Electrochemical Study of Poly(aniline N-alkylsulfonate)s

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Abstract: Electrochemical properties of self-dopable poly(aniline N-butylsulfonate)s in various acidic medium were investigated by spectroelectrochemical techniques. Cyclic voltammetric study showed more than two reversible process of one electron transfer, the potential and peak intensity of which were dependent on the acid concentration and dopant ion. Spectroscopic study at different oxidation level indicated that the electrochromic switching of the poly(aniline N-alkylsulfonate)s film involves structural changes from benzenoid ring to quinoid ring. Spectrocyclic voltammetry together with impedance spectra of the PANBUS film in 0.1 M LiClO4 solution of acetonitrile containing 0.46 M of perchloric acid showed two types of highly conductive states at the intermediate oxidation levels, which can be related to the metallic polaron states doped by two different process.

Keywords: poly(aniline N-alkylsulfonate)s, poly(aniline N-butylsulfonate)s, doping mechanism, spectroelectrochemistry, impedance study.

1. Introduction

Polyaniline has been of great interest because it exhibits a good environmental stability and its electrical properties can be modified by both the oxidation state of the polymer and protonation. Recently, substituted polyanilines have been of great interest due to improved processibility with good electrical properties [1-3]. Investigation of these substituted polyaniline derivatives are important to analyze complex problem of redox dynamics of the polymer as well as to establish structure-property relationships.

Although several investigations have been carried out on the ring substituted polyaniline, there are few investigation on N-substituted polyanilines. In general, N-substitution decreases the conductivity of polymer but increases electrochemical stability. In our recent paper, we reported the synthesis of new water soluble polyaniline derivatives, the film of which showed good electrochromic properties plus high redox stability in acidic acetonitrile media [4]. In principle, these poly(aniline N-alkylsulfonate)s can lose a proton or other monovalent cation concomitant with electron loss to produce self-doped polymer, in which the covalently bound alkylsulfonates act as counter ions for the positively charged quinoid center (eq. 1).
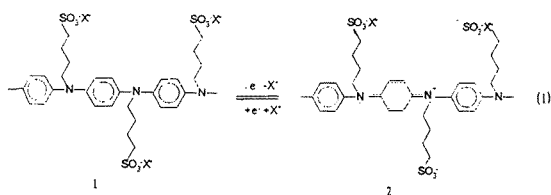
Verification of this cation popping mechanism of self-doped polymers was reported for poly(thiophene butanesulfonate) by Heeger et. al. [5]. We have examined the redox process of poly(aniline N-butylsulfonate)s, PANBUS, on the basis of self-doping process but found that the electrochemical behavior of PANBUS was rather complicated. Furthermore, the cation-popping mechanism leading a self-doped polymer has been questioned in other self-dopable polymers, particularly in the ring sulfonated polyanilines in the presence of acid.

In this context study of redox structure and effect of acid on the electrochemical property of self-doped polymer are important to understand the redox dynamics of the self-dopable polymer.

In this paper we report electrochemical property of poly(aniline N-butylsulfonate) film and discuss possible doping mechanism in the presence of acid

2. Experimental

Materials. Poly(aniline N-propylsulfonate)s, poly(aniline N-butylsulfonate)s, poly(aniline N-pentylsulfonate)s, and poly(aniline N-hexylsulfonate)s, were electrochemically synthesized from the solution of monomer containing 5% (v/v) $HClO_4$ (0.014 M) and 0.1 M $LiClO_4$ in acetonitrile as described before [3, 6]. Acetonitrile (Merck, HPLC grade) was purified by distillation. Lithium perchlorate (Aldrich) and p-toluenesulfonic acid (p-TSA) were recrystallized and dried before use. Dodecybenzenesulfonic acid (DBSA), perchloric acid, sulfuric acid were used as received. Samples for N(1s)XPS analysis at different oxidation level were prepared on a platinum plate by electrochemical deposition, which were subjected to a constant potential of 0.5 and 0 V for oxidation and reduction, respectively, for 30 min. in monomer free 0.1 M $LiClO_4$ solution of acetonitrile containing 5 % of $HClO_4$ (0.014 M).

