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Electropolymerization of hydrophobic dipyrrolyls in aqueous medium based on inclusion chemistry

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The host–guest complexation of hydrophobic dipyrrolyl monomers **1**–**4** with β-cyclodextrin has been studied in aqueous solution by means of ^{1}H NMR spectroscopy, chemical analysis and electrochemical techniques. In each case, 1 : 2 stoichiometry is found, the cyclodextrin cavities being likely located on the extremities of the monomers. Polymeric materials were obtained from such inclusion compounds in water by either electrochemical or chemical oxidation. ESCA and elemental analyses show that the host molecule is absent from these polymers, whose characteristics are quite similar to those synthesized in organic media. A scheme for polymerization in the presence of cyclodextrin is proposed.

Introduction

Organizing the encounter of reagents *via* molecular self-assembly is an important challenge in chemistry. Within this context, some of the simplest assemblies start with cyclodextrins (CD) which are cyclic oligosaccharides formed by six (αCD), seven (βCD) or eight (γCD) D-glucopyranose units joined together by α-(1,4) bonds. Their ability to form stable inclusion complexes with hydrophobic molecules in aqueous solution has been established[1] and has led to many applications.[2] Most previous electrochemical studies of host–guest CD solutions fall into one of two classes: selective electrosynthesis based on CD complexation reactions[3] and electroanalytical techniques for studying the ability of cyclodextrins to hold, orient, conceal or separate guest molecules.[4] The electrochemical behaviour of electroactive species in the presence of CD has also been studied for the characterization of organized layers consisting of host–guest complexes[5] or CD-grafted polypyrrole films capable of molecular recognition.[6] Recently, CD complexes have been used to electropolymerize a hydrophobic monomer in water, hydroxypropyl-β-cyclodextrin (HPβCD) being the host and bithiophene the guest.[7] HPβCD was chosen since it is more soluble in water than simple βCD: the presence of hydroxypropyl groups on the external crown of the CD increases considerably the host solubility without modification of the hydrophobicity of the cavity. Cyclodextrins remain in the polymer film, suggesting that partial encapsulation of the polymer chains occurs. This behaviour can be explained by a high affinity of the hydrophobic inner cavity of the CD macrocycles for the growing chains of polybithiophene which favours the formation of poly-pseudorotaxane structures during electropolymerization.

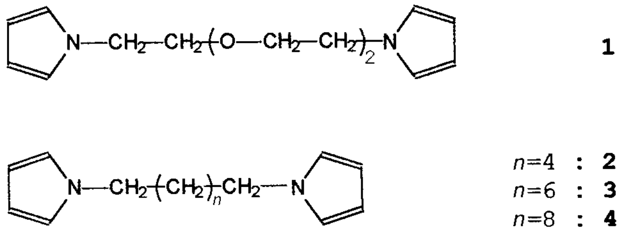
We have shown in a previous paper[8] that certain dipyrrolyl monomers can be used to form polymers presenting ladder-like structures, these monomers consisting of more or less rigid spacers, the extremities of which are bonded to the N atom of two pyrrolyl entities. The use of a rigid spacer leads undoubtedly to a ladder-structure whereas with long, flexible spacers intramolecular coupling may occur during polymer formation. Thus, depending on the structure of the complexes, encapsulation of such monomers by CDs could be a good way to make the spacers inflexible, or CD could be expelled into the bulk during the polymerization process.

This work is devoted to the study of the interaction of CD with dipyrrolyls having long, flexible spacers and to the subsequent behaviour of such complexes when they are oxidized by electrochemical or chemical means.

Results

Inclusion complexes

All the dipyrrolyl monomers studied here (see Scheme 1) are poorly soluble in water (10^{-3}, 2×10^{-4}, $<10^{-4}$ and $<10^{-4}$ M for **1**, **2**, **3** and **4**, respectively); this can be improved by the addition of 0.1 M of HPβCD (1.2×10^{-2}, 8×10^{-3}, 4×10^{-3} and 8×10^{-4} M, respectively). This behaviour implies the formation of inclusion complexes between the dipyrrolyl derivatives and the CD. ^{1}H NMR is the most reliable technique available to characterize this phenomenon. Studies on the two inner (H-3 and H-5) hydrogen atoms of CDs in the presence of a guest molecule provide valuable proof of inclusion.[9] Fig. 1 displays the characteristic upfield shifts of the H-3 and H-5 protons upon complexation with **1.** These small but significant shifts (0.024 and 0.042 ppm for H-3 and H-5, respectively) are related to an inclusion phenomenon with a low association constant.[10] Such shifts are observed in the 6–7 ppm spectral region corresponding to the pyrrolyl proton resonance. Conversely, the singlet peak at 3.58 ppm corresponding to the two central methylene groups of the spacer does not shift significantly upon complexation, indicating that the CDs interact much less with the aliphatic spacer chain. The stoichiometry of the complexes was determined by isolating the very slightly water-soluble βCD inclusion compounds. In every case 1 : 2 stoichiometry is found by chemical analysis (see Experimental section). These results are confirmed by ^{1}H NMR spectroscopy in DMSO-d_6 where the host molecules are unthreaded, and the resulting signals correspond to the free species. For



