ORIGINAL PAPER

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Poly(pyrroles) containing chiral side chains: effect of substituents on the chiral recognition in the doped as well as in the undoped state of the polymer film

Abstract The chiral discrimination of different poly(pyrroles) grafted by chiral side chains was investigated both in the doped and undoped state of the polymer films. To verify the enantioselective properties in the doped state, cyclic voltammograms were recorded in acetonitrile in the presence of the enantiomers of camphorsulfonic acid and the potentiodynamic polymerization of the appropriate monomers was performed using the same chiral electrolytes. The enantiomericrecognition in the undoped state was investigated by the application of these modified electrode surfaces in the enantioselective electroreduction of the prochiral ketones 4-methyl benzophenone and 2,5-dimethyl benzophenone. One polymer exhibits a recognition ability in the doped state; the investigation for the undoped state is in progress. A second polymer does not show enantioselective properties either in the doped nor in the undoped state.

Keywords Poly(pyrrole) · Chiral modified electrodes · Chiral discrimination · Enantioselective Electrosynthesis

Introduction

From the viewpoint of chiral economy, the use of chiral chemically modified electrodes in enantioselective electrosynthesis has attracted electrochemists since 1975 [1, 2, 3, 4, 5]. This approach seems to be excellent, because asymmetric induction can be achieved using extremely small amounts of inducing reagent, permanently immobilized at an electrode surface. Moreover, the use of electrogenerated conducting polymers like poly(pyrrole) derivatives offers several advantages for the preparation of modified electrodes. Their electrochemical generation leads to direct precipitation on the electrode surface and allows the preparation of electrodes with a maximum density of chiral centers.

In 1984, Komori and Nonaka [6] reported the kinetic resolution of racemic 2,2-dimethyl-1-phenyl-1-propanol using a lead dioxide anode modified by poly-S-valine grafted onto a poly(pyrrole) film that itself was anchored at the electrode surface by chemical derivatization. In this case, 43% of optical pure S-enantiomer was recovered unreacted when the racemate was oxidized to the ketone. Moutet and co-workers [7] showed in 1998 that asymmetric induction in electrosynthesis can be achieved by the use of a carbon felt electrode modified by oxidative electropolymerization of a rhodium(III) complex catalyst with pyrrole-substituted chiral bipyridyl ligands. They performed the enantioselective reduction of prochiral aromatic ketones. The best optical yield (12%) was achieved for the hydrogenation of acetophenone. These are the only two examples found the literature for the application of conducting polymers in enantioselective electrosynthesis. Furthermore, the first example describes an application of poly(pyrrole) in the doped state whereas the second one discussesan application in the undoped state.

Our goal is the investigation of chiral discrimination of poly(pyrroles) grafted by chiral side chains in the doped as well as in the undoped state. We have recently reported the preparation of poly(pyrroles) from chiral monomers **1** and **2** (Fig. 1) via electropolymerization on Pt sheets and Pt/Rh grids in acetonitrile (AN) in the presence of various supporting electrolytes, including their electrochemical as well as their enantioselective behavior [8, 9, 10, 11].

Concerning the enantioselective behavior, both polymers (poly-**1**, poly-**2**) possess a chiral recognition ability in the doped as well as in the undoped state. To

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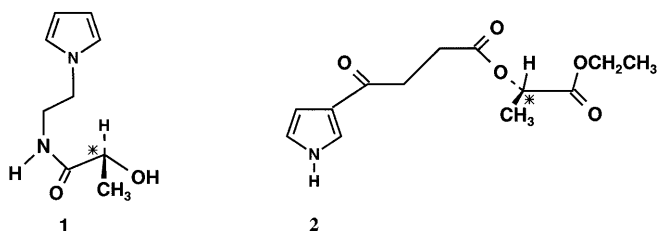E-mail: susanne.pleus@uni-oldenburg.de
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Fig. 1 Chiral pyrrole derivatives 1 [8] and 2 [8]

Fig. 2 Chiral pyrrole derivatives 3 and 4

verify the enantioselective properties in the doped state, the cyclic voltammograms recorded in AN using optically active supporting electrolytes, i.e. the enantiomers of camphor-10-sulfonic acid (CSA) [(S)-(+)-CSA, (R)-(−)-CSA)] were compared (the so-calledrecognition effect [12]). Owing to the low differences in current densities, the investigation of the film-forming abilities in solution in the presence of the enantiomers of CSA as supporting electrolyte was more meaningful. In both cases, electropolymerization was easily achieved in AN containing (S)-(+)-CSA. However, polymerization was completely inhibited using the R-enantiomer [9].

The enantioselective properties in the undoped state of the polymer-coated electrode surface were proved by the application of these electrodes in enantioselective electrosynthesis, i.e. by the electroreduction of prochiral ketones at these modified electrode surfaces.

One could also examine the chiral recognition in the doped state as well by an application in electrosynthesis, e.g. electrooxidation of a racemic alcohol. In fact the polymers are stable over a wide potential range (–3.0 to +1.1 V vs. Ag/0.01 M AgNO₃), but the anodic stability is the limiting factor for an oxidative reaction. In addition, we believe that a higher asymmetric induction can be expected for a reduction. In this case the prochiral compound has to diffuse through the insulating polymer film in order to react at the negatively charged electrode surface. The chiral environment forces the substrate in a definite geometric order, which is reflected by the extent of the asymmetric induction. On the other hand, during an oxidation the polymer film is conducting and the oxidative reaction of the substrate will occur mainly at the surface of the polymer. Therefore the influence of the chiral auxiliary on the substrate should be of minor importance.

