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Host–guest complexation: a convenient route to polybithiophene composites by electrosynthesis in aqueous media. Synthesis and characterization of a new material containing cyclodextrins

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An inclusion compound with hydroxypropyl-β-cyclodextrin (HPβCD) as host molecule has been used to electropolymerize bithiophene in aqueous medium. The complexation of bithiophene by HPβCD has been investigated by fluorescence, showing that BT molecules are tightly bound to cyclodextrin hosts. The electrochemical behaviour of this inclusion compound is irreversible in aqueous solution in the presence of HPβCD. The anodic electropolymerization of the BT–HPβCD complex has been performed in aqueous medium under galvanostatic or potentiodynamic conditions. Characterization of the deposited films supports the notion that polybithiophene (PBT) composites are formed. Although they show the usual features of PBT, the structure of the films appears to be considerably modified by the presence of cyclodextrins within the material but not grafted onto the polymeric backbone.

Introduction

In recent years, the synthesis and characterization of electroactive polymers have become an important research area in polymer science.[1] Among these polymers, polyheterocycles such as polypyrrole (PPy) and polythiophene (PT) have been widely studied on account of their good chemical stability and interesting redox properties.[1,2]

In contrast to PPy that can be obtained in aqueous media, PT is generally synthesized in organic media (in acetonitrile or nitrobenzene[3,4]). The insolubility of the monomer in aqueous media and the fact that its redox potential is higher than that for the decomposition of water are the two main reasons why thiophene does not electropolymerize in water. In addition to these reasons, the high reactivity of the thienyl radical cation with water molecules would lead to the formation of defects in the polymer or may impede electropolymerization. For industrial and practical applications (low cost of fabrication, environmental safety), water is however the most attractive solvent. Recently, acidic solutions or anionic micellar media have been successfully used to electropolymerize thiophene[5,6] and water-insoluble (or weakly soluble) thiophene derivatives such as 3,4-ethylenedioxythiophene (EDOT)[7] and bithiophene (BT).[8] It was shown that the films generated have properties and structures similar to those formed in organic media.

Cyclodextrins (CD) are toroidally shaped cyclic oligosaccharides with a hydrophobic internal cavity and a hydrophilic outer side. They are soluble in water and form stable inclusion complexes with hydrophobic guests that fit tightly (but without any formation of covalent bonds) inside the cyclodextrin cavity.[9] Cyclodextrins are not electroactive but they do form inclusion complexes with suitable redox-active guests. Numerous studies have been devoted to studying the electrochemical behaviour of these redox-active molecules included in cyclodextrin.[10–12] All these studies point to similar conclusions: the heterogeneous electron transfer reaction takes place only on the free guests, provided that the inclusion complexes remain kinetically labile. For instance, the oxidation of ferrocene guests occurs only after dissociation of the inclusion complex. This is probably the reason why there are hardly any observations involving the electropolymerization of inclusion compounds used as starting monomers whereas the chemical polymerization of inclusion compounds has been widely reported.[13–15] In a previous communication, we showed that the use of host–guest complexation makes it possible to grow polybithiophene in aqueous medium by anodic oxidation of a BT–HPβCD inclusion compound.[16]

In this paper, we wish to present a detailed study of this approach through the design, the synthesis and the characterization of these new molecular building blocks. We will demonstrate that although the PBT films present the usual pattern of the polythiophene family, cyclodextrins have a dramatic effect on the structure of the material, which may be viewed as a composite.

Experimental

Bithiophene (Acros), lithium perchlorate (Acros), βCD (Aldrich) and HPβCD (MS=0.8; Aldrich) were used as received. Distilled water was purified by a Millipore system.

Preparation of the BT–βCD complex

BT (59.5 mg, 7 mM) was added to a saturated βCD solution (0.74 g, 10 mM at 20 °C). The mixture was stirred at 60 °C under Ar for 15 min, then allowed to cool to room temperature. The precipitate (white solid) was isolated by filtration, washed with H_2O and ether, then dried under vacuum for 4 h (Calcd. for $C_{50}H_{76}O_{35}S_2\cdot3H_2O$: C 44.31; H 5.61; O 41.4; S 4.73; Found: C 44.16; H 6.07; O 43.8; S 4.62%).

Fluorescence spectra

All measurements were performed at 23 ± 0.1 °C. Fully corrected fluorescence spectra were recorded on an Aminco Bowman series 2 luminescence spectrophotometer. The excitation wavelength was 300 nm. The emission was monitored between 320 and 480 nm (the emission maximum is at 365 nm).

To study the complexation equilibrium, the samples were prepared as follows: 25 mL aqueous solution of BT was prepared from a stock solution of BT in absolute ethanol. The final concentration in water (containing 5% v/v ethanol) of BT was 5 μM. Then variable small amounts of HPβCD from a 0.1 M HPβCD aqueous stock solution were added in order to obtain the desired HPβCD concentration. After each HPβCD addition, spectra were recorded on a 3 mL sample. This method limits the dilution effect.