Instrumentation. Cyclic voltametric measurement was carried out using a CV-27 Bio Analytical System and BAS 100B electrochemical analyzer. In situ spectroelectrochemical system was consisted of a PC interfaced spectrophotometer using a GuidedWave Model 260 spectrophotometer and electrochemical subsystem (BAS 100B). The impedance measurements were carried out at r. t over a frequency range from 10 mHz to 1 M Hz with an amplitude of 10 mV. Measurements were controlled by an IM5d impedance analyzer. The electrochemical cell was a standard three-electrode spectroelectrochemical cell using either an ITO glass or a platinum wire as a working electrode. The reference electrode was Ag/AgCl in 3 M NaCl solution and the counter electrode was a spiral platinum wire or an ITO glass. Throughout this study, anaerobic conditions were maintained with an argon atmosphere.

3. Result and Discussion

Cyclic voltammetry of PANBUS. Voltammogram for PANBUS film measured in 0.1 M $LiClO_4$ solution of acetonitrile containing 5 % aq- $HClO_4$ (0.46 M) is shown in Fig. 1a. The voltammogram displays more than two reversible process of one electron transfer at 0.53, 0.71 V, and ~ 0.8V vs Ag/AgCl, with the anodic and cathodic peak separations for the first two peaks of 120, 50 mV, respectively. The second redox peak was discernible at a slower scan rate, implying that the process may relate to a chemical process.

The peak current (i_p) was neither correlated with the scan rate nor the square root of the scan rate indicating that the redox reaction of PANBUS involves quite complicating process in the presence of strong acid.

Reducing the concentration of $HClO_4$ to 0.2 M changed the voltammogram and significant changes were observed in the voltammogram when the concentration of $HClO_4$ was below 0.1 M (Fig 2a and Fig.2b). In this weakly acidic condition, the first redox peak shifted toward negative with significant current decrease as the concentration of $HClO_4$ was decreased (Fig.2b) and the potential shifts were linearly dependent on the acid concentration with a correlation coeffcient of 0.99 as follows:
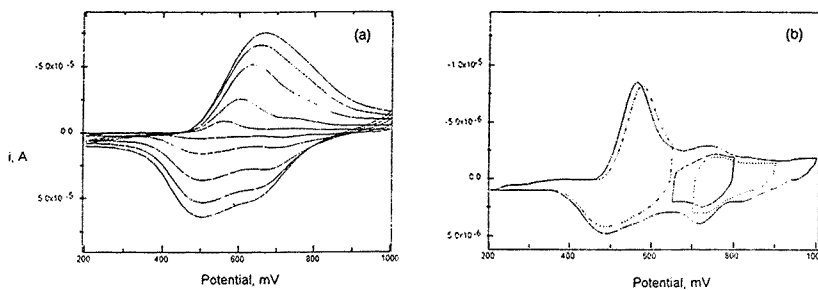
$$P1a = 0.19 + 4.5 \, [HClO_4] \quad (2)$$

Fig.1. (a) Cyclic voltammograms of PABUS film at different scan rate (100, 80, 50, 20, 10. 5 mV/s) in 0.1 M LiClO$_4$ solution of acetonitrile containing 0.46 M (5 % v/v) HClO$_4$. (b) CV of PANBUS at different potential ranges: scan rates of 5 mV/s.
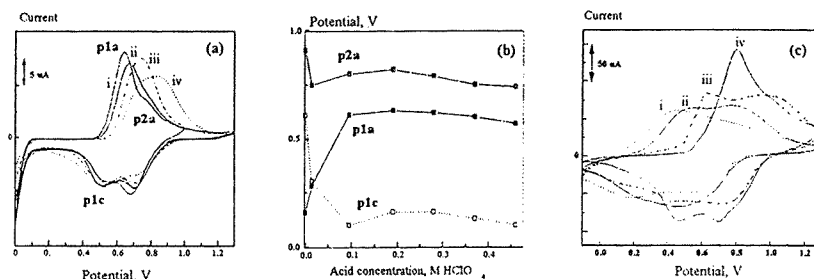