The potentiostatically performed electroreduction of the prochiral aryl ketones 4-methyl benzophenone and acetophenone at poly-1 and poly-2 in DMF/LiBr in the presence of phenol as a proton donor led to optically purities up to 17% or 55% of the corresponding alcohols. The enantioselectivity depends on the substrate, the electrode material, and on the electrolyte used for the polymerization [10, 11].

We have extended our investigations to further pyrrole derivatives 3 and 4 (Fig. 2). A mirror image behavior of poly-3 compared to that of poly-1 is expected. We also report the use of poly-4 in the asymmetric reduction of prochiral benzophenones, i.e. 4-methyl

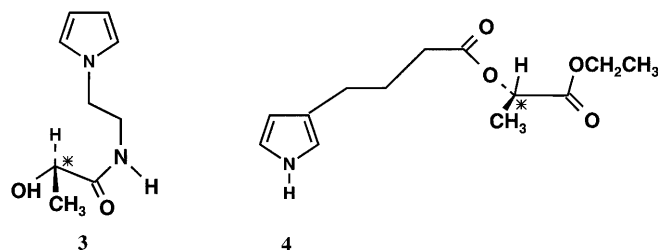benzophenone (5) and 2,5-dimethyl benzophenone (6). We compare the results with those obtained at poly-2 to investigate whether any influence could be observed of the carbonyl group in the α-position of the pyrrole nucleus on the enantioselectivity of the reaction.

The electrochemical behavior of poly-3 and poly-4 will also be presented and compared with poly-1, poly-2, and polypyrrole (PPy). For comparison purposes, all electrolyses were performed at bright platinum under the same conditions.

Experimental

Equipment

¹H NMR spectra were recorded on a Bruker AM 300 MHz instrument, using CDCl₃ as solvent and tetramethylsilane (TMS) as internal standard. Optical rotation was measured with a Perkin-Elmer polarimeter M343. TLC was performed on aluminum foil precoated with silica gel (Merck 60 F₂₅₄).

The electrochemical experiments were performed using a potentiostat (BANK POS 73) coupled with a Wenking model VS672 voltage scan function generator (BANK) and a x,y-recorder PM 8132 (Philips). The film preparations, the electrochemical investigations, and the electrolyses were performed in a three-compartment cell with working volumes of 10 mL for cyclic voltammetry and of 15 mL (anolyte) and 160 mL (catholyte) for electrolyses, respectively. The working electrode was a polymer-coated platinum sheet (1 cm² for cyclic voltammetry and 6 cm² for electrolysis, respectively) and the counter electrode a bright platinum sheet (1 cm²). An Ag/0.01 M AgNO₃ system was used as a reference electrode. The anolyte and catholyte compartments were separated by a fine-pore glass frit G3.

Materials

Monomer 3 was synthesized as outlined [8]. Instead of the ethyl L-(−)-lactate, the antipodean ethyl D-(+)-lactate was used as the chiral unit; $[\alpha]_D^{21} = +9.6°$ (CHCl₃, c 0.986). Monomer 4 was synthesized based on the literature [13]: starting from 2 [8] the reduction to 4 was accomplished with NaBH₃CN/ZnI in dichloroethane. A mixture of 1.4 g (5 mmol) of 2, 2.4 g (7.5 mmol) ZnI, and 2.35 g (37.5 mmol) NaBH₃CN in 50 mL dichloroethane was heated under reflux for 4 h, cooled, and 100 mL of cooled NH₄Cl/10% 6 M HCl were added. The layers were separated and the organic one was dried over Na₂SO₄. After evaporation of the solvent and purification by column chromatography on silica gel (eluent hexane/ether 2:1), 20% of 4 was obtained as a colorless oil; $[\alpha]_D^{21} = -23.5°$ (CHCl₃, c 1.25). ¹H NMR (CDCl₃) δ: 8.3 (br, 1H, NH), 6.7 (m, 1H, Hpyr), 6.6 (m, 1H, Hpyr), 6.1 (m, 1H, Hpyr), 5.1 (dd, 1H, CH), 4.2 (m, 2H, CH₂), 2.6 (m, 2H, CH₂), 2.5 (m, 2H, CH₂), 1.95 (m, 2H, CH₂), 1.5 (d, 3H, CH₃), 1.3 (m, 3H, CH₃). Analysis calculated for C₁₃H₁₉NO₄: C 61.64, H 7.56, N 5.53; found: C 60.36, H 7.80, N

5.37. 4-Methyl benzophenone was synthesized according to the literature [14]. 2,5-Dimethyl benzophenone (Aldrich), phenol (Merck), and AN (Scharlau, HPLC grade) were of commercial origin. DMF (Riedel de Haën) was dried over CaH_2, distilled under reduced pressure, and stored over 4 Å molecular sieve. LiBr (Fluka) was dried under high vacuum at 150 °C.

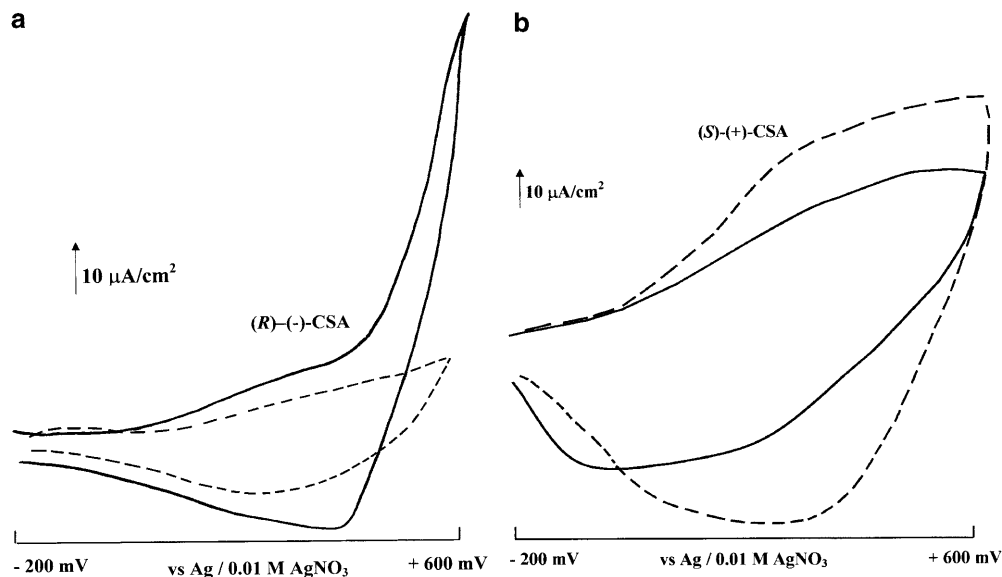### Electropolymerization and electrochemical characterization

