

# Electrochemical polymerization of chiral pyrrole derivatives in electrolytes containing chiral camphor sulfonic acid

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**Abstract:** *N*-Substituted pyrrole derivatives with chiral side groups have been synthesized and electrochemically polymerized in acetonitrile containing tetrabutylammonium perchlorate (TBAClO<sub>4</sub>) and (*S*)-(+)-camphor-10-sulfonic acid ((*S*)-(+)-CSA) or (*R*)-(–)-camphor-10-sulfonic acid ((*R*)-(–)-CSA). The resulting *N*-substituted polypyrrole films were characterized by cyclic voltammetry, infrared, Raman and X-ray photoelectron (XPS) spectroscopies. XPS results demonstrated that the as-grown polymer films are preferably doped by CSA anions when the monomer and the CSA anion have the same optical rotation dispersion (ORD). Furthermore, the conductivities of the polymers synthesized in the media containing CSA with the same ORD of the corresponding monomers were measured to be about 2–10 times higher than those of polymers obtained from electrolytes without CSA.

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**Keywords:** chiral pyrrole derivatives; electropolymerization; XPS; Raman spectra

## INTRODUCTION

Conducting polypyrroles have potential applications in many areas, such as electronics, electrochromic devices, polymeric batteries, antielectrostatic coatings and functional membranes.<sup>1</sup> Pyrrole derivatives have been synthesized and electropolymerized for fabrication of modified electrodes. Conducting chiral polymers are of considerable interest in view of their potential applications as electrodes for electrochemical asymmetric synthesis and stereoselective analyses.<sup>2,3</sup>

Most studies on chiral conducting polymers have concentrated on polypyrroles and polythiophenes. Salmon and Bidan<sup>4,5</sup> introduced (*S*)-(+)-camphor-10-sulfonic acid ((*S*)-(+)-CSA) with an alkyl spacer as a chiral graft to the nitrogen atom of pyrrole. Kotkar *et al*<sup>6</sup> introduced the (*S*)-(+)-(2-methylbutyl) group and (*S*)-(+)-(2-methylbutyl) group to the 3-position of thiophene, and the conductivity and mechanical properties of the freestanding chiral polymer were evaluated. The chiral pyrrole derivatives bring an optical active amide group at the 3-position of pyrrole ring and (*1S*)-(+)-*N*-(1-phenylethyl)pyrrole, (*1R*)-(–)-*N*-(1-phenylethyl)pyrrole were also synthesized and electropolymerized.<sup>7</sup> Pleus *et al*<sup>1,8</sup> reported the electrochemical polymerization of chiral pyrrole monomers containing (–)-ethyl L-lactate as the chiral

functional group either at nitrogen- or 3-position of pyrrole. They also investigated the properties of the polymer as enantioselective electrodes. Polypyrroles with amino acid substituents exhibit chirality in their main chain because of an asymmetric induction originating from the chiral substituents.<sup>9</sup> The chiral groups were introduced into pyrrole or thiophene by an alkyl spacer in previous papers.<sup>1,4–8</sup> Here, we report the polymerization and characterization results of *N*-substituted pyrrole with a chiral center bonded to a nitrogen bound atom or the chiral center to the nitrogen atom by an alkyl spacer.

## EXPERIMENTAL

### Chemicals

2,5-Dimethoxytetrahydrofuran (Acros 99 %), (*R*)-(–)-CSA (Fluka 98 %) and (*S*)-(+)-CSA (Fluka 98 %) were used without purification. All other chemicals were reagent grade. Acetonitrile (AN) was purified according to the literature,<sup>10</sup> and tetrabutylammonium perchlorate (TBAClO<sub>4</sub>) was dried under vacuum at 80 °C for 12 h before use. The *N*-substituted pyrroles were synthesized by condensation of 2,5-dimethyltetrahydrofuran with the primary amines according to published procedures (Scheme 1).<sup>11,12</sup>

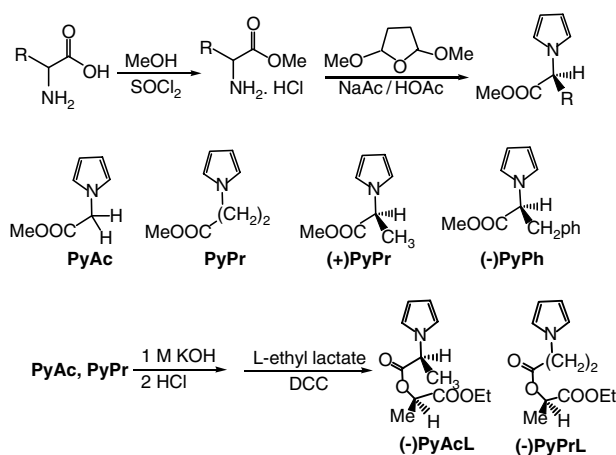
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Scheme 1. Synthesis of the *N*-substituted pyrroles used.

