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Choo Hwan Chang, Pyung Soo Son, Ji-Hoon Yang, and Seong-Ho Choi*

Department of Chemistry, BK 21 NanoBiosensor Research Team, Hannam University, Daejeon 305-811,
Republic of Korea
(2009. 1. 29 접수)

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(Received January 29, 2009)

주제어: Electrochemical polymerization, Functionalized pyrrole, 1-pyrrolyl-6-tetrahydropyranyloxyhexane, 6-pyrrolyl-hexane-1-ol, (*R*)-6-(pyrrolyl)hexyl 1-(naphthalenyl)ethylcarbamate

Keywords: Electrochemical polymerization, Functionalized pyrrole, 1-pyrrolyl-6-tetrahydropyranyloxyhexane, 6-pyrrolyl-hexane-1-ol, (*R*)-6-(pyrrolyl)hexyl 1-(naphthalenyl)ethylcarbamate

INTRODUCTION

Poly(pyrrole) and its derivatives have been received a great deal of attention due to its high electrical conductivity, good environmental stability, relatively easy synthesis and good redox reversibility. These properties are favorable to its applications in the areas of secondary batteries, electrocatalysis, electrochromic display devices, light-emitting devices, chemical sensors and biosensors.¹⁻⁵ However, poly(pyrrole) structure needs to be modified in order to use for the chemical sensor and biosensor fields because it has no functional group.^{6,7} Several approaches were tried to chemically introduce functional groups onto poly(pyrrole) backbone.^{8,9} Among them, copolymerization could be a desirable way because it not only provides facile functionalization but also improves chemical stability of the polymers.^{10,11}

The electrochemical polymerization is commonly

used for the fabrication of biosensors due to excellent electrocatalytic properties and rapid electron transfer ability of conducting polymers. Also, the conducting polymers permit a charge transfer to produce electrochemical signals between the electrode and the immobilized biomolecules.^{12,13} For the biosensor applications, the conducting polymers have been functionalized with carboxyl, amino, formyl or succinimidyl carbonate groups, and conjugated directly with various electronic mediators or bio-recognizable molecules to facilitate immobilization.

In our previous studies, we have prepared the poly(thiophene) with carboxylic acid groups in order to immobilize HRP via the copolymerization of thiophene and 3-thiopheneacetic acid in acetonitrile.¹⁴ However, the amounts of HRP on the surface of poly(thiophene) electrode with carboxylic acid groups are very low. We have also applied the Au nanoparticles as a spacer in order to

increase the immobilized HRP amounts.¹⁵ However, the lifetime of HRP for H₂O₂ sensing is short, because the HRP is degraded on the surface of polymer electrode. In order to overcome the short lifetime of HRP, the epoxy group-modified thiophene was synthesized, and then copolymerized with thiophene by electrochemical polymerization.¹⁶ We used the epoxy group to introduce the HRP for biosensor. However, there are only few reports about preparation of the poly-(pyrrole)-based polymer biosensor. Moreover, there was no report about synthesis of the functionalized pyrrole (F-Py) with ether, alcohol and amide groups, to our knowledge.

In this paper, we carried out electrochemical polymerization of the F-Py monomers on the ITO electrode surface, and electrochemical copolymerization of pyrrole in the presence of F-Py on ITO electrode. The obtained poly(F-Py) and Poly(Py-co-F-Py) conducting copolymers with functional group were characterized by SEM, AFM, and water contact angle, respectively.

EXPERIMENTAL

Chemicals

Pyrrole (Py), tetrabutylammoniumhexafluorophosphate (TBAF₆P), 1-bromo-6-tetrahydropyran-oxohexane, dimethylformamide (DMF), tetrahydrofuran (THF), acetonitrile, and *p*-toluenesulfonic acid were purchased from the Aldrich-Sigma chemical Co. (USA). (*R*)-(-)-1-(1-naphthyl)ethyl isocyanate was obtained from TCI Co., LTD. (Japan).

