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Preparation of highly conducting and spin-probed polypyrroles using coupled electrochemical-chemical synthesis in the presence of nitroxyl radicals

P. Rapta, A. Bartl, L. Dunsch *

Institut für Festkörper- und Werkstofforschung Dresden e.V.,
Helmholtzstrasse 20, D-01069 Dresden, Germany

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SUMMARY: A new method for the synthesis of conducting polypyrroles (PPy), based on chemical and combined electrochemical-chemical oxidation of pyrrole monomers in the presence of nitroxyl radical (TEMPOL - 2,2,6,6-tetramethyl-4-hydroxy-1-oxy-piperidyl) as oxidation agent (in its oxidation state) and redox mediator respectively is described. The PPy films obtained are extremely porous and the electrical conductivity (σ) of the resulting PPy samples ranges from 1 to 100 S cm^{-1}. PPy prepared in aqueous solutions has a lower conductivity $\sigma \sim 1$ S cm^{-1} as compared to the PPy prepared in acetonitrile solutions with conductivity of about 100 S cm^{-1}. The PPy films are quite compact and thick films (1 mm) can be pealed off from the electrode surface and pressed as a disc for further studies. Only after partial reduction of polypyrrole film the spin-probed PPy was obtained. The concentration of nitroxyl radicals incorporated in the polymer matrix can be changed using various degrees of polymer reduction. The anisotropic broadening of the observed ESR lines indicates a low mobility of incorporated nitroxyl radicals in the PPy matrix. The electronic interaction between the nitroxyl groups and the paramagnetic centers of the polymer chains, polarons, causes an ESR line broadening of polaron signal both on air (1.1 mT) and in vacuum (0.7 mT) as compared to unmodified PPy (0.2 mT on air, 0.05 mT in vacuum).

Introduction

The main procedure for the formation of both free standing membranes and adhering films of highly conducting polypyrrole (PPy) is the electrochemical polymerization (1). Recently, the high conductivity of the polypyrrole and its composites formed chemically was achieved by optimizing the experimental conditions (2). It is well known that the electrical conductivity and film morphology of PPy prepared both electrochemically and chemically strongly depends on the polymerization conditions. The application of the electrochemical polymerization technique in parallel to a chemical one opens new ways for the production of new types of PPy films with various morphology and chain structure at the electrode surface (3). In (3, 4) the parallel chemical *and* electrochemical synthesis of PPy by the electrochemical polymerization of pyrrole from solutions containing an oxidation agent (pyridinium chlorochromate) was described. Electropolymerization of pyrrole in the presence of bromide ions (5) or 2,5-dihydroxy 1,3-benzene disulfonic acid (6) was reported to be a catalytic process. The coupled electrochemical-chemical (ECH-CH) synthesis of PPy described in this paper has not been published up to now.

Nitroxyl radicals (NR) are widely used as spin probes or labels in the investigation of the structure and dynamic properties of various chemical systems and especially in polymers (7, 8). Recently an aqueous solution of 2,2,6,6-tetramethyl-1-oxipiperid-4-ylacetic acid was used as supporting electrolyte to produce PPy films by pyrrole polymerization at potentials of electrolyte discharge with the detectable nitroxyl radical

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* Corresponding author

content inside the PPy matrix (9). Furthermore PPy was modified during electrochemical synthesis with nitroxyl radicals by doping with anionic probes (10) or by a copolymerization with labelled bipyrrols (11) but no electron spin resonance (ESR) signals of nitroxyl radicals were observed. The presence of nitroxyl radicals in the polymer matrix was concluded from the increase of line broadening in comparison to the standard PPy film and from the cyclovoltammetric experiments (11). Changes in the PPy morphology, lower electrical conductivity and lower spin concentration after immobilization of NR were also observed (10).

We report here a new method for the synthesis of spin-probed conducting polypyrroles, based on chemical and combined electrochemical-chemical oxidation of corresponding monomers in the presence of nitroxyl radical (TEMPOL - 2,2,6,6-tetramethyl-4-hydroxy-1-oxy-piperidyl) which functions as oxidation agent in its oxidation state and redox mediator, resp.

