

# Soluble and Conductive Copolymers from 1-(Hydroxyalkyl) Pyrroles

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**ABSTRACT:** 1-Substituted pyrroles such as 1-(hydroxymethyl)pyrrole, 1-(3-hydroxypropyl) pyrrole, 1-*H*-1-pyrrolylmethyl 4-methyl-1-benzenesulfonate, 1-*H*-1-pyrrolylpropyl 4-methyl-1-benzenesulfonate, and 1-*H*-pyrrolylmethyl octanoate were synthesized and oxidatively polymerized and copolymerized with pyrrole by using  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$  and  $\text{FeCl}_3$ . Some of the copolymers were slightly soluble in

DMF and DMSO. The products were characterized by FTIR,  $^1\text{H-NMR}$ , and four-point probe conductivity. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 1830–1834, 2005

**Key words:** soluble polypyrrole; conducting polymers; solution properties; 1-hydroxyalkyl pyrrole; synthesis

## INTRODUCTION

Functional groups on the carbon or nitrogen atoms of the pyrrole ring were previously produced and polymerized to give derivatives of polypyrrole (PPy), and thus significant progress toward processibility and solubility of PPy derivatives has been made.<sup>1</sup> For example, 3-butyl sodium sulfonate pyrrole polymers and poly(3-alkylpyrrole) are soluble in some common organic solvents.<sup>2,3</sup> Because of the presence of 3,4-alkyl substituents, the crosslinking is hindered, and the processibility of poly(3,4-dimethylpyrrole) is greater than that of PPy.<sup>4</sup> Another way of obtaining soluble PPy is to use a special dopant. For example, PPy becomes solvent soluble if a long-chain dopant, such as dodecylbenzene sulfonic acid, is added to the reaction media during the polymerization.<sup>5</sup>

To improve electrochemical and/or thermal behavior of pyrrole-derived polymers, for instance, pyrrole-based liquid crystals<sup>6–8</sup> and 3-cyanopropyl pyrrole, pentafluorophenyl 1-*H*-pyrrole,<sup>9</sup> 1-substituted crown pyrroles,<sup>10</sup> and 1-alkyl pyrroles<sup>11</sup> were synthesized and polymerized. Attempts to electrochemically polymerize 1-hydroxyalkyl pyrroles and tosylated 1-hydroxyalkyl pyrroles were not successful because of the steric hindrance when the alkyl chain has 2 or 3 carbon atoms.<sup>12–14</sup>

The copolymerization of pyrrole with other monomers or oligomers also produces copolymers with various properties.<sup>15</sup> For example, pyrrole/1-

methylpyrrole copolymers have higher air and thermal stability than that of PPy.<sup>16</sup> Soluble and conductive polypyrrole copolymers have recently been produced with chemical oxidative polymerization with  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$  by using methyl ethyl ketone-formaldehyde resin<sup>17</sup> and silicon tegomers.<sup>18</sup> Their conductivities vary from  $10^{-6}$  to 6 S/cm, depending on the polymerization parameters such as the mole ratio of resin/pyrrole, the addition order of components, the concentration of Ce(IV), and the structure of the resin.

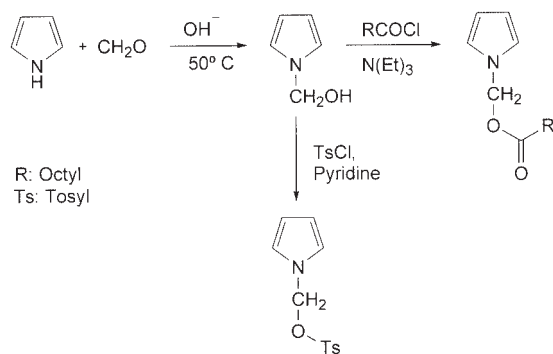
This article reports on the synthesis and polymerization of 1-hydroxyalkylpyrroles and their tosylated and octanoate ester derivatives, to produce conductive polymers. The effect of the substituted groups and the polymerization conditions on the conductivity and solubility of PPy copolymers were examined.

## EXPERIMENTAL

### Materials

Pyrrole (Py), acetonitrile,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , octanoyl chloride, DMSO, paraformaldehyde, 2,5-dimethoxy tetrahydrofuran, glacial acetic acid, 3-amino-1-propanol,  $\text{CHCl}_3$ , and benzyl(*N,N,N*-trimethyl) ammonium hydroxide were purchased from Merck (Darmstadt, Germany). Other products include DMF (Carlo Erba Reagenti, Milan, Italy); pyridine and  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$  (BDH AnalaR, Merck), THF (Riedel-de Haën, Seelze, Germany), and tosyl chloride (Fluka Chemika, Buchs, Switzerland).  $\text{CH}_2\text{Cl}_2$  and acetone were distilled before usage.

