown viscous liquid was purified by dissolving in acetone or chloroform and then poured in petroleum ether.

Infra-red (film) in cm^{-1} : 3010 (aromatic C-H stretching); 2900 (aliphatic C-H stretching); 1600, 1500 (aromatic ring stretching); 1450 (CH_2 bending); 1350 (CH_3 bending); 1150 (C-O stretching); 800 (C-H bending out of plane of benzene-*para* substituted); 700-750 (C-Cl stretching). UV-vis (THF solution) λ_{max} in nm: 277; 284.

Preparation of Emeraldine Base *N*-Substituted Polyaniline with Chlorinated Triton X-100, EB (*N*-Tri)

A sample of emeraldine base (EB, 0.60 g, 3.3 mmol *N*-H) was dissolved in totally dried DMSO. After passing the argon gas through the solution for 15 min, sodium hydride (0.1485 g, 4.95 mmol) was added to the solution (1:1.5 mol ratio). The reaction mixture was stirred under argon at room temperature for less than 5 min. An amount of chlorinated Triton X-100 (3.30 g) equal to that of NaH was dissolved in 5 mL DMSO and added to the reaction mixture. The reaction was stirred under argon at 60 C for 90 min. The mixture was poured over excess of 10% ammonium hydroxide aqueous solution. The precipitated dark blue polymer was filtered, washed with water and dried. The yield of polymer was 1.639 g. The precipitate looks like a sticky gel and even after placing in oven and drying it preserves its sticky property. For separating the soluble part from its insoluble part, the obtained polymer was dissolved in CH_2Cl_2 or THF. The solvent of the soluble part was evaporated by a rotary and after adding diethylether to the residue, precipitates were collected. The precipitate was washed with diethylether and dried under vacuum.

FTIR (KBr pellet) in cm^{-1} : 2868 (aliphatic C-H stretching); 1595 (quinoid C=N and C=C stretching); 1503 (aromatic ring stretching); 1317 (aromatic C-N



Scheme 1. Chemical structure of EB (*N*-Tri).

stretching); 1248 (aliphatic C-N stretching); 1109 (C-O stretching); 831 (aromatic C-H bending out of plane).

UV-vis (THF solution) λ_{\max} in nm: 277, 284, 321, 605. ^1H NMR (CDCl_3) in ppm: 0.69 (9H, S, *t*-butyl); 1.032 (6H, S, 2 CH_3); 1.679 (2H, S, CH_2); 3.62, 3.817 (36H, S, $-\text{CH}_2-\text{CH}_2-\text{O}-$); 2.5 (2H, broad, CH_2 bonded to N); 4.1 (2H, S, CH_2 bonded to phenoxy); 6.805, 6.95, 7.23 (broad, all the aromatic ring protons).

Characterization

^1H NMR Spectrum was recorded on a Bruker 500 MHz spectrometer. Infra-red spectra were obtained using Shimadzu DR-408 FTIR spectrophotometer. Cyclic voltammogram was recorded with a Autolab model PGSTAT 20, the working electrode was a platinum, the auxiliary and reference electrode were Pt and saturated calomel electrode, respectively. Thermal gravimetry analysis was carried out in N_2 Using Dupont 951 US instrument. UV-vis Spectrum was measured using UV-vis spectrophotometer (SHIMADZU 256) in the wavelength range 200-900 nm. Conductivity measurements of doped samples were carried out by using the four-point probe method with bars prepared from pressed pellets of the polymer at room temperature.

Cyclic voltammogram was recorded by using a one compartment cell fitted with a Pt disc electrode, that coated with EB (*N*-Tri), Pt electrode wire, and SCE as working, auxiliary and reference electrodes, respective-

Table 1. Solubility of EB (*N*-Tri) in common organic solvents.

Polymer	THF	CHCl_3	CH_2Cl_2	DMSO	DMF
EB (<i>N</i> -Tri)	+	+	+	+	+
ES (<i>N</i> -Tri)*	±	-	-	-	±

(+) soluble; (±) poor soluble; (-) in soluble.

(*) Doped EB with H_2SO_4 1N (emeraldine salt).

ly. As an electrolyte, used solution of HCl 1N and scanning took place at the potential range from -200 mV to 800 mV with scan rate of 50 mV/s.

RESULTS AND DISCUSSION

Chemical Structure

The chemical structure of the obtained polymer, EB (*N*-Tri) is given in Scheme I.

The number of repeating units (a) indicates that some of the hydrogens bonded to nitrogen atoms are not replaced by the substituent in the emeraldine base.

Solubility

The solubility of EB (*N*-Tri) in common organic solvents is shown in Table 1.

