Alternating copolymers based on 1-methylpyrrole and thiophene - synthesis and electrochemical studies

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Summary

The synthesis and electrochemical polymerisation behaviour of a series of monomers containing 1-methylpyrrole and thiophene is reported. These monomers provide copolymers of well defined monomer sequence in the backbone.

Introduction

Poly(thiophene) and poly(pyrrole) have been widely investigated as potential materials in the field of molecular electronics. They are of great interest due to their redox and photochemical properties and were proposed as sensors (1), batteries (2), molecular wires (3) and light-emitting diodes (4).

These polyaromatics form oxidatively stable films with high conductivity and good mechanical properties which are great practical improvements in comparison to poly(acetylene) in applications. Poly(thiophene) and poly(pyrrole) can also be regarded as cis-poly(acetylene) containing sulfur and nitrogen as bridging heteroatoms. The preparation of hybrid polymers containing both thiophene and pyrrole units are interesting for tailoring several properties (5). Under this aspect copolymers have been obtained either by anodic oxidation of a mixture of the monomers (6) leading to random copolymers or by the use of mixed oligomers as monomers (7) which already contain the copolymer structure. According to this, alternating copolymers could be achieved via symmetric comonomers. Oxidative polymerisation of such symmetrically derivatised monomers is a way to well defined copolymers with a higher degree of order as investigated by several groups (8). If the heteroaromat with the highest reactivity is chosen as the terminating group, in order to have a low oxidation potential at the end of the comonomer, the degree of branching could be limited and a more regular structure of the copolymer is achieved (9). A detailed study of various bis(1-methylpyrrole-2yl)arenes as comonomers for electrochemical polymerisation was recently published (10).

Now our interest was to study the influence of different conjugated structures and alternating repetitive units of thienylpyrrole precursor monomers, such as dimeric, trimeric or mixed tetramer oligomers on the resulting copolymer properties.

Experimental

All melting points are uncorrected. Infrared spectra were taken on a Bruker Equinox 55 FTIR spectrometer. All NMR spectra were recorded in $CDCl_3$ on a Bruker WP 80 SY (80 MHz) spectrometer for ^1H nuclei and Bruker AM 400 (400 MHz) for ^{13}C nuclei,

respectively. Chemical shifts are reported in parts per million (δ) using tetramethylsilane as internal standard. Mass spectra were recorded by a Finnigan MAT 312 spectrometer. UV/Vis spectroscopy was performed in $CHCl_3$ by a Perkin-Elmer model Lamda 5. Cyclic voltammetry measurements were performed in a Kiesele type cell with integrated drying tube for the used electrolyte (0.1 mol·L^{-1} $(C_4H_9)_4NPF_6$ in superdry CH_2Cl_2, $c_{oligomer} = 1·10^{-3}$ mol·L^{-1}). The working electrode was a platinum disk, the counter electrode a platinum wire and the reference a AgCl covered silver wire. All potentials are calibrated against ferrocene ($E^o_{(Fc/Fc+)} = 0.35$ V vs. Ag/AgCl). Cyclic voltammograms were recorded using a computer linked Heka PG 285 potentiostat with the LabVIEW-Software package from National Instruments.

Bulk electrolysis experiments were performed in an one-compartment cell employing a AgCl covered silver wire as reference electrode and platinum foils (A = 2.25 cm^{-2}) as working and counter electrodes. The electrolyte consisted of $5·10^{-2}$ mol·L^{-1} $(C_4H_9)_4NPF_6$ in purified CH_2Cl_2, the concentration of the given oligomer was $2.5·10^{-2}$ mol·L^{-1}. Purification of CH_2Cl_2 was performed according to the literature (10). Conductivities were measured by a standard four-probe method at room temperature on pressed pellets or films by using osmium contacts.

General procedure for preparation of compounds **1, 2, 3** and 1-methylpyrrole-2-yl zinc chloride, respectively: To a stirred solution of 13.5 mL (150 mmol) 1-methylpyrrole in 150 mL dry THF was added dropwise 100 mL (150 mmol) 1.5 M tert.-butyllithium (hexane solution) at -76°C. After 30 min the yellow solution was stirred for further 30 min at room temperature. Then the solution was transferred under ice cooling into a suspension of 21.8 g (160 mmol) $ZnCl_2$ in 100 mL dry THF and stirred for 3 h. The reaction mixture was added to a solution of 25 mmol of the aromatic dibromo or monobromo compound and 300 mg Ni(dppp)Cl_2 in 100 mL dry THF at -40°C. After reaching ambient temperature the mixture was refluxed. The reaction time varied as well as the work-up procedure.

