

Host-guest complexation: a new strategy for electrodeposition of processable polythiophene composites from aqueous medium

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For the first time host-guest complexation is used to (i) electrosynthesize polybithiophene in an aqueous medium and (ii) generate polybithiophene with electroactivity in water, enhanced solubility in common solvents and processability.

Electropolymerization of aromatic and heteroaromatic compounds, leading to anodic deposition of films, is one of the most valuable techniques for obtaining electrically conducting organic polymers which suffer from very low solubility and poor processability. With the exception of polyaniline and polypyrrole, which are sometimes electrosynthesized in aqueous solutions, most conducting polymers are synthesized in organic media.^{1,2} The reasons are the very low water-solubility of monomers, whose oxidation potential is, moreover, higher than that of water decomposition, and the relatively high reactivity of the initially formed radical cations with water molecules.² For practical and industrial applications, however, water is the ideal solvent. Acidic solutions of various compositions³⁻⁵ and anionic micellar media have been proposed for the electrosynthesis of polythiophene (PT) films in aqueous solution.⁶ Furthermore, soluble and processable conducting polymers are needed in terms of industrial and practical applications. To enhance the processability of these materials, grafting long alkyl groups onto the polymer backbone has been used. This strategy induces modifications of the interchain interactions and makes, for instance, poly(octylthiophene) soluble in most common solvents.⁷ We report here a new strategy which allows the synthesis of soluble polythiophene composites from an aqueous medium with no covalent modification of the polymer backbone. It uses host-guest complexation, without any covalent bonds being formed⁸ prior to the electropolymerization step, cyclodextrin being the host, bithiophene being the guest.

Cyclodextrins have been widely studied because of their ability to form inclusion compounds with a large variety of molecules. They are cyclic oligosaccharides consisting of six, seven or eight glucose units (α -, β - and γ -cyclodextrins) with a hydrophobic inner cavity and a hydrophilic outer side. They, therefore, readily form inclusion compounds with hydrophobic species in aqueous media.⁹ We have chosen to use hydroxypropyl- β -cyclodextrin (HP β CD), because of the size of its cavity and its good water-solubility, and bithiophene (BT) as the monomer, because it fits the β -cyclodextrin's cavity, is a rather hydrophobic molecule and has a lower oxidation potential than water.

The water-solubility of BT is very low ($<10^{-4}$ M) but is dramatically increased in the presence of HP β CD. Aqueous solutions of 10^{-3} and 10^{-2} M BT can be easily prepared with 10^{-1} M HP β CD, indicating the formation of an inclusion compound between BT and HP β CD. Fluorescence analyses were carried out by increasing the HP β CD concentration progressively. Emission spectra exhibit variations showing a change in the chemical environment of BT: the fluorescence intensity increases with the HP β CD concentration. This fluorescence amplification is typical of an inclusion phenomenon.¹⁰

BT was electropolymerized in aqueous HP β CD. Polybithiophene (PBT) thin films can be produced by electrooxidation of an aqueous solution of 10^{-2} M BT, $5 \cdot 10^{-2}$ M HP β CD and 10^{-1} M LiClO₄ at platinum electrodes, using cyclic voltammetry and the galvanostatic method. Multicycle voltammograms were recorded between -0.2 and 1.15 V vs. SCE at a scan rate of 100 mV s⁻¹. The first anodic sweep shows a wave at 1.0 V vs. SCE, corresponding to the oxidation of BT; additional anodic and cathodic peaks increase regularly with the number of successive cycles (Fig. 1). A thin, homogeneous and adherent film is obtained at the platinum electrode. It shows electroactive and electrochromic properties (Fig. 2) whereas PT and PBT films prepared from an organic solution (without cyclodextrins) do not show any electroactivity upon electrochemical cycling in aq. LiClO₄ solutions. Depending on the applied potential, the film is red (reduced state) or green (oxidized state). Similar films can be synthesized by applying constant current densities of 0.05 , 0.1 and 0.2 mA cm⁻² for 15 min. The chronopotentiometric responses of the electrode exhibits an instantaneous rise of the potential close to 1 V. Using higher current densities leads to non-adherent films.

