

# Interfacial polymerization of pyrrole and in situ synthesis of polypyrrole/silver nanocomposites

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## Abstract

We present a new synthetic approach leading to the formation of polypyrrole architectures in submicron level and to silver/polypyrrole nanocomposites via an interfacial polymerization in a water/chloroform interface. The oxidizing agent was either Ag(I) or Fe(III). In the first case, silver nanoparticles resulted. The mean diameter of the polypyrrole structures is in the range of 200–300 nm according to the addition or not of various surfactants. The progress of the reaction was studied by UV–visible spectroscopy, which also revealed the formation of a polaron band during the growth of the oligomers. The crystal structure of the polymers was examined by X ray diffractometry and all samples appeared to be amorphous, while the samples were further characterized by thermogravimetric analysis and FT-IR spectroscopy.

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## 1. Introduction

Recent advances in the field of electrically conducting polymers have attracted an increasing interest in the study of submicron or nanostructural electroactive polymers [1]. For example, polyaniline nanotubes or nanofibers with diameters less than 100 nm have been synthesized by polymerizing the monomer in either “hard” or “soft” templates. The former includes zeolites [2], polycarbonate [3], anodized alumina [4], micelles [5], liquid crystals [6] and polyacids [7]. Recently, the synthesis of polyaniline [8] and polypyrrole nanotubes [9] or nanofibers via a template seeding route has been described. The size of these polymeric nanotubes can be controlled in the range of 20–100 nm according to the kind of template used in the synthesis [9]. Expanding the reported

structures that fall within the submicron level, hollow polyaniline or polypyrrole spheres have also been reported [10]. Moreover, interfacial polymerization has been applied for the synthesis of polyaniline nanofibers [11]. However, several factors affecting the formation of the various nanostructures and the corresponding polymerization mechanisms are yet to be clearly identified.

In addition, silver nanoparticles exhibit significantly interesting conductive and optical properties [12]. Their size and shape dependent optical properties arise from their surface plasmon resonance frequency, characteristic of noble metals with free electrons such as Au and Ag which results in a characteristic absorption in the UV–visible spectrum [13]. The novel features of metal nanoparticles and conductive polymers lead to an increasing interest in the synthesis of composite materials consisting from finely and homogeneously dispersed nanoparticles in polymer matrices [14]. Specifically Ag(I) has been previously reported to initiate the polymerization of pyrrole leading to polypyrrole and silver nanostructures

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[14a]. However, one major problem when synthesizing nanocomposite materials derived from the dispersion of nanoparticles in polymer matrices is the aggregation of nanoparticles [15].

This article describes the polymerization of pyrrole in the boundary of two immiscible solvents which can be applied for the synthesis of silver/polypyrrole nanocomposites. To our knowledge no previous work has been reported to describe the interfacial polymerization of pyrrole. An important aspect of the interfacial polymerization procedure is that it enables the addition of various surfactant molecules, either negatively or positively charged, to the organic phase or even hydrophilic surfactants to the aqueous phase. As a result, the morphological and structural characteristics of the polymer can be easily controlled according to the reaction conditions. The aim of our work is to extensively study the interfacial polymerization of pyrrole and to synthesize nanocomposite materials with finely dispersed silver nanoparticles of low mean diameter.

## 2. Experimental part

### 2.1. Chemicals

Reagent grade  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , dodecyltrimethylammonium bromide (DTAB) and sodium dodecylsulfate (SDS) were used as received from Aldrich, Eastman and Fluka, respectively. Pyrrole (Aldrich) was distilled under nitrogen before use.  $\text{Ag}(\text{NO}_3)$  was purchased from Riedel De Haan (99.5%).

