Role of Substituent in Electrooxidation of Poly(1-substituted pyrrole) Films

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ABSTRACT: Poly(1-substituted pyrrole)s were prepared on a platinum electrode with different electrolysis times, and their properties were studied by cyclic voltammetry. The oxidation potential for most of the poly(1-alkylpyrrole)s were almost 0.3 V versus the Ag/Ag$^+$ reference electrode, except for poly(1-butylpyrrole). The electron transfer rate in polymer films depends on the electrolysis time and the size of the substituent. The difference of the redox peak potential of poly(1-phenylpyrrole) was smaller than that of poly(1-anisylpyrrole) films. The role of a substituent in the electrochemical behavior of the polymer main chain is discussed. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 471–475, 1998

Key words: substituents; poly(1-substituted pyrrole); cyclic voltammetry; electrolysis

INTRODUCTION

It is very important for industry to increase the solubility of a conducting polymer in popular solvents. Conducting polymers with high solubility to some solvents were recently synthesized by introducing alkyl and other substituents on the conducting polymer chain.[1,2]

An alkyl substituted conducting polymer, however, usually shows lower conductivity than the original unsubstituted polymer. Diaz et al. measured the conductivity of poly(1-alkylpyrrole) polymer films and found that the conductivity decreased as the size of the substituent increased.[3] They also found that the oxidation potential of poly(1-alkylpyrrole) films depends on the size of the substituent. Electroconducting polymer has a π-conjugation system along the polymer chain, and the nature of the conjugation system is reflected on the oxidation potential of the polymer.[4] The electronic and steric structure of a substituent both contribute to the polymer π-conjugation system.[5] However, the steric factor of n-alkyls is usually not so different from each other.[6–8] On the other hand, the packing and orientation of polymer molecules in a solid are the important factors in understanding its electric conductivity.[9,10] Substituents on the polymer chain may change these factors.

We are interested in the role of substituent size on the electrochemical properties of conducting polymer film, and we studied the poly(1-substituted pyrrole) films on the electrode by cyclic voltammetry.

EXPERIMENTAL

Materials

1-Propylpyrrole (PP), 1-butylpyrrole (BP), 1-octylpyrrole (OP), and 1-dodecylpyrrole (DP) were

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prepared from alkyl bromide and pyrrole in alkaline dimethyl sulfoxide.[11] 1-Methylpyrrole (MP) was obtained form Aldrich. These pyrroles were purified by distillation. 1-Anisylpyrrole (AnP) was synthesized using 2,5-dimethoxytetrahydrofuran and *p*-anisidine in acetic acid.[12] 1-Phenylpyrrole (PhP) was obtained from Tokyo Kasei Co. Ltd. and recrystallized from methanol. All the synthesized pyrroles were identified by NMR, IR, and comparison to other physical data in the literature.

Alkyl halides and pyrrole were obtained from Tokyo Kasei Co. Ltd. and distilled prior for use. 2,5-Dimethoxytetrahydrofuran was obtained from Tokyo Kasei Co. Ltd. and was used as received. Tetraethylammonium fluoroborate (TEAFB) was obtained from Aldrich and was recrystallized from a methanol/petroleum ether mixture and dried under reduced pressure. HPLC grade acetonitrile was obtained from Wako Chemicals and was dried over 3-Å molecular sieves for a few days. Then it was fractionally distilled over calcium hydride.

Electrochemical Experiments

Electrochemical experiments were performed with a Hokuto HA-301 potentiostat/galvanostat and a Hokuto HB-111 function generator. Cyclic voltammograms were recorded on a Rikadenshi *X–Y* recorder. A one-compartment cell equipped with a platinum disk (1 mm in diameter), a working electrode, a platinum wire counterelectrode, and an Ag/Ag$^+$ reference electrode were used for the electrochemical experiments.

Electrochemical polymerization and cyclic voltammetry were carried out in acetonitrile containing 0.1 mol dm^{-3} TEAFB as the electrolyte.

Preparation of Polymer Films

A 1-substituted pyrrole (SP) was electropolymerized on a platinum electrode in acetonitrile. The concentration of the SP was 50 mmol dm^{-3}. The potential was repeatedly swept between −0.2 and 1.0 V at a scan speed of 50 mV s^{-1}. The material produced on the electrode was electrochemically undoped. The chemical structure of the material was identified by FTIR. Different amounts of several films on the electrode were prepared by a potential sweep with a different number of scans. The amount of the polymer on the electrode was assumed to be proportional to the oxidation peek current I_{pa}.