Electrochemistry

All voltammetric and galvanostatic experiments were performed in a one-compartment, three-electrode cell by means of an EG&G PAR Model 362 potentiostat/galvanostat. The counter-electrode was a stainless steel grid, and an SCE electrode was used as reference. Electrochemical behaviour studies were carried out with a Pt disk (2 mm in diameter) or a glassy carbon electrode (3 mm in diameter), polished with diamond paste and rinsed in acetone with ultrasonic stirring before each experiment. For Raman, IR and XPS studies, films were deposited on an electrode consisting of a glass plate (10 mm × 30 mm) covered with a thin layer of Pt (*ca.* 500 nm) deposited by cathodic sputtering using a Balzers-Sputron II and a Pt target (Balzers, purity 99.9%). For UV–Vis measurements, transparent ITO plates were used as working electrodes. For the EQCM experiments, a 9-MHz quartz crystal (giving a sensitivity of 1.1 ng Hz^{-1}) metallized with Pt was used.

Spectroscopic experiments

Raman spectra were recorded on a Dilor XY double monochromator spectrometer in the backscattering configuration. The films deposited on the electrode were excited with a focused 514.5 nm laser beam. The power was always kept very low (*ca.* 4 mW) to avoid destruction of the films. FTIR experiments were performed on a Nicolet FTIR 60-SX spectrometer. The XPS spectra were obtained with a Vacuum Generators Escalab MKII spectrometer with an Al Kα X-ray source (power applied to the anode 200 W) at *ca.* 10^{-8} mbar pressure. The analyser was operated at constant pass energy (20 eV). The spectra were digitized, summed, smoothed and reconstructed using mixed Gaussian–Lorentzian components (Lorentzian $<20\%$). Binding energies are referred to C_{1s} at 285 eV. MALDI-MS spectra were recorded using a Voyager-Elite-Time-of-Flight Mass Spectrometer (PerSeptive Biosystems) and were averaged over 32 laser shots by a Tektronix TDS 520 oscilloscope. The sample was dissolved in DMF, then diluted to 10% in a matrix [1,8-dihydroxyanthracen-9(10*H*)-one].

All the films analysed were previously reduced, then carefully rinsed with water and acetone and air-dried. In some cases, the films deposited on the electrode were washed for three days with distilled water; they were dipped in a flask containing fresh water that was often renewed and vigorously stirred.

Results and discussion

a) Bithiophene inclusion in the host

Since one of the key parameters for forming inclusion compounds is the size of the host (as compared to the size of the guest), β-cyclodextrin (which consists of seven glucose units) is used. The size of its cavity (internal diameter 6.5 Å) fits well the size of BT molecules. The solubility of BT in water is very low ($<2\times10^{-5}$ M) but is dramatically increased in the presence of βCD but not with equivalent quantities of glucose. The complex between BT and βCD was prepared (see Experimental Section). It uses the fact that the complex is less soluble in water than free CD. Elemental analysis indicates a 1 : 1 stoichiometry for BT–βCD. The ^{1}H NMR spectrum of the complex in deuteriated DMSO (in which dissociation of the complex occurs) confirms this result: the ratio of proton signal attributed to H^1 of the βCD (Scheme 1) to the proton H_A of bithiophene is found to be 7 : 2.

However, low solubility of BT in water (0.5 mM) is reached with βCD. Since electropolymerization exhibits a concentration threshold, a rather high monomer concentration is important (10^{-2} M for bithiophene). The use of a substituted βCD, hydroxypropyl-β-cyclodextrin (HPβCD) whose solubility is up to 7×10^{-1} M in water, allows an increase in the solubility of BT in water. Then, aqueous solutions of 10^{-3} to 5×10^{-2} M BT can easily be prepared with 10^{-1} M HPβCD. The formation of the inclusion compound between BT and HPβCD is studied by fluorescence measurements.

Fluorescence. Fig. 1 shows a series of BT (5 μM) emission spectra recorded at HPβCD concentrations between 15 μM and 1.5 mM. Absorbance measurements were also tried as a method of monitoring complexation. Indeed, we observe systematic changes in the BT absorption spectrum on increasing the HPβCD concentrations. However, the changes are small compared to those observed in fluorescence spectra, making this latter method preferable. In this case, intermolecular stacking (aggregation) of BT can be ruled out, since BT obeys the Beer–Lambert law at concentrations below 10 μM. The fluorescence intensity decreases as the HPβCD concentration is increased, indicating that the fluorescence quantum yield of the inclusion complex is smaller than that of the free molecule (Fig. 1).

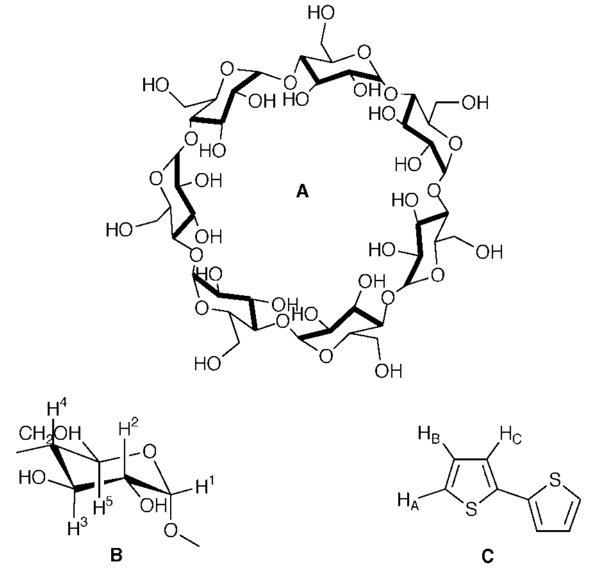
The spectra of Fig. 1 were fitted assuming formation of a 1 : 1 complex [eqn. (1)].

$$\mathrm{BT} + \mathrm{HP\beta CD} \rightleftharpoons \mathrm{HP\beta CD} - \mathrm{BT} \qquad (1)$$

