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Elaboration and characterization of carboxylic acid-functionalized polypyrrole films

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ABSTRACT

Conducting polymers such as polypyrrole and its derivatives are highly attractive for a number of applications including biology, sensing and molecular electronics. For these purposes, poly(*N*-carboxyalkylpyrroles) are of interest since they contain a terminal carboxyl group that can be easily modified with biological or chemical moieties. In the present study, pyrrole monomers were modified by grafting, on the N-position of the pyrrole monomer, of an alkyl chain, whose length varied from 1 to 10 carbons, terminated by a carboxyl group. The substitution significantly decreased the solubility of the monomers but it was although possible to solubilize them in acetonitrile. So, the anodic oxidation of these N-substituted pyrroles was performed in acetonitrile leading to the electrodeposition of substituted polypyrrole films. The morphological features (topography, thickness, roughness) were determined and compared with the ones of polypyrrole and poly(*N*-alkylpyrroles) having the same chain length. The morphology of the polymer films was shown to be strongly dependent on the alkyl chain since non-substituted polypyrrole exhibited granular structure when substituted ones had a fibrillar structure. The substitution also significantly impacts on the wettability of the films because an increase of the substituted chain length led to the increase of the hydrophobicity of poly(*N*-carboxyalkylpyrroles).

1. Introduction

Conducting polymers are an exciting new class of electronic materials, which have attracted an increasing interest since their discovery in 1977 [1]. They have many advantages, as compared to the non-conducting polymers, which is primarily due to their electronic and optical properties. Thus, they have been used for many different applications including: energy storage [2,3], field-effect transistors [4], electrochromism [5], (bio)sensing [6,7], or artificial muscles [8]. Among the numerous heterocyclic polymers, polypyrrole (PPy) and its derivatives are frequently used because they are environmentaly stable and provide high electrical conductivity [9,10]. Polypyrrole can be obtained either by electrochemical polymerization or by oxidative chemical polymerization. However, fabrication of PPy films by electropolymerization is probably the most attractive technique since it allows the pyrrole monomer, dissolved in a solvent and containing an anionic dopant, to be easily oxidixed at the electrode surface by application of an anodic potential, forming a polymer film and since it allows to easily control the thickness of this film.

To tune properties of conducting polymers, a strategy consists in using organic chemistry to synthesize original electropolymerizable monomer units. For this purpose, chemical modifications to the pyrrole monomer leading to N-substituted derivatives and corresponding derivative electropolymerizations have already been done [11–18]. For example, a series of poly-*N*-alkylpyrroles have been electrosynthesized and it was evidenced that the conductivity of the films decreased with the introduction of *N*-alkyl substituents [11]. 3-methyl-1H-pyrrole and 3,4-dimethyl-1H-pyrrole were also electropolymerized and used as actuators for soft microrobotics [12]. A series of *N*-alkyl derived pyrrole monomers, where the substituent of the alkyl chain is a hydroxyl or a tosyl group, was prepared by Bidan et al. [13]. Their electropolymerization was shown to be possible except for hydroxylated pyrrole monomers where it was blocked for short alkyl chains. Several carbazole-pyrrole-based carboxylated monomers were also synthesized and a successful electropolymerization was obtained when a carbazole/pyrrole unit ratio greater than or equal to one was used [14,15]. An important work was also realized by Kumar et al. who studied the structure-reactivity relationship of twenty one different N-substituted pyrrole derivatives showing the importance of steric effects on the electropolymerization reaction.