Monomers **3** and **4** (0.1 M) were electropolymerized potentiodynamically on a platinum sheet electrode in AN in the presence of various electrolytes (0.1 M) [$LiClO_4$, Et_4NClO_4, Bu_4NClO_4, (R)-(–)-CSA, and (S)-(+)-CSA] as outlined [9]. For comparison purposes, PPy was deposited under the same conditions using AN/$LiClO_4$ [9]. The electrochemical investigations were carried out in monomer-free solutions of the same concentration of supporting electrolytes as the ones used previously [9]. All solutions were degassed by purging with argon for 20 min prior to electrochemical investigation. To compare the different polymer films, the deposition process was stopped as soon as a peak current density of 50 $\mu A\ cm^{-2}$ for the respective polymer oxidation was noted. After polymerization the films were reduced at –200 mV in case of poly-**3** and at –500 mV in case of poly-**4** until the current was negligible. The coated electrodes were rinsed several times with dry AN to eliminate residual traces of monomer and stored in AN.

Enantioselective properties

The investigation of the enantiomeric recognition in the doped state was performed by cyclic voltammetry in the presence of the enantiomers of CSA as described previously [9].

The proof of chiral recognition in the undoped state was realized by the electroreduction of the ketones **5** and **6**. The reduction potentials of **5** and **6** were determined by cyclic voltammetry as peak potentials vs. $Ag/AgNO_3$ in the same electrolyte as used for preparative electrolysis (DMF/LiBr) [10, 11]. Thus 30 mmol of **5** or **6** were potentiostatically reduced in DMF/0.5 M LiBr at –2.2 V vs. $Ag/AgNO_3$ in the presence of phenol (60 mmol) as proton donor as described previously [10, 11]. The electrolysis was stopped after 2×10^{-2} F had been consumed. The optical yield of the reduction product of **5**, phenyl(p-tolyl)methanol (**5a**), was determined by the optical rotation of the phthalic monoester [15, 16]. The enantiomeric excess of the corresponding alcohol of **6**, 2,5-dimethylphenyl(phenyl)methanol (**6a**), was determined by HPLC using a (R,R)-Whelk-0-1 (Merck) column.

Results and discussion

Poly-3

Enantioselective properties

In order to verify the enantioselective properties of poly-**3** in the doped state, we compared the cyclic voltammograms recorded in AN using the enantiomers of CSA. As shown in Fig. 3a, a mirror image behavior for poly-**3** compared to poly-**1** (Fig. 3b [9]) was observed. This means higher current densities were noticed in presence of the *R*-isomer for poly-**3**, whereas the antipodean poly-**1** shows higher current densities in the presence of the *S*-enantiomer.

Concerning the film-forming ability of monomer **3** in the presence of the enantiomers of CSA as supporting electrolyte, as shown in Fig. 4 a mirror image behavior compared to **1** was observed as well. Electropolymerization of **3** can easily be achieved in AN containing *R*-CSA (Fig. 4a). In contrast to **1** (Fig. 4c and d [9]), the polymerization of **3** is completely inhibited using the *S*-enantiomer (Fig. 4b). Compound **3** polymerizes in the racemic mixture of CSA as well as **1** [9].

In summary, poly-**3** exhibits enantioselective properties in the doped state. The expected mirror image behavior compared to poly-**1** as mentioned in the Introduction is confirmed. These results emphasize once again the chiral recognition ability of these poly(pyrroles) grafted by chiral side chains, as already published [9]. Investigations concerning the enantioselective behavior of poly-**3** in the undoped state are in progress.