According to eqn. (2), the binding constant K_1 was determined by a non-linear fit

$$I = \frac{I_0 + I_\infty K_1[\mathrm{HP\beta CD}]_T}{1 + K_1[\mathrm{HP\beta CD}]_T} \qquad (2)$$

where I_0, I and I_∞ denote the fluorescence intensity of BT in pure water, at a given intermediate HPβCD concentration and in the fully complexed form, respectively. The value of K_1 is 3570 ± 90 M^{-1}. This large value suggests a strong interaction between BT and HPβCD as a consequence of the low water solubility of BT. This value is very close to that reported by Shen and co-workers[17] ($K_1=3760\pm25$ M^{-1}) for the BT–βCD



Scheme 1 Structures of (A) β-cyclodextrin, (B) the D-glucose unit and (C) bithiophene.

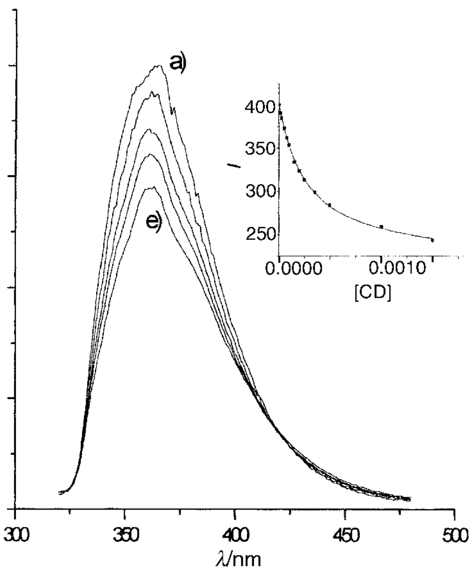


Fig. 1 Fluorescence spectra of BT (5 μM) with increasing HPβCD concentration: 0 M (a), 5×10^{-5} M (b), 1.5×10^{-4} M (c), 2.5×10^{-4} M (d), 5×10^{-4} M (e). Inset: plot of the fully corrected emission of BT at 365 nm at various HPβCD concentrations (■) experimental data (−) fit based on eqn. (2).

complex. It can be deduced that the hydroxypropyl substituent on the upper rim of the host does not greatly affect the complexation equilibrium between BT and β-cyclodextrins.

Electrochemical behaviour of the BT–HPβCD complex. Cyclic voltammograms of 10^{-3} M BT, 10^{-1} M $LiClO_4$ solutions containing HPβCD at various concentrations: 3×10^{-3} M, 5×10^{-3} M, 7×10^{-3} M, 10^{-2} M, 3×10^{-2} M, 5×10^{-2} M and 8×10^{-2} M were recorded. For all HPβCD concentrations, the cyclic voltammograms retain their irreversible shape, indicating that the coupling of BT radical cations is most likely to occur (Fig. 2) in this medium. The BT oxidation peak (Ep) is observed at *ca.* 0.98 V instead of 1.3 V in acetonitrile. Then the electropolymerization of BT in water could be achieved without serious competition from the electrochemical decomposition of water. This effect may be due to a better solvation of the radical cation (resulting from the BT oxidation) in water than in acetonitrile.

The effect of complexation of BT by HPβCD is also evident through comparison of the voltammograms (Fig. 2). A substantial reduction of the anodic peak current is observed upon addition of HPβCD. This is a common feature observed in these host–guest associations.[10] This decrease is caused by the fact that much of the BT exists as the more slowly diffusing inclusion compound[10] since no noticeable increase in solution viscosity is expected over the range of 0–50 mM HPβCD. A larger decrease in peak current occurs for the lowest HPβCD concentrations (up to 30 mM). With increasing HPβCD concentration, the peak current continues to decrease but tends to approach a limiting value. At HPβCD concentrations near to 30 mM, the ratio of the concentration of complexed BT to that of free BT is 100: most of the BT molecules have then bound with HPβCD and the peak current tends to be governed by diffusion of the complex. Besides, the peak potential is shifted to values that are more positive (by about 90 mV) when the HPβCD concentration increases from 3 to 30 mM.[18] This may indicate that BT is more difficult to oxidize when it is more strongly bound to HPβCD (from a thermodynamic point of view). However, it is worth noticing that the shift remains quite small. This observation may indicate that dissociation of the complex precedes the actual electrochemical process. Indeed a larger shift would be observed if direct oxidation of the complex occurred as shown by Kaifer *et al.* for the oxidation of a redox-active ferrocene locked in a host cavity.[19] When the scan rate is varied between 0.1 and 1 V s^{-1}, broadening of the anodic wave is observed with increasing HPβCD concentration (Fig. 2). This observation may suggest that the presence of HPβCD slows down the kinetics of the radical cation formation.[20] This result is in agreement with recent work using the pulse radiolysis technique[21] where a decrease in the oxidation rate of methylbipyrrole upon addition of cyclodextrin was observed. This latter study also showed that the reaction of BT radical cations is similar to that in organic solvents. In particular, it follows a second-order decay.[21] It is worth emphasizing this point because it shows that BT radical cations do not react with water or with HPβCD (in this case an apparent first-order decay would be observed). Moreover, this work shows that BT radical cations are not encapsulated when dimerization occurs.[21] Kinetic studies using laser flash photolysis are currently being performed in order to confirm this result and further analyse the behaviour of the BT radical cation in media containing HPβCD.[23]