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Poly(*N*-carboxyalkylpyrroles) are among the most interesting polypyrrole derivatives since the presence of carboxyl groups can lead to the formation of amide linkages by the condensation reaction of the carboxyl groups with amino groups of chemical or biological moieties. Thus, carboxylic acid-functionalized conductive polypyrroles was prepared by Lee et al. and successfully used as substrate for the culture of human umbilical vein endothelial cells [16,17]. These polypyrrole derivatives were prepared by grafting of the substituent either at the N-position of the polymer backbone [16] or at its Cα-position [17]. 3-pyrrolylacrylic acid and 5-(3-pyrrolyl)-2,4-pentadienoic acid were also synthesized and were successfully used for DNA sensing [18]. The polymerization of pyrrole-3-carboxylic acid [19] and pyrrole-2-carboxylic acid [20] was also recently reported. Poly(pyrrole-2-carboxylic acid) was polymerized by electrochemical oxidation and used for the amperometric detection of catechol [20]. Poly(pyrrole-2-carboxylic acid) was also synthesized by chemical oxidative polymerization catalyzed by an enzyme and used for the covalent attachment of biologically active materials as bioreceptors [21].

Taking into account this literature, the present study aimed at synthesizing a series of *N*-carboxyalkylpyrroles and *N*-alkylpyrroles for comparison. Then, the solubilization and the electrooxidation of the synthesized N-substituted pyrroles were studied in water and acetonitrile. The properties (morphology, thickness, roughness, wettability) of the resulting substituted polypyrrole films were also investigated to determine the influence of the grafted alkyl chain length and terminal carboxy group on these properties.

2. Experimental

2.1. Reagents

All reagents used to prepare monomers and dry DMSO (Acroseal®) were purchased from Acros and used as received unless otherwise stated. Pyrrole was distilled under reduced pressure prior to use. Lithium perchlorate was from Sigma Aldrich and used as electrolytic salt. The solvent used was either acetonitrile from Fisher Scientific or double deionized water (Milli-Q, resistivity 18 MΩ cm).

2.2. Synthesis

Chromatography was carried out on Teledyne Isco Rf Lumen+ Flash Chromatographer or by Dry-Column-Vacuum-Chromatography (DCVC) [22]. ^{1}H and 13C NMR were recorded on a Bruker Avance 300 spectrometer. Melting points were recorded on a Stuart SMP 10 melting point apparatus and are uncorrected.

2.2.1. *Pyrrole*-N-*propanoic acid (P2C)*

In a three-necked round-bottomed flask are successively placed pyrrole (3.8 mL; 54 mmol) and a 40% solution of benzyltrimethylammonium hydroxide in methanol (0.3 mL). Acrylonitrile (2.9 mL; 43 mmol) is added dropwise while maintaining temperature below 40 °C. The reaction mixture is stirred at room temperature for 17 h. Then, aqueous 10 mol/L potassium hydroxide (50 mL) is added to the flask and the content is refluxed for 12 h. After cooling to room temperature, the pH of the solution is adjusted to 2 by the dropwise addition of concentrated hydrochloric acid. The solid so obtained is filtered and washed with deionized water (50 mL). Aqueous layer is extracted with ethyl acetate (4 × 30 mL). Organic layers are combined, washed with brine (75 mL), dried over sodium sulfate and concentrated. The crude brown oil is purified by flash chromatography to afford P2C (4.34 g; 71%) as a colorless oil which solidifies as a white solid (Mp = 62 °C) upon standing. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 6.68 (br s, 2H, N-C**H** = pyrrole), 6.16 (br s, 2H, C**H** pyrrole), 4.22 (t, 2H, J = 6 Hz, N-C**H$_2$**-), 2.84 (t, 2H, J = 6 Hz, −C**H$_2$**-COOH). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 177.8, 120.7, 108.7, 44.5, 36.4.