### Synthesis of methyl aminoacid ester hydrochloride

Excess  $\text{SOCl}_2$  (10 ml) was dropped into a suspension of aminoacid in anhydrous methanol. The mixture was stirred at room temperature for 2 h, and then the solution was refluxed for 30 min. After the solution was cooled to room temperature, diethyl ether was added and the precipitate was collected and dried under vacuum; yield: (75–90 %).

### Synthesis of pyrrole derivatives (PyAc, PyPr, (+)PyPr, (-)PyPh)

Methyl aminoacid ester hydrochloride (20 mmol) and anhydrous sodium acetate were dissolved into acetic acid (30 ml). The solution was heated to  $80^\circ\text{C}$  and stirred for 30 min, and 2,5-dimethoxytetrahydrofuran (3.0 ml) was added slowly into the solution under stirring. After a further 2 h reflux, the solution was diluted with water and extracted with dichloromethane. The organic phase was dried over anhydrous  $\text{MgSO}_4$  and solvents removed using a rotary-evaporator to give black oil. The rough product was purified by chromatography (silica gel, ethyl ether/petroleum ether = 1/3) and a light yellow oil was obtained; yield: ca 45 %.

*Methyl 2-(1H-pyrrolyl) acetate (PyAc)*.  $^1\text{H}$  NMR ( $\text{DCCl}_3$ ):  $\delta$  6.55 (m, 2H, 2,5-pyrrole H), 6.19 (m, 2H, 3,4-pyrrole H), 4.62 (s, 2H,  $-\text{CH}_2-$ ), 3.74 (s, 3H,  $-\text{OCH}_3$ ).

*Methyl 3-(1H-pyrrolyl) propionate (PyPr)*.  $^1\text{H}$  NMR ( $\text{DCCl}_3$ ):  $\delta$  6.64 (m, 2H, 2,5-pyrrole H), 6.12 (m, 2H, 3,4-pyrrole H), 4.18 (t, 2H,  $\mathcal{J} = 6.96$  Hz,  $\text{N}-\text{CH}_2-$ ), 3.67 (s, 3H,  $-\text{OCH}_3$ ), 2.75 (t, 2H,  $\mathcal{J} = 6.95$  Hz,  $-\text{CH}_2-$ ).

*Methyl (S)-(+)-2-(1H-pyrrolyl) propionate ((+)PyPr)*.  $^1\text{H}$  NMR ( $\text{DCCl}_3$ ):  $\delta$  6.74 (m, 2H, 2,5-pyrrole H), 6.18 (m, 2H, 3,4-pyrrole H), 4.76 (q, 1H,  $\mathcal{J} = 7.3$  Hz,  $-\text{COCH}-$ ), 3.70 (s, 3H,  $-\text{OCH}_3$ ), 1.71 (d, 3H,  $\mathcal{J} = 7.2$  Hz,  $-\text{CH}_3$ );  $[\alpha]_{\text{D}} = +6.13^\circ$  ( $\text{CHCl}_3$ ,  $c = 1.06$ ).

*Methyl (S)-(-)-3-phenyl-2-(1H-pyrrolyl) propionate ((-)PyPh)*.  $^1\text{H}$  NMR ( $\text{DCCl}_3$ ):  $\delta$  7.20 (m, 3H, 3, 4, 5-phenyl H), 7.01 (m, 2H, 2, 6-phenyl H), 6.71 (m, 2H, 2, 5-pyrrole H), 6.14 (m, 2H, 3, 4-pyrrole H), 4.74 (t, 1H,  $\mathcal{J} = 7.21$  Hz,  $\text{N}-\text{CH}-$ ), 3.68 (s, 3H,  $-\text{OCH}_3$ ), 3.28 (m, 2H,  $-\text{CH}_2-$ );  $[\alpha]_{\text{D}} = -83.8^\circ$  ( $\text{CHCl}_3$ ,  $c = 0.67$ ).

### Synthesis of pyrrole derivatives ((-)PyAcL, (-)PyPrL)

The compound PyAc or PyPr was dissolved in an ethanol/water mixture solution of 1 M KOH and hydrolyzed for 24 h at room temperature. The pH of the solution was adjusted to ca 3–4 by adding dilute HCl solution, the product was extracted with  $\text{HCCl}_3$ . The organic phase was dried over anhydrous  $\text{MgSO}_4$  and solvent evaporated using a rotary-evaporator to give a white powder (85 %). The white powder was dissolved in ethyl L-lactate (5 ml), a slight excess of  $\text{N,N}'$ -dicyclohexylcarbodiimide (DCC) added to the solution, and the mixture was stirred at room temperature for 24 h. Excess solvent was then evaporated under vacuum. The pure product (40 %) was obtained as light yellow oil through column chromatography (silica gel, ethyl ether/petroleum ether = 1/3 v/v).