b) Electropolymerization of the BT–HPβCD complex: synthesis of the material

BT can be easily electropolymerized on platinum electrodes from an aqueous solution of 10^{-2} M BT, 10^{-1} M HPβCD and 10^{-1} M $LiClO_4$. Fig. 3 shows multicycle voltammograms recorded between −0.3 and 1.1 V at a scan rate of 0.1 V s^{-1}. The first anodic sweep presents a wave at *ca.* 1.0 V, corresponding to the oxidation of BT. Additional anodic and cathodic peaks appear to increase with the number of successive cycles and usual electrochromic behaviour can be observed during the synthesis, *i.e.* depending on the polarization potential, the film is red (reduced state) or green (oxidized state). The growth of the polymer depends on the electrochemical conditions.[23] Indeed, the observed electroactivity appears in some cases restricted to the additional layer that has just been deposited, and the polymer signal stops growing even though the film thickness is still increasing.[23] Thin, homogenous and adherent films are obtained at the platinum electrode. The material remains slightly electroactive in aqueous 2×10^{-1} M $LiClO_4$ whereas PBT films prepared from an organic solution (without cyclodextrin) do not show any electroactivity upon cycling under the same conditions. This result indicates that PBT films prepared from an aqueous solution using the host–guest strategy are structurally different from those prepared from organic media. The former may allow partial water and counter-ion penetration whereas the latter are highly hydrophobic and may inhibit the penetration of water and counter ion.

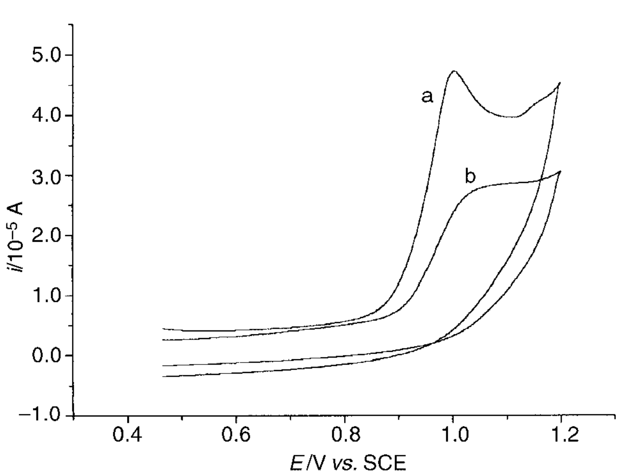


Fig. 2 Cyclic voltamogramms at 0.1 V s^{-1} scan rate for aqueous 10^{-1} M $LiClO_4$ and 10^{-3} M BT containing HPβCD, 3×10^{-3} M (a) and 3×10^{-2} M (b).

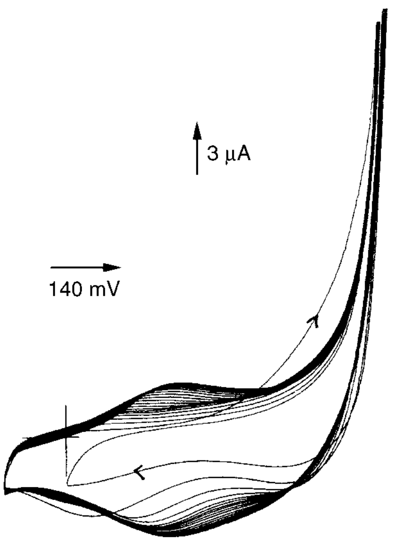


Fig. 3 Electrosynthesis of PBT on a Pt electrode using cyclic voltammetry from aqueous 10^{-1} M $LiClO_4$, 10^{-2} M BT, 10^{-1} M HPβCD. $v = 0.1$ V s^{-1}. The arrow denotes the first scan.

PBT films can also be synthesized from aqueous solutions of 10^{-2} M BT, 10^{-1} M HPβCD and 10^{-1} M $LiClO_4$ by applying constant current densities of 0.05, 0.1 and 0.2 mA cm^{-2}. Fig. 4 shows the chronopotentiometric responses of the electrode. In the first stage of polymerization, the potential is close to 1 V, varying from 0.98 to 0.96 V. Then a second deposition regime occurs in which the potential starts to rise sharply from 1 V. This result indicates that the polymer generated is initially (first regime) conductive and suggests that its conductivity changes during electrodeposition. This suggests that the structure of the upper layers of the material is different from that of the inner layers. Interestingly, such PBT do not exhibit electroactivity in aqueous 2×10^{-1} M $LiClO_4$ solution and, therefore, are much more similar to PBT prepared in organic media than the films generated by cyclic voltammetry.

c) Film characterizations

The films were studied by Raman, UV–Vis, FTIR and XPS spectroscopies. The *ex-situ* Raman spectra are similar to those of PBT films formed in organic media.[16] They display an intense band at 1455 cm^{-1} which is assigned to the symmetric stretching mode of the aromatic C=C band (v_s) while a weaker band at 1495–1492 cm^{-1} is attributed to the antisymmetric stretching vibration (v_{as}). It has been shown that, for the latter, the wavenumber and the intensity decrease monotonically as the average conjugation length increases;[24,25] thus, the v_{as} are 1556 (BT), 1530 (terthiophene), 1519 (quaterthiophene) and 1507 cm^{-1} (sexithiophene)[24] whereas literature results for electrochemically synthesized PT are below 1500 cm^{-1}.[24,25] It appears then that the PBT chains generated from aqueous HPβCD solutions have a longer average conjugation length than sexithiophene.