Scheme 1 Monomers **1**–**4**.

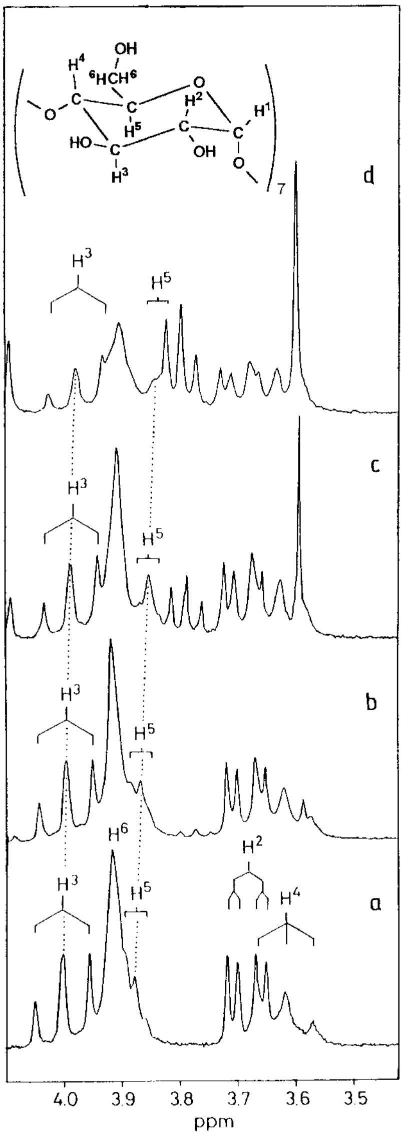


Fig. 1 Partial 200 MHz ^{1}H NMR spectra of βCD in D_2O: (a) no additive; after addition of **1** with [host/guest] ratios of (b) 3.3, (c) 1.1 and (d) 0.25 (only host protons are assigned).

example, Fig. 2 exemplifies the results obtained with the **3**–βCD complex: the peak at 4.83 ppm corresponds to the seven H^1 protons of the cyclodextrin and those at 5.95 and 6.72 ppm correspond to the four H_B and H_A of the dipyrrolyl derivative, respectively. The relative integrated intensities of these peaks give the proton ratio (3.236/7):(1.05/4), that is nearly 2:1. The same results are obtained with the other monomers. It should be noted that spacer length does not affect the stoichiometry of the complex and, conversely, the longer the spacer, the less the resulting complex is water-soluble. This, added to the NMR study described above, indicates that the two pyrrolyl rings of the monomers constitute the complexation sites, the spacer remaining free. This assumption is in good agreement with a study of the complexation of ferrocene derivatives containing *n*-alkyl chains, where it was demonstrated that βCD interacts much less effectively than αCD with aliphatic chains.[11] Any attempt to obtain complexes of the monomers with αCD in good yields failed, although αCD is known to complex alkyl or PEG chains,[12] possibly because it is difficult for the cavity to thread into the pyrrolyl ring and reach the spacer chain.

In what follows, we will devote our attention to the most soluble complex, being given the necessary concentrations to carry out polymerization reactions under good conditions.