Instrumentation

The surface morphology of the samples was characterized by using field emission-scanning electron microscopy (FE-SEM, JSM-7000F, JEOL Ltd., Japan) and atomic force microscopy (AFM, PICO Station, Germany). Cyclic voltammetry was performed at 25 °C using a Potentiostat/Galvanostat model 283 (Ametek PAR, U.S.A). Fourier transform infrared (FT-IR) spectra were recorded in the range 400–4000 cm⁻¹ with a 4 cm⁻¹ resolution from

KBr pellets on a Perkin-Elmer Spectrum 1000 system (Perkin-Elmer life and analytical sciences, USA). Also, contact angle measurements were performed using a Phoenix 300 goniometer (Surface Electro Optics Co., Ltd., Korea).

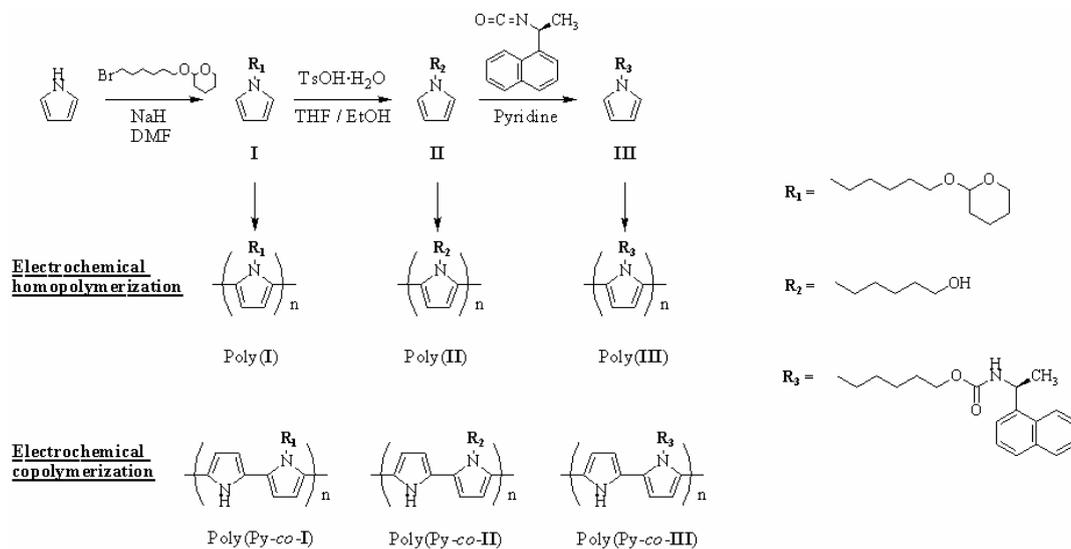
Synthesis of the F-Py (I, II, and III)

Scheme 1 shows the synthesis and electrochemical polymerization of the F-Py monomers. The detailed synthesis and electrochemical polymerization of F-Py is as follows:

Synthesis of 1-pyrrolyl-6-tetrahydropyran-oxohexane (I). I was synthesized by reaction of Py (14.0 mmol) and 1-bromo-6-tetrahydropyran-oxohexane (15.0 mmol) in DMF (40 mL) with 60% NaH (17.5 mmol) at 0 °C for 1 hr. Subsequently, the reaction was performed at room temperature for 3 hrs. The conversion yield was ~ 80.9%. TLC Rf : 0.7 Hexane/EA(5:1) as mobile phase. Spectroscopic data of I: ¹H NMR (CDCl₃, TMS): δ 6.6 (d, 2H, Py), 6.1 (d, 2H, Py), 4.6 (t, 1H, O-CH-O), 3.8 (t, 2H, N-CH₂-C), 3.7 (t, 2H, tetrahydropyran), 3.5 (t, 2H, C-CH₂-O), 3.3 (t, 2H, tetrahydropyran), 1.7 (t, 2H, tetrahydropyran), 1.5-1.3 (m, 10H, methylene).

Synthesis of 6-pyrrolyl-hexane-1-ol (II). II was synthesized by reaction of Py derivative (I) (7.6 mmol) and *p*-toluenesulfonic acid (0.05 mmol) in THF/EtOH 1:1 (100 mL) at room temperature for 20 hrs. The conversion yield was ~ 98.3%. TLC Rf : 0.1 methylene chloride as mobile phase. Spectroscopic data of (II): ¹H NMR (CDCl₃, TMS): δ 6.6 (d, 2H, Py), 6.1 (d, 2H, Py), 3.8 (t, 2H, N-CH₂-C), 3.6 (t, 2H, C-CH₂-OH), 1.7-1.2 (m, 8H, methylene). FT-IR (KBr): 3350 (OH), 1280 (C-N), 1500 (C=C) cm⁻¹.