2-(1-Methylpyrrole-2-yl)thiophene **1**: After a reaction time of 2 h the mixture was cooled down, hydrolysed with H_2O and extracted several times with diethylether. The combined organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was chromatographically purified on silica gel with petrolether/diethylether (1:1) yielding 3.59 g (88 %) 2-(1-methylpyrrole-2-yl)thiophene **1** as yellow oil: ^{1}H-NMR ($CDCl_3$), δ (ppm): 3.72 (s, 3H), 6.16 (t, 1H), 6.33 (dd, 1H), 6.70 (t, 1H), 7.04 (m, 2H), 7.26 (dd, 1H); MS (relative intensity): 164 (M+1, 34), 163 (M^+, 100), 162 (60), 148 (39), 121 (36), 80 (27), 69 (30); IR (kap. film) [cm^{-1}]: 3102, 2943, 1562, 1508, 1472, 1444, 1299, 1244, 1058, 1018, 940, 844, 698, 606; UV/Vis ($CHCl_3$): $\lambda_{max} = 296$ nm; E^1_{pa}: 0.48 V vs. Fc/Fc^+.

2,5-Bis(1-methylpyrrole-2-yl)thiophene **2**: After a reaction time of 16 h the mixture was cooled to room temperature, added to H_2O and extracted several times with diethylether. The combined organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was chromatographically purified on silica gel with petrolether/diethylether (1:1) to give 2',5'-bis(1-methylpyrrole-2-yl)thiophene **2** (3.45 g, 57 %) as yellow crystals after recrystallisation from heptane: m.p. 72°C; ^{1}H-NMR ($CDCl_3$), δ (ppm): 3.72 (s, 6H), 6.16 (dd, 2H), 6.34 (dd, 2H), 6.68 (dd, 2H), 6.94 (dd, 2H); ^{13}C-NMR (400 MHz, THF-d8) δ (ppm): 35.3, 108.4, 110.4, 124.9, 125.3, 127.6, 134.9; HRMS: calc. 242.0878, found 242.0887; IR (KBr) [cm^{-1}]: 3095, 2979, 2948, 1576, 1509, 1495, 1456, 1409, 1326, 1285, 1215, 1202, 1082, 1059, 953, 924, 799, 782, 733, 707, 664, 606; UV/Vis ($CHCl_3$): $\lambda_{max} = 332$ nm; E^1_{pa}: 0.10 V vs. Fc/Fc^+.

2,5-Bis(1-methylpyrrole-2-yl)bithiophene **3**: After a reaction time of 12 h the mixture was cooled to room temperature, hydrolysed with H_2O and extracted several times with diethylether. The combined organic layers were dried over Na_2SO_4 and the solvent was removed in vacuo. The crude product was chromatographically purified on silica gel with petrolether/diethylether (2:1) yielding 6.48 g (80 %) 2',5'-bis(1-methylpyrrole-2-yl)bithiophene **3** as golden crystals after recrystallisation from EtOH: m.p. 143°C; ¹H-NMR (CDCl₃), δ (ppm): 3.76 (s, 6H), 6.18 (m, 2H), 6.37 (dd, 2H), 6.72 (m, 2H), 6.92 (d, 2H), 7.11 (d, 2H); ¹³C-NMR (400 MHz, THF-d8) δ (ppm): 35.4, 108.6, 110.6, 124.4, 125.3, 125.4, 135.2, 136.2; MS (relative intensity): 326 (M+2, 10), 325 (M+1, 41), 324 (M⁺, 80), 323 (100), 308 (48), 282 (11), 162 (46), 141 (9), 91 (12), 69 (23); HRMS: calc. 324.0759, found 324.0755; IR (KBr) [cm⁻¹]:3060, 2922, 1558, 1502, 1480, 1443, 1406, 1310, 1275, 1232, 1171, 1053, 1012, 882, 859, 795, 721, 704, 669, 577; UV/Vis (CHCl₃): λ_{max} = 379 nm; E^1_{pa}: 0.08 V vs. Fc/Fc⁺.