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Scheme 1

### Analyses

Infrared (IR) spectra were recorded on a Jasco FT-IR 5300 Fourier transform infrared spectrometer (Jasco, Tokyo, Japan).  $^1\text{H-NMR}$  spectra were obtained from  $\text{CDCl}_3$  solution on a Bruker AC (250 MHz; Bruker, Darmstadt, Germany).

### Conductivity measurements

To measure the electrical conductivity of polymers, compact thin pellets were prepared under 8–10 tons/ $\text{cm}^2$  pressure. Dimensions of a typical sample were 13 mm diameter and 0.8 mm thickness. Conductivity measurements of polymers were performed by the four-probe technique and calculated from the following equation:

$$\sigma = V^{-1}I(\ln 2 / \pi d_n)$$

where  $V$  is the potential in volts,  $I$  is the current in amperes, and  $d_n$  is the thickness of the samples in centimeters.

### Preparation of 1-hydroxymethyl pyrrole

Preparation of this starting molecule was adapted from a previously published method.<sup>19</sup> A mixture of pyrrole (0.20 mol), anhydrous paraformaldehyde (0.38 mol), and benzyl(*N,N,N*-trimethyl) ammonium hydroxide (1 mL 40%) was heated to 50°C under nitrogen atmosphere and restricted from light. After 15 min, paraformaldehyde was dissolved and the reaction became exothermic. Cooling was used to keep the

reaction temperature from rising above 50°C. After dissolving, the solution was kept at 45–50°C and stirred for 4 h. A yellow-colored crude product was obtained. The mixture was cooled and filtered, after which it was vacuum distilled at 55 to 60°C (1.5 mmHg).

FTIR data: 3400  $\text{cm}^{-1}$  (broadband OH), 3127 and 3104  $\text{cm}^{-1}$  (aromatic CH), 1565, 1500, and 1410  $\text{cm}^{-1}$  (C=C pyrrole ring), 1030  $\text{cm}^{-1}$  (C—O primer alcohol).  $^1\text{H-NMR}$  [in  $\text{CDCl}_3$ ,  $\delta$  (ppm)]: 3.81 (s, OH), 5.15 (s, 2H,  $\text{CH}_2\text{—OH}$ ), 6.24 (m, 2H, pyrrole ring), 6.73 (m, 2H, pyrrole ring).

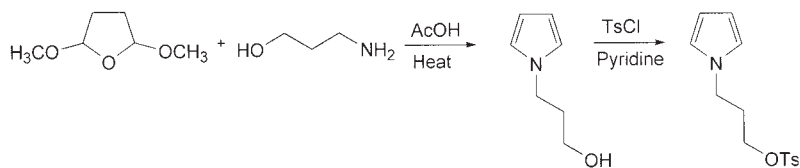
### Preparation of 1-*H*-pyrrolylmethyl octanoate

A mixture of 1-(hydroxymethyl)pyrrole (7 mmol) and triethylamine (1 mL) and dichloromethane (5 mL) was cooled at 0°C. Octanoyl chloride (7 mmol) was added by portions in 30 min. The crude product was cooled to  $-25^\circ\text{C}$  and filtered. Octanoic acid salt was separated as colorless crystal. 1-*H*-Pyrrolylmethyl octanoate was obtained as a red-brown semisolid.

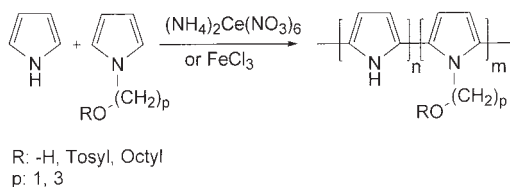
FTIR data: 3123 and 3106  $\text{cm}^{-1}$  (pyrrole CH aromatic), 2957, 2928, 2859  $\text{cm}^{-1}$  (octyl CH), 1744  $\text{cm}^{-1}$  (ester carbonyl), 1559, 1497, 1456  $\text{cm}^{-1}$  (pyrrole C=C).  $^1\text{H-NMR}$  data [in  $\text{CDCl}_3$ ,  $\delta$  (ppm)]: 0.88 (t,  $^3J = 6.5$  Hz, 3H), 1.25 (m, 6H), 1.59 (m, 2H), 2.30 (t,  $^3J = 7.5$  Hz, 2H), 5.79 (s, 2H), 6.19 (s, 2H, pyrrole ring), 6.82 (s, 2H, pyrrole ring).