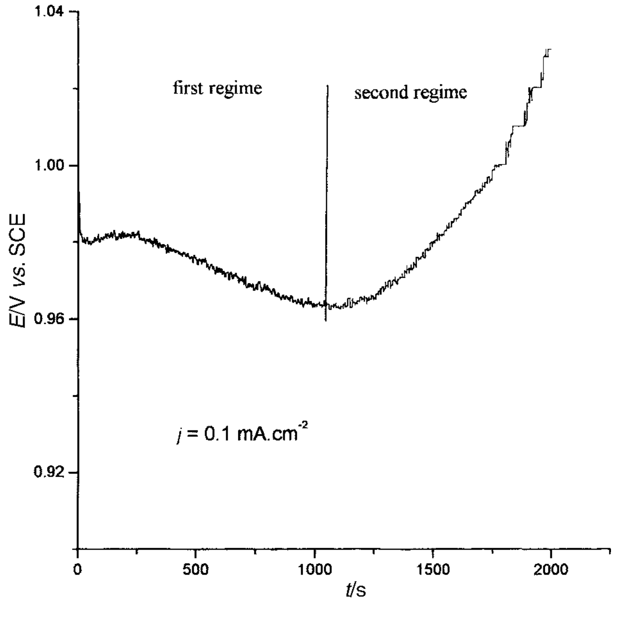


Fig. 4 Electrosynthesis of PBT on a Pt electrode using galvanostatic method ($j = 0.1$ mA cm^{-2}) from aqueous 10^{-1} M $LiClO_4$, 10^{-2} M BT and 10^{-1} M HPβCD. Variation of the potential during the synthesis indicates the presence of two regimes for the deposit.

The electronic absorption spectra of conducting polymers provide some information concerning the molecular structure of the material. The linear relationship of the energy gap (Eg in eV at the absorption maximum) of thiophene oligomers (in $CHCl_3$) *vs.* the inverse of the thiophene units ($1/n$) would allow the determination of the average conjugation length (Nc) for the polymer by extrapolation.[26] UV–Vis spectra were recorded on fully reduced films deposited on ITO electrodes. They are similar to those reported for PBT generated in organic media and do not depend upon the electropolymerization procedure (multiple cyclic voltammetry or galvanostatic method). They exhibit absorption maxima at $\lambda_{max} = 475$–480 nm. These values are the same as those reported for solid state neutral PBT generated from organic media.[27–29] Available data reported for long thiophene oligomers[30,31] could support the notion that we formed PBT with long conjugated chains as suggested by the Raman results. Moreover, if we assume that the solid state and solution spectra are identical, Nc can be estimated to be *ca.* 14–15 thiophene units by using the linear relationship between Eg and $1/n$.

However, this outcome remains quite qualitative because the assumption that solid state and solution spectra are identical is not generally true as severe hypsochromic shifts are observed between solid state and solution spectra for alkyl-substituted polythiophene.[32] UV–Vis absorption spectra of neutral thin films dissolved in DMF were recorded. They show a band at $\lambda_{max} = 430$–440 nm. The λ_{max} are more than 40 nm smaller than those obtained for the solid state spectra. This last value would correspond to an apparent conjugation length in solution of six thiophene units. As the solubility of the PBT–HPβCD films is relatively limited, one may assume that DMF could extract the smallest conjugated chains up to six units long. However, the films are insoluble in CH_2Cl_2 and, consequently, this conclusion would be inconsistent with such a chain length, since sexithiophene is soluble in CH_2Cl_2 (1 g L^{-1}).[33] PBT–HPβCD films must, therefore, be formed with longer polymeric conjugated chains, and the dramatic hypsochromic shift observed between solid state and solution spectra probably reflects a high loss of π-conjugation. It may indicate that the chains are very twisted in solution.[34,35] This may be due to the highly polarizable nature of the sulfur atom making the thiophene rings easily deformable, as reported by Barbarella *et al.* for quaterthiophene derivatives.[35]

The FTIR spectra of carefully rinsed films are also very similar to those of PBT films prepared in organic media.[36] They exhibit bands at 795 and 695 cm^{-1} (Fig. 5). It has been shown that these bands correspond to the out-of-plane C–H bending vibrations of disubstituted and monosubstituted thiophenes.[37] By using the ratio of the area intensities of these bands, it is possible to evaluate the average degree of polymerization (DP) according to the empirical eqn. (3).[37]

$$\mathrm{DP} = 2\left(\frac{R_0}{R} + 2\right) \qquad (3)$$

where $R = I_{695}/I_{795}$ and $R_0 = 1.07$, value obtained for sexithiophene.

On the basis of 11 samples, DP is estimated to be in the range of 12–40 with an average value of 23 for the PBT films generated from aqueous solution using the host–guest strategy. These values are very close to those obtained for PT generated in organic media (10–35).[24,25,37] They can also be compared with those measured for PBT generated in organic solution which are generally lower (DP = 13 for PBT prepared in acetonitrile[38]) although PBT films obtained from BT in nitrobenzene (at 5 °C) can have a DP value equal to 40.[25] Accordingly, despite the use of far from classical conditions of electropolymerization, the synthesis of PBT having relatively high DP values can be achieved from aqueous HPβCD solutions. This result is in agreement with the UV–Vis and Raman results, but the DP values are higher than Nc ones, indicating that some defects (α–β linkage, distortion from planarity) may occur during the electropolymerization.