Results and discussion
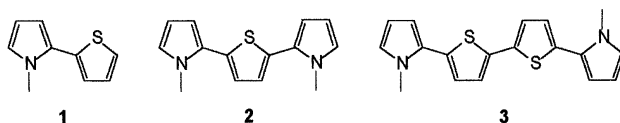
The comonomers **1** and **3** were first synthesised and elctrochemically studied by Niziurski-Mann and coworkers (11). For comparable values we synthesised them analogue to bis(1-methylpyrrole-2-yl)thiophene **2** (10) by the nickel-catalyzed coupling reaction of the 1-methylpyrrole-2-yl anion with 2-bromo-thiophene, 2,5-dibromo-thiophene and 2,2'-dibromo-bithiophene for compound **3**, respectively. Using (Ni(dppp)₂Cl₂) as catalyst the oligomers were obtained in high yields compared to other methods reported in literature (11).

All monomers were characterised by cyclic voltammetry (see Fig.2) and show an irreversible behaviour suggesting the generation of an unstable and reactive radical cation which couples rapidly with another monomer unit, leading to the formation of polymers or higher oligomers. In Table 1 the peak potentials and properties for the thienylpyrrole monomers and corresponding copolymers are shown.
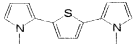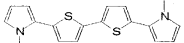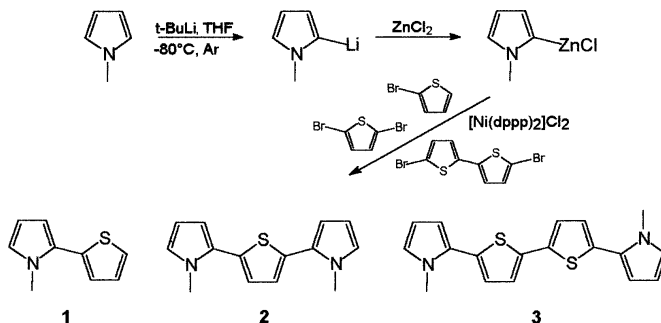

Fig. 1: Synthesis of mixed oligomers via (Ni(dppp)₂Cl₂) catalysed coupling

Table 1. Peak potential vs. Fc/Fc⁺ for the oligomers and polymers in the thienylpyrrole series.

Oligomer	E^1_{pa} [V]	λ_{max} / nm	Torsion Angle[a]	Polymer E_{pa} [V]	σ / S·cm⁻¹
1	0.48	296	26°	0.17	$5 \cdot 10^{-3}$
2	0.10	331	28°	-0,03	$2 \cdot 10^{-3}$
3	0.08	379	26° (5°)	0.13	2

[a] The torsion angle was calculated by the PC-programm *Alchemy III* from Tripos, only for qualitative comparison

The oxidation potential of the monomers increases as expected with the longer conjugation segment, whereas the three-ring system **2** shows nearly the same E^1_{pa} as the tetrameric system **3** with a central bithiophene unit due to the higher amount of pyrrole (ratio 2:1). In accordance to this the UV/Vis results indicate a clear blue shift of the maximum absorption peak from 296 nm in the case of dimer **1** compared to bis(1-methylpyrrole-2-yl)bithiophene **3** (379 nm) due to the conjugated structure of the oligomers.

The cyclic voltammetry measurements on the copolymers support the suggestion that the use of symmetric comonomers like **2** (ABA) or **3** (ABBA) leads to well defined structures if polymer defects resulting from β-coupling reactions are ignored. CV measurements of polymer **1** show a broad oxidation wave whereas polymers of **2** and **3** are more uniform in redox behaviour indicating a regular structure of alternating copolymers. It is also interesting to note that the oxidation potential of the alternating bis(1-methylpyrrole)bithiophene copolymer (E_{pa} = 0,13 V) is slightly lower compared to the potential of the random copolymer derived from the dimeric unit **1** (E_{pa} = 0,17 V). Although conductivities and mechanical properties of the copolymers are appreciable different, conductivities of the polymers derived from **1** and **2** are both in the range of 10^{-3} S·cm⁻¹. Formation of free standing films could only be observed in the case of the dimer and trimer. Poly(bis(1-methylpyrrole-2-yl)bithiophene) is electrolytically deposited as a homogeneous powder and shows a conductivity of 2 S·cm⁻¹, which is the highest conductivity for a copolymer based on 1-methylpyrrole and thiophene reported in the literature so far. All doped and neutral polymers are insoluble in common organic solvents, thus aggravating investigations on structure-properties relationships.