Experimental

ECH-CH polymerization: PPy layers were prepared potentiostatically on gold electrodes (surface area 1 cm^2) by electropolymerization in aqueous or acetonitrile (MeCN) solutions containing 0.01 M pyrrole, 0.01-0.05 M TEMPOL (2,2,6,6-tetramethyl-4-hydroxy-1-oxy-piperidyl) and 0.1 M $LiClO_4$. The electrolyte solutions were rigorously degassed with nitrogen before polymerization. A conventional three-electrode cell for electrochemical experiments was equipped with a gold sheet as the working electrode and a platinum sheet as the counter electrode. A commercial saturated calomel electrode SCE (Sensortechnik Meinsberg) for aqueous solutions and a home made Ag/AgCl electrode for MeCN solutions separated from the solution *via* a junction containing saturated LiCl in ethanol served as reference electrodes. After electrochemical polymerization the films were washed with monomer-free electrolyte and than reduced at -600 mV *vs.* SCE at various electrolysis times (in the range of 10 to 60 min.) in 0.1 M $LiClO_4$ monomer-free electrolyte. PPy films adhering at the electrode and used in spectroscopic experiments were washed by water, toluene and trichlorobenzene (TCB), and then dried under vacuum. After washing and drying porous PPy layers could be stripped from the electrode for further investigation.

Chemical polymerization: In the case of the chemical synthesis the glass cell was filled with the solution containing TEMPOL (0.01-0.05 M), 0.1 M 4-toluenesulfonic acid (tosylate) or acidic 0.1 M $LiClO_4$ and purged with nitrogen. Then pyrrol was added to the solution (final pyrrole concentration 0.01 M) and purged with nitrogen again. After polymerization the solution was filtered and the PPy powder obtained was washed with toluene and dried at 40 °C under vacuum. Porous PPy films as well as polymer powder were pressed using a pressure of about $10^7 N m^{-2}$ to get disks for electrical conductivity measurements.

Materials: Pyrrole monomer (Fluka) was distilled under nitrogen and kept cool and in the dark prior to use. Acetonitrile (MeCN), $LiClO_4$, HCl and 4-toluenesulfonic acid (tosylate) were analytical grade commercial products (Fluka). TEMPOL (2,2,6,6-tetramethyl-4-hydroxy-1-oxy-piperidyl) was prepared by Dr. G. Jansen (TU Dresden). Aqueous solutions were made from bidestilled water.

Characterisations and measurements: All electrochemical experiments were carried out with the PAR 173 potentiostat-galvanostat (EG&G) driven by a computer.

The thickness of the films was measured using an electromagnetic layer-meter ULTRAMETER INCO A91 (Poland). For ESR-spectroscopy an X-band spectrometer ERS 221 (ZWG Berlin) with an H_{110}-cavity was used applying a 100 kHz modulation and a microwave power of 1 or 2 mW. Because the ESR signal of PPy samples is very sensitive to oxygen (12), the ESR investigations were carried out both under vacuum ($p<10^{-3}$ Pa) and on air. The pressure in the ESR sample tubes was controlled by a vacuum-meter VM 1500 (ebro). The measurements of electrical conductivity were performed by a four probe method using a home made apparatus.

Results and discussion

In order to find a correlation between the type of polymer formation and the experimental conditions (solvent, kind of dopand, TEMPOL concentration) four different reaction systems were studied.

(1) Aqueous (or MeCN) solutions containing 0.1 M $LiClO_4$ + TEMPOL (0.01-0.05 M)
(2) Aqueous (or MeCN) solutions containing 0.1 M tosylate + TEMPOL (0.01-0.05 M)
(3) Aqueous solutions containing 0.1 M $LiClO_4$ + TEMPOL (0.01-0.05 M) + HCl
(4) Aqueous (or MeCN) solutions containing 0.1 M tosylate.

System 1: The cyclic voltammograms of these solutions show a reversible anodic peak at the potential +660 mV *vs.* SCE corresponding to the nitrosonium ion production (13, 14). In this case no changes were observed after addition of pyrrole into this mixture. The solution has a yellow-orange colour which is typical for dissolved TEMPOL (λ_{max}= 280 nm). If the deoxygenated solution is electrolyzed at a potential in the range of 500 to 1000 mV *vs.* SCE a very high current densities (in the range 15-25 mA cm^{-2}) and a strong polymerization at the gold working electrode are found. This high reaction rate reached in that procedure enables the preparation of PPy films with a thickness of about 100 µm within a few minutes (in general 5 minutes). The PPy films obtained are extremely porous similar to that PPy structures prepared by a parallel electrochemical *and* chemical synthesis using pyridinium chlorochromate (3, 4) or by the catalyzed electrochemical polymerization (5, 6). The electrical conductivity (σ) of the resulting PPy samples ranges from 1 to 10 S cm^{-1}. Generally, PPy layers prepared in aqueous solutions exhibits lower conductivity ($\sigma \sim 1$ S cm^{-1}) to compare to the PPy prepared in MeCN solutions ($\sigma \sim 10$ S cm^{-1}). The PPy films are quite compact (especially those prepared in aqueous solutions). Thicker films (1 mm) can be pealed off from the electrode surface and pressed as a disc for further studies.