The FTIR spectra show additional bands that are not visible in the FTIR spectra of PBT films prepared in organic media. Strong bands at 3400, 2960 and 2930 cm^{-1} are observed (Fig. 5). These bands, attributed to the stretching modes of the O–H bond and of the alkyl C–H bonds (symmetric and antisymmetric), respectively, are characteristic of cyclodextrin. A film washed in water for three days with vigorous stirring in order to eliminate residual cyclodextrins still exhibits these strong bands, showing that cyclodextrins remain in the polymer film and that these molecules are not absorbed on the surface of the electrode. This result is quite surprising since dethreading of the inclusion compound occurs during electropolymerization as explained above. Moreover, similar experiments with terthiophene[39] and dipyrrolyl compounds[40] did not lead to material containing cyclodextrins.

Another proof of the presence of cyclodextrins in the material is provided by X-ray photoelectron spectroscopy (XPS). Since XPS can give qualitative, quantitative and chemical-state information on the surface layers of solid state, it is interesting to use this technique to estimate the amount of cyclodextrins incorporated in the material. XPS analyses were performed on a set of samples electrosynthesized under different conditions (Table 1). The most intense signals were attributed to C_{1s}, S_{2p}, S_{2s} and O_{1s} photoelectrons. Curve analyses of the C_{1s} signal are shown in Fig. 6 for films prepared by various electrochemical procedures. The signal can be deconstructed into three components at 285, 287 and 289 eV. It allows the identification of carbon species that are present in the polymer although a precise identification is beyond the resolution of the technique. Table 1 shows the C : S ratio and the contribution of each peak to the C_{1s} signal for the different samples. The signal at 285 eV is attributed to the α and β carbons of the polymeric backbone.[41] This peak is usually the major part of the C_{1s} signal for PBT electrosynthesized in organic media (Fig. 6a, and PBT 6 in Table 1).[42,43] For PBT–HPβCD films (PBT 1–5 in Table 1), one observes that the $C_{285}:C_t$ ratio decreases while the $C_{287}:C_t$ and $C_{289}:C_t$ ratios increase as compared to PBT 6. The peaks at 287 and 289 eV related to C–OH and O–C–O bonds can be attributed mainly to HPβCD, although some other surface species could also contribute to these signals; for example C=O from surface oxidation, C–Cl and C–O–Cl in the cycled samples.[43,44] Obviously, these observations are also associated with an excess of carbon (*versus* sulfur) (C : S ratio) as compared to PBT 6 (Table 1). Accordingly, these results indicate that cyclodextrins are incorporated in the material since the extensive rinsing procedure used is likely to remove most of the adsorbed cyclodextrins. Furthermore, the C : S ratio allows a crude estimation of the amount of cyclodextrins incorporated in the upper layers of the material per BT unit (y) by assuming an elementary formula of $C_8H_4S_2 + yC_{61}H_{119}O_{42}$. In most cases, one cyclodextrin for 10 BT units is detected in the upper layers of the film, but PBT 4 and PBT 5 show y values between 12 and 45% (Table 1). It should be noted that the y values

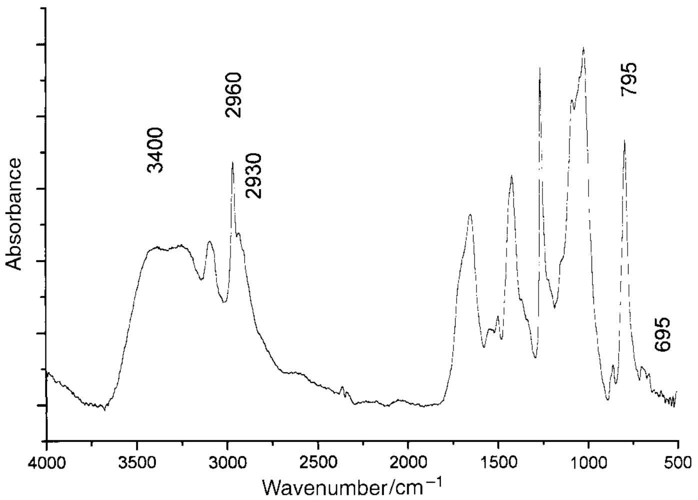


Fig. 5 FTIR spectrum of PBT films formed on a Pt electrode from aqueous 10^{-1} M $LiClO_4$, 10^{-2} M BT and 10^{-1} M HPβCD.

Table 1 XPS analyses for different PBT films

	C : S	y (%)	$C_{285}:C_t$	$C_{287}:C_t$	$C_{289}:C_t$
PBT 1	6.24	7.4	0.63	0.25	0.12
PBT 2	5.74	6	0.67	0.2	0.13
PBT 3	5.69	5.5	0.68	0.24	0.08
PBT 4	7.73	12	0.48	0.44	0.08
PBT 5	17.6	45	0.29	0.55	0.16
PBT 6	3.8	0	0.85	0.10	0.05

PBT 1–5 synthesized from aqueous 10^{-1} M $LiClO_4$, 10^{-2} M BT and 10^{-1} M HPβCD: PBT 1: galvanostatic deposit ($j = 0.1$ mA cm^{-2}, $R = [HP\beta CD]/[BT] = 10$); PBT 2: ($j = 0.1$ mA cm^{-2}, $R = 5$); PBT 3: cyclic voltammetry (−0.2 to 1.1 V, $v = 0.1$ V s^{-1}, $R = 10$, polarized at 0.2 V); PBT 4: (−0.2 to 1.1 V, $v = 0.1$ V s^{-1}, $R = 10$, polarized at −0.2 V); PBT 5: (−0.2 to 1.1 V, $v = 20$ V s^{-1}, $R = 10$, polarized at −0.2 V); PBT 6 synthesized from 10^{-1} M $LiClO_4$ and 10^{-2} M BT, in acetonitrile solution ($j = 0.1$ mA cm^{-2}).