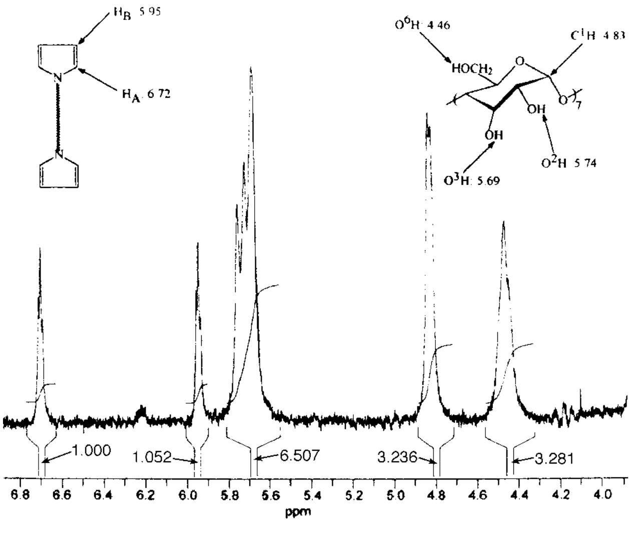


Fig. 2 Partial 200 MHz ^{1}H NMR spectrum of **3**–βCD inclusion complex in DMSO-d_6. Chemical shifts in ppm; 1:2 stoichiometry is deduced from integration of monomer and CD peaks.

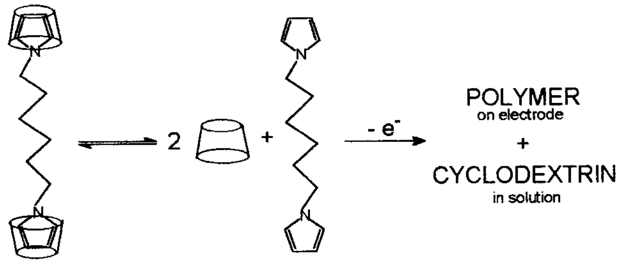
Electrochemical oxidative polymerization

The most water-soluble monomer complex '**1**–CD' was first investigated electrochemically at 20 °C in water. The voltammetric behaviour of **1** is characterized by the irreversible oxidation of the pyrrolyl group as in an organic medium.[8] Whereas monomer **1** oxidizes at 1.21 V in acetonitrile, its oxidation potential becomes 1.09 V in water in the presence of a 10-fold excess of HPβCD. This potential shift could be explained by a greater stabilization of the cation-radical in aqueous medium. As can be seen in Table 1, addition of βCD causes the peak oxidation current to decrease, indicating that much of the monomer exists as the more slowly diffusing inclusion complex, since no change in the solution viscosity is expected over the range of 0–10 mM βCD.[13] Simultaneously, the oxidation peak potential of **1** is shifted substantially to a more positive value, indicating that **1** is more difficult to oxidize in the presence of βCD. Such effects are also observed with HPβCD addition. Evans *et al.* observed the same behaviour in voltammetric studies of ferrocenecarboxylic acid in the presence of βCD and conclusively demonstrated the prevalence of a CE (C: chemical; E: electrochemical) mechanism[13] in which the complex first dissociates followed by the oxidation of the free ferrocene derivative. We conclude that the same mechanism applies for the oxidation of the dipyrrolyl derivative (see Scheme 2).

Regular film formation at 20 °C by electrochemical oxidation of a 10^{-2} M solution of monomer **1** in water and in the absence of HPβCD is impossible for solubility reasons: the electrode surface is covered with submicronic polymer islets (Fig. 3), resulting from the polymerization of droplets of **1** in suspension in water. It becomes possible when HPβCD is added at a ratio of 10 HPβCD per monomer, using the galvanostatic method or cyclic voltammetry. Fig. 4 shows a multicycle voltammogram recorded between 0 and 1.0 V at a scan rate of 50 mV s^{-1}. The first anodic sweep reveals a wave

Table 1 Current and potential peaks measured on a carbon graphite electrode immersed in 0.1 M KNO_3 containing 1.0 mM **1** and various concentrations of HPβCD. Scan rate: 50 mV s^{-1}; reference electrode: SCE.

10^3 c HPβCD/M	i/μA	E/V
0	61.5	1.05
1	53	1.07
10	42	1.09



Scheme 2 Proposed mechanism of oxidative polymerization of **1** in presence of HPβCD.

with an onset at 0.75 V, corresponding to the oxidation of **1**; additional anodic and cathodic peaks increase regularly with the number of successive cycles. The electroactivity of the resulting poly-**1** films in water is similar to that for films obtained in acetonitrile (Fig. 5). This behaviour is quite unusual for a polypyrrole (PPY) derivative. For instance, when PPY is synthesized in organic medium, the cyclability performance of the film in water is much worse than in the synthesis solvent. The presence here of ether functions, which are well known to increase the ionic conductivity of the polymer,[14] in the crosslinking spacers probably induces a permeability sufficient to allow free movements of the counter ions. This could explain the great reversibility of the oxidoreduction of the poly-**1** in water independently of the medium used for the electrosynthesis.

