전기화학적으로 합성한 폴리아닐린의 ESR 연구

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ESR Study of Electrochemically Synthesized Polyaniline

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요 약 : 여러가지 다른 전위와 pH에서 전기화학적으로 합성한 폴리아닐린의 ESR 스펙트럼을 연구하였다. 폴리아닐린의 전기화학적 산화의 여러 단계에 대하여 반응 메카니즘을 제안하였다. 폴리아닐린을 산화시키면 제1단계에서 라디칼 양이온 즉 폴라론이 형성된다. 더 산화시키면 라디칼 양이온이 점차 없어지고 벤조이드 구조가 퀴노이드 구조로 변한다. 폴리아닐린의 전기전도도와 ESR 신호의 세기가 거의 같은 경향을 가지고 변한다는 점을 고려할 때, 이 실험에서 얻은 데이타는 폴리아닐린의 전기전도도에 대한 라디칼 양이온 메카니즘을 뒷받침 해준다.

Abstract : ESR spectra of polyaniline which had been synthesized electrochemically under various potentials and pH's were studied. A reaction scheme has been proposed for the stepwise electrochemical oxidation of polyaniline. Upon oxidation of polyaniline, radical cations, i. e. the polarons are formed in the first step. Upon further oxidation, the radical cations gradually disappear and the quinoid structures are formed at the expense of the benzoid structures. Considering that the electrical conductivity of polyanilline varies with the oxidizing potential almost in the same fashion as the relative ESR intensity, it is concluded that the ESR data obtained in this experiment are supportive of the radical cation mechanism for the electrical conductivity of polyaniline.

INTRODUCTION

Polyaniline is one of the most frequently studied conducting polymers mainly because it can be easily synthesized in aqueous media. Nevertheless, the mechanism of electrical conduction is among the least understood. There have been some controversies on the conduction mechanism of polyaniline. MacDiarmid et al.[1,2] considered the fully oxidized form as the conducting form, while McManus et al.[3,4], from the spectroscopic studies and conductivity measurements, concluded that the form at the intermediate oxidation state was responsible for electrical conduction. They also identified that the form at the intermediate oxidation state was the radical cation, i. e. the polaron state. Genies and Lapkowski[5], from the

ESR and electrochemical studies, proposed that the complete redox mechanism involves four one-elecron steps and two polaron-bipolaron states. Glarum and Marshall[6] noticed that upon oxidation of polyaniline in the potential range of -0.1 to $0.5V$ (vs. SCE), the ratio of the number of produced-spins to the consumed-charge in the oxidation was one Curie spin per electronic charge. Kuzmany, Sariciftci, Neugebauer, and Neckel[7] suggested two step oxidation mechanism of polyaniline, namely an insulator-to-metal transition in the first oxidation step and a metal-to-insulator transition in the srcond oxidation step. They also concluded that the radical cations are the conducting species of polyaniline. On the other hand, Kaya, Kitani, and Sasaki[8] concluded that the electron spins had no direct correlation with the electrical conductivity of the polyaniline film. Focke, Wnek, and Wei[9] found that the proton played an important role in the electrical conduction of polyaniline, while the type of the anion was less important than the redox state of the film and the pH of the solution. Furukawa, Ueda, Hyodo, Harada, Nakajima, and Kawagoe[10] identified two different conducting forms by means of vibrational spectro scopy. However, the two conducting forms of Furukawa et al. can be considered to be virtually the same form in that the two forms have the identical cation polymer chain differing only in the type of the counter-anions.

In this study ESR spectroscopy and cyclic voltammetry have been used to reveal the mechanism of electrochemical oxidation and to identify the conducting form of polyaniline.

EXPERIMENTAL

Aniline was purified by vacuum distillation of the commercially available products. Polyaniline was systhesized electrochemically in aqueous media using a three electrode system in which platinum wire was used as a working electrode and a saturated calomel electrode was used as a reference electrode. The concentration of the monomer was 0.1M and the electrolyte was 1M aqueous HCl solution. Polyaniline film was coated on the Pt-wire electrode under a cycling potential between -0.2 and 1.0 V vs. SCE at a rate of 50mV / s. Then the electrode system was placed in a solution which contained no monomer but the electrolyte, HCl. The pH of the solution was controlled by HCl. The potential was maintained at a fixed value. After the current dropped almost to zero at the given potential, the polyaniline-coated Pt-wire was carefully inserted into an ESR tube as shown in Fig. 1.