Synthesis of (R)-6-(pyrrolyl)hexyl 1-(naphthalenyl)ethylcarbamate (III). III was synthesized by reaction of II (3.0 mmol) and (*R*)-(-)-1-(1-naphthyl)ethyl isocyanate (3.9 mmol) in pyridine (25 mL) at 90 °C for 24 hrs. The conversion yield was ~ 89.9%. TLC Rf : 0.5 Hexane/EA(5:2) as mobile phase. Spectroscopic data of III: ¹H NMR (CDCl₃, TMS): δ 8.1 (d, 1H, naphthalene), 7.8 (d, 1H, naphthalene), 7.7 (d, 1H, naphthalene), 7.5~7.4 (m, 4H, naphthalene), 6.6 (d, 2H, Py), 6.1



Scheme 1. Synthesis and electrochemical polymerization of pyrrole derivatives (I, II and III)

(d, 2H, Py), 4.9 (m, 1H, asymmetric center), 4.0 (t, 2H, C-CH₂-O), 3.8 (t, 2H, N-CH₂-C), 1.7~1.2 (11H, methylene and methyl). FT-IR (KBr): 3330 (N-H), 1700 (C=O) cm⁻¹. LC-MASS : 365.2

Electrochemical polymerization of pyrrole with functionalized pyrrole. Electrochemical polymerization of the F-Py such as I, II, and III was performed by cycling the potential between -2.5 V to +2.5 V in acetonitrile containing TBAF₆P as the background electrolyte, respectively. And the electrochemical copolymerization of the mixture of Py and the F-Py (I, II, and III) was also examined. The molar ratio of the Py:F-Py was fixed to be 2:1. All experiments were carried out with a conventional three-electrode system having ITO electrode (working area 0.7 x 1.1 cm², 10 resistance, Republic of Korea) as a working electrode, a platinum wire as an auxiliary electrode, and a Ag/Ag⁺ (containing 0.1 M acetonitrile) electrode as a reference electrode. Electro-oxidative polymerization and copolymerization were carried out in acetonitrile containing 0.05 M of TBAF₆P at a scan rate of 50 mV s⁻¹.

RESULTS AND DISCUSSION

Figure 1 shows the cyclic voltammograms

recorded during the electrochemical polymerization of Py (50 mM) (a), I (b), II (c) and III (d), and copolymerization with Py-I (e), Py-II (f), and Py-III (g) on ITO electrode in acetonitrile electrolyte containing 0.05 M TBAF₆P. The molar ratio of Py:F-Py was to be 2:1. In Figure 1(a), the starting oxidation peak of Py was appeared at +1.6 V, and the reduction peaks of poly(pyrrole) were observed at -1.2 V and -0.4 V in the CVs. L. Niggyuan and coworkers have published a possible mechanism for the polymerization of Py [10]. Electrochemical polymerization of F-Py and copolymerization with Py on an ITO electrode as a working electrode was also examined. The redox peak potentials of F-Py and a mixture of F-Py and Py were found to be slightly different from that pure poly(pyrrole).

Figure 2 represents the SEM images of poly(pyrrole) (a), poly(I) (b), poly(II) (c), poly(III) (d), poly(Py-co-I) (e), poly(Py-co-II) (f), poly(Py-co-III) (g) on the ITO electrode prepared by electrochemical polymerization. The surface morphology of the poly(pyrrole) electrode appeared fractal-like growth patterns with smooth surface. The electrodes were shown as round, well-featured pattern forms for poly(I), dotted pattern forms for poly(II), wrinkles pattern forms for

