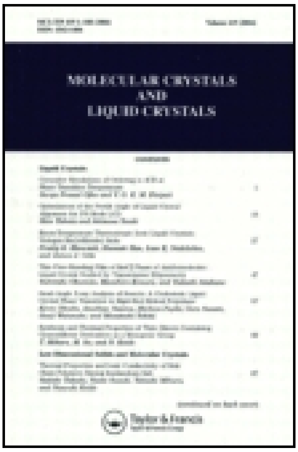

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Electrochemical Polymerization of Pyrrole Derivatives

T. Inagaki [a c] , M. Hunter [a] , X. Q. Yang [a] , T. A. Skotheim [a] , H. S. Lee [b] & Y. Okamoto [b]

[a] Division of Materials Science, Brookhaven National Laboratory, Upton, NY, 11973

[b] Department of Chemistry, Polytechnic University, Brooklyn, NY, 11201

[c] UBE Industries Fellowship Recipient

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Electrochemical Polymerization of Pyrrole Derivatives

T. INAGAKI†, M. HUNTER, X. Q. YANG and T. A. SKOTHEIM
Division of Materials Science, Brookhaven National Laboratory, Upton, NY 11973

and

H. S. LEE and Y. OKAMOTO
Department of Chemistry, Polytechnic University, Brooklyn, NY 11201

Electrochemical copolymerization of pyrrole and 3-(6-ferrocenyl-6-hydroxyhexyl)pyrrole (P-Fc) yields a ferrocene functionalized polypyrrole with a controlled amount of ferrocene functionalization.

Similarly, copolymers of pyrrole and 3-(4-(2,5-dimethoxyphenyl)butyl)pyrrole (P-MP) can be made by electrochemical polymerization and converted to the copolymers containing pH dependent electroactive hydroquinone moieties.

INTRODUCTION

Polypyrrole provides a unique substrate for the design of surface materials with specific electrochemical properties. Redox species can be incorporated in the polymer matrix utilizing their own chemical reactivities to effect the tailoring of surface catalysts or redox couple probes for electroanalytical techniques on a versatile electrode surface.

The methodologies reported for derivatizing polypyrrole films with electroactive species are: 1) chemical synthesis of derivatized pyrrole monomers followed by electrochemical polymerizations,[1–7] 2) cova-

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†UBE Industries Fellowship Recipient.

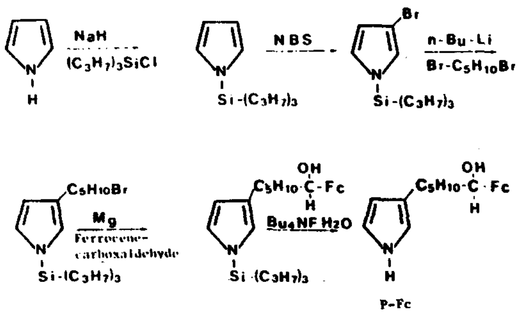
lent bonding to active sites in the polymer,[8] 3) incorporation of electroactive and electro-optic molecules as counterions.[9–13]

Here we report the synthesis and the electrochemical behavior of copolymers of pyrrole with 3-(6-ferrocenyl-6-hydroxyhexyl)pyrrole (P-Fc) or 3-(4-(2,5-dihydroxyphenyl)-butyl)pyrrole (P-HQ). These materials are of interest as modified electrodes for organic- and bioelectrochemistry.

EXPERIMENTAL

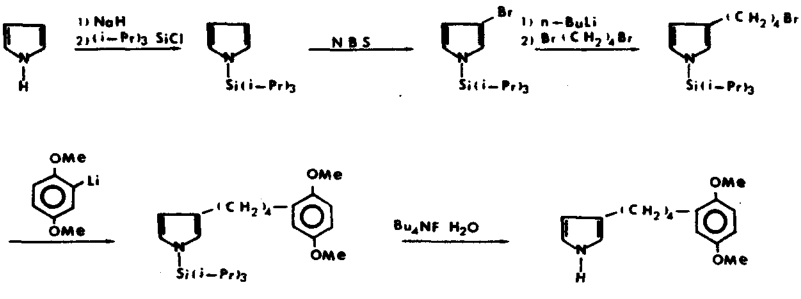
Preparation of derivatized pyrrole monomers

3-(6-Ferrocenyl-6-hydroxyhexyl)pyrrole (P-Fc) and 3-(4-(2,5-dimethoxyphenyl)butyl)pyrrole (P-MP) were prepared according to the following schemes.