*2-(1H-pyrrolyl) acetic acid-1-(S)-(-)-ethoxycarbonyl-ethyl ((-)PyAcL)*.  $^1\text{H}$  NMR ( $\text{DCCl}_3$ ):  $\delta$  6.65 (m, 2H, 2,5-pyrrole H), 6.17 (m, 2H, 3,4-pyrrole H), 5.09 (q, 1H,  $\mathcal{J} = 7.10$  Hz,  $-\text{CH}-$ ), 4.69 (s, 2H,  $\text{N}-\text{CH}_2-$ ), 4.18 (q, 2H,  $\mathcal{J} = 7.16$  Hz,  $-\text{OCH}_2-$ ), 1.46 (d, 3H,  $\mathcal{J} = 7.09$  Hz,  $-\text{CH}_3$ ), 1.24 (t, 3H,  $\mathcal{J} = 7.12$  Hz,  $-\text{CH}_3$ );  $[\alpha]_{\text{D}} = -45.7^\circ$  ( $\text{CHCl}_3$ ,  $c = 1.10$ ).

*3-(1H-pyrrolyl) propionic acid-1-(S)-(-)-ethoxycarbonyl-ethyl ester ((-)PyPrL)*.  $^1\text{H}$  NMR ( $\text{DCCl}_3$ ):  $\delta$  6.68 (m, 2H, 2,5-pyrrole H), 6.14 (m, 2H, 3,4-pyrrole H), 5.06 (q, 1H,  $\mathcal{J} = 7.07$  Hz,  $-\text{CH}-$ ), 4.22 (m, 4H,  $\text{N}-\text{CH}_2-$  and  $-\text{OCH}_2-$ ), 2.86 (t, 2H,  $\mathcal{J} = 6.99$  Hz,  $-\text{CH}_2-$ ), 1.46 (d, 3H,  $\mathcal{J} = 7.06$  Hz,  $-\text{CH}_3$ ), 1.27 (t, 3H,  $\mathcal{J} = 7.05$  Hz,  $-\text{CH}_3$ );  $[\alpha]_{\text{D}} = -45.1^\circ$  ( $\text{CHCl}_3$ ,  $c = 1.27$ ).

### Instruments

Electrochemical polymerization and characterization were performed in a one-compartment cell with platinum plate as working and counter electrodes with a model 283 potentiostat-galvanostat (EG & G Princeton Applied Research) under computer control. All the potentials were referred to a saturated calomel electrode (SCE). The solutions were degassed by bubbling dry  $\text{N}_2$  gas for 10 min prior to polymerization and a slight overpressure was maintained during experiments.  $^1\text{H}$  NMR spectra were recorded with a Bruker AC 200P spectrometer operating at 200 MHz. Optical rotation angles were measured with a WZZ-ZA automatic polarimeter. XPS examinations were carried out with a PHI5300 ESCA/610SAM spectrometer under a pressure lower than  $10^{-8}$  torr. Infrared spectra were recorded on an AVATAR 360 FTIR spectrometer