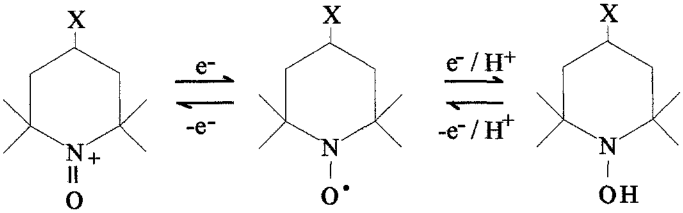
System 2: The yellow aqueous or MeCN tosylat solutions of TEMPOL (λ_{max}= 245 nm) show a decreasing ESR triplet signal of about 30% in comparison to the solution of TEMPOL in the absence of tosylate in *system 1*. In contrary to the solution of TEMPOL without tosylate the presence of protons causes a disproportionation of nitroxyl radicals in *system 2* to form hydroxylamine and nitrosonium ion $R_2N{=}O^+$ (7). After addition of pyrrole to this mixture a rapid polymerization of pyrrole in the bulk of the solution and the formation of dark precipitates were observed. The colour of the solution changed from yellow to blue-green. In this chemically oxidative polymerization of pyrrole in the presence of TEMPOL using MeCN as solvent, tosylat as counter ion and the concentration ratio of TEMPOL to pyrrole 5:1, it is possible to prepare PPy with an electrical conductivity of about 100 S cm^{-1}.

System 3: In this case a similar behaviour as in *system 2* was observed. The polymerzation rate decreases in comparison to *system 2* and changes in dependence on the concentrations of TEMPOL and HCl as well as the type of solvent and supporting electrolyte. Generally, with increasing acidity as well as TEMPOL concentration the polymerization rate increases. The electrical conductivity of pressed polymer powder ranging from 0.001-0,01 S cm^{-1} is about two orders of magnitude lower than that of the films prepared by ECH-CH synthesis or polymer powder prepared chemically using MeCN tosylat solutions.

System 4: After addition of pyrrole, the mixture was electrolyzed at various current densities (from 1 to 10 mA cm^{-2}). Typical PPy films produced by this electrochemical polymerization with an electrical conductivity ranging from 1 S cm^{-1} (aqueous solutions, low current densities) to 100 S cm^{-1} (MeCN solutions, high current densities) were prepared.

The above described observations can be explained as follows: Chemical reduction of nitroxyl radicals in the presence of electron donors requires obviously protons (7). After disproportionation of nitroxyl radical in acidic medium the cation $R_2N{=}O^+$ acts as an oxidizing agent. In the chemical polymerization in *system 2* the protons were added by tosylate and pyrrole acts as an electron donor. Thus a rapid oxidation of pyrrole is found. The same behaviour was observed in *system 3* after the addition of protons by HCl but with a considerably slower rate as compared to *system 2*. In the coupled ECH-CH synthesis protons are produced in the initial stage of electropolymerization (15) initiating the simultaneous chemical polymerization by nitrosonium ions present in the solution. In addition, during the anodic polymerization the oxidation of nitroxyl radical and hydroxylamine (produced by reduction of NR) to nitrosonium ion takes also place as it is known from the literature (7).

Scheme 1. Redox states of nitroxyl radicals (X = OH for TEMPOL)



The pyrrole oligomers and the polymer chains produced in solution in *system 1* are immediately deposited on the surface of the working electrode. As no colour changes in the solution are observed, in contrary to rapid colour changes from yellow to blue-green in chemical oxidation of pyrrole in *systems 2* and *3*, the rapid electrocoagulation of coloured oligomeric products on the electrode surface is confirmed. After both chemical and coupled ECH-CH synthesis of PPy using nitroxyl radicals only a single narrow ESR line is found in the polymer layer or polymer powder on air (linewidth $\Delta H = 0.25$ mT) and in vacuum (linewidth $\Delta H = 0.06$ mT). This result indicates that nitroxyl radicals are transformed into new chemical states which are ESR inactive: hydroxylamine by reduction and nitrosonium ion by its two electron oxidation in the presence of protons (7). After potentiostatic electrolysis at -600 mV of that PPy prepared by coupled ECH-CH method the intensity of the ESR triplet signal of TEMPOL is found besides the broad ESR signal of the polymer measured both in air and in vacuum. In this cathodic step it is possible to prepare nitroxyl radicals inside the PPy matrix by reduction of the nitrosonium ion. Using various times of reduction ESR spectra of modified PPy were observed differing in the ratio of the spin probe triplet and the polaron singlet.