All the ESR measurements were carried out at room temperature using a Bruker (ER 200E-SRC) ESR spectrometer. A cyclic voltammetric system (BAS CV-1B) in conjuction with a potentiostat (AMEL 533) was used for the electro-chemical system.

All the potential values used in this work are referenced to the saturated calomel electrode (SCE), unless otherwise described.

RESULTS AND DISCUSSION

A typical ESR spectrum of polyaniline is shown in Fig. 2. The g-value was 2.002 which is a value indicating the presence of free radicals in the polymer. As shown in Fig. 3 to Fig. 6 the intensity
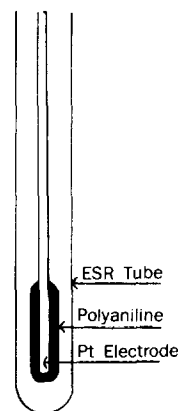

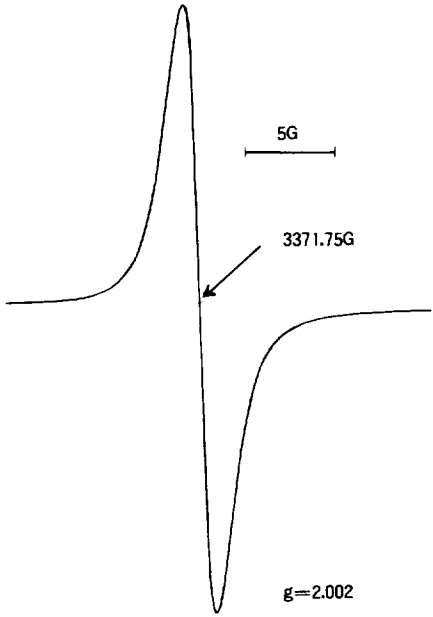Fig. 1. Polyaniline-coated pt-wire in an ESR tube.

Fig. 2. A typical ESR spectrum of polyaniline. The g-value was 2.002.
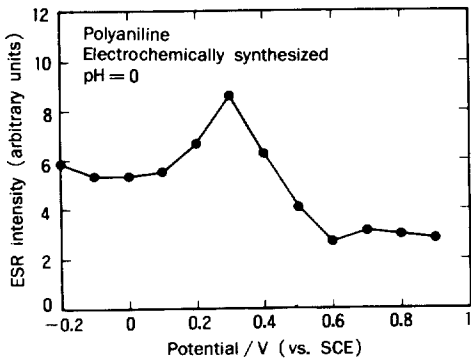
Fig. 3. Variation of the relative intensity of the ESR signal with potential at pH=O.

Fig. 4. Variation of the relatiive intensity of the ESR signal with potential at pH=1.

Fig. 5. Variation of the relative intensity of the ESR signal with potential at pH=2.

Fig. 6. Variation of the relative intensity of the ESR signal with potential at pH=3.

of ESR signal varies with the pH and the potential at which the sample was kept until the current decayed to nearly zero. It is very interesting to note that, at a constant pH, the ESR intensity shows a mximum as the potential changes. In the pH range of 0 to 3, as the potential increased to anodic direction, from somewhere around 0 V (vs. SCE), the radicals began to be formed,
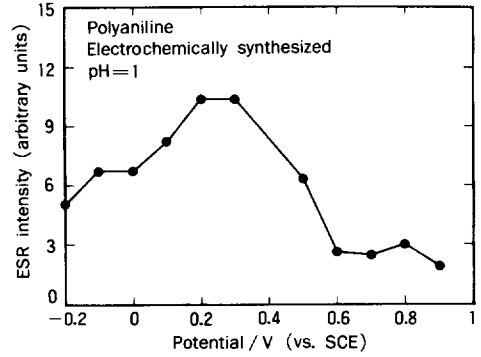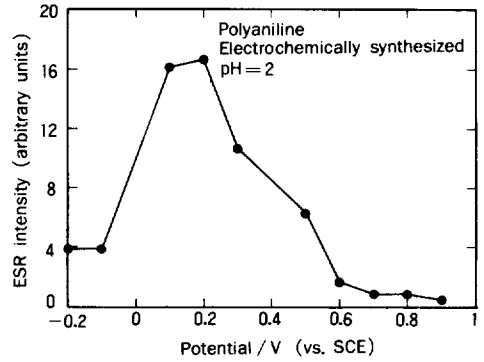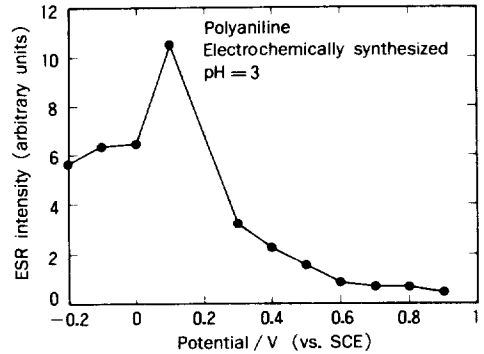
then disappeared under sufficiently anodic conditions. Furthermore, as can be seen in Fig. 3