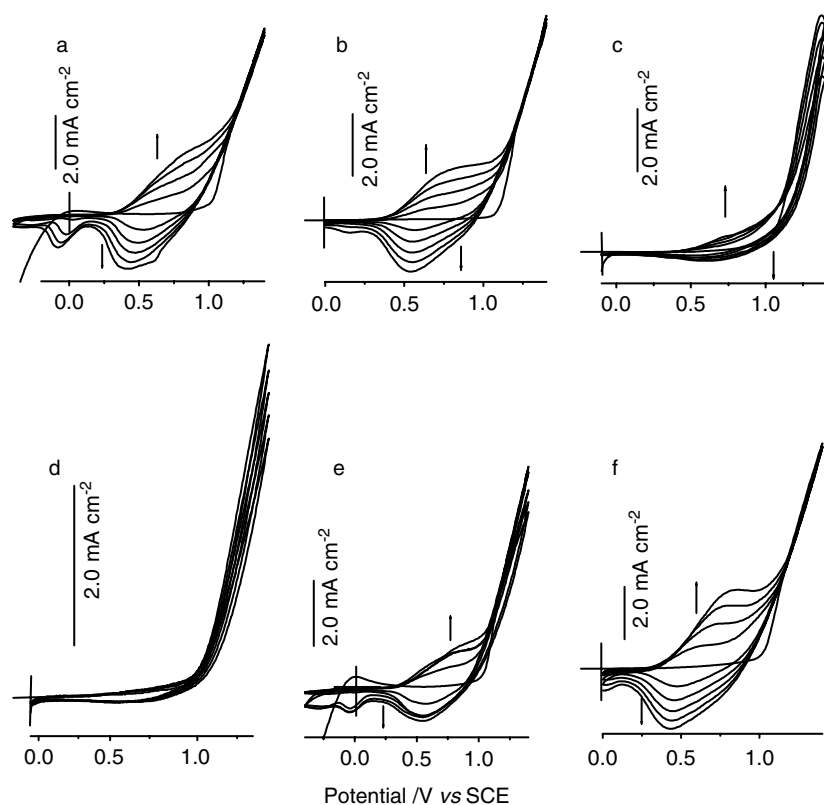
with KBr pellets. Raman spectra were recorded with a RM 2000 microscopic confocal Raman spectrometer (Renishaw PLC, UK) employing a 633 nm laser beam and a charge-coupled detector (CCD) with  $4\text{ cm}^{-1}$  resolution. The dc conductivity of the polymers was measured by the conventional four-probe technique.

## RESULTS AND DISCUSSION

### Electrochemical polymerization

Typical successive cyclic voltammograms (CV) of the monomers during the process of electrochemical polymerizations are shown in Fig 1 and the oxidation potentials of the monomers (corresponding to the

beginning of their oxidation processes) are listed in Table 1. The polymerization rates of monomers in acetonitrile containing only 0.1 M (*S*)-(+)-CSA or (*R*)-(–)-CSA are very low. In order to get a thin film in a convenient time period, a certain amount of TBAClO<sub>4</sub> (0.1 M) was added into the medium to increase the ionic conductivity of the electrolyte and accelerate the reaction. During the process of CV scanning, the color of the solution close to the working electrode surface changed from transparent to light brown because part of the monomer was oxidized into oligomers, which were dissolved or dispersed in the solution. Each CV showed a couple of broad redox waves of the polymer except that of



**Figure 1.** Successive voltammograms of 0.1 M monomer in acetonitrile containing  $0.1\text{ mol l}^{-1}$  TBAClO<sub>4</sub> +  $0.1\text{ mol l}^{-1}$  (*S*)-(+)-CSA: (a) PyAc; (b) PyPr; (c) (+)PyPr; (d) (–)PyPh; (e) (–)PyAcL; (f) (–)PyPrL at potential scan rate of  $50\text{ mV s}^{-1}$ .

**Table 1.** Oxidation potentials of various monomers (corresponding to the beginning of their oxidation processes) in different media<sup>a,b</sup>

Monomer <sup>c</sup>	$E_{\text{ox}}$ (V)			$(E_a + E_c)/2$ (V) and $(i_a/i_c)^d$		
	Medium 1	Medium 2	Medium 3	Sample 1	Sample 2	Sample 3
PyAc	1.11	0.99	1.02	0.74 (1.08)		
PyPr	1.09	1.03	1.02	0.57 (1.05)		
(+)PyPr	1.11	1.06	1.05	0.79 (1.33)	0.82 (1.50)	0.84 (2.21)
(–)PyPh	1.19	1.09	1.09			
(–)PyAcL	1.17	1.05	1.07	0.80 (1.29)	0.78 (1.22)	0.78 (1.17)
(–)PyPrL	1.10	1.02	1.03	0.69 (1.24)	0.67 (1.23)	0.67 (1.27)

<sup>a</sup> Medium 1, 2 and 3 represent the acetonitrile solutions of 0.1 M monomer and containing 0.1 M TBAClO<sub>4</sub>, 0.1 M TBAClO<sub>4</sub> + 0.1 M (+)CSA or 0.1 M (–)CSA, respectively.

<sup>b</sup> Samples 1, 2 and 3 represent the polymer films prepared from the acetonitrile solutions of 0.1 M monomers and containing 0.1 M TBAClO<sub>4</sub>, 0.1 M TBAClO<sub>4</sub> + 0.1 M (+)CSA or 0.1 M TBAClO<sub>4</sub> + 0.1 M (–)CSA, respectively.

<sup>c</sup> + and – indicate the optical rotation dispersion of the monomer.

<sup>d</sup> The electrochemical scan rate:  $50\text{ mV s}^{-1}$ .