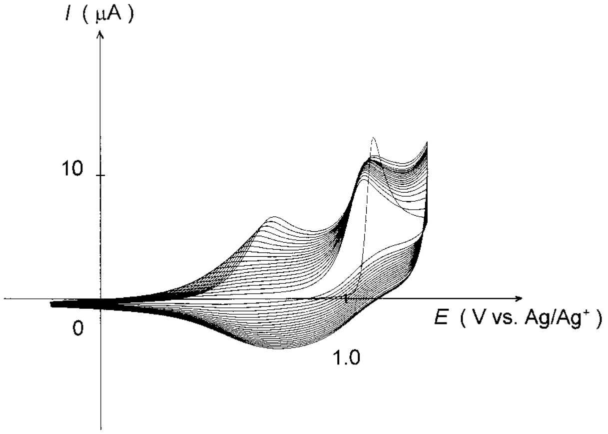

Figure 1 Cyclic voltammograms of a DP containing solution during electrolysis. [DP] = 50 mmol dm^{-3}; [TEABF] = 0.1 mod dm^{-3}; scan rate = 50 mV s^{-1}.

Cyclic Voltammetry of Polymers

Experimental conditions for cyclic voltammetry were almost the same for electrochemical polymerization. The polymer coated electrode was moved to a monomer free electrolysis cell, and cyclic voltammetry was carried out. The potential sweep rate for a typical measurement was 100 mV s^{-1}, and the sweep range was from −0.2 to 1.0 V.

RESULTS AND DISCUSSION

Growth of Polymer Film

Figure 1 shows cyclic voltammograms of an OP containing solution during electrolysis. The oxidation wave of the monomer changed at around 1.1 V, and a new oxidation and reduction wave appeared at 0.3 V. By continuing the electrolysis, the peak current of the new oxidation wave I_{pa} increased and the oxidation peak potential E_{pa} shifted anodically. After the electrolysis, the working electrode was covered with a brownish film. The same kind of changes were observed on the cyclic voltammogram of the SP solutions during the electrolysis.

Cyclic Voltammetry of Polymer Film

Figure 2 shows cyclic voltammograms of polyDP prepared with different scan times. With increasing scan times, the oxidation peak current increased. The polySP showed the same behav-

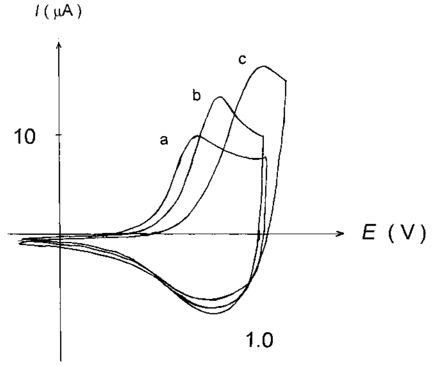

Figure 2 Cyclic voltammograms of polyDPs electrochemically polymerized with scan times of (a) 15, (b) 20, and (c) 30. Scan rate = 100 mV s^{-1}.

ior, too. The I_{pa} should be proportional to the amount of substance oxidized on the electrode. For a more quantitative expression of the amount of polymer on the electrode, we used I_{pa} as the scale.

Plots of E_{pa} versus I_{pa} for polyAPs are shown in Figure 3. The plots for the polymer with a large substituent shows a large shift of E_{pa} with increasing I_{pa}. The half-wave potential $E_{1/2}$ was calculated for polyAnP and polyPhP from their E_{pa} and E_{pc}. The $E_{1/2}$ also changed with the I_{pa}. Extrapolation of the $E_{1/2} - I_{pa}$ plots and the $E_{pa} - I_{pa}$ plots gave almost an equal intercept.