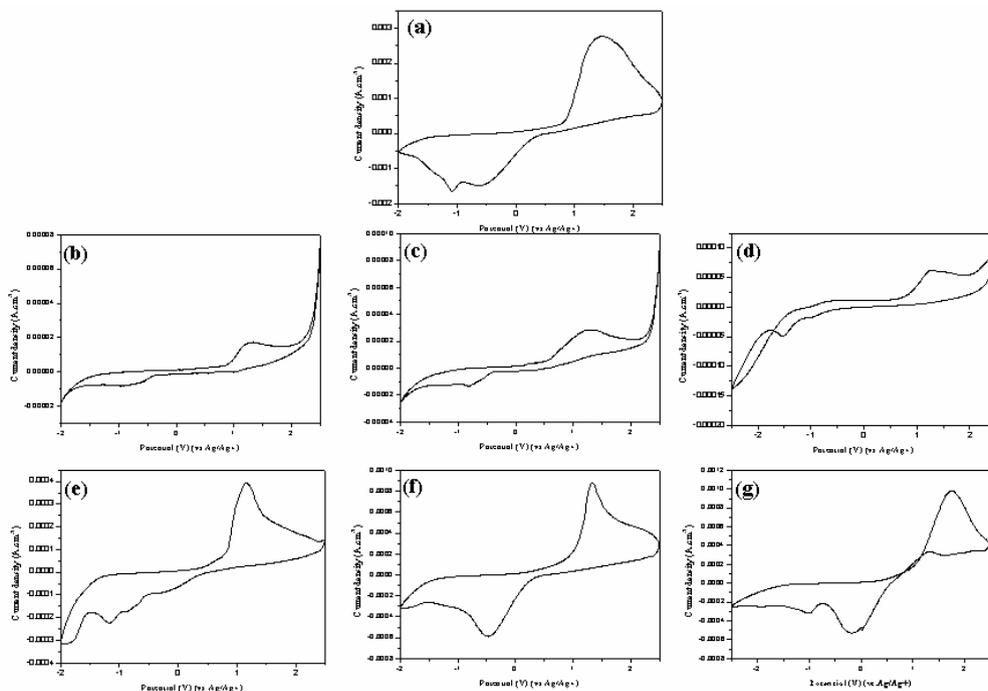


Fig. 1. Cyclic voltammograms recorded during electrochemical polymerization in acetonitrile containing 50 mM of TBAF₆P electrolyte. Scan rate 50 mVs⁻¹. poly(Py) (a), poly(I), poly(II) (c), poly(III) (d), poly(Py-co-I) (e), poly(Py-co-II) (f), and poly(Py-co-III) (g).

poly(III), respectively. On the other hand, the surface morphology of poly(Py-co-I), poly(Py-co-II), and poly(Py-co-III) was displayed as like spherical patterns, blend patterns, and amorphous patterns, respectively. As results, the functionalized conducting polymers were successfully prepared by electrochemical polymerization.

Figure 3 shows 3D projection images by AFM for poly(Py) (a), poly(I) (b), poly(II) (c), poly(III) (d), poly(Py-co-I) (e), poly(Py-co-II) (f), poly(Py-co-III) (g) prepared by electrochemical polymerization. The surface of poly(Py) film was very rough with fractal-like patterns, while the surface morphology of poly(I), poly(II) and poly(III) was dramatically changed to smooth fractal behavior.

Figure 4 represents the contact angle measurement images poly(Py) (a), poly(I) (b), poly(II) (c), poly(III) (d), poly(Py-co-I) (e), poly(Py-co-II) (f), poly(Py-co-III) (g) on ITO electrode prepared by electrochemical polymerization. The contact angle

of water at ITO glass surface was 73°. An decrease to 63° of the contact angle was noticed with a deposition of poly(Py). The contact angle of poly(I), poly(II) and poly(III) surface was at 67°, 55°, and 57°, respectively. The contact angle of poly(II) and poly(III) become much lower than 63° at poly(Py) surface due to increased hydrophilic properties from the hydroxyl and carbamate group. On the other hand, the contact angle of poly(Py-co-I), poly(Py-co-II) and poly(Py-co-III) was at 68°, 56°, 27°, respectively, because of changes in surface roughness between the polymer surface of poly(Py-co-F-Py) as shown by SEM and AFM images and the functional groups. Thus, the functionalized polymer electrodes can be successfully prepared. In order to know chiral sensing ability of a chiral polymer electrode, poly(III), we performed the chiral sensing for (D)-phenylalanine, (L)-phenylalanine, (D)-alanine, and (L)-alanine, respectively. However, the chiral sensing on chiral poly(III) electrode in phosphate buffer solution