Fig 1d. The increase of the redox wave currents of the polymer imply that the amount of the polymer on the electrode was increased. However, in the case of electrolysis of  $(-)$ PyPh, with CV scanning, the color of the solution changed from transparent to black brown, but no polymer film was formed on the electrode surface during the process of successive cyclic voltammetric scanning. The redox waves of the polymer were also not observed (Fig 1d). This is mainly due to the fact that the large grafted group of  $(-)$ PyPh close to the nitrogen atom increased the steric hindrance so that it is difficult for  $(-)$ PyPh to form long polymer chains. Therefore, the polymer could be dissolved into the electrolyte at low potentials and not deposited on the electrode during the CV process. The oxidation potentials of the monomers in acetonitrile solution containing both TBAClO<sub>4</sub> and CSA are *ca* 50–100 mV lower than those determined in acetonitrile solution containing only TBAClO<sub>4</sub> (Table 1). This is mainly due to the fact that CSA can increase the ionic conductivity of the media and that H<sup>+</sup> can catalyze the polymerization of pyrrole derivatives in accord with the fact that polymerization of pyrrole is catalyzed by an acid.<sup>13</sup>

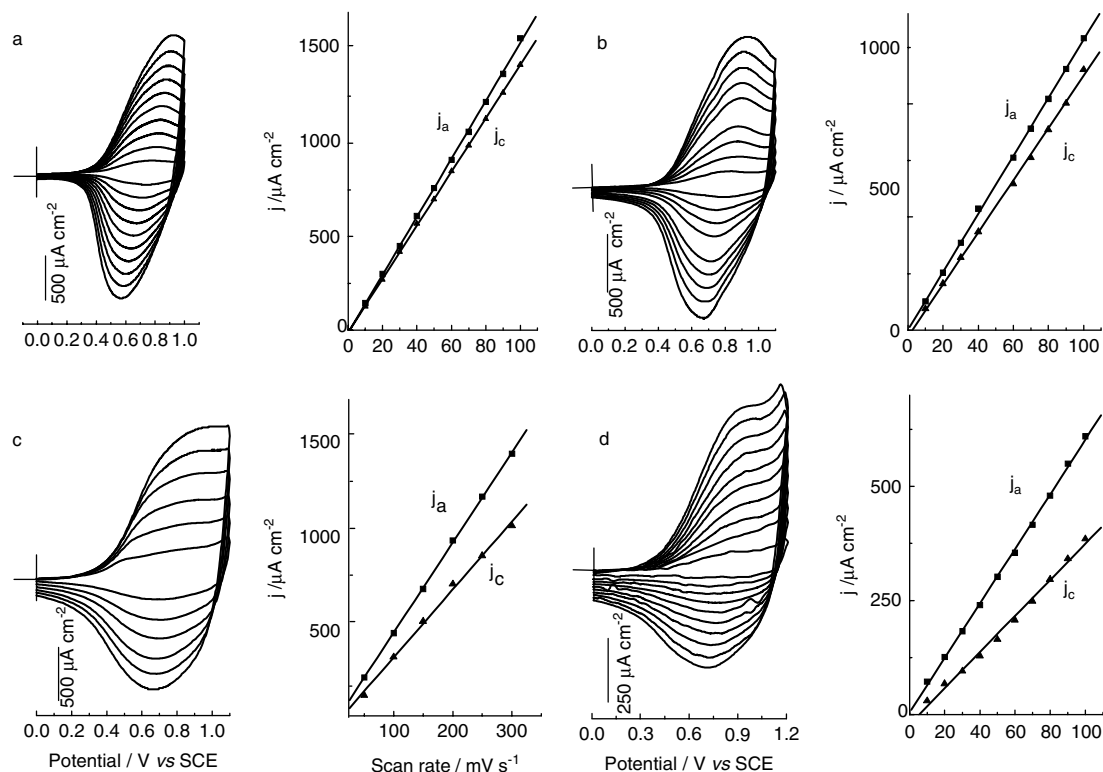
### Electrochemical studies

The electroactivity of the polymer samples described above were studied in monomer-free acetonitrile solutions containing 0.1 M TBAClO<sub>4</sub> as supporting electrolyte. Cyclic voltammograms and plots of wave