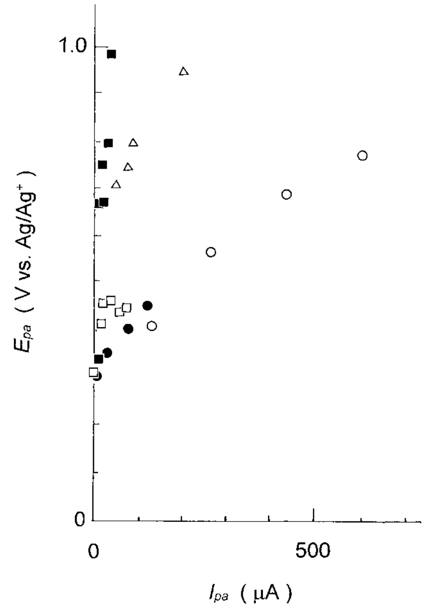

Figure 3 Plots of E_{pa} versus I_{pa} for (○) polyMP, (●) polyPP, (△) polyBP, (□) polyOP, and (■) polyDP.

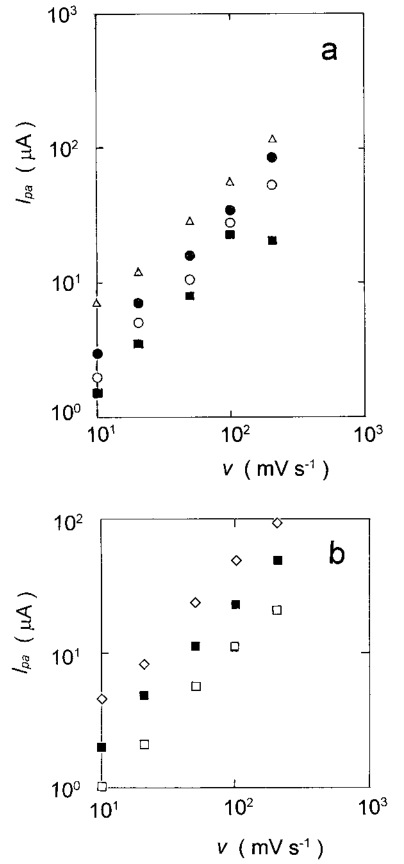

Figure 4 Plots of I_{pa} versus v. Scan times: (a) polyPhP: (■) 2, (○) 4, (●) 8, and (△) 12; (b) polyAnP: (□) 10, (■) 19, and (◇) 30.

At the intercept, chemical and structural changes of the polymer film can be negligible. Therefore, we attributed the intercept $E_{pa,0}$ to the oxidation potential of the polymer itself. The $E_{pa,0}$ for polyPhP, polyAnP, polyMP, polyPP, polyBP, polyOP, and polyDP, was 0.40, 0.24, 0.27, 0.28, 0.55, 0.29, and 0.25 V, respectively. The experimental error for these values was within 10%.

Influence of Scan Rate on I_{pa}

Voltammograms of polyPhP and polyAnP were recorded for scan rate v in the 10–200 mV s^{-1} range. The I_{pa} versus v plots are shown in Figure 4. These plots demonstrate that the peak current tends to be proportional to v. These results suggest that the electrochemical behavior is limited by the electron transfer rate. This is in good agreement with a literature result for polyPhP in a mixture of polyvinylidene fluoride and carbon

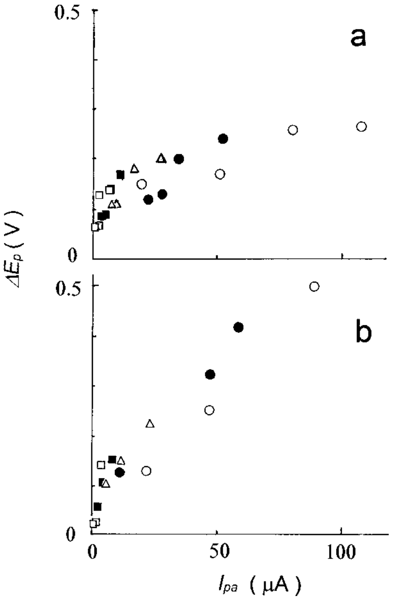

Figure 5 Plots of ΔE_p versus I_{pa} of (a) polyPhP and (b) polyAnP. Scan rate: (□) 10, (■) 20, (△) 50, (●) 100, and (○) 200 mV s^{-1}.

black.[13] From the electrochemical point of view, the difference between E_{pa} and E_{pc}, ΔE_p, gives an estimate of the rate of electron transfer. These values were measured for the polyPhP and polyAnP and are plotted against I_{pa} in Figure 5. The ΔE_p between polyAnP and polyPhP increased with the increase of I_{pa}. This means that the electron transfer process in polyAnP is slower than in polyPhP.