Fc : Ferrocenyl Group

SCHEME 1 Preparation of 3-(6-ferrocenyl-6-hydroxy-hexyl)pyrrole



P-MP

SCHEME 2 Preparation of 3-(4-(2,5-dimethoxyphenyl)-butyl)pyrrole

Electrochemical polymerization

Thin polymer films (1000–5000 Å) were grown by electrochemical oxidation of monomers from acetonitrile (MeCN) solution on sputtered Pt-on-glass electrodes with a Pt counter electrode and a saturated calomel reference electrode. All potentials are referred to the saturated calomel electrode (SCE).

MeCN was freshly distilled twice over CaH_2 and tetraethylammonium tetrafluoroborate ($TEABF_4$) was recrystallized twice from MeOH. The solutions were thoroughly deoxygenated prior to polymerization. The films obtained were rinsed thoroughly with MeCN and placed in fresh $TEABF_4$-MeCN solution for cyclic voltammetry studies.

Copolymerization of P-Fc and pyrrole

Copolymer films of P-Fc and unsubstituted pyrrole were grown at a constant potential of 1.00 V and the charge passed was 100 mC/cm^2. Homopolymers of P-Fc were difficult to produce in thin film form and resulted only in uneven film deposits on the electrode. The copolymers were made from electrolyte-monomer solutions containing 0.02 M of P-Fc, 0.1 M of $TEABF_4$ and various concentrations of freshly distilled pyrrole (1.0 M, 0.5 M and 0.1 M) in MeCN. The thicknesses of films were determined with a Dektak surface profilometer (Sloan Technology Corporation), and were 4000 Å, 1600 Å and 1000 Å respectively.

Copolymerization of P-MP and pyrrole

The films were grown at a constant potential of 1.00 V and the charge passed was 30 mC/cm^2. The polymerization solutions contained 0.02 M of P-MP, 0.2 M of pyrrole and 0.1 M of $TEABF_4$ in MeCN. The films obtained were dipped into a solution of Me_3SiI in dried CH_2Cl_2 under N_2 atmosphere for 48 hr and subsequently washed with MeOH, aqueous $NaHCO_3$ solution and H_2O.[14] This resulted in a conversion of the dimethoxyphenyl moiety to dihydroxyphenyl moiety. The procedure for this conversion is shown in Scheme 3.

SCHEME 3 Conversion of Dimethoxyphenyl Group in the Copolymer to Dihydroxyphenyl Group

The cyclic voltammogram studies of these copolymer films were carried out in aqueous KCl (0.1 M) solution with various pH values. AcOH-NaOAc (total concentration of Acetate:0.1 M) was used as a buffer for pH values of 3.8, 4.6 and 5.5 and KH_2PO_4-K_2HPO_4 (total concentration of Phosphate: 0.1 M) for pH 7.1.

The cyclic voltammograms of these films were compared with those of hydroquinone (H_2Q) or methylhydroquinone (MH_2Q) (1.0 mM) in aqueous KCl (0.1 M) solution with the same series of buffers both with a bare Pt electrode and a polypyrrole-BF_4 coated Pt electrode. In the latter case, polypyrrole was freshly coated on a sputtered Pt-on-glass electrode from an acetonitrile solution containing 1.0 M of pyrrole and 0.1 M of $TEABF_4$ at a constant potential of 1.00 V with 35–45 mC/cm^2.

RESULTS AND DISCUSSION

Copolymer film incorporating ferrocene moiety

The cyclic voltammograms reveal two different redox processes corresponding to the reduction/oxidation of the polypyrrole backbone and the ferrocene moiety respectively. The $E^{1/2}$ value of the ferrocene moiety in the copolymer film is not appreciably different from that of the pyrrole-ferrocene monomer or unsubstituted ferrocene in solution (Figure 1).