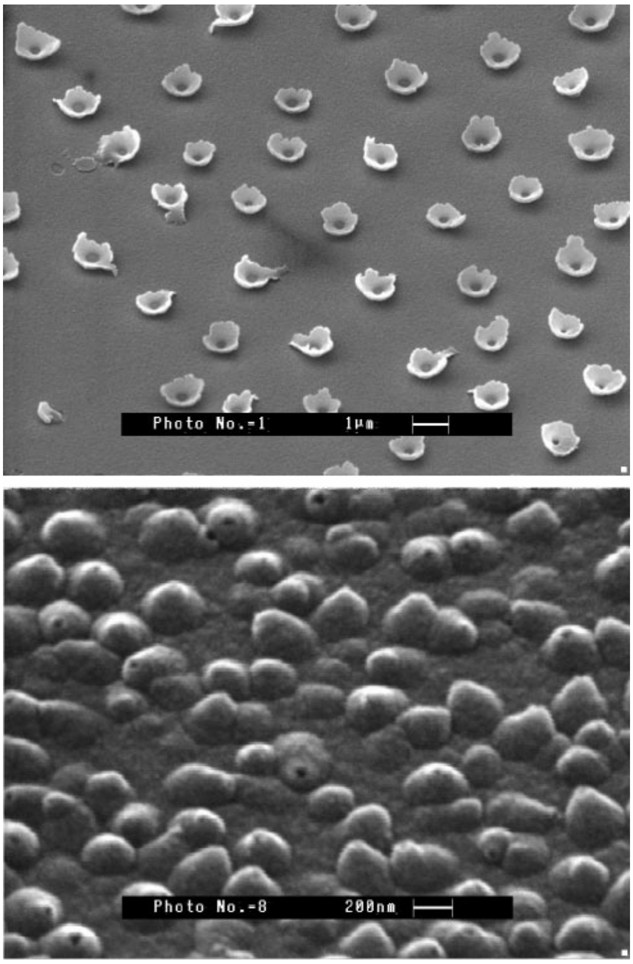


Fig. 3 SEM photographs of poly-**1** deposited on platinum from a 10 mM **1** solution in water; top: without HPβCD; bottom: with 0.1 M HPβCD. Supporting electrolyte: 0.1 M $LiClO_4$.

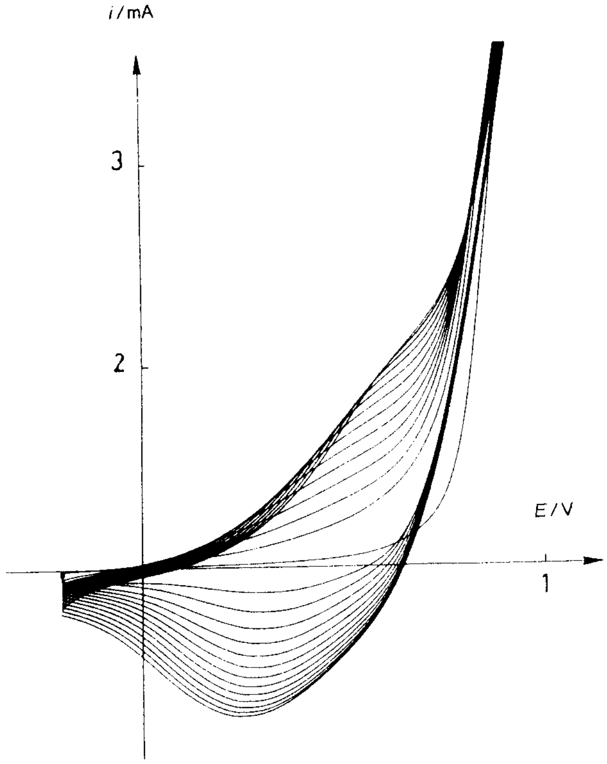


Fig. 4 Potentiodynamic multisweep electrodeposition and redox cycling ($50\ mV\ s^{-1}$) of poly-**1** on Pt in aqueous 0.1 M $LiClO_4$ and 0.1 M HPβCD ($S = 1.5\ cm^2$). Monomer concentration: 10 mM; reference electrode: SCE.