current density versus potential scan rate are illustrated in Fig 2. As can be seen from this figure, all the polymers show broad oxidation and reduction waves in the potential scale of *ca* 0.4–1.1 V and the polymers have good electrochemical stability. The oxidation and reduction potentials of these polymers are substantially more positive than those of polypyrrole and close to those of polypyrroles containing nitrogen substituents.<sup>7</sup> The wave currents have linear relationships with potential scan rates, which are the characteristics of mass transfer in the electroactive film on the electrode. The cyclic voltammetric data are summarized in Table 1 (data are based on three repeated experiments), and the current ratios of oxidation and reduction waves ( $i_a/i_c$ ) are also listed in Table 1. It can be seen from Table 1 that, in acetonitrile solutions of TBAClO<sub>4</sub>, the values of  $i_a/i_c$  are close to unity for the polymers made from monomers without chiral substituents (PyAc, PyPr), indicating a relatively reversible redox process. However, for polymers prepared from chiral monomers ( $(+)$ PyPr,  $(-)$ PyAcL, and  $(-)$ PyPrL),  $i_a/i_c$  ratios were higher than 1. This indicates that the redox process was relatively irreversible because the structure of the polymers prepared from chiral monomers may be relatively unstable during the redox process.

### Spectroscopic characterization

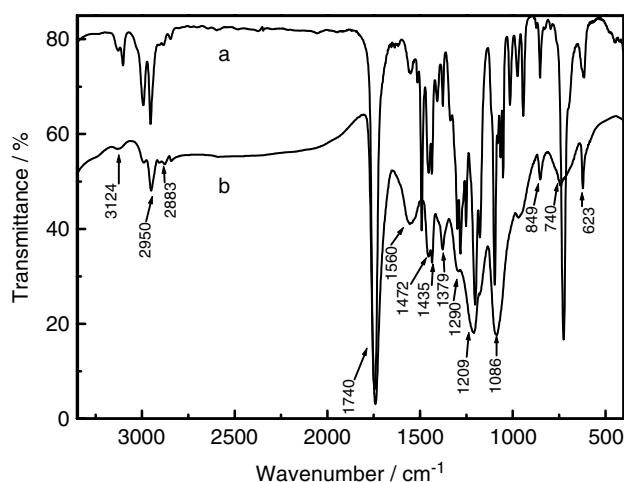
Doping levels of the polymer samples<sup>14–16</sup> were determined by XPS from the peak areas unified by



**Figure 2.** Cyclic voltammograms of as-grown polymer films in acetonitrile containing 0.1 M TBAClO<sub>4</sub> and plots of wave current density versus potential scan rate for polymers prepared from PyAc in acetonitrile solution containing 0.1 M TBAClO<sub>4</sub>, scan rate *ca* 10–100 mV s<sup>-1</sup> (a); from  $(-)$ PyAcL in acetonitrile solution containing 0.1 M TBAClO<sub>4</sub> and 0.1 M  $(R)$ - $(-)$ -CSA, scan rate of *ca* 10–100 mV s<sup>-1</sup> (b); from  $(+)$ PyPr in acetonitrile solution containing 0.1 M TBAClO<sub>4</sub>, scan rates of *ca* 50–300 mV s<sup>-1</sup> (c) and containing 0.1 M TBAClO<sub>4</sub> and 0.1 M  $(R)$ - $(-)$ -CSA, scan rate of *ca* 10–100 mV s<sup>-1</sup> (d).

atomic sensitivity factors of the core level spectra, and the atomic ratios of S/N (sulfur/nitrogen), Cl/N (chloride/nitrogen), (Cl + S)/N of the polymer samples are listed in Table 2. It is clear from this table that the total doping levels of the polymer samples are in the range *ca* 15–20%. In the case of (+)PyPr, a positive optical rotation monomer, the polymer prepared in acetonitrile solution of TBAClO<sub>4</sub> + (*S*)-(+)CSA has a higher S/N ratio (16.0) than that of the polymer obtained from the acetonitrile solution containing TBAClO<sub>4</sub> + (*R*)-(–)CSA (7.7). In contrast, the polymer prepared from a negative optical rotation monomer such as (–)PyAcL or (–)PyPrL in acetonitrile solution of TBAClO<sub>4</sub> + (*R*)-(+)CSA had a lower S/N ratio than that of the polymer obtained from the acetonitrile solution containing TBAClO<sub>4</sub> + (*S*)-(–)CSA. From these results we can imply that the polymers have some selectivity towards the doping anion when the doping anion and the monomer have the same optical rotation dispersion. Furthermore, it is also clear from Table 2 that the polymers prepared from (+)PyPr contained more CSA doping anions than those prepared from (–)PyAcL and (–)PyPrL. This is possibly due to the fact that the relative large steric hindrance of (+)PyPr increases the volume between the polymer chains, thus weakening the interactions between the polymer chains so that the film becomes looser; therefore the big doping anion CSA having large steric hindrance can be easily introduced into the polymer.