Fig.2.(a) CV for PABUS film in 0.1 M LiClO$_4$ solution of acetonitrile containing perchloric acid (i) 0.46 M, (ii) 0.37 M, (iii) 0.19 M, (iv) 0.095 M, (b) peak potential dependency on acid concentration, and (c) CV for PABUS film in 0.1 M LiClO$_4$ solution of acetonitrile containing 0.1 M of (i) acetic acid (ii) trifluoroacetic acid, (iii) dodecybenzenesulfonic acid, (iv) p-toluenesulfonic acid: scan rate of 10 mV/s, PANBUS area of 0.031 cm^2 for (a) and 0.3 cm^2 for (c).

Such an acid effect on the evolution of the redox system of PANBUS→PANBUS$^+$ can be ascribed to one electron/one proton reaction (eq.3), which has been described for the pH dependence of polyaniline [7].
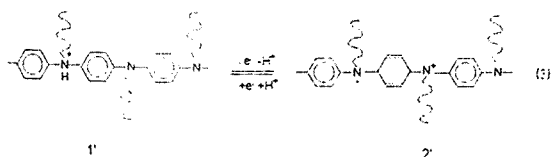
Since the intensity of the first redox peak is dependent on the perchloric acid concentration, quinoid center of 2' in eq. (3) may be counterbalanced by perchlorate. The second redox peak, discernible at a slower scan rate (*Fig. 1a*), was also influenced by acid concentration.

Peak potential and the extent of peak broadening for the redox process of PANBUS were dependent to a great extent on the acidity and structure of the dopant as shown in *Fig.2 (c)*. This result support that the redox process of

PANBUS involves external doping

PANBUS film soaked in non-acidic media showed different CV. which may indicate that the different doping process occurs. Dramatic decrease in the peak intensity was observed for the CV of PANBUS measured in 0.1 M LiClO$_4$ in acetonitrile. The voltammogram of the latter displays broad reversible peaks centered at 0.2 and 0.9 V. The peak current rises   linearly with the square root of the scan rate indicating that the redox process involves rate determining diffusion step.

CV study described above could be related to redox structure of polymer. In order to characterize the redox structure of the polymer at different oxidation level, spectroscopic study was carried out in acidic media.

Spectroelectrochemical study. Oxidation of the poly(aniline N-alkylsulfonate) films with a potential higher than 0.3 V (vs Ag/AgCl) effected coloration of the film with dark green hue. which was changed to a dark blue at above 0.7 V but changed to a purple at higher potential. Spectroelectrochemical study in acidic medium

is shown in *Fig. 3*, where the quantitative effects of color changes were apparent in the UV spectra by appearance of new absorption bands at ~ 420, 700 ~ 990 nm.

In the reduced state (0 V), the color of the PANBUS film was yellowish green and UV spectra showed two absorption bands at 420 and 920 nm, indicating that the polymer is protonated [7]. The band at 350 nm for PANBUS can be assigned to the aromatic π-π* transition based on the earlier studies on the polyaniline and its N-substituted derivatives [8-10]. In the intermediate oxidation state, the color of the film was darker, showing increased absorbance at 990 nm and 700 nm as shown in *Fig 3 (b)*. Those bands can be assigned as the absorption of the metallic polaron band of the conducting form as an intermediate species in the two step oxidation of polymer [11-12]. New bands at 630 nm at highly oxidized state (0.9 V) can be attributed to the formation of a dication (Structure 3).