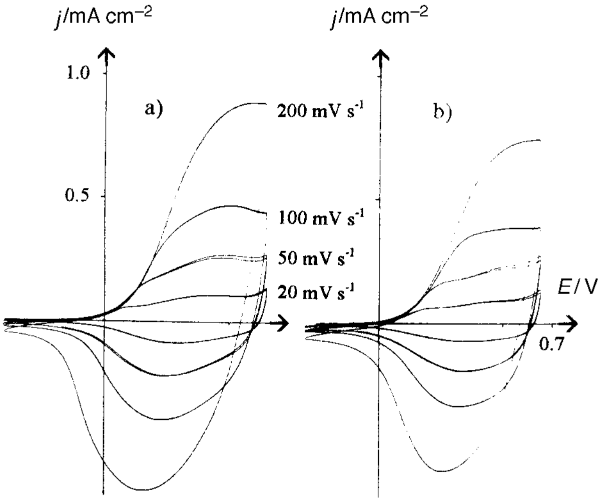


Fig. 5 Electroactivity in aqueous 0.1 M $LiClO_4$ at different scan rates of poly-**1** films generated in galvanostatic mode using a charge of $132\ mC\ cm^{-2}$ from: (a) 10 mM **1** aqueous + 0.1 M HPβCD; (b) 10 mM **1** in acetonitrile.

Surface analyses of these films in the oxidized state have been performed by XPS in order to estimate the doping level and to determine whether CD remained in the material. The results are given in Table 2. The comparison with theoretical stoichiometry strongly suggests that no CD remains, and that the doping level is in the order of 15%, this being slightly lower than the value of 20% found previously for such films formed in acetonitrile.[8] The observed excess of oxygen atoms in the materials may be provided from an over-oxidation process during the electrosynthesis, as evidenced by IR spectroscopy (see below). The perpendicular conductivity of free standing films, *ca.* 1 µm thick, was measured: poly-**1** films have a conductivity of 6×10^{-6} and $4 \times 10^{-7}\ S\ cm^{-1}$ when generated in the galvanostatic mode at $0.1\ mA\ cm^{-2}$ in acetonitrile and water + HPβCD, respectively. These modest values,

Table 2 Empirical formulae deduced from ESCA analysis of thin films of poly-**1** films in oxidized state and calculated by assuming no CD incorporation and a ratio of 0.15 ClO_4^- per pyrrolyl ring (*i.e.* a doping level of 15%). Sample (1) was obtained in galvanostatic mode by cycling between −0.2 and 1.0 V at a scan rate of 50 mV s^{-1}, and sample (2) was obtained in galvanostatic mode using a current of 0.2 mA cm^{-2} and a total charge of 72 mC cm^{-2}. Monomer concentration: 10^{-2} M in 0.1 M HPβCD and 0.1 M $LiClO_4$ aqueous solution

Sample	Empirical formula
Calcd. for poly-**1**+30% ClO_4^-	$C_{14}N_2O_{3.2}Cl_{0.3}$
Found for (1)	$C_{14}N_{2.3}O_{4.7}Cl_{0.28}$
Found for (2)	$C_{14}N_{1.9}O_{4.3}Cl_{0.24}$

when compared with classic poly-*N*-alkylpyrrole,[16] are due to a great steric effect of the spacer which could highly disturb the ring–ring planarity. However, these results are in accordance with the respective doping levels of the two polymers.

Mass measurements were compared with the theoretical masses for 100% yield and without CD incorporation. A doping level of 15% and a consumption of four electrons per monomer are assumed (the two pyrrolyl moieties are assumed to be involved in the polymerization process), as previously found in acetonitrile.[8] Table 3 gives the masses of some poly-**1** generated in water at different current densities. Although the polymerization yields do not always reach 100%, possibly due to some oligomer dissolution, these new results confirm that cyclodextrin is not incorporated in the films.

Moreover, the IR spectra of such poly-**1** films are very similar to those generated in acetonitrile, as can be seen in Fig. 6: the two spectra show a series of peaks characteristic of the polymer without CD (see Table 4). The dramatic increase in intensity of the IR band near 1700 cm^{-1} observed in the film generated in water may be due to the introduction of carbonyl groups as end groups which is favoured in this medium[15] whereas the weak band at 3360 cm^{-1} is attributable to residual water. Nevertheless, if substantial amounts of HPβCD were incorporated in great quantity in poly-**1** films obtained in aqueous medium, the bands at *ca.* 1100 and 3400 cm^{-1} would be at least as strong as that at 2900 cm^{-1}, as can be seen in the IR spectrum of HPβCD (see Fig. 6). This is not the case here, which confirms the absence of constitutive CD from the material.