The resonance Raman spectra (Fig. 3), performed *ex situ* with an excitation wavelength of 514.2 nm on a reduced film, are similar to those of PBT films formed in organic media. The most intense band at 1455 cm⁻¹ is assigned to the symmetric stretching mode of the aromatic C=C band, while a weaker band at 1492 cm⁻¹ is attributed to the antisymmetric stretching vibration. Other, weaker bands at 1364 and 1268 cm⁻¹ are

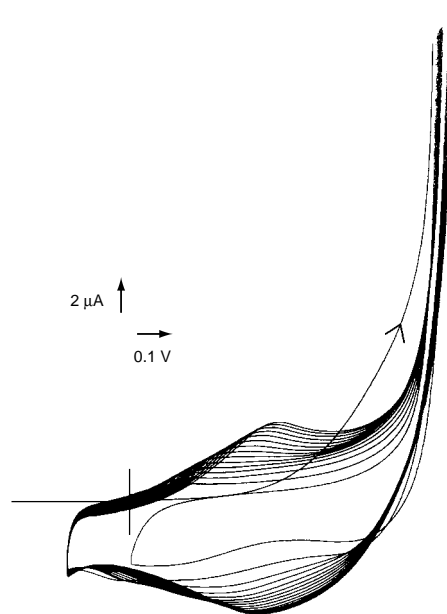


Fig. 1 Voltametric synthesis of PBT film from aq. BT (10^{-2} M), HP β CD (5×10^{-2} M) and LiClO₄ (10^{-1} M) on Pt electrode ($v = 100$ mV s⁻¹): (arrow denotes first cycle)

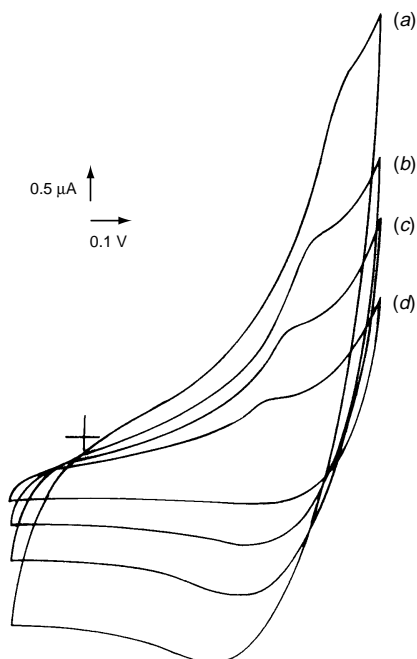


Fig. 2 Electroactivity of a PBT composite in aq. LiClO_4 (2.10–1.00 M) for various scan rates: (a) 200, (b) 100, (c) 50 and (d) 20 mVs^{-1}

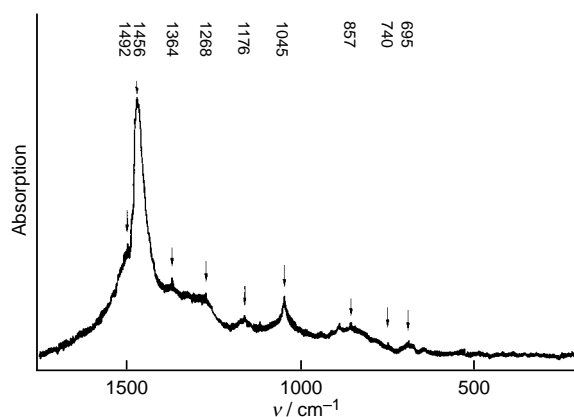


Fig. 3 Resonance Raman spectrum of PBT films deposited from aq. $\text{HP}\beta\text{CD}$

assigned to the stretching mode of the single C–C bond and the C–C inter-ring bond, respectively. The bands at 1045 and 695 cm^{-1} are attributed to the deformation modes of the C–H bond and the C–S–C aromatic bond (Fig. 3). The FT-IR spectra are

also very similar to those of PBT films prepared in organic media but display strong bands at 3400, 2960 and 2930 cm^{-1} characteristic of cyclodextrins. A film washed in water for three days in order to eliminate residual cyclodextrins molecules still exhibits these strong bands, showing that cyclodextrins remain in the polymer film. The PBT films deposited from aq. $\text{HP}\beta\text{CD}$ solutions are soluble in DMF, DMSO and THF, while PBT films prepared in MeCN are insoluble in these solvents. Since it is well-known that, for β -substituted oligothiophenes, the variation of the absorption maximum energy as a function of the inverse of the chain length is linear,¹¹ an average conjugation length of 15 thiophene units is estimated from UV–VIS spectroscopy (performed on the fully reduced film), indicating that the material does not consist of low molecular weight oligomers.

We have demonstrated that electropolymerization of BT in an aqueous solution of $\text{HP}\beta\text{CD}$ is possible and leads to a homogeneous films similar to that produced in organic media. According to our first analyses, it seems that cyclodextrins persist in the film. The abnormal solubility in common solvents of PBT films electrosynthesized in aq. $\text{HP}\beta\text{CD}$, associated with a high conjugation length, strongly suggests that the polymer chains are partially encapsulated by cyclodextrins. Further work is in hand to confirm this interpretation.

Notes and References

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Received in Cambridge, UK, 3rd November 1997; 7/07862E