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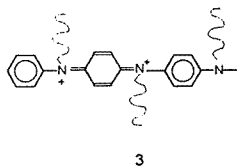
UV spectra of PANBUS film in non-acidic electrolyte medium is compared in *Fig 4*, in which the reduced form (at 0 V, transparent yellow) showed no absorbance above 700 nm, indicating that the polymer is deprotonated (structure 1 in eq.1).

Alkyl chain length of the alkylsulfonate group effected only little change in λmax for oxidized polymers. These result indicate that the absorbance changes are mainly due to the redox reaction of pi-system of the polymer main chain, which can be interconverted from the benzenoid to quinoid structure.
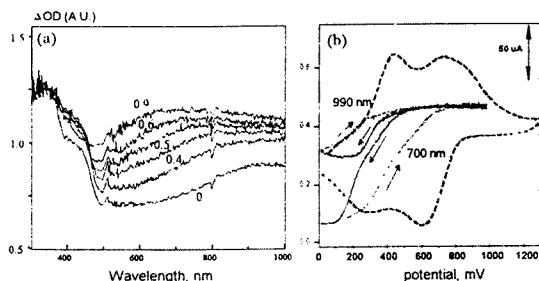

Fig. 4. UV Spectra of PANBUS at 0.9, 0.6, 0.5, 0.4, 0.3, and 0 V (top to bottom) in 0.1 M LiClO₄/AN.

XPS Study. N(1s)XPS core-level spectra of the oxidized and reduced films of PANBUS showed three component peaks centered at 399.3, 401.2, and 403.3 eV, with the fwhm of 1.4, 2.2, and 3.0 eV, respectively, by spectral deconvolution. The area fractions of these peaks are summarized in Table I. Kang et. al [13] have pointed out that the peaks at lower binding energy (399.3 ± 0.1 eV for polyaniline) represents the nitrogen of amine units. Kumar and Inoue et. al.[14] have found that the higher binding energy can be attributed to the polaron(BE = 400.8 for polyaniline) and bipolaron (BE = 402.2 eV for polyaniline). Furthermore Nakajima et al.[15] and Chen et al. [16] have reported that the tail can be referred to the radical cation (NH$^{·+}$, BE = 400.8 eV) and cationic nitrogen (NH$_2^+$, BE = 402.3 eV). Thus for the present study, the N(1s) peaks at 399.3, 401.2, and 403 eV can be assigned to the amine nitrogen, cation radical (NR$^{·+}$; R = N-alkylsulfonate), and cationic nitrogen (NR$^+$), respectively. Thus the area fractions of three peaks listed in Table II indicate that the benzenoid to quinoid (B/Q) ratio are 2.8 and 0.8 for oxidized and reduced PANBUS, respectively. It was noticeable that the Li content was much less than N and S for the oxidized PANBUS.

Fig 3. (a) UV Spectra at 0.9, 0.6, 0.5, 0.4, 0.3, and 0 V (top to bottom) and (b) Spectrocyclic voltammogram measured at 990 nm and 700nm and CV for PANBUS film in electrolyte containing 5 % HClO₄ (0.014 M), scan rate of 5 mV/s.
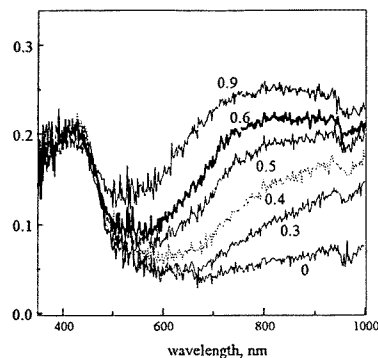
Table 1. N(1s)XPS core-level spectral data for PANBUS film by spectral deconvolution.

eV	integration Result (% area)	
	reduced	Oxidized
399.3	0.24 (74)	0.22(40)
401.2	0.077(24)	0.27(50)
403.3	0.009(3)	0.055(10)

Impedance study Impedance spectra measured at different oxidation level identified the in-situ conductivity of the PANBUS film. In this technique, the system is only infinitesimally perturbed with respect to the state and thus the electrical properties of interface in between electrode/polymer and polymer/electrolyte could be calculated [17-20].