As shown in the Table 1, due to incorporation of polyether side chains to the polymer backbone, solubility of EB (*N*-Tri) has been increased in the low boiling point solvents such as THF, CH_2Cl_2 , and CHCl_3 . But due to the polarity obtained by ether groups, solubility in polar solvents is also preserved. The emeraldine salt of EB (*N*-Tri) and ES (*N*-Tri), only have poor solubility in polar solvents.

Spectroscopic Characterization

Our initial work was focused on the spectroscopic characterization of the chemically synthesized EB (*N*-Tri).

The UV-vis spectra of EB (*N*-Tri) and chlorinated Triton X-100 are shown in Figure 1.

The first absorption with maxima at 321 nm is assigned to $\pi \rightarrow \pi^*$ transition of benzoid rings on the basis of studies of polyaniline [8]. The second absorption with maxima at 605 nm is assigned to the exciton transition of quinoid rings [9]. Two bands with the maxima at 277 and 284 nm are related to the $\pi \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of the polyether chain, respectively.

The FTIR spectrum (KBr pellet) of EB (*N*-Tri) is shown in Figure 2. The ring stretching of quinoid and benzenoid forms are observed at 1595 and 1503 cm^{-1} ,

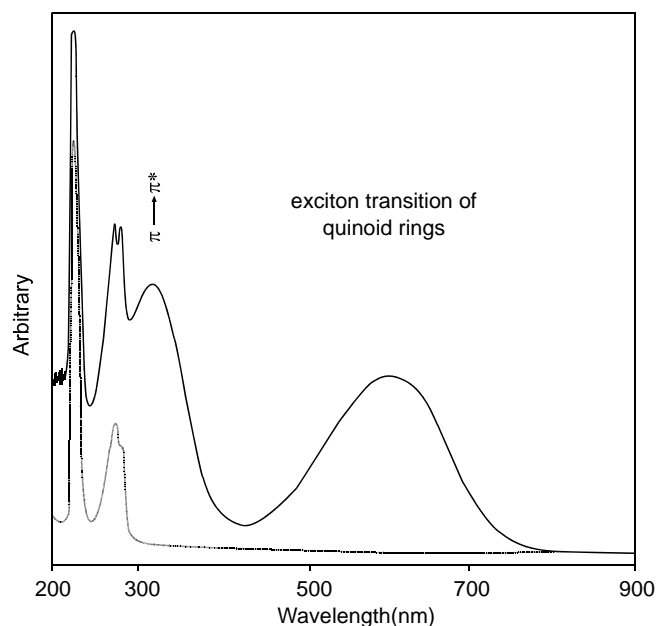


Figure 1. UV-vis spectra of EB (*N*-Tri) (—) and chlorinated Triton X-100 (---) in THF.

respectively [10]. The $C-N_{(aromatic)}$ stretching band of an aromatic amine appears at 1317 cm^{-1} [10]. The presence of the absorption peak at 2868 cm^{-1} , characteristic of the aliphatic C-H stretching vibration, indicates the existence of aliphatic group in the polymer backbone. The $C-N_{(aliphatic)}$ stretching band appears in 1248 cm^{-1} and indicates that the aliphatic substituent is linked on the amine nitrogen. The absorption peak at 1109 cm^{-1} is related to C-O stretching vibration. The presence of the absorption peak at 831 cm^{-1} (as in the emeraldine base) indicates the C-H out-of-plane bending vibrations of the 1,4-disubstituted benzene ring [10].

The $^1\text{H NMR}$ spectrum of EB (*N*-Tri) in CDCl_3 is shown in Figure 3. The solvent gives a peak at 7.3 ppm from the residual CHCl_3 (used as internal reference), aromatic protons give a broad peak in the range of 6.8-7.4 ppm. (aromatic protons of polyaniline rings and the phenyl ring in Triton X-100). Protons of 3CH_3 (*t*-butyl) appears at 0.69 ppm. The protons of 2CH_3 , bonded to the carbon adjacent to the phenyl group of the poly-

Table 2. Estimation of functionality percent of EB (*N*-Tri).

Functionality (%)	Theoretical mass of polymer (g)	$H_{\text{arom. PANI}}/0.1H_{\text{polyether}}^*$	C (%)	H (%)	N (%)
45	1.557	4.44	70.66	7.765	6.04
50	1.64	4	70.3	7.89	5.66
Exp. results	1.639	4.45	66.57	7.09	6.18

(*) for 40 hydrogen atoms on polyether chain exist 4 hydrogen atoms on polyaniline aromatic rings and $H_{\text{Total Aromatic}} = H_{\text{arom. PANI}} + H_{\text{Arom. Triton}}$