Electrochemical properties

In order to characterize the redox behavior of the polymer-coated electrode surfaces, the relationship
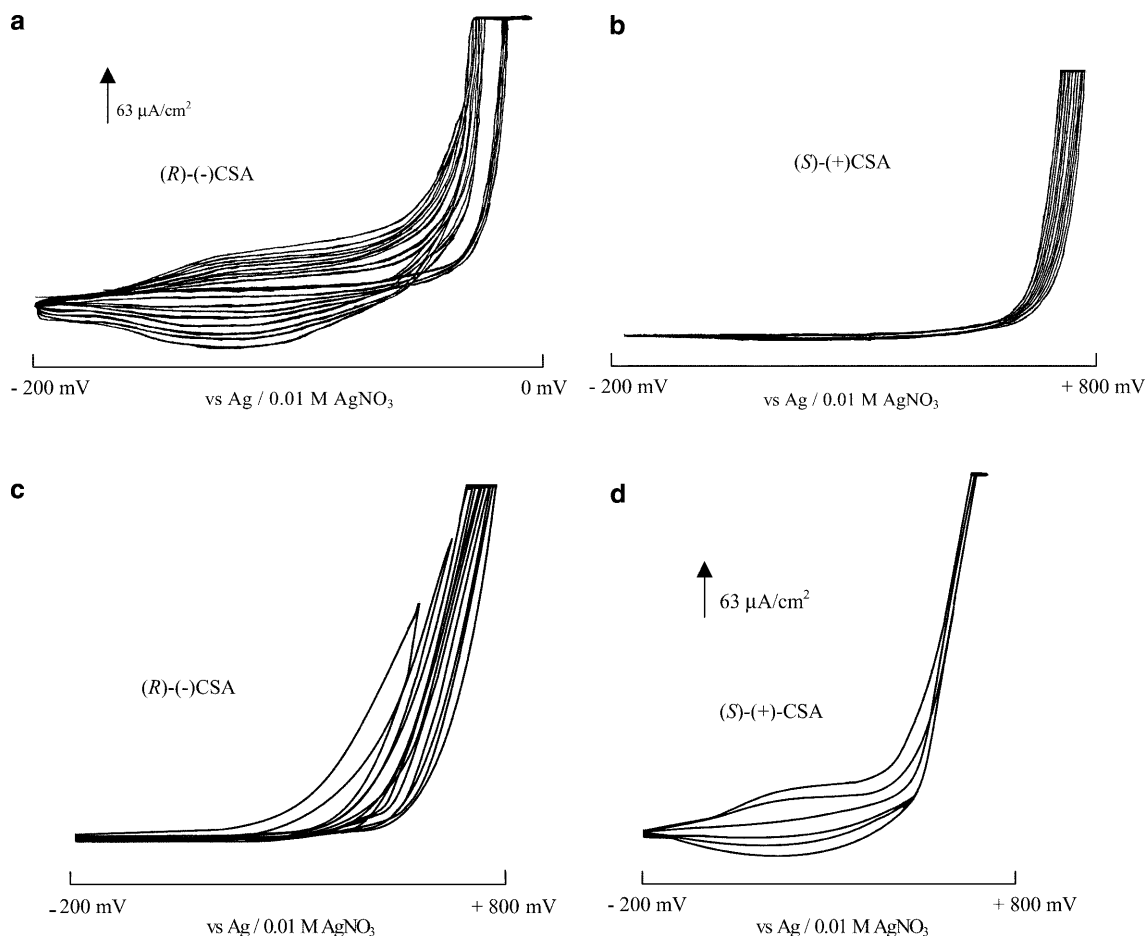
Fig. 3 Recognition effect: **a** poly-**3** and **b** poly-**1** [9] in AN containing (R)-(–)-CSA or (S)-(+)-CSA (0.1 M) as doping agent. Scan rate: 10 mV s^{-1}

a

10 μA/cm²

(R)–(-)-CSA

- 200 mV   vs Ag / 0.01 M AgNO₃   + 600 mV

b

(S)-(+)-CSA

10 μA/cm²

- 200 mV   vs Ag / 0.01 M AgNO₃   + 600 mV

Fig. 4 Electropolymerization of **3** (**a** and **b**) and of **1** (**c** and **d**) [9] in AN in the presence of (R)-$(-)$-CSA/Bu$_4$NClO$_4$ or (S)-$(+)$-CSA/Bu$_4$NClO$_4$. Scan rate: 10 mV s^{-1}

between scan rate and the current response at poly-**1** (Fig. 5a) as well as at poly-**3** (Fig. 5b) was studied. It is well known that this relationship shows the characteristics of mass transfer in the electroactive film on the electrode. As expected for a surface-localized material, the current values of poly-**1** and poly-**3** scale linearly with sweep rate between 10–90 mV s^{-1} (poly-**1**) and 10–100 mV s^{-1} (poly-**3**), respectively. Although monomers **1** and **3** have only one distinguishing feature, i.e. the configuration of the chiral C-atom in the side chain of the pyrrolic unit, the electrochemical behavior of poly-**1** and poly-**3** is different as the comparison of the voltammograms shows (Fig. 5a, b). In contrast to poly-**3** (Fig. 5b), higher peak current densities were noticed for poly-**1** when using the same sweep rate (Fig. 5a). This result is valid independent from the doping agent used for polymerization.

For clarity the relevant potentials are combined in Table 1. The data are mean values (deviation: ±5 mV) based on the data derived from multiple experiments.

Owing to the electron withdrawing and steric effects of the side chain in **1** and **3**, the anodic peak potentials (E_{pa}) of **1** and **3** and also of the corresponding polymers
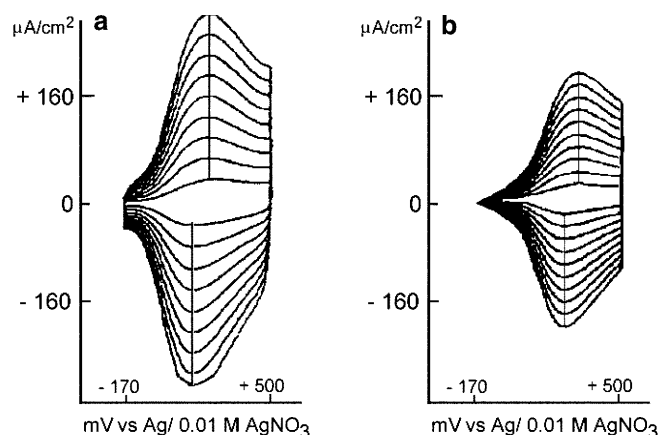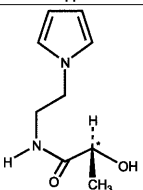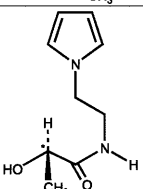

Fig. 5 Cyclic voltammograms of poly-1 (**a**) and of poly-**3** (**b**) in 0.1 M LiClO$_4$/AN. Scan rate: 10–90 mV s^{-1} (**a**) and 10–100 mV s^{-1} (**b**)

(poly-**1** and poly-**3**) are shifted anodically compared to pyrrole or PPy, respectively (Table 1). A surprising feature is that in contrast to poly-**1** the shift of the E_{pa} and also of the cathodic peak potential (E_{pc}) of poly-**3** goes on for about 100 mV. Consequently, the potential E measured midway between the cathodic and anodic peak potentials, $E = (E_{pa} + E_{pc})/2$, of poly-**3** is shifted to a more positive value compared to poly-**1** (Table 1).