Chemical oxidative polymerization

Monomers **1** and **2** were chemically polymerized in water in the presence of HPβCD. The other monomers were not investigated in this way for reasons of solubility. The synthesis conditions are given in the Experimental section. In both cases, a black powder was collected and analysed. The results are given in Table 5. When the measured percentage of each element is compared with the theoretical values based on various assumed compositions, only that with no CD incorporation and a doping level of 15% fits well. These new results are in good agreement with those obtained by electropolymerization, *i.e.* although the starting monomer is encapsulated in cyclodextrin in aqueous medium, it is unthreaded during the polymerization process and affords finally a material similar to that generated in an organic medium where ladder-like structures are formed.

Table 3 Calculated masses (m_{th}) by assuming no CD incorporation and a doping level of 15%, and experimental masses (m_{exp}) of deposited films of poly-**1** at varying current densities. *E* is the observed deposition potential. Electropolymerization was performed in aqueous solutions of 10^{-2} M monomer with 0.1 M HPβCD and 0.1 M $LiClO_4$

j/mA cm^{-2}	E/V	Q/C cm^{-2}	m_{th}/mg	±0.04 m_{exp}/mg
0.06	0.63	0.443	0.74	0.89
0.21	0.67	0.625	0.59	0.54
0.545	0.8→1.03	0.227	0.16	0.14

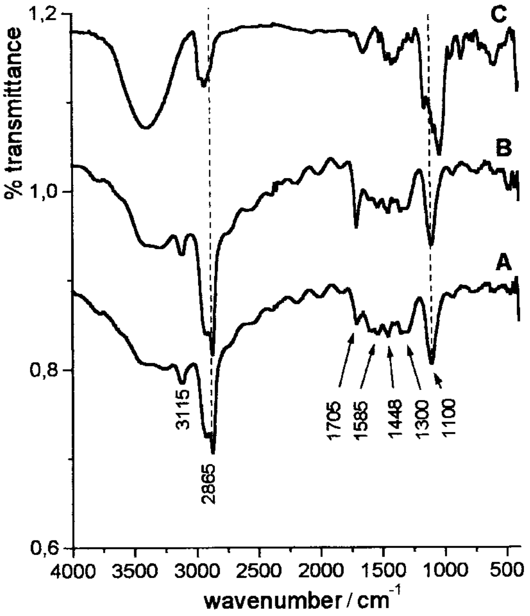


Fig. 6 A and B: IR spectra of reduced poly-**1** films deposited on platinum in potentiodynamic mode from 10 mM of **1** in: (A) acetonitrile; (B) water+0.1 M HPβCD; C: IR spectrum of HPβCD (1% dispersion in KBr).

Table 4 Frequencies (cm^{-1}) and assignments of the principal bands observed on thin films of poly-**1** deposited on a platinum electrode in either acetonitrile or aqueous 0.1 M HPβCD

Band position/cm^{-1}	Assignments
1100	ν (CH_2–O–)
1300	ν N–C(H_2)
1448	δ CH_2
1585	ν C=C out-of-phase
1705	ν C=O (default)
2865	ν CH_2
3115	ν (CH ring)

ν = stretching vibration. δ = deformation vibration.

In principle, two structures are possible for the CD complexes: i) an association of the monomer at the outside of the cavity, and ii) an inclusion inside the ring. ^{1}H NMR measurements show that the inner protons of the CD are affected upon complexation and that the partners form 1 : 2 complexes. These results make mechanism ii) more likely. Moreover, the materials formed either electrochemically or by chemical polymerization do not contain constitutive CD. This behaviour is consistent with a complex in which only the two pyrrolyl entities are encapsulated, the spacer remaining free. We can expect such complexes to be formed according to

Table 5 Results of elemental analyses of poly-**1** and poly-**2** obtained in aqueous HPβCD by chemical polymerization, using Fe^{3+} as oxidising agent. Theoretical percentages are calculated by assuming a doping level of 15% and total absence of CD