2.2.2. *Pyrrole*-N-*undecanoic acid (P10C)*

In a round-bottomed flask are successively introduced 11-aminoundecanoic acid (43.28 g; 215 mmol), glacial acetic acid (215 mL), 1,4-dioxane (285 mL) and 2,5-dimethoxytetrahydrofuran (32 mL; 247 mmol). The mixture is refluxed for 4 h and stirred at room temperature for 24 h. Solvent is removed under reduced pressure and the resulting oil is purified by DCVC (Dichloromethane/Ethanol 100:0–95:5 v:v). The resulting beige solid is further purified by recristallization from pentane to afford pure P10C (13.51 g; 20%) as a white solid (Mp = 63 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 6.66 (br s, 2H, N-C**H** pyrrole), 6.15 (br s, 2H, C**H** pyrrole), 3.88 (t, 2H, J = 7 Hz, N-C**H$_2$**-), 2.36 (t, 2H, J = 6 Hz, −C**H$_2$**-COOH), 1.30 (m, 16H, −(C**H$_2$**)$_8$-). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 180.5, 120.4, 107.8, 49.6, 34.1, 31.6, 29.4, 29.3, 29.2, 29.0, 26.7, 24.7.

2.2.3. N-*propylpyrrole (P2Me)*

A suspension of 85% powdered potassium hydroxide (8.80 g) in dry DMSO (200 mL) is stirred at room temperature under argon for half an hour. Pyrrole (4.50 g; 67 mmol) is added and the solution is stirred for 30 min. Propyliodide (11.39 g; 67 mmol) is then added and the reaction mixture is stirred at room temperature under argon for 24 h. The mixture is poured onto water (1000 mL) and the aqueous layer is extracted with dichloromethane (4 × 150 mL). Organic layers are combined, washed with water (3 × 150 mL), dried over sodium sulfate and concentrated. The crude product is purified by distillation under reduced pressure which affords pure P2Me (0.78 g; 11%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 6.70 (br s, 2H, N-C**H** pyrrole), 6.19 (br s, 2H, C**H** pyrrole), 3.88 (t, 2H, J = 9 Hz, N-C**H$_2$**-), 1.84 (sext., 2H, J = 9 Hz, −C**H$_2$**-CH_3), 0.96 (t, 3H, J = 9 Hz, CH_2-C**H$_3$**). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 120.7, 108.1, 51.5, 25.2, 11.6.

Alternatively, P2Me can be prepared according to the procedure by Guida and Mathre [23]: to a solution of 18-Crown-6 (0.80 g; 3 mmol) in dry ether (50 mL) are added potassium *tert*-butoxide (3.90 g; 35 mmol) and pyrrole (2.01 g; 30 mmol). The reaction medium is stirred at room temperature for 15 minutes. Then, a solution of *n*-propyl iodide (5.95 g; 35 mmol) in dry ether (20 mL) is added dropwise and the mixture is stirred at room temperature for 18 h. Water is added and the phases are separated. Aqueous layer is extracted with ether (2 × 20 mL). Organic layers are combined, washed with brine (50 mL), dried over sodium sulfate and concentrated. The crude product is purified by distillation under reduced pressure which affords pure P2Me (1.41 g; 43%) as a colorless oil.

2.2.4. N-*undecylpyrrole (P10Me)*

A suspension of powdered 85% potassium hydroxide (2.07 g; 31 mmol) in dry DMSO (50 mL) is stirred at room temperature under argon for half an hour. Pyrrole (1.06 g; 16 mmol) is added and the solution is stirred for 30 min. 1-Bromoundecane (3.70 g; 15 mmol) is then added and the reaction mixture is stirred at room temperature under argon for 24 h. The mixture is poured onto water (250 mL) and the aqueous layer is extracted with dichloromethane (3 × 50 mL). Organic layers are combined, washed with water (2 × 100 mL), dried over sodium sulfate and concentrated. The crude product is purified by flash chromatography which affords pure P10Me (0.50 g; 15%) as a light yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 6.77 (br s, 2H, N-C**H** pyrrole), 6.27 (br s, 2H, C**H** pyrrole), 3.98 (t, 2H, J = 6 Hz, N-C**H$_2$**−), 1.41 (m, 18H, −(C**H$_2$**)$_9$−), 1.04 (t, 3H, J = 6 Hz, CH_2-C**H$_3$**). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 120.5, 107.9, 49.7, 32.1, 31.8, 29.8, 29.7, 29.5, 29.4, 26.9, 22.9, 14.3.