Table 1 Cyclic voltammetric data for pyrrole [9], **1** [9], and **3**: monomer concentration 0.1 M in 0.1 M LiClO$_4$/AN and for the appropriate polymers PPy [9], poly-**1** [9], and poly-**3** in 0.1 M LiClO$_4$/AN; scan rate 10 mV s^{-1}; E vs. Ag/0.01 M AgNO$_3$

Pt AN/LiClO$_4$	monomer E_{pa} [V]	polymer			
		E_{pa} [V]	E_{pc} [V]	ΔE [V]	E [V]
pyrrole [9]	0.93	- 0.38	- 0.71	0.33	- 0.54
1 [9]	1.2	+ 0.20	+ 0.13	0.07	+ 0.18
3	1.2	+ 0.30	+ 0.23	0.07	+ 0.26

An enhanced redox reversibility for poly-**1** and poly-**3** for the electrochemical redox switching was obtained ($\Delta E = 70$ mV, Table 1) compared to PPy. In contrast to pyrrole, monomers **1** and **3** are not soluble in water. Thus, we conclude that the polymer matrix has a more lipophilic character than PPy owing to the substitution [9], which leads to better solvation by the organic solvent. Because of this, the ionic conductivity in the polymer increases and this leads to an enhanced redox reversibility for poly-**1** and poly-**3**.

Not only a distinction between the electrochemical properties of poly-**1** and poly-**3** is established, but also the polymerization process of **1** and **3** is different. The potentiodynamic experiment in particular provides useful information on the growth rate of conducting polymers. The increasing current densities with each cycle are a direct measure of the increasing surface of a redox-active polymer [17]. In both cases, a polymeric film was obtained using a potential range from –0.17 to + 0.75 V vs. Ag/0.01 M AgNO$_3$ at a scan rate of 10 mV s^{-1}. Independent from the doping agent, poly-**1** grows linearly in time as calculated from the peak current density of the respective polymer oxidation. In the case of poly-**3**, increasing current densities are observed from the 20th cycle onwards; then the current densities increase linearly with time. Compared with PPy, which also grows linearly in time, the increase of the current densities of PPy is considerably lower than that of its derivative poly-**1**, but higher than that of poly-**3**. This is surprising, because we use the same potential range for the polymerization of both monomers and also both pyrrole derivatives (**1** and **3**) possess the same E_{pa}, i.e. 1.2 V vs. Ag/0.01 M AgNO$_3$ in AN/LiClO$_4$ (Table 1). It is common knowledge that faster polymerization is supported by a high formation potential for polymers [13].

Based on the results mentioned above, we conclude that the configuration in the side chain of the pyrrolic unit, i.e. the configuration of the chiral C-atom, seems to have a profound effect on the structure of the polymer film, as reflected by the electrochemical and the enantioselective behavior. However, this result is highly unusual, because chiral compounds are normally indistinguishable with respect to their behavior towards achiral compounds or measurements. Similar behavior was reported in 1994 by Lamy and co-workers [18, 19, 20]. They suggested that unmodified polycrystalline and single-crystal platinum electrodes are "able to recognize the absolute configuration" of 2,3-butanediol molecules. Investigations carried out by Kuhn and Anson [21] have shown that the presence of an adsorbing poison in one of the two enantiomers could be responsible for behavior like this.

Monomers **1** and **3** show identical values for the optical rotation (in opposite directions). Therefore we do not really understand these results; we are trying to find explanations for this unexpected behavior. However, steric and electronic effects of the substituents in the side chain of five-membered heterocycles on electropolymerization and also on electrochemical properties of the polymer films have been extensively discussed in the literature [22, 23]. The influence of the supporting electrolyte used for the polymerization not only on the structure of the polymer (morphology) [24] but also on the permeability, conductivity, electroactivity, processibility, and mechanical strength of PPy films is known in the literature as well [25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36].

Poly-**4**

Enantioselective properties

Poly-**4** was produced to investigate the effects of the substituents in the side chain, i.e. the influence of the

carbonyl group in the α-position of the pyrrole nucleus, on the electrochemical and especially on the enantioselective properties of the resulting polymer. The current-voltage curves recorded in the presence of the enantiomers of CSA do not exhibit any differences. Additionally, polymerization of monomer 4 is possible in AN in the presence of (R)-(−)-CSA and (S)-(+)-CSA. This observation validates the concept of chiral recognition, known as the three-point rule [37]. This rule was formulated for chiral recognition relevant to liquid chromatographic separation of enantiomers. It means (restated in a slightly modified form for clarity) that recognition requires a minimum of three simultaneous interactions between a chiral auxiliary and at least one of the enantiomers, with at least one of these interactions being stereochemically dependent. Dalgleish [38] noted that derivatization of an amino or carboxyl function or the replacement of an aromatic side chain by an aliphatic group resulted in the loss of separation of enantiomers. He concluded that three simultaneous binding interactions are necessary for enantioselective discrimination. This can be transmitted to our systems. In the case of poly-4 the carbonyl function in the side chain of poly-2 was replaced by a CH_2 group. We assume that one possible selective intermolecular interaction, i.e. a π-donor-acceptor interaction or hydrogen bonding, as well as a steric interaction between the polymer and the doping agent in the transition state, might be missing, which is reflected by a negative recognition effect.

