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NOTES

Synthesis of New Polypyrroles by Oxidative Polymerization of *N*-(Benzylideneamino)pyrroles and Properties of the Polymers

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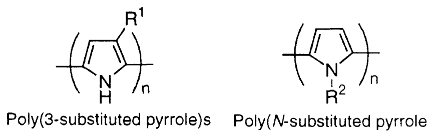
Polypyrrole has high and stable electrical conductivity in the doped state,[1–3] and has found its industrial application (*e.g.*, electrode for capacitors[3] and materials to remove static electricity). However, the polymer is insoluble, and its poor solubility and processibility have prevented revealing its basic properties (*e.g.*, optical properties) and chemical structure.[4] From this background, synthesis of soluble polypyrroles by introducing substituents and investigation on their chemical and physical properties have been carried out. For example, soluble poly(3-alkylpyrrole)s and poly(3-acylpyrrole)s shown in Chart 1 have been synthesized by electrochemical polymerization of the corresponding monomers.[5] Poly(*N*-alkylpyrrole) has also been prepared by electrochemical[6] and chemical[7] methods and they also show good solubility in common organic solvents. Preparation of new types of polypyrroles, however, is still desired from view points of basic polymer chemistry as well as development of industrially valuable materials.


Poly(3-substituted pyrrole)s Poly(*N*-substituted pyrrole)s

R^1 = $-(CH_2)_mCH_3$, $-CO(CH_2)_mCH_3$, etc.
R^2 = $-(CH_2)_mCH_3$, $-CH_2CH_2OH$, $-CH_2CH_2COCH_3$, etc.

Chart 1. Soluble polypyrroles.

We have also been concerned with π-conjugated polymers constituted of 5-membered ring hetero-aromatic units including polypyrroles, and herein report synthesis of new soluble type polypyrroles.

EXPERIMENTAL

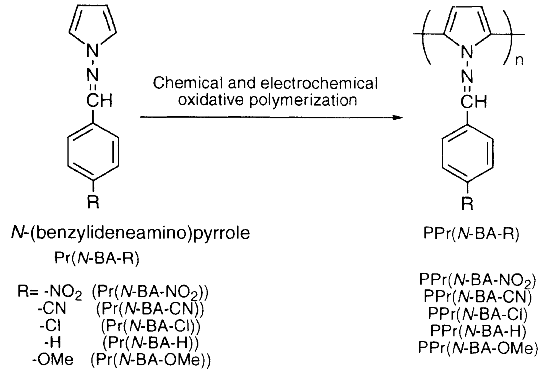
The polymers have been prepared by chemical and electrochemical oxidative polymerization of the following *N*-(benzylideneamino)pyrroles.

One of the monomers, Pr(*N*-BA–H), was prepared by a reaction of *N*-aminopyrrole and benzaldehyde according to the literature method.[8] Other monomers were prepared analogously, by using the corresponding benzaldehydes, as analytically pure compounds. The oxidative polymerization was carried out by using $FeCl_3$ (4.0 mol per 1 mol of Pr(*N*-BA–R)) in chloroform for 5 h at room temperature. The reaction mixture was poured into methanol to obtain a black preticipate, which was washed with methanol twice and dried under vacuum to yield the polymer. The polymer is considered to be formed as a *p*-doped material and *p*-undoped during the treatment in methanol. Polymers were obtained in 76—100% yield.

The electrochemical deposition of the polymer on a Pt-plate (1 cm × 1 cm) was carried out in a CH_3CN solution containing the monomer (0.01 M) and $[Et_4N]BF_4$ (0.1 M) at 1.0 V *vs.* Ag/Ag^+. The electrochemical polymerization of pyrrole proceeds at 1.0 V *vs.* Ag/Ag^+, whereas those of the present monomers required oxidation potential higher than 1.0 V *vs.* Ag/Ag^+.

