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A. Kitani^a, H. Munemura^a, Y. Ota^a, K. Takaki^a & S. Ito^a

^a Faculty of Engineering, Hiroshima University, Kagamiyama, Higashi-Hiroshima, 739, Japan

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ELECTROCHEMICAL, OPTICAL AND ELECTRICAL PROPERTIES OF POLY-*N*-HEPTYLANILINES

AKIRA KITANI, HIROSHI MUNEMURA, YOSHIFUMI OTA,
KEN TAKAKI AND SOTARO ITO

Faculty of Engineering, Hiroshima University,
Kagamiyama, Higashi- Hiroshima, 739 Japan

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Abstract Poly-*N*-(3,6-dioxaheptyl)aniline (poly-NDHAN), containing two oxyethylene units in the side chain, was prepared electrochemically to improve electrochemical redox activity of polyaniline. The cyclic voltammogram of poly-NDHAN showed a reversible redox peak around 0.6 V (vs. SCE) and another irreversible redox couple at -1.2 V and -0.1 V in acetonitrile solution containing LiClO₄. The latter couple was attributed to the n-type doping and undoping reactions. Poly-NDHAN unlike polyanilines had an absorption maximum in the visible region even in its neutral form. The molecular weight of poly-NDHAN was high (1,200,000), and the conductivity value was $1 \times 10^{-3} \text{ Scm}^{-1}$. The effect of polymerizing conditions on the conductivity of poly-*N*-heptylaniline was also studied. Poly-*N*-heptylaniline with a higher conductivity was obtained by constant potential polymerization at 1.2 V in acetonitrile solution containing H₂SO₄.

Keywords : Poly-*N*-(3,6-dioxaheptyl)aniline, Oxyethylene unit,
Poly-*N*-heptylaniline, Electrochemical behavior, Optical property

INTRODUCTION

Polyaniline has occupied a prominent position in electric conducting polymers because of its unique and useful characteristics. However, an improvement of various properties is necessary for industrial applications. Among various properties, processability is an important factor for practical use. Several soluble, ring-substituted¹⁻³ and *N*-substituted⁴⁻⁶ polyalkylanilines have been prepared to enhance their processability.

In the case of polythiophene, Roncali and coworkers introduced oxyethylene

units to β -alkyl chain of thiophene and reported the increase of redox activity of resulting polymer⁷⁻¹⁰. In this paper, we have studied on the properties of *N*-3,6-dioxaheptyl-substituted polyaniline, which has two oxyethylene units in the side chain, in order to improve processability and redox activity of polyanilines. We have also found electrochemical polymerization conditions for the preparation of poly-*N*-heptylanilines having a conductivity higher than those of polyalkylanilines already reported.

EXPERIMENTAL

N-(3,6-Dioxaheptyl)aniline (NDHAn, substituent = $(\text{CH}_2\text{CH}_2\text{O})_2\text{CH}_3$) was synthesized from 2-anilinoethanol and 2-chloroethyl methyl ether according to the procedure of Williamson's ether synthesis¹¹. *N*-Heptyl-, *N*-octyl- and *N*-decyl-anilines were synthesized from aniline and corresponding alkylbromides¹². The structures of the synthesized aniline derivatives were confirmed with a 270 MHz NMR (^1H and ^{13}C) and an FT-IR spectroscopy. Other *N*-alkylaniline derivatives were obtained from Tokyo Kasei Co. Ltd.

Unless otherwise specified, electrochemical polymerization was performed under potentiostatic conditions at 1.2 V in the acetonitrile (AN) solution containing 50 mM NDHAn and 0.2 M H_2SO_4 under nitrogen atmosphere. A Pt plate was used as a working electrode and an aqueous SCE was used as a reference electrode. The polymer powder collected from Pt surface was washed with AN and dried under vacuum. An ITO-glass electrode was used for spectroscopic and electrochemical measurements.

Electrochemical properties of polymers were investigated with cyclic voltammetry. The quantity of electricity passed for the preparation of polymer modified electrode was 100 mCcm^{-2} . Electrical conductivities of polymer pressed pellets were determined with four-probe DC method. Molar mass measurements were performed with GPC using *N,N*-dimethylformamide as an eluent and monodisperse polystyrene as an internal standard.