### Preparation of 1-(3-hydroxypropyl)pyrrole<sup>20</sup>

3-Amino-1-propanol (5.7 mL) was added with efficient agitation to glacial acetic acid (11.4 g), and cooled in an ice-salt mixture at a rate such that the temperature was maintained at 15–25°C. When the addition was completed, 2,5-dimethoxytetrahydrofuran (3 mL) was added in one portion, and the reaction vessel was removed from the cooling bath and set up for downward distillation. The reaction flask was placed in an oil bath and the temperature was raised 100–120°C, at which point the distillation of a liquid began. After 1.5 h at this temperature some distillate had been collected. The residual liquid in the reaction vessel was cooled to room temperature, diluted with water, and the product was extracted with  $\text{CH}_2\text{Cl}_2$ . The extract was washed successively with saturated aqueous solutions of NaCl and  $\text{Na}_2\text{CO}_3$ , dried with  $\text{MgSO}_4$ , and then the solvent was removed in vacuum. The residue, which consisted mainly of 1-(3-hydroxypropyl) pyrrole and a lesser amount of the corresponding



Scheme 2



Scheme 3

acetate was dissolved in methanol; 20% NaOH (50 mL) was added, and the solution was maintained at room temperature for 1 h. The solution was poured into saturated NaCl solution (60 mL), the product was extracted into  $\text{CH}_2\text{Cl}_2$ , and the extract was dried with  $\text{MgSO}_4$ . The solvent was removed in vacuum, leaving an oily product.

FTIR data: 3395  $\text{cm}^{-1}$  (broadband OH), 3125 and 3100  $\text{cm}^{-1}$  (aromatic CH), 2934 and 2882 (CH), 1643, 1562, 1501, and 1450  $\text{cm}^{-1}$  (C=C aromatic), 1053  $\text{cm}^{-1}$  (C—O primer alcohol).  $^1\text{H-NMR}$  data [in  $\text{CDCl}_3$ ,  $\delta$  (ppm)]: 1.72 (m, 2H), 3.16 (s, OH), 3.57 (t,  $^3J = 6.7$  Hz, 2H), 4.02 (t,  $^3J = 6.8$  Hz, 2H), 6.21 (s, 2H), 6.72 (s, 2H).

#### Preparation of 1-hydroxyalkylpyrrole toluene-4-sulfonate esters

1-Hydroxymethyl pyrrole (0.06 mol) or 1-(3-hydroxypropyl) pyrrole was dissolved in 0.3 mol of dry pyridine. The flask was surrounded by a bath sufficiently cold to lower the temperature of the mixture to about  $0^\circ\text{C}$ . Toluene-*p*-sulfonyl chloride (0.07 mol) was added to this solution by portions to prevent the temperature from rising above  $0^\circ\text{C}$ . The mixture was stirred for 3 h at a temperature below  $20^\circ\text{C}$ . Then the solution was stirred at room temperature for an addi-

tional 2 h. The crude product was diluted and extracted with  $\text{CH}_2\text{Cl}_2$ , after which pyridine was neutralized by diluted HCl solution. The product was dried over  $\text{Na}_2\text{SO}_4$  and obtained as an orange oil.

#### Spectroscopic data of 1-*H*-1-pyrrolylmethyl 4-methyl-1-benzenesulfonate

FTIR: 3123 and 3104  $\text{cm}^{-1}$  (aromatic pyrrole and benzene CH), 2961, 2924, 2855  $\text{cm}^{-1}$  ( $\text{CH}_2$ ), 1595, 1500, 1402  $\text{cm}^{-1}$  (aromatic C=C), 1370 and 1171  $\text{cm}^{-1}$  (S=O), 1063  $\text{cm}^{-1}$  (S—O), 1020  $\text{cm}^{-1}$  (C—O), 955  $\text{cm}^{-1}$  (S=O).  $^1\text{H-NMR}$  [in  $\text{CDCl}_3$ ,  $\delta$  (ppm)]: 2.42 (s, 3H), 5.34 (s, 2H), 6.17 (m, 2H, pyrrole ring), 6.79 (m, 2H, pyrrole ring), 7.35 (d,  $^3J = 7.5$  Hz, 2H, benzene ring), 7.78 (d,  $^3J = 7.5$  Hz, 2H, benzene ring).