The amount of ferrocene in the film can be controlled by varying the composition of the electropolymerizing solution as described in detail in a separate publication.[15] Higher relative concentrations of pyrrole-ferrocene results in less efficient film formation due to parasitic current for the oxidation of ferrocene.

Copolymer film incorporating hydroquinone moiety

Cyclic voltammograms in aqueous KCl solutions reveal a pH dependent electroactivity. The plots of $E^{1/2}$ values vs. pH values gave linear relationship with slopes of 47 ~ 56 mV/pH (Figure 2). $E^{1/2}$ values of H_2Q-Q with polypyrrole-BF_4 coated electrode are smaller than those with Pt electrode.

Figure 3 shows typical cyclic voltammograms of (a) H_2Q in solution with bare Pt electrode, (b) H_2Q in solution with polypyrrole-BF_4 coated Pt electrode, (c) polypyrrole and (d) copolymer possessing dihydroxyphenyl moiety. As can be seen from the large peak separation in Figure 3(a), the two electron reduction/oxidation of hydro-

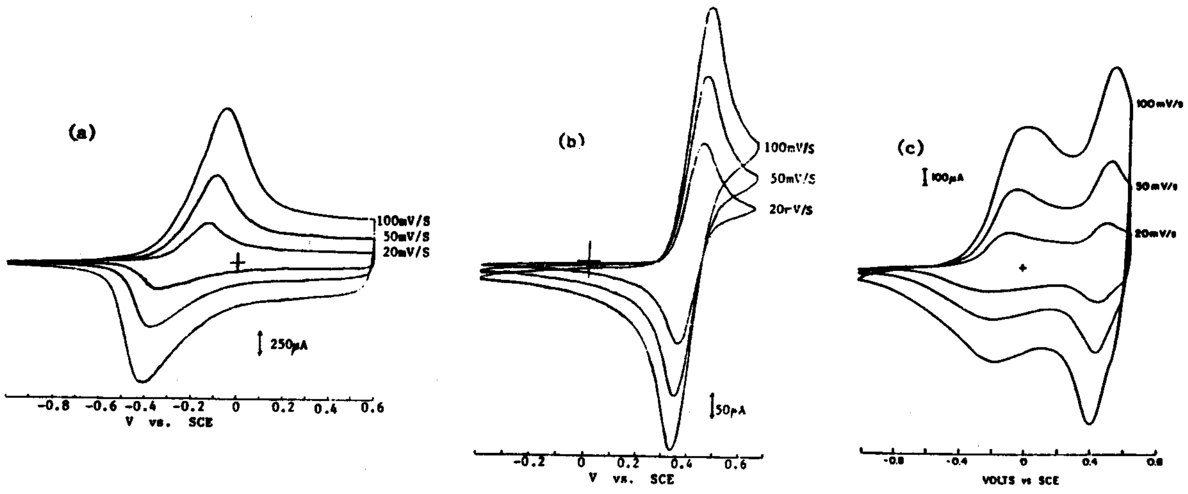


FIGURE 1 Cyclic voltammograms of: (a) Polypyrrole, (b) P-Fc monomer in MeCN, (c) copolymer of P-Fc with pyrrole with 0.1 M of $TEABF_4$ in MeCN.