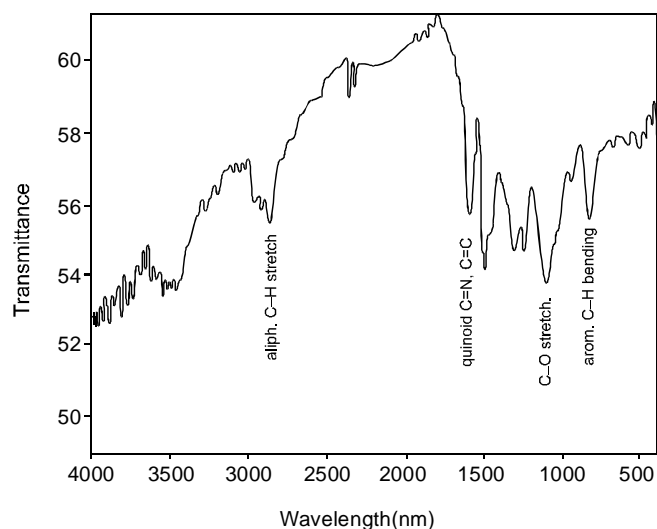


Figure 2. FTIR Spectrum of EB (*N*-Tri).

ether chain appear at 1.32 ppm. The protons of CH_2 group bonded to the *t*-butyl group appear at 1.68 ppm. The protons of CH_2 group in the repeating units of $(-\text{CH}_2-\text{CH}_2-\text{O}-)$ appear in the range of 3.62-3.82 ppm. The broad peak at 2.5 ppm is related to the protons of CH_2 bonded to nitrogen and the sharp peak at 4.1 ppm is related to the protons of CH_2 bonded to phenoxy.

The Percentage of Functionality

In Table 2, the percentage of functionality, calculated by elemental analysis data, $^1\text{H NMR}$ and the weight of the obtained polymer are shown. On the basis of theoretical and empirical data, the percentage of functionality is 45%.

Cyclic Voltammogram

Cyclic voltammogram of EB (*N*-Tri), with scan rate of 50 mV/s in the electrolytic solution of HCl 1N is shown in Figure 4.

The voltammogram shows that this polymer is electroactive. Two distinct pairs of peaks can be seen in the voltammogram. Two anodic peaks (E_{pa}) appeared

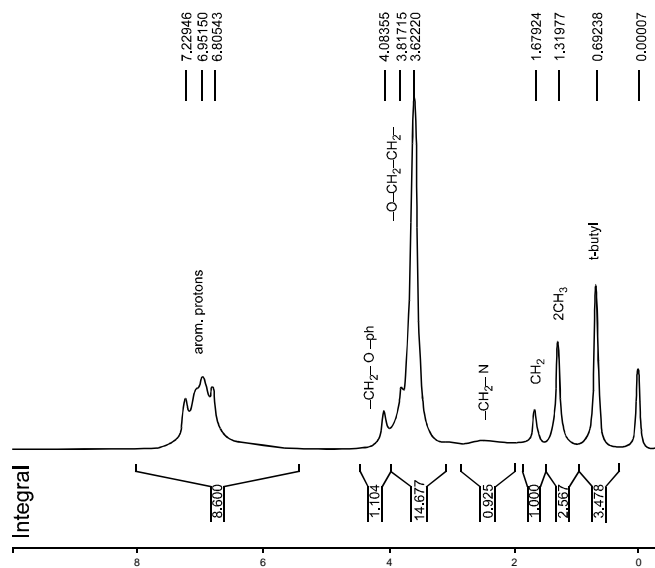
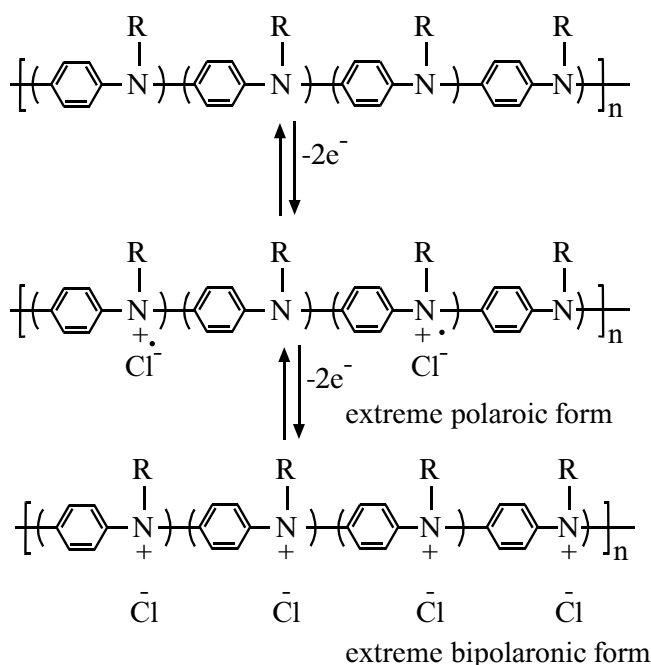


Figure 3. ¹H NMR Spectrum of EB (*N*-Tri) in CDCl₃.

clearly at 0.342 and 0.67 V and the two cathodic peaks (E_{pc}) at 0.21 and 0.575 V. As shown in Figure 4, cyclic voltammogram of EB (*N*-Tri) exhibits some quantitative similarities with those of unsubstituted polyaniline. According to the other workers' results [11,12], the peaks are ascribed to polaronic and bipolaronic transitions for the first and second peaks, respectively, as seen in Scheme II.