#### Spectroscopic data of 1-*H*-1-pyrrolylpropyl 4-methyl-1-benzenesulfonate

FTIR: 3124 and 3101  $\text{cm}^{-1}$  (aromatic pyrrole and benzene CH), 2957, 2928, 2895  $\text{cm}^{-1}$  ( $\text{CH}_2$ ), 1562, 1497, 1452  $\text{cm}^{-1}$  (aromatic C=C), 1367, 1157  $\text{cm}^{-1}$  (S=O), 1066  $\text{cm}^{-1}$  (S—O), 1020  $\text{cm}^{-1}$  (C—O), 956  $\text{cm}^{-1}$  (S=O).  $^1\text{H-NMR}$  [in  $\text{CDCl}_3$ ,  $\delta$  (ppm)]: 2.05 (m, 2H), 2.46 (s, 3H,  $\text{CH}_3$ ), 3.43 (t,  $^3J = 5.5$  Hz, 2H), 3.95 (t,  $^3J = 6.5$  Hz, 2H), 6.08 (m, 2H, pyrrole ring), 6.50 (m, 2H, pyrrole ring), 7.35 (d,  $^3J = 7.5$  Hz, 2H, benzene ring), 7.78 (d,  $^3J = 7.5$  Hz, 2H, benzene ring).

#### Polymerization procedure

The mixture of pyrrole and 1-hydroxyalkylpyrrole or its derivatives such as octanoates and tosylates, which were separately dissolved in acetonitrile, was prepared and  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  solution in acetonitrile was added to this mixture while stirring. After 1 h, the polymerization was halted and the dark precipitate

TABLE I  
Conductivity and Solubility Data of 1-Hydroxymethylpyrrole and Pyrrole Copolymers

No.	[Py]	[1-Hydroxymethylpyrrole]	[Fe(III)]	Conductivity (S/cm)	Solubility in DMF <sup>a</sup>
M1	0.150	0.151	0.187	$10^{-6}$	i
M2	0.150	0.002	0.187	0.2	i
M3	0.327	0.075	0.475	$10^{-4}$	i
M4	0.654	0.075	0.950	$10^{-3}$	i

<sup>a</sup> i, insoluble.

TABLE II  
Conductivity and Solubility Data of 1-*H*-pyrrolylmethyl Octanoate and Pyrrole Copolymers

No.	[Py]	[1- <i>H</i> -pyrrolylmethyl octanoate]	[CAN] <sup>a</sup>	Conductivity (S/cm)	Solubility in DMF <sup>b</sup>
PO1	0.225	0.045	0.270	$10^{-4}$	sl
PO2	0.315	0.045	0.360	$6 \times 10^{-5}$	sl
PO3	0.450	0.045	0.495	$2 \times 10^{-6}$	sl

<sup>a</sup> [CAN], cerium ammonium nitrate.

<sup>b</sup> sl, slightly soluble.

**TABLE III**  
Effect of Pyrrole and Cerium Ammonium Nitrate [CAN] Concentration on the Conductivity and Solubility of the Copolymers of 1-*H*-1-pyrrolylmethyl 4-methyl-1-benzene Sulfonate [0.02M] and Pyrrole

No.	[Py]	[CAN]	Conductivity (S/cm)	Solubility in <sup>a</sup>	
				DMF	DMSO
M S-1	0.05	0.07	$4 \times 10^{-3}$	sl	sl
M S-2	0.10	0.12	6	s	s
M S-3	0.20	0.22	$10^{-2}$	s	s
M S-4	0.10	0.06	6	i	i
M S-5	0.10	0.24	$5 \times 10^{-5}$	s	s

<sup>a</sup> s, soluble; i, insoluble; sl, slightly soluble.

was filtered and washed sequentially with acetonitrile and then with water several times. A similar polymerization procedure was carried out by using  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$  solution in acetonitrile instead of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  solution.

## RESULTS AND DISCUSSION

1-Hydroxymethylpyrrole was produced by the reaction of pyrrole with paraformaldehyde solution at a temperature below 50°C. Above this temperature, 1-hydroxymethylpyrrole rearranges to 2,5-dihydroxymethylpyrrole.<sup>19</sup> 1-Hydroxymethylpyrrole was reacted with octanoyl chloride or tosyl chloride to produce its appropriate derivatives (Scheme 1). Other 1-hydroxyalkylpyrroles and tosyl derivatives were synthesized accordingly (Scheme 2).