In Fig.1 the ESR spectra of polypyrrole prepared using *system 1* (0.1 M $LiClO_4$, 0.01 M pyrrole, 0.05 M TEMPOL aqueous solution polymerized at +700 mV *vs.* SCE and reduced after polymerization at -600 mV *vs.* SCE in 0.1 M $LiClO_4$ solution at various times) are presented. The pattern of the ESR signals indicates different concentrations of both spin probe and polymer paramagnetic centres (polarons) in polymer matrix in dependence on the extension of reduction.

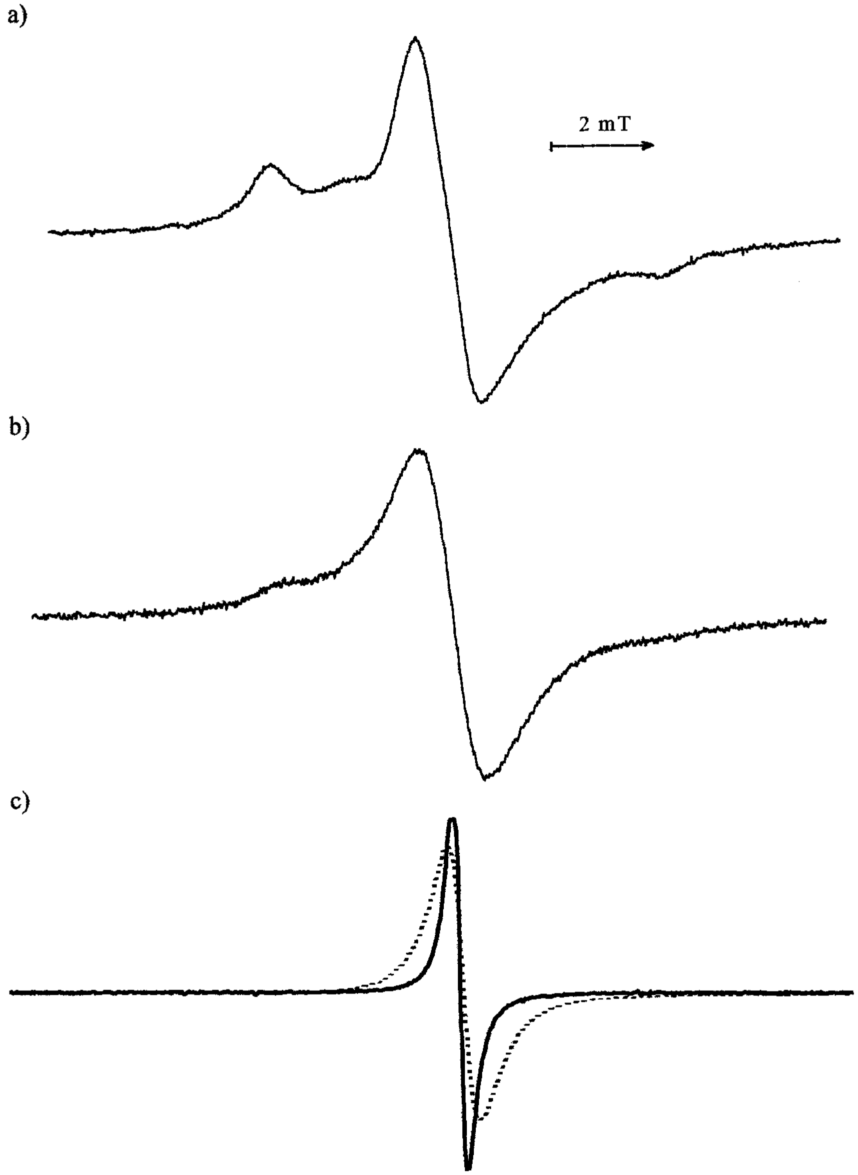


Figure 1. ESR spectra of nitroxyl radical-modified PPy at different degrees of film reduction measured at room temperature in toluene (solid line) and on air (dashed line). (a) after prolonged reduction, $c_{NR} >> c_{PPy}$; (b) after partial reduction, $c_{NR} \approx c_{PPy}$ and (c) without reduction, $c_{NR} << c_{PPy}$. (c_{NR} -concentration of nitroxyl radicals in PPy matrix, c_{PPy} - concentration of polarons in PPy matrix).