In comparison to polymer of **3**, the unsubstituted dimeric derivative of **1** has been polymerised electrochemically by Naitoh and coworkers (12) and the conductivity of the corresponding poly(thienylpyrrole) film was reported to be up to 3 S·cm⁻¹, which is at least one order of magnitude higher than the conductivities of the homopolymers doped with the same anion. We are sure that steric factors can not be the only reason for the observed low conductivities of the copolymers from **1** or **2** and the significant difference to poly(bis(1-methylpyrrole-2-yl)bithiophene), respectively. As the torsion angle between the 1-methylpyrrole and thiophene rings is almost the same in all monomers, only in tetramer **3** the central, nearly planar bithiophene unit causes a better conjugation. The reasons for the

different polymer properties, for example the conductivity behaviour, should also be related to the reactivity of the comonomer and the corresponding radical cation, concerning the selectivity of coupling reactions, the degree of branching and polymerisation as well as the tertiary structure. Further investigations under this aspect are in progress.
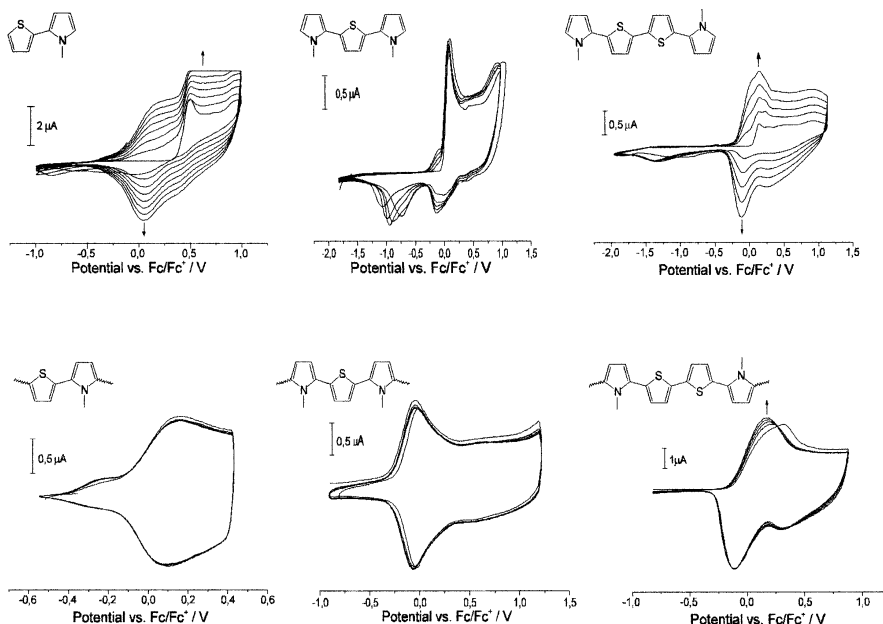

Fig.2: Cyclic voltammetry measurements of monomers and galvanostatically deposited polymers ($Q = 66$ µgC·cm^{-2}), scan rate 100 mVs^{-1}

These results are in contrast to the general behaviour of the electropolymerisation of extensively conjugated molecules as thiophene, pyrrole and mixed oligomers. Thus conductivities of poly[oligo-(1-methylpyrrole)]s (13) and poly[oligo-(thiophene)]s (14) electrochemically polymerised under similar conditions are typically in the range of 10^{-4} to 10^{-2} S·cm^{-1}, comparable to poly(ter-thiophene), poly(ter-1-methylpyrrole), poly(quater-1-methylpyrrole) and can be explained by a limited conjugated π-system in the polymer. The reactivity of the monomer and the stability of the corresponding radical cation determines the polymerisability as well as the relative reactivity of the α-positions which influence the stereoselectivity during polymerisation.

Acknowledgements

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