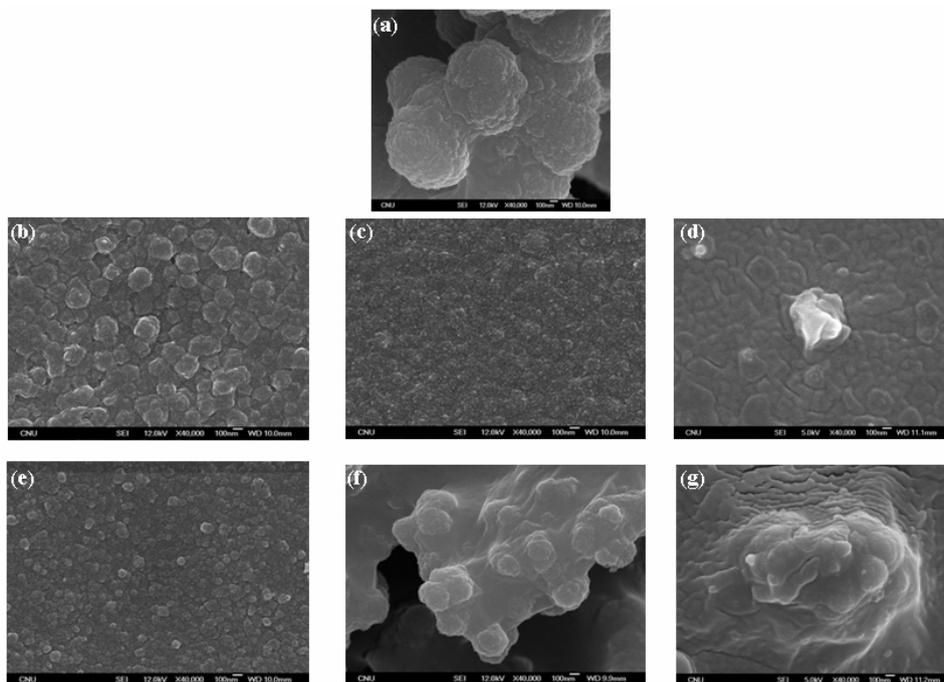


Fig. 2. SEM images(*40,000) of poly(Py) (a), poly(I) (b), poly(II) (c), poly(III) (d), poly(Py-co-I) (e), poly(Py-co-II) (f), and poly(Py-co-III) (g).