At room temperature the anisotropic broadening of the NR lines can already be observed. That means that the NR has a low mobility in the PPy matrix and the size of the pore where the radical is localised does not exceed 1 nm (9). The electronic interaction between the nitroxyl groups and the paramagnetic centers of the polymer chains causes an ESR line broadening of polarons both on air (1.1 mT) and in vacuum (0.7 mT) as compared to unmodified PPy (0.2 mT on air, 0.05 mT in vacuum).

Taking all reactions in the polymerization mixture into account a reaction mechanism of PPy synthesis in presence of NR is proposed. In the coupled ECH-CH synthesis nitroxyl radicals act in protic media after disproportionation *via* nitrosonium cations as oxidant of pyrrole being reduced to hydroxylamine which is re-oxidized by the electrochemical two electron step to form nitrosonium ions according to the equations:

$$\mathrm{nPy} - 2\mathrm{ne}^- \rightarrow (\mathrm{Py})_n + 2\mathrm{nH}^+ \qquad (1)$$

$$2\mathrm{R_2NO}^\bullet + 2\mathrm{H}^+ \rightleftharpoons \mathrm{R_2N{=}O}^+ + \mathrm{R_2NOH_2}^+ \qquad (2)$$

$$\mathrm{R_2NO}^\bullet - \mathrm{e}^- \rightleftharpoons \mathrm{R_2N{=}O}^+ \qquad (3)$$

$$\mathrm{mPy} + \mathrm{mR_2N{=}O}^+ \rightarrow (\mathrm{Py})_m + \mathrm{mR_2NOH_2}^+ \qquad (4)$$

$$\mathrm{R_2NOH_2}^+ - 2\mathrm{e}^- \rightleftharpoons \mathrm{R_2N{=}O}^+ + 2\,\mathrm{H}^+ \qquad (5)$$

Furthermore the copolymerization of reduced nitroxyl radicals in PPy seems to be possible as the reaction mechanism similar to that of the oxidative polymerization of pyrrole and quinone (16) or to that of the electrochemical polymerization of pyrrole and squaric acid as referred in (17). Further investigations will decide where the nitroxyl radicals are located in holes in the polymer matrix either without any chemical bond to the polymer backbone or in a copolymer structure in the main or the side chain *via* covalent bonds to pyrrole.

In summary it was shown that nitroxyl radicals in aqueous and nonaqueous solutions can cause an oxidative polymerization of pyrrole in the presence of protons to form polypyrrole with reduced as well as oxidized forms of NR incorporated in the PPy matrix. The protons resulting from electrochemical polymerization at the electrode and the nitrosonium ions produced by the electrochemical oxidation of NR are the reason for a coupled electrochemical-chemical polymerization of pyrrol. Nitrosonium ions present in polymer matrix can be electrochemically reduced in an one-electron step to form the nitroxyl radicals. ESR spectra indicate that even at room temperature the incorporated NR have a restricted rotational mobility in the polymer matrix.

The PPy deposited at the electrode surface is characterized by the following new properties:

- nitroxyl radicals incorporated in the polymer matrix can be applied in spin studies of the polymer (9, 10). Their concentration can be changed using various degrees of polymer reduction as illustrated Figure 1.
- both the porosity of the films and the film stability on the electrode surface enable the incorporation of special molecules like catalysts, redox mediators and others inside the polymer matrix (11)
- the electrical conductivity of PPy prepared by the coupled ECH-CH synthesis and chemical synthesis using MeCN tosylat solutions is significantly higher (in two orders of magnitude) in comparison to the PPy prepared by chemical synthesis using NR in its oxidation state as the only oxidizing agent in aqueous solutions.

A study of various pyrrole oligomers (and their oxidized forms) produced in the solution during chemical polymerization with nitroxyl radical and the application of ESR spectroscopy in reaction kinetic studies of this pyrrole reaction using the unique property of this free spin oxidizing agent is currently in progress.

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