PROPERTIES OF POLYANILINE CONTAINING OXYETHYLENE UNITS

Electrochemical Properties of Poly-NDHAn

Figure 1 shows the cyclic voltammogram of poly-NDHAn between 0 and 1.2 V. Poly-

NDHAn was electroactive and showed one reversible redox peak around 0.6 V. This redox process should be the oxidation of polymer chain to form cationic polymer, then the reduction of cations to neutral polymer (so called p-type doping and undoping reactions). The peak current was proportional to the square root of sweep rate, indicating the redox process was controlled by diffusion of anions in polymer matrix.

Unlike the electrochemical behaviors of ordinary polyaniline, both the redox current and reversibility were affected by the kind of cations in solution. As shown in Fig. 1, highest redox current was observed in LiClO_4 / AN solution with good reversibility. This may be due to the interaction between lithium cation and oxyethylene units. It is well-known that polyethyleneoxide / lithium salt composite material acts as an excellent solid polymer electrolyte due to the coordination of ethereal oxygen to lithium cation.

The most striking feature of electrochemical behavior of poly-NDHAn in AN solution containing Li cation was the appearance of a new reduction peak at more negative potential region. When cathodic limiting potential was shifted to -1.5 V, the new cathodic peak appeared at -1.2 V and the corresponding anodic peak appeared at -0.1 V (Fig. 2). No such reduction peak was observed for unsubstituted polyaniline. This new cathodic peak may be attributed to the reduction of polymer chain to form anion radical, followed by the insertion of Li cation into polymer matrix (n-type doping reaction).

TABLE 1 Atomic concentration of poly-NDHAn polarized at each potential determined with XPS.

Sample	Potential (V vs. SCE)	Atomic concentration / %				
		C(1s)	N(1s)	O(1s)	S(2p)	Li(1s)
A	1.2	68.8	4.7	23.6	2.9	-
B	-1.2	60.3	3.3	11.7	-	24.8
C	0.0	77.5	4.3	18.2	-	-

Sample A (As prepared) ; Obtained at 1.2 V from a solution of 0.05 M NDHAn in 0.2 M H_2SO_4 / AN.

Sample B (Reduced form) ; Obtained by holding sample A at -1.2 V for 30 min in 0.2 M LiClO_4 / AN.

Sample C (Neutral form) ; Obtained by holding sample B at 0 V for 30 min in 0.2 M LiClO_4 / AN.

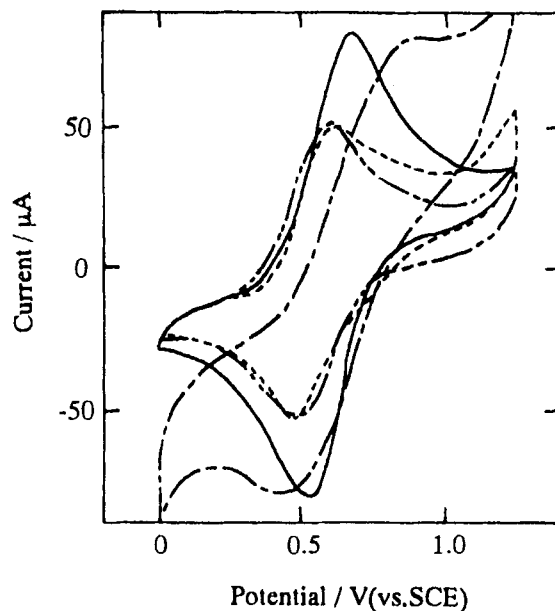


FIGURE 1 Effect of cations on electrochemical redox activity of poly-NDHAn in AN solution.

Supporting electrolyte : LiClO_4 (—), HClO_4 (— — —), NaClO_4 (— · — · —), $(\text{But})_4\text{NClO}_4$ (· · · · ·); Sweep rate : 100 mV s^{-1}

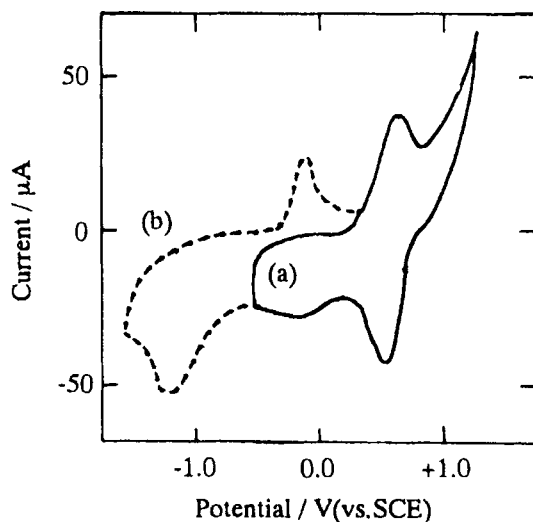


FIGURE 2 Cyclic voltammogram of poly-NDHAn in $0.2 \text{ M LiClO}_4 / \text{AN}$ solution at 50 mV s^{-1} between -0.5 and 1.2 V (curve a) or between -1.5 and 1.2 V (curve b).