The IR spectra of the polymers are similar, and a typical IR spectrum of monomer (+)PyPr and its polymer in acetonitrile containing TBAClO<sub>4</sub> + (*R*)-(–)CSA are shown in Fig 3. Compared with the IR spectrum of the monomer, the peaks of the polymer are broader and the peak at 727 cm<sup>–1</sup> weakened, which is evidence that a polymer has been synthesized. In the spectrum of the polymer, the weak peak at 3124 cm<sup>–1</sup> is assigned to ring C–H stretching of pyrrole ring. The peaks at 2950 and 2883 cm<sup>–1</sup> are attributed to asymmetric methyl C–H stretching. The very strong peak at *ca* 1740 cm<sup>–1</sup> is due to the stretching of carbonyl groups; the peak at 1560 cm<sup>–1</sup> is assigned to ring C=C vibration; bands at 1472, 1435 and 1379 cm<sup>–1</sup> are due to C–N vibrations and C–H deformations. The 1290 cm<sup>–1</sup> band may be due to the C–C inter-ring stretching. The band at 1209 cm<sup>–1</sup> is assigned to the group of –COOR stretching and the band at 1086 cm<sup>–1</sup> is assigned to doped ClO<sub>4</sub><sup>–</sup>



**Figure 3.** FTIR spectra of monomers (+)PyPr (a) and P((+)PyPr) (b) prepared from acetonitrile solution containing 0.1 mol l<sup>–1</sup> TBAClO<sub>4</sub> and 0.1 mol l<sup>–1</sup> (*R*)-(+)CSA.

and C–O stretching modes. Bands at 849, 740 and 623 cm<sup>–1</sup> may be attributed to C–H deformations and CH<sub>3</sub> rocking.<sup>17–22</sup>

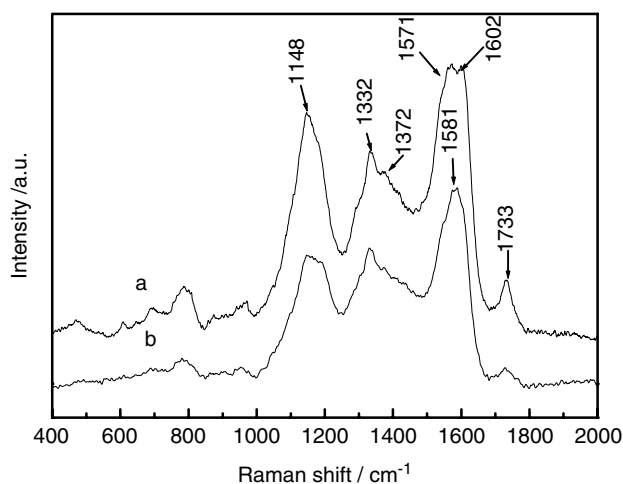
The Raman spectra of the monomers and CSA could not be obtained because of their low Raman activity. However, all the polymers showed Raman spectra with similar spectral characters. Typical Raman spectra of polymers prepared from (–)PyAcL in acetonitrile containing TBAClO<sub>4</sub> and (*R*)-(–)CSA are illustrated in Fig 4. The band at *ca* 1730 cm<sup>–1</sup> is assigned to the stretching of carbonyl groups. In the spectrum of as-grown polymer, the band at *ca* 1602 cm<sup>–1</sup> is attributed to the C=C bond stretching of the oxidized species and the band at *ca* 1570 cm<sup>–1</sup> is associated with the C=C stretching of the neutral species. The spectrum of reduced polymer sample, which was electrochemical reduced at –0.5 V versus SCE until the current was almost equal to zero, showed only one strong and broad band at *ca* 1580 cm<sup>–1</sup>, implying that the content in neutral species was increased in the polymer. The peaks at *ca* 1332 cm<sup>–1</sup> and 1372 cm<sup>–1</sup> are assigned to the ring stretching modes of polypyrrole. The broad band centered at *ca* 1148 cm<sup>–1</sup> originates from ring C–H deformations.<sup>21,22</sup> The spectral results described above confirm that the polymers have a structure of *N*-substituted polypyrrole and that the as-grown samples were in doped states.

**Table 2.** Relative atomic concentrations of as-grown polymers measured by XPS<sup>a,b</sup>

Polymer	P((+)PyPr)			P((–)PyAcL)			P((–)PyPrL)		
	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3
S/N × 100%	0	16.0	7.70	0	2.42	5.94	0	2.33	5.39
Cl/N × 100%	19.6	1.30	6.80	19.3	16.5	15.9	19.8	17.1	13.9
(Cl + S)/N × 100%	19.6	17.3	14.5	19.3	18.9	21.8	19.8	19.4	19.3

<sup>a</sup> Samples 1, 2 and 3 represent polymers prepared from acetonitrile solutions of 0.1 M monomers and containing 0.1 M TBAClO<sub>4</sub>, 0.1 M TBAClO<sub>4</sub> + 0.1 M (+)CSA or 0.1 M TBAClO<sub>4</sub> + 0.1 M (–)CSA, respectively.