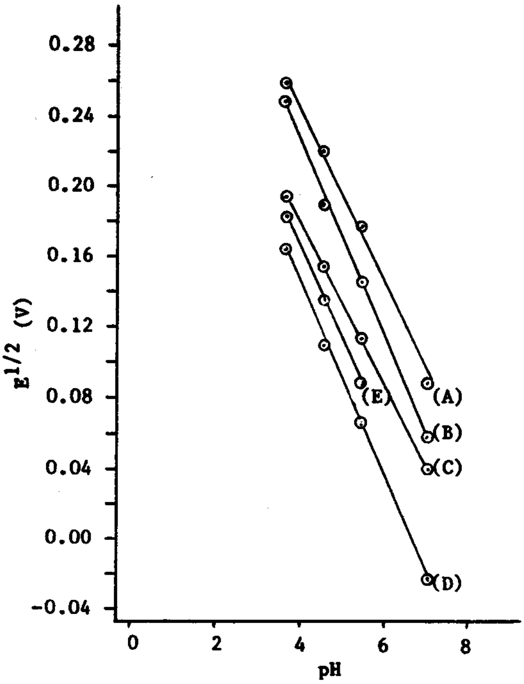


FIGURE 2 Relation between pH values and $E^{1/2}$ of H_2Q-Q redox system: (a) H_2Q in solution with Pt electrode; (b) H_2Q in solution with pp-BF_4 coated Pt electrode; (c) MH_2Q in solution with Pt electrode; (d) MH_2Q in solution with pp-BF_4 coated Pt electrode; (e) Dihydroxyphenyl group incorporated in the copolymer.

quinone (and also methylhydroquinone) is an irreversible process on a Pt electrode. The hydroquinone redox process is completely reversible on a polypyrrole coated Pt electrode, as seen in Figure 3(b) and appears to be electrocatalyzed by polypyrrole.[16] Similar behavior is observed for methylhydroquinone. Polypyrrole itself does not exhibit oxidation/reduction peaks in this voltage range (Figure 3(c)).

The redox process of hydroquinone (H_2Q) incorporated in the copolymer film is not perfectly reversible, as seen in Figure 3(d), with a peak separation of 115 ~ 175 mV. A reversible redox process for a surface bound species wold entail no peak separation since no diffusion of the electroactive species to the electrode surface is involved. The irreversibility may be associated with ion movement in and out of the polymer film. The reversibility of H_2Q in solution with polypyrrole coated Pt electrode may therefore be associated with a surface process wihtout movement of H_2Q in and out of the polypyrrole films.