XPS measurements were carried out to detect the Li atom in polymer matrix. As listed in Table 1, Li cation was incorporated into polymer matrix when poly-NDHAn was polarized at -1.2 V in LiClO₄ / AN solution, while Li was not found for the sample kept at 0 V for 30 min. Therefore, the new redox couple observed at -1.2 V and -0.1 V was due to the n-type doping-undoping reactions of poly-NDHAn.

Optical and Electrical Properties of Poly-NDHAn

Usually the color of polyanilines was changed by electrochemical p-type doping-undoping reactions. In the case of poly-NDHAn, however, its deep green color was unchanged during continuous potential cycling between 0 and 1.2 V. Figure 3 shows the visible absorption spectra of poly-NDHAn. Polymer oxidized at 1.2 V (cationic form) showed absorption maxima at 630 nm and at near infra red region (> 900 nm). To our surprise, neutral sample reduced at 0 V (neutral form) showed a clear maximum at 880 nm. The absorption spectrum of neutral form indicates poly-NDHAn has a smaller band gap compared to ordinary polyanilines. This result is consistent with the occurrence of n-type doping of poly-NDHAn.

The electrical conductivity of poly-NDHAn prepared at 1.2 V was $1 \times 10^{-3} \text{ Scm}^{-1}$. This conductivity value is considerably high compared to poly-*N*-butylaniline (10^{-7} Scm^{-1})^{4,6}. The molar mass distribution was examined with GPC (Fig. 4). Although a small peak was observed at lower molecular weight portion, its molecular weight was determined to be 1,200,000. This value is also higher than those of poly-*N*-alkylanilines (40,000 - 70,000)⁶. These findings indicate that poly-*N*-alkylanilines with a higher conductivity could be obtained by changing polymerizing conditions.

PROPERTIES OF POLY-*N*-ALKYLANILINES

Properties of Poly-*N*-heptylaniline

Because poly-NDHAn has unique properties such as n-type doping, it is interesting to study the electrochemical polymerization of *N*-heptylaniline (NHAn), which has no oxyethylene unit in the alkyl chain. Poly-NHAn was prepared according to the procedure described in the experimental section. No cathodic peak was observed in the voltammogram of poly-NHAn in AN solution containing 0.2 M LiClO₄ between 0 and -2.0 V. In contrast to poly-NDHAn, poly-NHAn showed clear color change by electrochemical redox cycle. The color of polymer was deep blue in its fully oxidized state, but turned pale yellow by electrochemical reduction at 0 V (Fig. 3b).