These monomers were polymerized and copolymerized with pyrrole using either ferric chloride or cerium ammonium nitrate in a homogeneous solution of acetonitrile with various oxidant to monomer mol ratios (Scheme 3).

The conductivity of the copolymers changed with the mol ratio of 1-hydroxymethylpyrrole and pyrrole (Table I). The copolymers are insoluble in organic solvents. The conductivity of poly(1-hydroxymethylpyrrole) was not determined because the preparation of a pellet from the polymer powder could not be achieved as a result of its electrostatic properties. However, a pellet was easily prepared from this homopolymer produced with 0.15M of 1-hydroxymeth-

ylpyrrole using 0.15M  $\text{NH}_4\text{S}_2\text{O}_8$  in an aqueous solution and the conductivity of the pellet was measured as  $10^{-4}$  S/cm.

The results are summarized in Table II for the copolymers of pyrrole and octaonate ester of 1-hydroxymethyl pyrrole. The copolymers are slightly soluble in DMF and DMSO and have conductivities of about  $10^{-4}$  S/cm. The solubility and conductivity of the copolymers produced from tosylated derivative of 1-hydroxymethyl pyrrole are seen in Table III. The copolymers of the pyrrole with this monomer show rather interesting properties. One of the copolymers (MS-2 in Table III) is soluble in both DMF and DMSO and has a conductivity value as high as 6 S/cm.

The results of the 1-(3-hydroxypropyl) pyrrole and pyrrole copolymers are shown in Table IV. These copolymers are completely insoluble and have low conductivity. Homopolymerization of this monomer gives a product with a conductivity of  $1.5 \times 10^{-6}$  S/cm and slight solubility in DMF. It was reported earlier that the electrochemical polymerization of this monomer and its tosylated derivative was not possible and it was suggested that the steric hindrance of alkyl chains of 2–3 carbon atoms inhibited the oxidative polymerization of pyrrole rings.<sup>11–13</sup> In this work, the tosyl derivative of 1-(3-hydroxypropyl) pyrrole could be copolymerized with pyrrole to yield some slightly soluble conducting copolymers (Table V).

## CONCLUSIONS

1-Hydroxyalkylpyrroles and their derivatives were chemically polymerized and copolymerized with pyrrole using  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$  and  $\text{FeCl}_3$ . By using appropriate ratios of these pyrrole-derived monomers to pyrrole both soluble and conductive copolymers could be produced. 1-Hydroxymethylpyrrole and 1-hydroxyalkylpyrroles were synthesized from pyrrole and from primary amines, respectively. These 1-hydroxyalkylpyrroles could be derived by the reaction of the hydroxyl group with the reagents such as acid chlorides, acid anhydrides, *p*-toluene sulfonyl chloride, and the resulting N-derived pyrrole monomers could be polymerized and copolymerized chemically to produce polypyrrole copolymers with differ-

**TABLE IV**  
Conductivity and Solubility Properties of the Copolymers of Pyrrole and 1-(3-Hydroxypropyl)pyrrole

No.	[Py]	[1-(3-Hydroxypropyl)pyrrole]	[Fe(III)]	Conductivity (S/cm)	Solubility in DMF <sup>a</sup>
P1	0.02	0.02	0.04	—	i
P2	0.06	0.02	0.08	$2 \times 10^{-4}$	i
P3	0.10	0.02	0.12	$3 \times 10^{-3}$	i
P4	0.20	0.02	0.22	$10^{-4}$	i

<sup>a</sup> i, insoluble.

**TABLE V**  
**Conductivity and Solubility Properties of TsPPy and Pyrrole Copolymers**

No.	[Py]	[TsHPPy]	[CAN]	Conductivity (S/cm)	Solubility in DMSO <sup>a</sup>
P M-1	0.1	0.02	0.12	10 <sup>-4</sup>	sl
P M-2	0.1	0.04	0.12	10 <sup>-5</sup>	sl
P M-3	0.1	0.08	0.12	10 <sup>-5</sup>	sl

<sup>a</sup> sl, slightly soluble.

ent chemical and physical properties. The physical properties, such as solubility and conductivity of the copolymers, could be changed by the type and concentration of the N-derived pyrrole monomer.

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