reported in Table 1 cannot be seen as a precise determination of the rate of cyclodextrin incorporation into the material. On the one hand, it has been shown that significant discrepancies exist between the results obtained from the surface (XPS) and bulk analysis.[45] On the other hand, we must emphasise that *y* values are only indicative since poor reproducibility has been observed in these analyses. Among the different samples, PBT 4 and PBT 5 exhibit larger C : S ratios while $C_{287}:C_t$ becomes equal to and even higher than the $C_{285}:C_t$ ratio. This shows the presence of a large amount of cyclodextrins in the upper layers of the material even though it was thoroughly rinsed. The common feature of these latter films is that they have been reduced at −0.2 V prior to rinsing and XPS analysis. This result shows that the incorporation of cyclodextrins is easier when the material is reduced by polarization at −0.2 V.

This last point is, moreover, confirmed by electrochemical quartz crystal microgravimetry (EQCM) experiments. EQCM measurements under double-step chronopotentiometric conditions were performed. Fig. 7 shows the variation of mass during a 200 s pulse at +1 V followed by a 200 s pulse at −0.3 V. This mass variation reflects the growth of the material that is deposited on the electrode. Film formation is seen in the mass uptake during the first 200 s but the most striking feature is that a large mass increase is also observed during the polarization at −0.3 V, indicating that a foreign species (most probably HPβCD as evidenced by the XPS measurements) is incorporated. This mass increase can be more important than the mass of polymer deposited in the 200 s pulse at +1 V.[23]

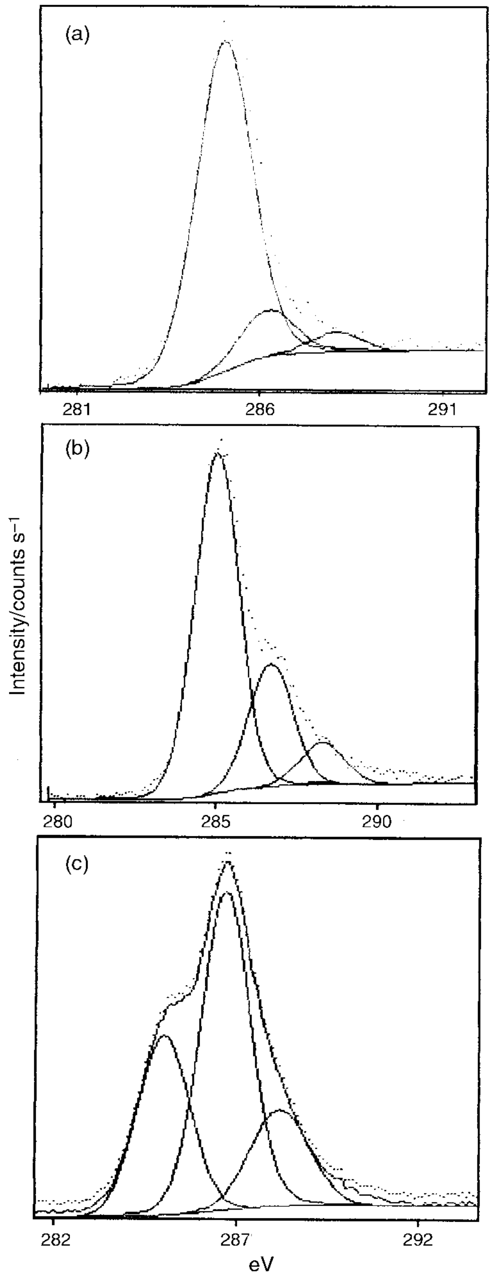


Fig. 6 Curve-fitting analysis of the C_{1s} signal obtained from XPS analysis: (a) is for a PBT film generated from acetonitrile + 10^{-1} M $LiClO_4$ (PBT 6 in Table 1); (b) and (c) are for PBT films electrosynthesized from aqueous 10^{-1} M $LiClO_4$ + HPβCD 10^{-1} M but (b) with polarization at +0.2 V (PBT 3) and (c) with polarization at −0.2 V (PBT 5).

The PBT films deposited from aqueous HPβCD solutions are slightly soluble (around 1 g L^{-1} in DMF) in DMF, DMSO and THF whereas PBT films prepared in acetonitrile are insoluble in these solvents. Such behaviour suggests that interchain interactions are severely modified by the presence of cyclodextrin in the material. However, at this point it is impossible to state whether cyclodextrin is incorporated in the material without any covalent bond being formed or if it is grafted onto the polymer backbone. Accordingly, possible structures of the polymeric material could be thought of as illustrated in Scheme 2.