Scheme II. Polaronic and bipolaronic transitions of *N*-substituted polyaniline [3].

Table 3. Conductivity of initial EB and functionalized EB with Triton X-100 after doping with H₂SO₄ 1N.

Polymer	Conductivity (S/cm)
EB	6.5×10^{-3}
EB (<i>N</i> -Tri)	0.0289

For the sake of clarity, the transitions are depicted as extreme forms, the observed doping level always being lower than 100%. As seen, the pair redox appeared in lower amount of potential in comparison with parent polyaniline.

Conductivity

The conductivity of EB (*N*-Tri) after doping with H₂SO₄ 1N and for 12 h doping time, that presented as emeraldine salt *N*-substituted polyaniline with chlorinated Triton X-100, ES (*N*-Tri), are shown in Table 3.

As seen in the Table 3, the conductivity of EB (*N*-Tri) shows an enhancement in comparison with primary polyaniline. The conductivity of EB (*N*-Tri) is caused by two factors, i.e. two conductivities interfere in the total conductivity. The first is the electronic and the second is the ionic conductivity. Probably ionic conductivity is caused by sulphate ions on the polyether chain.

Thermal Studies

Figure 5 shows the thermogravimetric measurement of the EB (*N*-Tri) in a nitrogen atmosphere. As shown in the thermogram, no trace of water is present in the polymer. The polymer is stable up to 208 C. The weight loss, from 208 to 340 C is related to cleavage of the polyether chains, and the weight loss from 340 to 590 C is related to the thermal decomposition of the main chain of the polyaniline. Thermogram from 340

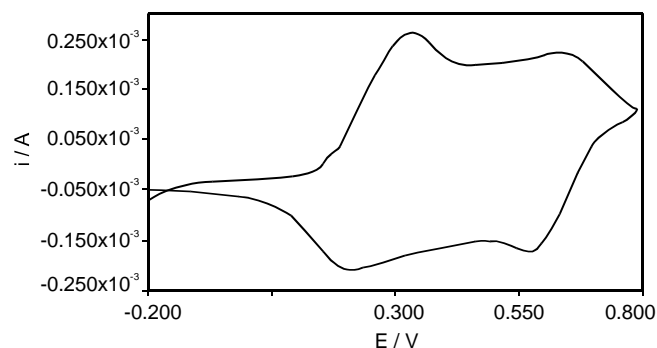


Figure 4. Cyclic voltammogram of EB (*N*-Tri), on the Pt electrode in HCl 1N electrolyte solution with scan rate of 50 mV/s.

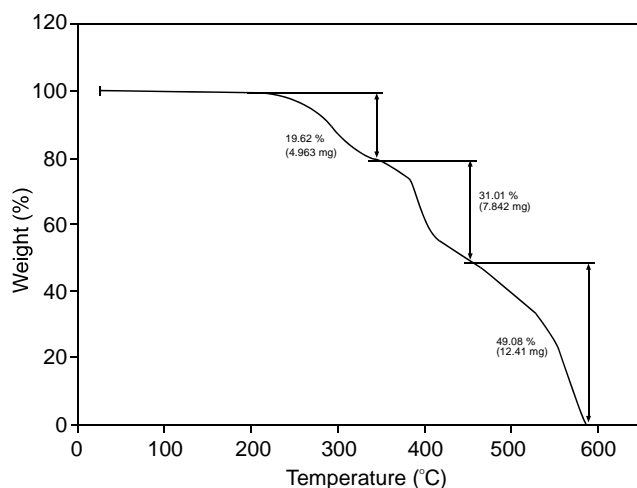


Figure 5. Thermogram of EB (*N*-Tri).

to 590 C exhibits similar decomposition pattern to the parent polyaniline [13].

CONCLUSION

EB (*N*-Tri) is prepared for the first time and its optical and spectroscopic properties are studied.

Electroactivity of EB (*N*-Tri) is similar to the parent polyaniline and its cyclic voltammogram shows two redox (cathodic and anodic) peaks.

The conductivity of doped EB (*N*-Tri) is higher than initial doped EB.

The percent of functionality, according to ¹H NMR, elemental analysis and weight increasing of product estimated about 45 percent.

The prepared *N*-substituted polyaniline has a desirable thermal stability up to 208 C.

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