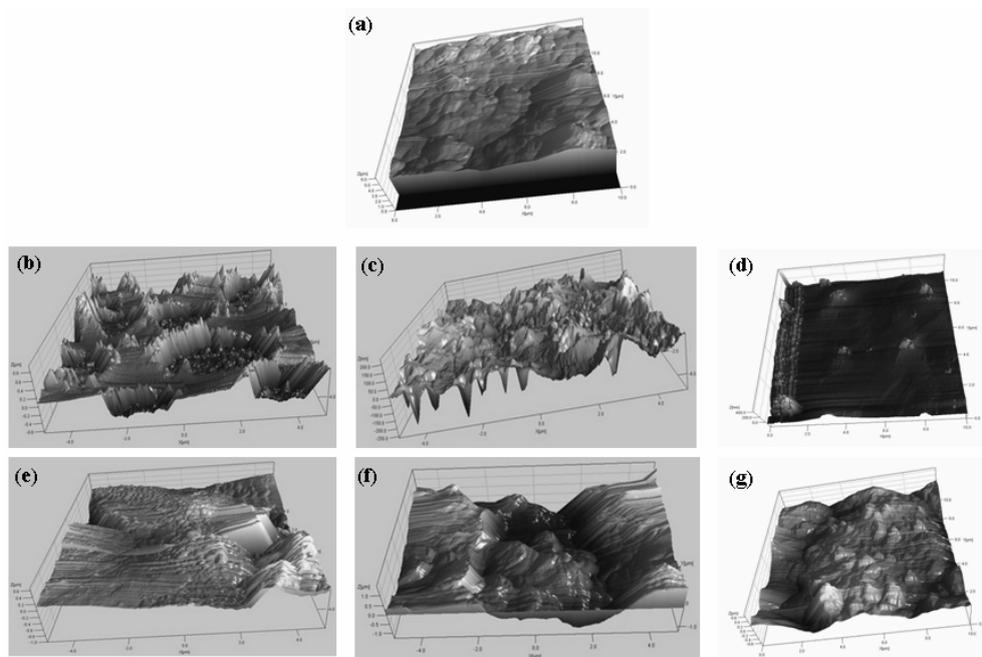


Fig. 3. AFM 3-D images of poly(Py) (a), poly(I) (b), poly(II) (c), poly(III) (d), poly(Py-co-I) (e), poly(Py-co-II) (f), and poly(Py-co-III) (g).

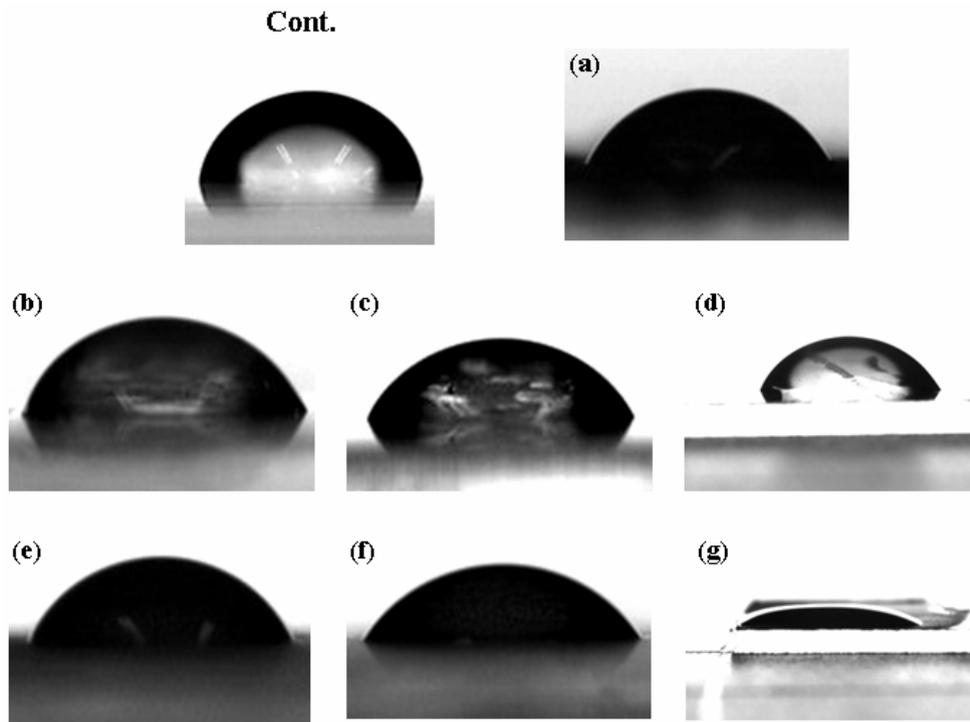


Fig. 4. Water contact angle for non-treatment ITO surface (Cont.), poly(Py) (a), poly(I) (b), poly(II) (c), Poly(III) (d), poly(Py-co-I) (e), poly(Py-co-II) (f), and poly(Py-co-III) (g). Angle of each samples; 75 (Cont.), 63 (a), 67 (b), 55 (c), 57 (d), 68 (e), 56 (f), 27 (g).

with amino acid can not be obtained. On the other hand, the functionalized polymer electrode with alcohol group can be used for biosensor after the enzyme immobilization.

CONCLUSION

From this study, we can prepare the novel functionalized conducting polymers by electrochemical polymerization of the new functional monomers based on pyrrole on an ITO electrode surface in acetonitrile. The functionalized polymer electrode with alcohol group can be used for biosensor after the enzyme immobilization.

Acknowledgments. This research was supported by the 2008 Hannam University Research Fund (2008A143).

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