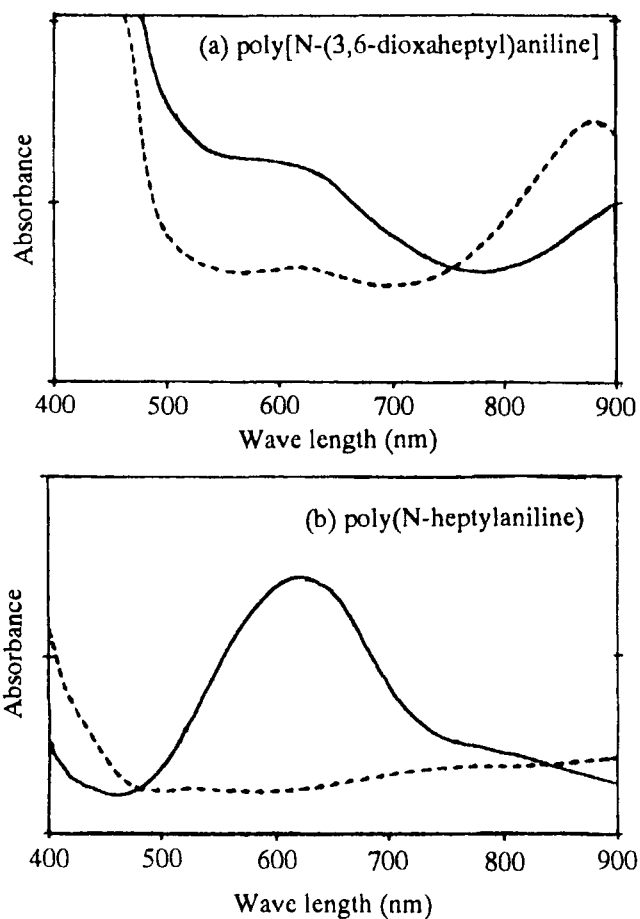


FIGURE 3 Visible absorption spectra of poly-NDHAN (upper, a) and poly-NHAN (lower, b) oxidized at 1.2 V (—) or reduced at 0 V (- - - -).

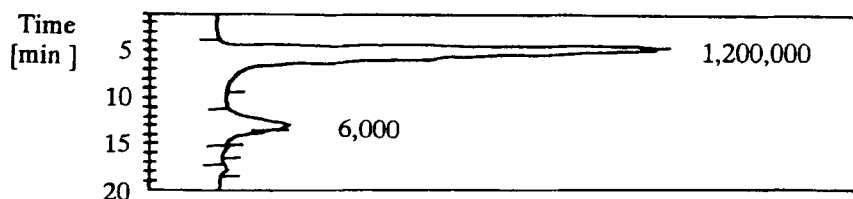


FIGURE 4 Molar mass distribution of poly-NDHAN measured with GPC.

These results suggest that unique electrochemical and optical properties of poly-NDHAn are mainly due to the presence of ethereal oxygen in the side chain, although the reason is not clear at this stage.

However, the conductivity ($2 \times 10^{-3} \text{ Scm}^{-1}$) and the molecular weight (1,000,000) of poly-NHAn were unaffected by the absence of ethereal oxygen. The effect of polymerizing conditions on the conductivity and the molar mass of poly-NHAn was studied. As summarized in Table 2, the electrical conductivity strongly depended on the kind of supporting electrolyte and solvent of the polymerizing solution. There was no direct correlation between the electrical conductivity and the molar mass of poly-NHAn.

TABLE 2 Effect of polymerizing conditions on electrical conductivity and molar mass of poly-*N*-heptylanilines.

Monomer	Acid	Solvent	Conductivity / Scm^{-1}	Molar mass / g
NDHAn	H_2SO_4	AN	1×10^{-3}	1,200,000
NHAn	H_2SO_4	AN	2×10^{-3}	1,000,000
NHAn	H_2SO_4	(AN + H_2O)*	4×10^{-6}	3,600
NHAn	H_2SO_4	(DMSO + H_2O)*	Insulator	4,600
NHAn	HClO_4	AN	1×10^{-7}	1,000
NHAn	HClO_4	(AN + H_2O)*	1×10^{-4}	9,600
NHAn	HClO_4	(DMSO + H_2O)*	Insulator	8,900

* : Equivolume mixture (DMSO = Dimethylsulfoxide)

Conductivity of Poly-*N*-alkylanilines

Several *N*-alkylanilines were polymerized electrochemically under two different conditions (Table 3). The one was H_2SO_4 / AN system , in which highest conductivity was obtained for poly-NHAn. The other was HClO_4 / (DMSO + H_2O) system, which was unsuitable for the polymerization of NHAn. Interestingly, H_2SO_4 / AN system was suitable for the polymerization of *N*-alkylanilines having long alkyl chains, while HClO_4 / (DMSO + H_2O) system was recommended for the preparation of poly-*N*-alkylanilines with short alkyl chains.

TABLE 3 Effect of length of linear alkyl chain on electrical conductivity of poly-*N*-alkylanilines prepared in 0.5 M H₂SO₄ / AN or 0.5 M HClO₄ / (DMSO + H₂O) solution.

Alkyl group	Conductivity / Scm ⁻¹	
	H ₂ SO ₄ / AN	HClO ₄ / (DMSO + H ₂ O)
Methyl	Insulator	2 x 10 ⁻³
Ethyl	Insulator	1 x 10 ⁻⁴
Butyl	Insulator	1 x 10 ⁻⁴
Heptyl	2 x 10 ⁻³	Insulator
Octyl	2 x 10 ⁻⁵	Insulator
Decyl	2 x 10 ⁻⁵	Insulator

DEDICATION

This article is dedicated to Professor Fumio Ogura for his outstanding achievements in the field of conducting organic solids.

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