### 2.2. Synthesis of polypyrrole

The synthetic procedure involves polymerization of pyrrole in a water/chloroform interface with pyrrole monomer and surfactants added to the organic phase, while  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  to the aqueous phase. The aqueous solution was slowly added to the organic medium. In a typical preparation, a solution of 300 mg  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (0.75 mmol) in 15 ml of  $\text{H}_2\text{O}$  was slowly spread to 15 ml chloroform containing 0.8 ml of pyrrole monomer (11 mmol) and 0.7 mmol of DTAB or SDS. As the reaction proceeded, without stirring, a black film appeared at the interface. A 24 h reaction time was sufficient to complete the growth of the polypyrrole film. The byproducts of the reaction were easily removed due to their solubility in the aqueous or organic media. The insoluble in organic or polar solvents film was isolated by decanting the solvents, washed several times with water and alcohol and air dried. During the reaction progress pyrrole oligomers were detected in the aqueous phase. Their solubility allowed the recording of the UV–visible spectra. The polypyrrole obtained without surfactants is designated as PPy/ $\text{NO}_3$ , while the samples with SDS and DTAB as PPy/SDS and PPy/DTAB, respectively.

### 2.3. Synthesis of silver/polypyrrole nanocomposites

$\text{AgNO}_3$  (130 mg, 0.75 mmol) used as an oxidant was dissolved in 15 ml  $\text{H}_2\text{O}$  and the solution was added to 7 mmol

of pyrrole (0.5 ml) in 15 ml of chloroform. The polymerization proceeded as described when Fe(III) was used as an oxidant. Sample name: PPy/Ag.

## 3. Characterization techniques

X ray diffraction patterns were recorded on powder samples by a Siemens 500 Diffractometer.  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) was used with a scan rate  $0.03^\circ/2 \text{ s}$ . Thermogravimetric measurements (TGA) were recorded on a Perkin–Elmer Pyris TGA/DTA apparatus under a continuous air flow with a heating rate  $10^\circ\text{C}/\text{min}$ . For the thermal analysis measurements about 3–4 mg of each sample was used. Infrared (FT-IR) spectroscopy studies were performed on a Bruker Equinox 55/S model spectrometer. The specimen was made by mixing the corresponding composites with KBr (Aldrich, 99%, FT-IR grade). The samples were dried at  $60^\circ\text{C}$  for 24 h before all measurements. UV–visible spectra of the aqueous solution were collected on a Shimadzu 2100 spectrometer in quartz cuvettes. Scanning electron microscopy images were recorded on a Carl Zeiss Supra 35 VP. Transmission electron microscopy images were recorded on a Philips CM20 operated at 200 kV.

## 4. Results and discussion

For the synthesis of polypyrrole films ferric ions ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) or silver cations ( $\text{Ag}(\text{NO}_3)$ ) were used as oxidizing agents. Following the transfer of reagent solutions to the reaction vessel the polymerization started and after a few hours a polypyrrole film was formed at the interface. It is important to note that while the oxidative polymerization of pyrrole in solution is a rapid and not controllable reaction, the corresponding reaction at the interface of two immiscible liquids involves the diffusion of the reactants to the interface, and thus the growth of the film is slow and completed in almost 24 h. We also note that while in the case of interfacial polymerization of aniline, the oxidized and protonated polyaniline are soluble in water and migrate to the aqueous phase, in the pyrrole case the resulting polypyrrole is insoluble in common organic or polar solvents and thus after completion of reaction, a black film is observed at the interface that is easily separated and dried.

The growth of the interfacial polypyrrole film can be inferred by tracking the evolution of the oligomers in the aqueous phase. Although, the oxidative polymerization occurs mainly at the interface, a small percentage of the pyrrole monomers diffuses to the aqueous phase where limited bulk polymerization leads to the formation of soluble pyrrole oligomers. When the molecular weight of the oligomers increases the polymers become insoluble in both solvents. It is interesting to note that in the absence of surfactant, the aqueous phase acquires a light red color within a few minutes, in contrast to a light green when SDS and DTAB were added.

The UV–visible spectra of the oligomers formed in the aqueous phase are shown in Fig. 1. At the start of reaction the spectrum is that of  $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ . As the reaction proceeds

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