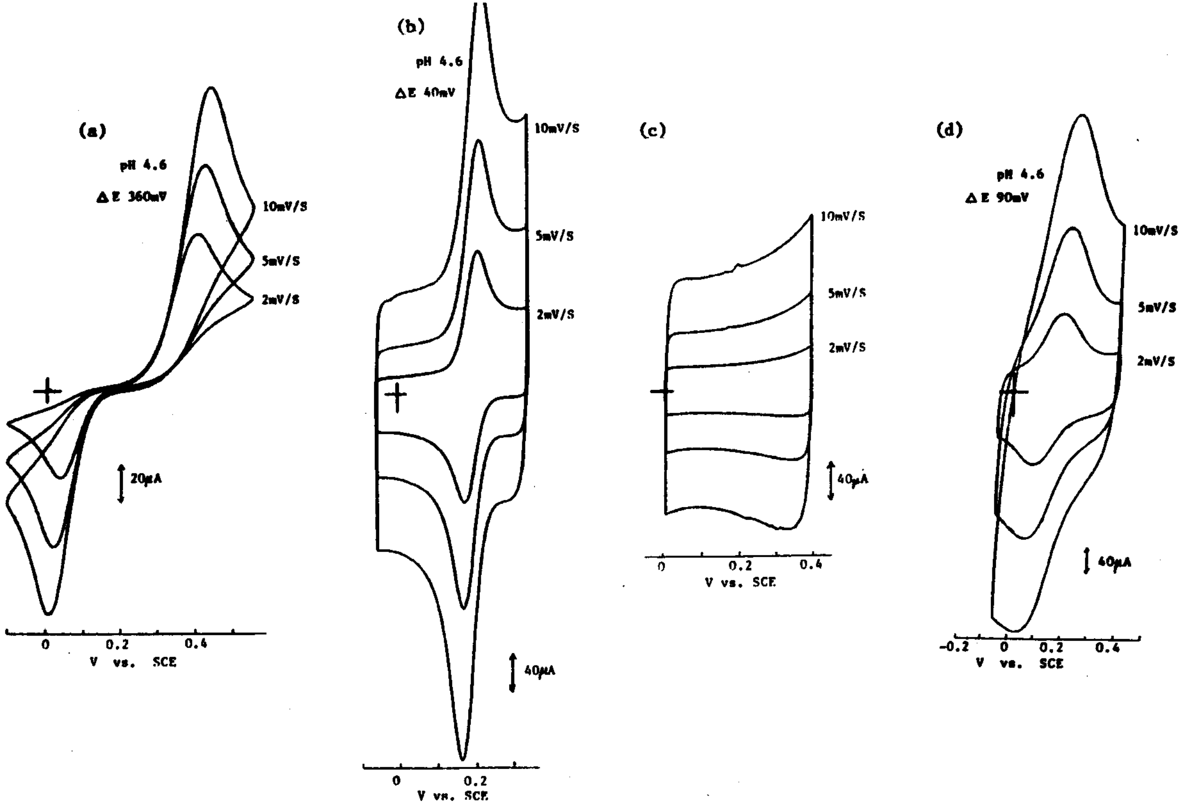


FIGURE 3 Cyclic voltammograms in KCl (0.1 M) aqueous solution with pH 4.6: (a) H_2Q in solution with Pt electrode; (b) H_2Q in solution with pp-BF_4 coated Pt electrode; (c) Polypyrrole-BF_4 deposited on Pt electrode; (d) copolymer incorporating dihydroxyphenyl group.

TABLE I

Cyclic voltammetry of H_2Q-Q system

		H_2Q in solution with Pt electrode		H_2Q in solution with pp-BF_4[a] on Pt electrode	
pH	Buffer	$E^{1/2}$ (V)	ΔE (mV)	$E^{1/2}$ (V)	ΔE (mV)
3.76	A	0.257	345	0.248	45
4.64	A	0.221	360	0.190	40
5.45	A	0.178	355	0.145	50
7.05	B	0.090	240	0.058	45

H_2Q: 1.0 mM; KCl: 0.1 M; Solvent: H_2O;
Buffer A: AcOH-NaOAc (Total Concentration of Acetate: 0.1 M)
B: KH_2PO_4-K_2HPO_4 (Total Concentration of Phosphate: 0.1 M);
Scan Rate: 2mV/S.
[a]For polymerization conditions, see text.

$E^{1/2}$ and ΔE values (peak-to-peak separation) of the hydroquinone/benzoquinone (H_2Q/Q) redox system under various pH values are summarized in Tables I, II and III.

CONCLUSIONS

We have described methods for systematically modifying polypyrrole films with electroactive groups to design electrode materials with specific electrochemical properties. The films obtained undergo redox reactions characteristic of the incorporated electroactive groups. The pyrrole polymer performs as an "organic wire," through which one

TABLE II

Cyclic voltammetry of MH_2Q-MQ system

		MH_2Q in solution with Pt electrode		MH_2Q in solution with pp-BF_4[a] on Pt electrode	
pH	Buffer	$E^{1/2}$ (V)	ΔE (mV)	$E^{1/2}$ (V)	ΔE (mV)
3.76	A	0.193	315	0.163	55
4.66	A	0.155	320	0.110	50
5.49	A	0.113	325	0.065	70
7.10	B	0.040	310	−0.023	55

MH_2Q: 1.0 mM; KCl: 0.1 M; Solvent: H_2O;
Buffer A: AcOH-NaOAc (Total Concentration of Acetate: 0.1 M)
B: KH_2PO_4-K_2HPO_4 (Total Concentration of Phosphate: 0.1 M);
Scan Rate: 2mV/S.
[a]For polymerization conditions, see text.

TABLE III

Cyclic voltammetry of H_2Q-Q system incorporated in the copolymer film[a]

pH	$E^{1/2}$ (V)	ΔE (mV)
3.76	0.183	115
4.64	0.135	160
5.45	0.088	175

KCl: 0.1 M; Buffer (AcOH-NaOAc) total Acetate: 0.1 M;
Solvent: H_2O; Scan Rate: 2 mV/S.

[a] For polymerization conditions, see text.

can perform specific reactions, such as electrocatalysis, or utilize these modified electrodes as probes in chemical analysis. The present work demonstrates that modifying the pyrrole monomer in the β-position does not interfere with the electroactivity of polypyrrole, in contrast to substitutions at the nitrogen atom. The electroactivity of the attached redox species is maintained in the polymer and the amount of electroactive species can be controlled by the polymerization condition. This allows a rational design of electroactive films.

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