The recognition ability in the undoped state was proved by the application of poly-4 in the enantioselective electroreduction of the prochiral ketones 5 and 6

to the corresponding alcohols 5a and 6a. The electrolyses were carried out at −2.2 V vs. Ag/0.01 AgNO$_3$. The correlation of the electrolyte used for polymerization of 4 and the enantioselectivity of the reduction was examined compared to 2 (influence of the carbonyl group in the α-position). In all cases the absolute configuration of the major enantiomer was determined to be R, based on the sign of its optical rotation. The results are mean values (deviation: ±2%) based on the data derived from at least three individual experiments. In all experiments the temperature of its reaction media never exceeded 30 °C.

By comparison of the results obtained at poly-2 and poly-4 for the reductive conversion of 5 (Table 2), two points are remarkable. In the case of poly-4 the absence of the carbonyl group in the α-position of the pyrrole nucleus leads to a decrease of the optical yield of about 60% compared to poly-2 (compare runs 1–3 [11] and runs 4–6). Furthermore, in contrast to poly-2, no influence of the electrolyte used for the polymerization can be noticed. For subsequent investigations of the influence of the carbonyl group on the enantioselectivity of the reaction, the electroreduction of another prochiral ketone was performed. For the electroreduction of 6, a higher optical yield of the resulting alcohol was expected compared to the reduction of 5 because in the case of 6 one of the aromatic rings of the prochiral center has a CH_3 group close to the prochiral center. As can be plainly seen in Table 3, independent from the supporting electrolyte used for the polymerization, an optical yield of only 2% was obtained. The investigations using poly-2 for the electrochemical reduction of 6 are in progress. The

Table 2 Stereoselective electroreduction of 5 in 0.1 M LiBr/DMF at –2.2 V vs. Ag/0.01 M AgNO$_3$ at poly-2, poly-4, and platinum, depending on the electrolyte used for the polymerization
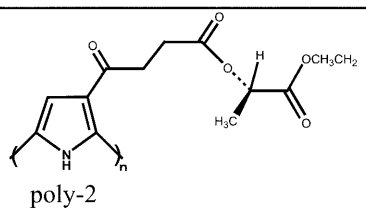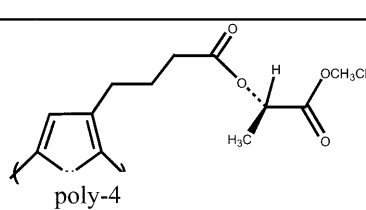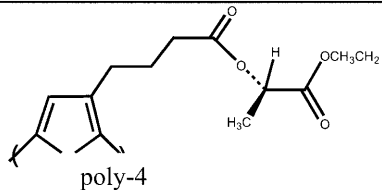
		Reductive conversion of 5		
run	Polymer / electrode	conducting agent used for polymerization	current yield [%] alcohol	op [%]
1 [11]	poly-2	LiClO$_4$	80	17
2 [11]		Et$_4$NClO$_4$	66	13
3 [11]		Bu$_4$NClO$_4$	43	8
4	poly-4	LiClO$_4$	55	5
5		Et$_4$NClO$_4$	52	5
6		Bu$_4$NClO$_4$	66	5
7 [11]	platinum		53	0

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		Reductive conversion of 6		
run	**polymer /electrode**	**conducting agent used for polymerization**	**current yield [%] alcohol**	**op [%]**
8	poly-**4**	LiClO$_4$	58	2
9		Et$_4$NClO$_4$	50	2
10		Bu$_4$NClO$_4$	50	2
11	platinum		75	0

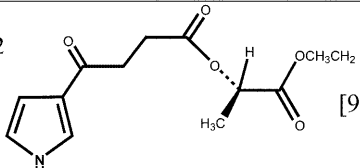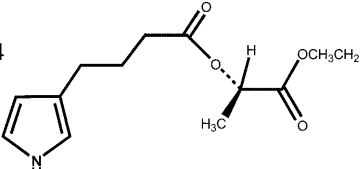reduction of **5** and **6** at bright platinum proceeds without stereoselectivity, as expected.

In conclusion, the enantioselective recognition of poly-**4** in the undoped state is similar to that in the doped state. It is obvious that the carbonyl group in the α-position of the pyrrole nucleus seems to be necessary to stabilize the interactions in the transition state between the chiral-modified electrode surface and the ketone. In case of the electroreduction of **5**, this causes a higher optical yield for the resulting alcohol at the polymer electrode possessing a carbonyl group in this position (poly-**2**). The influence of the electrolyte used for polymerization on the stereoselectivity of the reaction observed at poly-**2** might be caused by the formation of pores of different sizes due to the different sizes of the electrolyte cations (Li$^+$ < Et$_4$N$^+$ < Bu$_4$N$^+$). We assume that the smaller are the pores in the polymer matrix, the closer the interaction will be between the chiral environment and the prochiral ketone [11].

Electrochemical properties

By comparison of the characteristic electrochemical parameter for poly-**4** with the ones for poly-**2** and PPy (listed in Table 4), a clear trend becomes apparent. The introduction of a side chain (poly-**4**) and moreover the introduction of a carbonyl group in the α-position of the side chain (poly-**2**) leads to an anodic shift (due to the electronic and steric effects of the side chain [9]) of the electrochemical parameter. However, in the case of poly-**4**, only a slight anodic shift was observed compared to poly-**2**.