to Fig. 6, the maximum ESR intensity appeared successively at lower potentials as the pH of the solution increased, i. e. the peak potential was 0.3V (vs. SCE) at pH=0, 0.25V at pH=1, 0.15V at pH=2, and 0.1V at pH=3. Such behavior of shift in peak potential with the pH is plotted in Fig. 7.

The straight line in Fig. 7 shows the linear least square fit to the experimental data points. The slope of the straight line was 70 ± 7mV / pH. This indicates that, in the radical-forming reaction, the number of electrons and the number of protons involved are equal. This is a result which agrees very well with Glarum et al's.[6]

A typical cyclic voltammogram of polyaniline on Pt-wire electrode (Fig. 8) shows four anodic

peaks and four cathodic peaks. Among these, peaks B and B' is attributable to the soluble species, i. e. benzoquinone and hydroquinone produced from the hydrolysis of polyaniline[11,12]. Therefore, only 3 pairs of peaks are responsible for the electrochemical reactions of the polymer.

Judging from the peak potentials of peaks A (0.02V) and A' (0.22V), the half wave potential for A / A' pair should be 0.12V, which is about the same value as the potential at which the free radicals start to be formed at the pH (Fig. 3). Peak C and C' appeared at 0.51V which is the same potential as the one at which the ESR signal almost disappeared (Fig. 3). Therefore, it is reasonable to conclude that free radicals are formed in the first step of oxidation of polyaniline and disappears mostly in the second step.

The reaction scheme for the electrochemical oxidation of polyaniline is proposed in Fig. 9. According to McManus et al.[3,4] and Kuzmany et al.[7], the forms that exist in the potential range of 0.12 to 0.51 V are the radical cations. Therefore, the peak pair A / A is assigned to the oxidation / reduction between form Ⅰ and Ⅱ as shown in Fig. 9. According to MacDiarmid et al.[2] and Reiss,[3] in the fully protonated form of polyaniline,
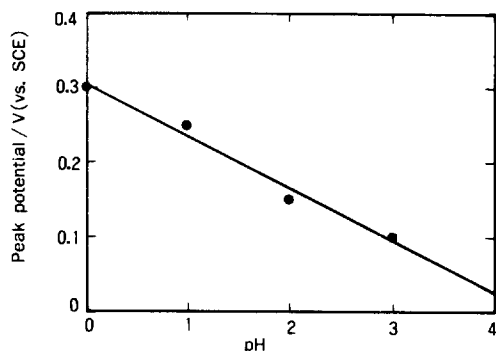

Fig. 7. Shift of the peak potential with pH.
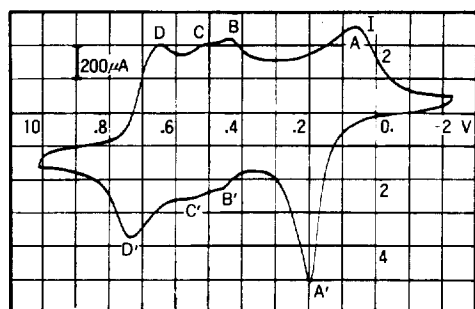
Fig. 8. A typical cyclic voltammogram of polyaniline in 1M HCl solution. Potential scan rate=50 mV / s.
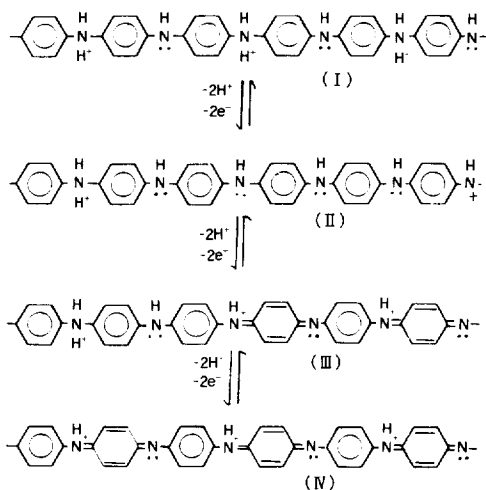

Fig. 9. Proposed structural change of polyaniline with potential.

approximately 50% of the repeating units are protonated, i.e. every other nitrogen atom in the polymer chain exists in $-NH^+_2-$ form as shown in Fig. 9(I).