In order to investigate this point, MALDI-MS experiments were performed. This technique, which has rarely been used for conductive polymer characterization,[46] allows mass analysis of the material without fragmentation. Recently, the MALDI spectra of poly(methoxythiophene) films generated from aqueous micellar medium were reported,[47] and oligomethoxythiophenes were evidenced. This suggests that grafted oligothiophenes can be easily identified using this technique whereas unsubstituted oligothiophenes are difficult to observe by this technique because of their low solubility (preparation of the matrix).[46] In our case, the main feature seen with this technique is unmodified HPβCD, with the usual statistical substitution pattern of 1 to 7 hydroxypropyl groups grafted on the CD core.[48] In particular, no evidence of HPβCD grafted by short oligothiophene can be observed. This indicates that unmodified HPβCD is incorporated into the PBT composite films without any covalent bond being formed and rules out structure A (Scheme 2).

Then structures B and C (Scheme 2) appear to be the most plausible structures. However, some experimental features are not in complete agreement with structure B. As mentioned before, similar experiments with terthiophene[39] and dipyrrolyl

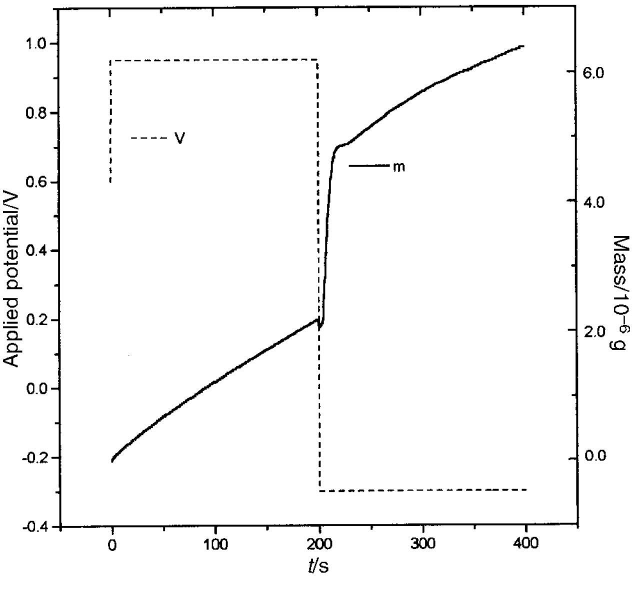
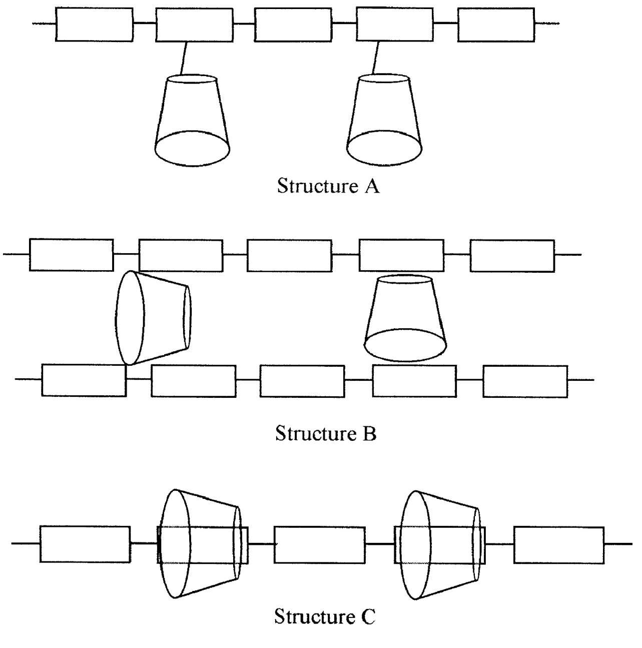


Fig. 7 Variation of mass during polymer growth. Electrosynthesis is performed under chronopotentiometric conditions from aqueous 10^{-1} M $LiClO_4$ and 10^{-1} M HPβCD.

compounds[40] did not lead to material containing cyclodextrins. In particular, it is very surprising that the material resulting from terthiophene does not contain any cyclodextrin, because the two starting monomers, bithiophene and terthiophene are of the same nature. Moreover, it has been shown that the material needs to be fully reduced in order to incorporate cyclodextrins to a major extent. It must be emphasised that cyclodextrin molecules have a hydrophilic outer surface whereas polybithiophene is strongly hydrophobic especially when the material is in its reduced state.[49] In this case, one can suggest that there is no affinity between the host molecules and the polymeric chains, apart from assuming that PBT chains are partially encapsulated by cyclodextrins. The abnormal solubility of the PBT films, which strongly suggests that the structure of the polymer is dramatically modified because of the insertion of cyclodextrins within the material, strengthens this assumption.

Conclusion

The complexation of BT into the host HPβCD has been studied and it has been shown that the association constant is large. It is demonstrated that electropolymerization of BT in an aqueous solution of HPβCD is possible and leads to homogenous films exhibiting common features of classical PBT films (generated in organic media), such as a high conjugation length. However, although dimerization occurs outside the cavity of the host, spectroscopic studies show that cyclodextrins remain steadily within the material without any covalent bond being formed between the polymeric backbone and the cyclodextrin molecules. The incorporation of cyclodextrins in the film is more efficient when the polymer is fully reduced by applying a potential of −0.2 V/SCE. Although cyclodextrins are not electroactive, electrochemical activation is required to trigger significant insertion of HPβCD. Then, the driving forces that make it possible to insert cyclodextrins into the polymer could be seen as electrochemically controlled molecular recognition forces.[50]



Scheme 2 Possible structures for the polymeric material: with covalent bonding between the PBT chains and cyclodextrins (A); without covalent bonding, consisting of an insertion of cyclodextrins between the polymeric chains (B) or consisting of a partial encapsulation of the PBT chains with cyclodextrins (C).

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