This now has serious consequences. It is generally known that autoxidation of PPy proceeds very fast in the undoped state owing to its low oxidation potential (E_{pa} = –0.38 V vs. Ag/AgNO$_3$). This is also given for poly-**4** (E_{pa} = –0.23 V vs. Ag/AgNO$_3$), proven by its long-term stability under redox cycling. In this case the peak current densities decrease rapidly with each cycle (to 50% after 40 cycles). It should be noted that the

Pt **AN/LiClO$_4$**		**monomer** **E_{pa} [V]**	**polymer**			
			E_{pa} [V]	**E_{pc} [V]**	**ΔE [V]**	**E [V]**
pyrrole	[9]	0.93	- 0.38	- 0.71	0.33	- 0.54
2	[9]	1.1	+ 0.54	+ 0.47	0.07	+ 0.5
4		0.82	- 0.23	- 0.3	0.07	- 0.27

solutions for the cyclic voltammetric experiments were purged with argon. Thus long-term damage may arise after the electrodeposition process. Now after electro-polymerization the polymer films were reduced, rinsed with AN, and stored in AN, but the AN was not de-gassed with argon. So oxidation by atmospheric oxygen of the polymer film in the undoped state may be as-sumed. This was checked in an experiment. All solutions were degassed with argon and all investigations were performed under an argon atmosphere. Under this condition, poly-**4** exhibits a good long-term stability. However, poly-**2** (also poly-**1** and poly-**3**) exhibits high electrochemical stability under redox cycling. Several tens of voltammetric cycles can be performed without any loss of electroactivity.

Because of the instability of poly-**4** in the undoped state as mentioned above, we assume that the micro-structure and the "porosity" of the polypyrrole film might be changed during electrolysis. Consequently, no influence of the electrolyte can be observed, as the results in Tables 2 and 3 show. The consequence of the insta-bility of poly-**4** in the undoped state for chiral economy is that the modified electrodes are not reusable, in con-trast to poly-**2** as well as poly-**1**. These latter electrodes were both reusable without any effects on the current yield and on the stereoselectivity of the reaction.

From Table 4 it is also visible that the redox revers-ibility of poly-**2** and poly-**4** ($\Delta E = 70$ mV) is enhanced compared to PPy, owing to substitution as mentioned above for poly-**1** and poly-**3**. In addition to the expla-nation given for poly-**1** and poly-**3**, the pendant ether and ester chains in poly-**2** and poly-**4**, known for their cation-solvating properties, lead to a higher mobility of the electrolyte in the polymer matrix [39].
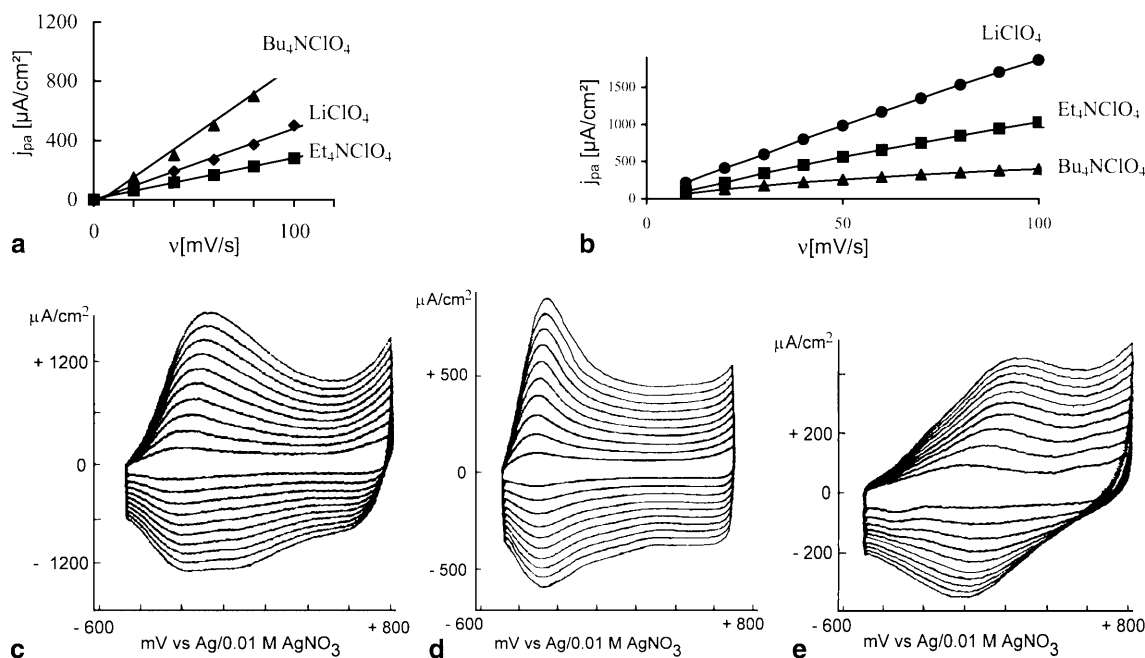
Additionally, owing to the substitution, the polymer backbone of poly-**2** and poly-**4** becomes more lipophilic. Thus, both monomers are insoluble in water. This leads in case of poly-**2** to increasing electroactivity in the presence of Bu_4N^+ compared to the electroactivity in the presence of more hydrophilic cations, e.g. Li^+ and Et_4N^+, as emphasized in Fig. 6a. However, in the case of poly-**4** the highest electroactivity was observed in the presence of Li^+ followed by Et_4N^+ and Bu_4N^+ (Fig. 6b). This leads to the assumption that the polymer matrix in the case of poly-**4** is more lipophilic than in the case of PPy but not as lipophilic as in the case of poly-**2**.