RESULTS AND DISCUSSION

The chemical oxidative polymerization expressed by eq 1 proceeds smoothly at room temperature to give the corresponding poly[*N*-(benzylideneamino)pyrrole]s, PPr(*N*-BA–R)s, in 76—100% yields.



(1)

Among the monomers, those with the highly electron withdrawing substituents such as NO_2 and CN groups gave polymers, PPr(*N*-BA–NO_2) and PPr(*N*-BA–CN), which were highly soluble in organic solvents such as dimethyl sulfoxide (DMSO), *N*,*N*-dimethylformamide (DMF), and *N*-methylpyrrolidone (NMP). On the other hand, other monomers with $-C_6H_4Cl$-*p*, $-C_6H_5$, and $-C_6H_4OMe$-*p* yielded polymers that were insoluble in organic solvents. Since various electron-donating aromatic compounds are susceptible to the oxidative polymerization, the polymerization may also occur at benzene ring in the latter monomers, and the insolubility of these polymers seems to be attributable to the crosslinking due to additional oxidative polymerization at the side chain. On the other hand, the monomers with NO_2

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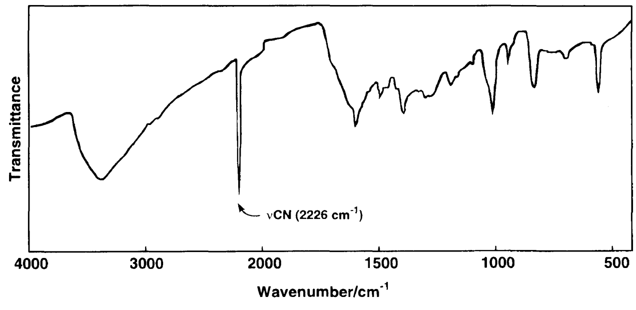

Figure 1. IR spectrum of PPr(*N*-BA–CN).

and CN groups do not seem to receive such side chain reaction.

The IR spectrum of PPr(*N*-BA–CN) (Figure 1) is reasonable for the structure of the polymer. The ν (C$\equiv$N) absorption peak at 2226 cm^{-1} has almost the same intensity as that of the corresponding monomer, indicating that cleavage of the –CH$=$N– bond during the polymerization, if any, is negligible. Polypyrrole is susceptible to various hydrogenation reaction, oxidation reaction, and substitution reactions and its solid ^{13}C NMR spectrum shows absorption due to aliphatic carbons,[4,9] however, the ^{1}H NMR spectrum of PPr(*N*-BA–CN) shows only signals due to aromatic and the –CH$=$N– protons in a range of δ 7.0—8.3. These results indicate that PPr(*N*-BA–CN) has high chemical stability and maintains the basic structure originated from the monomer unit.

PPr(*N*-BA–NO$_2$) and PPr(*N*-BA–CN) have number average molecular weights (M_n) of 6000 ($M_w/M_n=2.01$) and 9500 ($M_w/M_n=2.67$), respectively, as estimated by GPC (eluent: DMF; polystyrene standards).

UV-Vis spectra of PPr(*N*-BA–CN) and PPr(*N*-BA–NO$_2$) in DMF exhibited absorption peaks at 333 and 357 nm, respectively, with their onset at about 700 nm. The absorption peaks are shifted to longer wavelengths from those of monomers (Pr(*N*-BA–CN): 324 nm, Pr(*N*-BA–NO$_2$): 350 nm), however, the degree of the bathochromic shift is much smaller than those observed with pyrrole (210 nm)-polypyrrole (370 nm) and thiophene (230 nm)-polythiophene (420—480 nm) couples. The CPK molecular model as well as MOPAC (AM 1) calculation indicates twisting out of the main chain due to the presence of a steric repulsion between the N$=$CH hydrogen and 3-H in the pyrrole ring and this twisting of the main chain explains the small degree of the bathochromic shift. A film of PPr(*N*-BA–CN) showed a UV-Vis peak at 333 nm (the same position as that observed with the solution), and the film exhibited a shift of the absorption peak to 374 nm when doped with I$_2$.