The anodic shift of oxidation potential can be explained by the change of electron transfer rate in the polymer film. What then changes the electron transfer rate in these polymer films? Novák and Vielstich studied electrochemical degradation of polypyrrole by nucleophilic contaminants such as water. Degradation of a conjugated polymer results in an anodic shift of its oxidation peak.[14] The substituent effect could be explained by the degradation: the conjugation system of polyAnP was cut during electrochemical preparation, because polyAnP was easily oxidized. However, degradation of the electronic structure cannot explain the relationship between the anodic shift of E_{ap} and the size of the substituent of the polymer.

The electron transfer rate can also be changed by the distance between polymer chains. Because a substituent of a polymer can act as a spacer between polymer chains, the electron transfer rate for a polymer that has large substituents is expected to be slow.

Because the larger anodic shift of E_{pa} is observed for polymers that have larger substituents, the size of the substituent is the controlling factor for the electron transfer rate in the polymer film.

Influence of Substituent on Oxidation Potential

The $E_{pa,0}$ of polyBP and polyPhP are more anodic than the others. The steric factor of phenyl is obviously larger than n-alkyl. The difference between anisyl and phenyl probably comes from their different electronic structures. On the other hand, the steric factor based on the van der Waals radius of butyl is almost the same as that of octyl and dodecyl.[7,8]

The low $E_{ap,0}$ of polyOP and polyDP may be explained by the interaction between substituents. The structure change of poly(3-alkylthiophene)s has been studied by many workers.[15] According to these results, most of the poly(3-alkylthiophene)s shows thermochromism, which could be the result of a change of the conjugation length along the polymer chain. This kind of phenomena was not observed for the polymers with short substituents. Therefore, long alkyl substituents in the polymer may order the structure of the polymer main chain.

CONCLUSIONS

The influence of the n-alkyl substituent in polySP does not appear on the electronic structure of the polymer molecule, instead appearing on the electrochemical behavior of the polymer film. The substituent acts as a spacer between polymer chains and controls the electron transfer rate in the polymer film.

REFERENCES

1. X.-L. Wei, Y. Z. Wang, S. M. Long, C. Bobeczko, and A. J. Epstein, *J. Am. Chem. Soc.,* **118,** 2545 (1996).
2. S. Hotta, S. D. D. V. Rughoopth, A. J. Heeger, and F. Wudl, *Macromolecules,* **20,** 212 (1987).
3. A. F. Diaz, J. Castillo, K. K. Kanazawa, J. A. Logan, S. Salmon, and O. Fajardo, *J. Electroanal. Chem.,* **133,** 233 (1982).

4. A. F. Diaz, J. Crowley, J. Bargon, and J. B. Torrance, *J. Electroanal. Chem.,* **121,** 355 (1981).
5. D. D. Cunningham, L. Lagure–Davidson, H. B. Mark, Jr., C. V. Pham, and H. Zimmer, *J. Chem. Soc., Chem. Commun.,* 1021 (1987).
6. R. W. Taft, in *Steric Effects in Organic Chemistry,* M. S. Newman, Ed., Wiley, New York, 1956, p. 556.
7. M. Charton, *J. Am. Chem. Soc.,* **97,** 1152 (1975).
8. M. Charton, *J. Org. Chem.,* **41,** 2217 (1976).
9. M. Holb and P. Ehrlich, *J. Polym. Sci.: Polym. Phys.,* **15,** 627 (1977).
10. Y. W. Park, M. A. Druy, C. K. Chiang, A. G. MacDiarmid, A. J. Heeger, H. Shirakawa, and S. Ikeda, *J. Polym. Sci.: Polym. Lett.,* **17,** 195 (1979).
11. H. Heaney and S. V. Ley, *J. Chem. Soc. Perkin I,* 499 (1973).
12. A. D. Josey and E. L. Jenner, *J. Am. Chem. Soc.,* **27,** 2466 (1962).
13. E. M. Genies, A. A. Syed, and M. Salmon, *Synth. Metals,* **11,** 353 (1985).
14. P. Novák and W. Vielstich, *J. Electrochem. Soc.,* **137,** 1036 (1990).
15. K. Tashiro, K. Ono, Y. Minagawa, K. Kobayashi, T. Kawai, and K. Yoshino, *J. Polym. Sci., Part B: Polym. Phys.,* **29,** 1223 (1991).