There is a general consensus between the re-searchers[1~7,9~13] that in the fully oxidized form of polyaniline in acidic media, every other repeating unit has the quinoid structure as shown by structure IV in Fig. 9. Form I in Fig. 9 should loose one electron per repeating unit to be transformed into form IV in Fig. 9. The cyclic voltammogram in Fig. 8 shows that the area enclosed by the peak pair A / A' is approximately one third of the total area. This means that approximately one out of three repeating units has lost an electron in the first step, i.e. in average about one third of the nitrogen atoms in structure II exist in $-NH^+-$ form. It has already been explained that the number of protons and the number of electrons involved in each step of Fig. 9 should be the same. It has to be pointed out that the electrical conductance also shows a maximum in this potential range[3,4]. This is a strong evidence that the radical cations are the conducting forms.

The equilibrium between structure II and III in Fig. 9 is responsible for the peak pair C / C' in Fig. 8. By oxidizing form II, some of the benzoid structures are transformed into the quinoid structrures. The number of quinoid structures formed in this reaction is the same as the number of electrons transfered. Notice that the number of electrons transfered is the same as the number of protons transfered and at the same time the same number of free radicals disappear, as has been indicated in Fig. 9. The electrical conductance also decreased with the disappearance of the radical cations.[4] This observation supports the radical cation mechanism for the electrical con-ductivity in polyaniline.

The last step of the oxidation / reduction equilibrium is responsible for the peak pair D / D' in Fig. 8. Oxidation of form III transforms more of the benzoid structures into the quinoid structures. Thus, in the fully oxidized form of

polyaniline, every other repeating unit has the quinoid tructure.[1~7,9~13] It is important to note that the fully oxidized form, form IV in Fig. 9, is not the conducting form as was concluded in some literatures.[1,2]

In conclusion, the radical cations are produced in the initial stage of the electrochemical oxidation of polyaniline. However, upon further oxidation, the quinoid structures are produced at the expense of the benzoid structures. It is also concluded that the radical cation form is the conducting form while the fully oxidized form is nonconducting.

REFERENCES

1. A. G. MacDiarmid, J. -C. Chiang, M. Halpern, W. -S. Huang, S. -L. Mu, N. L. D. Somasiri, W. Wu, and S. Y. Yaniger : *Mol. Cryst. Liq. Cryst.*, **121**, 173(1985).

2. W. -S. Huang, B. D. Humphrey, and A. G. MacDiarmid : *J. Chem. Soc., Faraday Trans. 1*, **82**, 2385(1986).

3. P. M. McManus, S. C. Yang, and R. J. Cushman : *J. Chem. Soc., Chem. Commun.*, 1556(1985).

4. R. J. Cushman, P. M. McManus, and S. C. Yang : *Makromol. Chem., Rapid Commun.*, **8**, 69(1987).

5. E. M. Genies and Lapkowski : *Synthetic Metals*, **24**, 61(1988).

6. S. H. Glarum and J. H. Marshall : *J. Phys. Chem.*, **90**, 6076(1986).

7. H. Kuzmany, N. S. Sariciftci, Neugebauer, and Neckel : *Phys. Rev. Lett.*, **60**, 212(1988).

8. M. Kaya, A. Kitani, and K. Sasaki : *Chemistry Letters (Japan)*, 147(1986).

9. W. W. Focke, G. E. Wnek, and Y. Wei : *J. Phys. Chem.*, **91**, 5813(1987).

10. Y. Furukawa, F. Ueda, Y. Hyodo, I. Harada, T. Nakajima, and T. Kawagoe : *Macromolecules,*

21, 1297(1988).

11. D. E. Stilwell and S. -M. Park ; in "Corrosion Protection by Organic Coatings", Proceedings Vol. 87-2 (M. W. Kendig and H. Leidheiser, Jr. ed.) The Electrochemical Society, Inc.,

Pennington, NJ, 1987.

12. D. E. Stilwell ; Ph. D. dissertation, University of New Mexico, 1987.

13. H. Reiss ; *J. Phys. Chem.*, **92**, 3657(1988).