The polymers, PPr(*N*-BA–R)s, can also be prepared by the electrochemical oxidation (eq 1). The electrochemical polymerization of the monomer required somewhat higher potential (*e.g.*, 1.0 V *vs.* Ag/Ag$^+$ for Pr(*N*-BA–CN)) compared with electrochemical polymerization of pyrrole, reflecting less electron-donating properties of the present monomer due to the electron-withdrawing imine –CH$=$N– nitrogen in the side chain. The electrochemical polymerization gives smooth films of the polymer. As for the electrochemically prepared PPr(*N*-BA–CN), it was obtained as a *p*-doped material with BF$_4^-$ dopant, and work up including treatment with MeOH gave undoped sample, which showed essentially the same IR spectrum as PPr(*N*-BA–CN) prepared by the chemical oxidation.

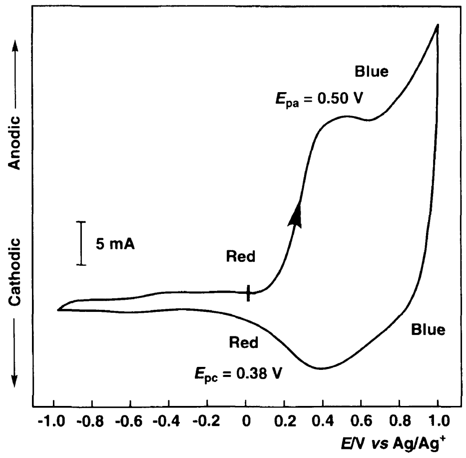

Figure 2. Cyclic voltammogram of the PPr(*N*-BA–CN) film on a Pt electrode in a CH$_3$CN solution of [Et$_4$N]BF$_4$ (0.10 M). Sweep rate$=$100 mV s^{-1}.

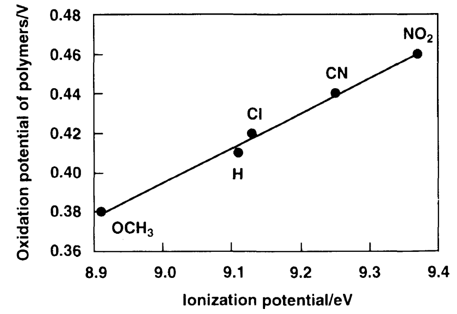

Figure 3. Oxidation potential of polymers *vs.* IP of monomer units. Oxidation potential is determined by CV. IP is estimated by MOPAC (AM 1) calculation.

Figure 2 shows cyclic voltammogram of the electrochemically prepared PPr(*N*-BA–CN) on the Pt-plate in an acetonitrile solution of [Et$_4$N]BF$_4$. The polymer film gives an electrochemically active cycle with an anodic peak at 0.50 V *vs.* Ag/Ag$^+$ and a cathodic peak at 0.38 V, which is about 0.3 V higher than the corresponding peak potential of polypyrrole, due to its having the electron withdrawing substituent in the side chain.[10] The electrochemically active cycle for the present polymers was stable during repeated scanning. The color of the film changes from red to blue on the electrochemical oxidation (or *p*-doping) and returns to red by the reduction (or *p*-undoping) as depicted in Figure 2. The polymer film was inert in the reduction region up to -1.0 V *vs.* Ag/Ag$^+$.

By the electrochemical polymerization, all of the monomers shown in eq 1 give polymer films on the Pt electrode. As shown in Figure 3, oxidation potential (E^0) of the polymers determined by the CV measurements increases linearly with increase in the ionization potential of the corresponding monomer Pr(*N*-BA–R) estimated by MOPAC (AM 1) calculation.

As described above, new poly[*N*-(benzylideneamino)-pyrrole]s have been obtained by the oxidation polymerization, and some of the polymers are soluble. They are electrochemically active and show electrochromism.

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