However, in case of poly-**4** the peak potentials of the anodic process shift to more anodic values and the ones of the cathodic process to more negative values with increasing scan rate, resulting in an increase of ΔE [$\Delta E = 150$ mV (LiClO$_4$), 100 mV (Et$_4$NClO$_4$), 250 mV (Bu$_4$NClO$_4$) at 100 mV s^{-1}], as shown in Fig. 6c–e. This experimental evidence reflects again the instability of poly-**4** caused by the low oxidation potential compared to poly-**2**. In summary, the electrochemical behavior of poly-**4** is more similar to that of PPy than to poly-**2**.

Conclusion

The influence of the substituents on the chiral discrimi-nation of poly-**3** and poly-**4** in the doped as well as in the undoped state was investigated. Poly-**3** exhibits a rec-ognition ability in the doped state; the investigation of the undoped state is in progress. Poly-**4** does not show enantioselective properties either in the doped or in the undoped state. In case of poly-**3**, an influence of the configuration of the chiral C-atom in the side chain of

Fig. 6 Plot of i_{pa} vs. v (scan rate: 10–100 mV s^{-1}) for poly-**2** (**a**) and for poly-**4** (**b**) in AN containing various electrolytes. Cyclic voltammograms of poly-**4** in 0.1 M LiClO$_4$/AN (**c**), 0.1 M Et$_4$NClO$_4$/AN (**d**), and 0.1 M Bu$_4$NClO$_4$/AN (**e**); scan rate: 10–100 mV s^{-1}

the pyrrole nucleus on the structure of the polymer film, as reflected by the enantioselective and electrochemical behavior, is proposed. In the case of poly-**4**, we conclude that the absence of the carbonyl group in the α-position of the pyrrole nucleus leads to a decrease of the electrochemical stability and of the chiral recognition.

References

1. Moses PR, Wier L, Murray RW (1975) Anal Chem 47:1882
2. Roncali J (1992) Chem Rev 92:711
3. Merz A (1990) Topics in current chemistry, vol 152. Springer, Berlin Heidelberg New York, pp 51–89
4. Nonaka T (1993) In: Lund H, Baizer MM (eds) Organic electrochemistry, 3rd edn. Dekker, New York, pp 1131–1195
5. http://www.electrosynthesis.com/news/w5content.html
6. Komori T, Nonaka T (1984) Chem Lett 509
7. Moutet J-C, Duboc-Toia C, Menage S, Tingry S (1998) Adv Mater 10:665
8. Pleus S, Schwientek M (1997) Synth Commun 27:2917
9. Pleus S, Schwientek M (1998) Synth Met 95:233
10. Pleus S, Schwientek M, Schulte B, Stroot J, Hamann CH (1999) In: Russow J, Sandstede G, Staab R (eds) Elektrochemische Reaktionstechnik und Synthese. (Dechema monograph 14) Spengler, Frankfurt, p 173
11. Schwientek M, Pleus S, Hamann CH (1999) J Electroanal Chem 461:94
12. Lemaire M, Delabouglise D, Garreau R, Guy A, Roncali J (1988) J Chem Soc Chem Commun 658
13. Lau CK, Dufressne C, Bélanger PC, Piétre S, Scheigetz J (1986) J Org Chem 51:3038
14. Ador E, Rilliet AA (1879) Ber Dtsch Chem Ges 12:2298
15. Davies AG, Kenyon J, Lyons BJ, Rohan TA (1954) J Chem Soc 3474
16. Jarrousse MJ, Regnier MT (1951) Ann Pharm Fr 321
17. Heinze J, Hinkelmann K, Land M (1988) In: Russow J (ed) Organische Elektrochemie-Angewandte Elektrothermie. (Dechema monograph 112) Schön & Wetzel, Frankfurt, p 75
18. Hilmi A, Belgsir EM, Léger JM, Lamy C (1995) J Electroanal Chem 382:53
19. Hilmi A, Dupont M, Belgsir EM, Léger JM, Lamy C (1995) J Electroanal Chem 380:177
20. Hilmi A, Dupont M, Belgsir EM, Léger JM, Lamy C (1994) J Electroanal Chem 376:161
21. Kuhn A, Anson FC (1996) J Electroanal Chem 410:243
22. Lemaire M, Garreau R, Roncali J, Delabouglise D, Youssoufi HK, Garnier F (1989) New J Chem 13:863
23. Waltman RJ, Bargon J (1986) Can J Chem 64:76
24. Skotheim TA (ed) (1986) Handbook of conducting polymers, vols I and II. Dekker, New York
25. Delabouglise D, Garnier F (1990) Synth Met 39:117
26. Pickup PG (1987) J Electroanal Chem 255:273
27. Garnier F, Youssoufi HK, Srivastava P, Yassar A (1994) J Am Chem Soc 116:8813
28. Otero TF, Arévalo AH (1994) Synth Met 66:25
29. Shimidzu T, Ohtani A, Honda K (1988) Bull Chem Soc Jpn 61:2885
30. Pernaut JM, Peres RCD, Juliano VF, De Paoli M-A (1989) J Electroanal Chem 270:225
31. Kuwabata S, Nakamura J, Yoneyama H (1989) J Electrochem Soc 137:2147
32. Boyle A, Geniès E, Fouletier M (1990) J Electroanal Chem 279:179
33. Walton DJ, Hall CE (1991) Synth Met 45:363
34. Walton DJ, Hall CE, Chyla A (1992) Analyst 117:1305
35. Panero S, Prosperi P, Scrosati B (1992) Electrochim Acta 37:419
36. Gao Z, Bobacka J, Lewenstam A, Ivaska A (1994) Synth Met 62:117
37. Pirkle WH, Pochapsky TC (1989) Chem Rev 89:347
38. Dalgleish CE (1952) J Chem Soc 3940
39. Delabouglise D, Garnier F (1990) Adv Mater 2:91