Impedance measured for PANBUS film in 0.1 M LiClO$_4$/AN containing 0.46 M HClO$_4$ changed significantly in the frequency range of 100 Hz ~ 10 mHz by the potential changes, while it remained almost constant at the frequency above 10,000 Hz. The Nyquist plot obtained at intermediate oxidation level (bet. 0.5 and 0.8 V) showed a semicircle in the frequency range of 1 ~ 20,000 Hz. Such a semicircle can be associated with the charge transfer resistance of the polymer and double layer capacitances (Cd) of the polymer/electrolyte interface [19-20].

The charge transfer resistance R$_{CT}$ was calculated from the simulation based on an equivalent circuit derived from the Randels model. Addition to this, C (capacitance)-E (potential) and R (resistivity)-E curve were traced by measuring impedance at single frequency (1 Hz or 10 Hz) during potential sweep. The R-E curve for the PANBUS film in 0.1 M LiClO$_4$ solution of acetonitrile containing 0.46 M HClO$_4$ matched well with the result determined by Nyquist plot showing two minimum resistivity at 0.58 and 0.72 V, respectively, where the first two redox process were observed by CV (*Fig. 1a*).

Fig 5 shows plots of conductivity vs E and capacitance-E obtained from the single frequency analysis. The conductivity determined from the impedance study was similar to the dc conductivity of 10^{-6} S/cm measured for a pellet prepared from the oxidized PANBUS.

The maximum conductivity at two different potential can arise from the formation of two types of semiquinone radical cation structures, which are different only by ionic environment. Since the first redox process involve external doping, the first state can be assigned as externally doped semiquinone radical cation structure. The second peak may then be attributed to the self-doped semiquinone radical cation structure, which are prominent at slower scan rate and could be thermodynamically stable due to steric reason.
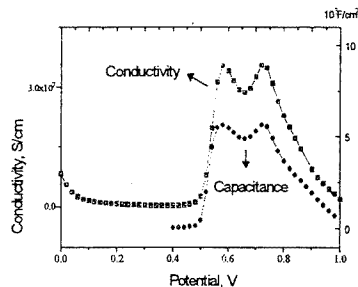

Fig 5. In-situ conductivity and capacitance for PANBUS film in 0.1 M LiClO$_4$ solution of acetonitrile containing 0.46 M (5 %, v/v) HClO$_4$.

In accord with the R-E curve, the C-E curve showed two maximum point at the same potentials probably due to maximum dielectric separation at highly conductive states. The reduced state (0 - 0.2 V) and highly oxidized state (0.9 V) showed high resistance that can be estimated from *Fig.5*. High resistivity at a potential greater than 0.9 V is possibly due to the formation of a dicationic structure (3).

From the spectroscopic and impedance analysis we suggest the external doping of self-dopable polymer in the presence of acid. In the first oxidation process, the protonated form of the phenyleneamine structure (eq. 3, 1 '), the reduced structure of polyaniline main chain, is oxidized to the semiquinone radical cation structure and its delocalized state accompanying external doping. In weakly acidic medium, partial protonation may result in the peak potential shift toward negative for the first process as observed in *Fig 2 (b)*.

The second redox pair seems to be related to the self-doping process that extrudes HClO$_4$ to form self-doped structure, which produce the quinonediimine cation structure (3) via one electron transfer.

Finally, third peak in Fig 1a can be attributed to the formation of the quinonediimine cation structure possibly from the externally doped semiquinone radical cation structure via one electron transfer.

Further studies on the doping mechanism and redox switching of the self-doped polyaniline derivatives is in progress and will be published elsewhere.

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