<sup>b</sup> + and – indicate the optical rotation dispersion of the monomers.



**Figure 4.** Raman spectra of a polymer prepared from monomer (-)PyAcL in acetonitrile solution containing 0.1 M TBAClO<sub>4</sub> and 0.1 M (R)-(-)-CSA: (a) the film as-grown; (b) the film as reduced at -0.5 V vs SCE.

### Conductivities

Conductivities of the polymers were measured by using pressed discs of the polymers because free-standing films of the polymers could not be obtained. The conductivity of the polymers are listed in Table 3. It was found that both the monomer structure and the conditions of polymerization influence the electronic properties of the polymers. The conductivity of polymer P(PyAc) prepared by electrolysis of PyAc in acetonitrile solution of TBAClO<sub>4</sub> is about ten times lower than that of polymer P(PyPr) made from PyPr. This is possibly due to the fact that the carbonyl group of PyAc is closer to the pyrrole nitrogen atom, which causes a larger steric hindrance than PyPr. Furthermore, polymer P((+)PyPr) prepared from (+)PyPr in acetonitrile solution of TBAClO<sub>4</sub> has the lowest conductivity because this monomer bears the largest substituted group connected to the nitrogen atom of the pyrrole ring.

The conductivities of the polymer samples prepared from the monomer without chiral group, P(PyPr) or P(PyAc), are almost constant whether the electrolyte contained chiral CSA anions or not. However,

**Table 3.** Conductivities of the as-grown polymers prepared in different media<sup>a</sup>

Polymer <sup>b</sup>	Conductivity (S cm <sup>-1</sup> )		
	Sample 1	Sample 2	Sample 3
P((-)PyPrL)	$1.9 \times 10^{-4}$	$4.6 \times 10^{-4}$	$1.1 \times 10^{-3}$
P(PyPr)	$2.2 \times 10^{-4}$	$1.7 \times 10^{-4}$	$1.6 \times 10^{-4}$
P((-)PyAcL)	$3.3 \times 10^{-5}$	$6.9 \times 10^{-5}$	$4.4 \times 10^{-4}$
P(PyAc)	$2.5 \times 10^{-5}$	$2.9 \times 10^{-5}$	$2.1 \times 10^{-5}$
P((+)PyPr)	$6.4 \times 10^{-6}$	$2.2 \times 10^{-5}$	$1.1 \times 10^{-5}$

<sup>a</sup> Samples 1, 2 and 3 represent the polymer films prepared from acetonitrile solutions of 0.1 M monomer and containing 0.1 M TBAClO<sub>4</sub>, 0.1 M TBAClO<sub>4</sub> + 0.1 M (+)CSA or 0.1 M TBAClO<sub>4</sub> + 0.1 M (-)CSA, respectively.

<sup>b</sup> + and - indicate the optical rotation dispersion of the monomers.

P((-)PyAcL) or P((-)PyPrL), which bear a chiral group, and its monomer, show a negative optical rotation, and the conductivity of the polymer sample prepared in acetonitrile containing TBAClO<sub>4</sub> + (-)CSA was almost ten times higher than that obtained from the medium containing only TBAClO<sub>4</sub>. However, P((+)PyPr), shows positive optical rotation. It was found that the conductivity of the polymer sample prepared in acetonitrile containing TBAClO<sub>4</sub> + (+)CSA was almost twice that of the polymer sample obtained from the medium containing TBAClO<sub>4</sub> + (-)CSA, and about four times that of the polymer synthesized in the electrolyte containing only TBAClO<sub>4</sub>. These results demonstrate that polymers prepared from chiral monomers of pyrrole derivatives exhibit selectivity towards chiral CSA doping anions. When the structure of the doping anion fits the structure of the monomer or of the repeat units of the polymer chains, the contents of the CSA counter ions and the conductivities of the as-grown polymers are relatively high.

### CONCLUSION

Several pyrrole derivatives with nitrogen-substituted chiral groups can be electrochemically polymerized in acetonitrile containing TBAClO<sub>4</sub> as a supporting salt. The addition of chiral CSA into the solutions can lower the oxidation potentials of the monomers and accelerate their polymerization. The conductivity of as-grown polymers depend on the structure of the monomers and the conditions of electrolysis. Doping with chiral CSA counter-ions improved the electronic properties of the polymer. Furthermore, the as-grown polymer films favored doping by CSA anions with the same optical rotation dispersion as that of the monomer.

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