X	Elemental analysis (%)
1	Found: C: 59.8, H: 5.8, N: 9.5, O: 21.0, Cl: 3.2
	Calcd.: C: 61.3, H: 5.8, N: 10.2, O: 18.7, Cl: 3.9
2	Found: C: 67.4, H: 7.3, N: 10.1, O: 10.5, Cl: 4.0
	Calcd.: C: 69.5, H: 6.6, N: 11.6, O: 7.9, Cl: 4.4

X: starting monomer.

equilibria (1) and (2),

$$S + L \rightleftharpoons SL \quad (1)$$

$$SL + L \rightleftharpoons SL_2 \quad (2)$$

where S and L denote Substrate (monomer) and Ligand (CD), respectively. Even if the monomer is made soluble by complexation of the two pyrrolyl rings, the resulting complex is subject to association/dissociation phenomena. Oxidation of the pyrrolyl rings involves only the free species, and this is immediately followed by a coupling step which leads to insoluble oligomers. Since the polypyrrole chains are substituted on the N atoms of each pyrrole ring, leading to a ladder-like structure, no binding site is available for subsequent inclusion of the chains by surrounding CD.

In conclusion, these first experiments show that electropolymerization of highly hydrophobic dipyrrolyl derivatives can be performed in aqueous media with the help of host–guest chemistry. Quite surprisingly, the electrochemical properties of the resulting films are very similar to those of films generated in acetonitrile. This could be explained by similar interchain organization during the film growth in water as in organic medium, the CD having a minor influence on the structure of the film itself. Different characteristics could be observed for materials formed starting from such monomers in which the spacer moieties are also and remain complexed by CD during electropolymerization. Experiments with this aim are under investigation.

Conclusion

The interaction in water of dipyrrolyl monomers with β-cyclodextrin has been studied by ^{1}H NMR spectroscopy and chemical analyses. It is demonstrated that the two pyrrolyl rings are encapsulated, the cyclodextrin being positioned at the extremities of the monomer. The solubility of the CD complex depends mainly on the length of the spacer. This peculiar structure of the inclusion compound leads to polymers free of host molecule, resulting from the polymerization of the two pyrrolyl rings, both by electrochemical and chemical polymerization. The polymers thus formed present electrochemical characteristics similar to those obtained in organic medium. Moreover, the presence of ethoxy groups in the spacer could explain the peculiar electroactivity of the polymer in water, by favouring the formation of a reticulated, non compact material in which the movement of the doping ions can easily take place during the doping–dedoping process.

In this work inclusion chemistry has been proved to be a good strategy for forming polymeric materials in aqueous media starting from hydrophobic monomers. This demonstrates that the applications of cyclodextrin can still be extended, in particular in the field of polymeric film electrosynthesis in non-polluting media.

Experimental

General methods

^{1}H NMR spectra were recorded on a Bruker W 200 (200 MHz) spectrometer in D_2O and DMSO-d_6; chemical shifts (δ) are given relative to tetramethylsilane as internal standard.

IR spectra were recorded on a Nicolet SX 60 Fourier transform spectrometer.

ESCA spectra were recorded on a Vacuum Generator Escalab MK2 Spectrometer equipped with an unmonochromated Al-Kα X-ray source (power applied to the anode 200 W) at pressures in the 10^{-8} mbar range. The analyser was operated at constant pass energy (20 eV). The spectra were digitized, summed, smoothed and reconstructed using Gaussian-shaped components. Binding energies were referenced to C_{1s} 285 eV. For quantitative analysis, each peak area was corrected by the appropriate experimentally determined sensitivity factor.

Table 6 Conditions for synthesis of poly-**1** and poly-**2** by chemical oxidation

Synthesis solution	Added dropwise	T/°C	Yield (%)
0.1 M HPβCD + 0.01 M **1**	0.046 M $Fe(ClO_4)_3$	20	25
0.4 M HPβCD + 0.04 M **2**	0.200 M $Fe(ClO_4)_3$	50	30

The electrochemical studies were carried out in a single-compartment three-electrode cell using an EG&G PAR 362 potentiostat in the potentiodynamic or galvanostatic mode. Glassy carbon (disk area = 7.1×10^{-2} cm^2) and platinum coated glass (plate area = 2 to 3 cm^2) were used as anodes. The counter-electrode was in all cases a platinum grid. All potentials were measured with respect to a saturated calomel electrode (SCE). The electrolyte solution consisted of acetonitrile (CH_3CN) (Prolabo Chromanorm HPLC grade, used without further purification) or water (purified on a MilliQ Water System, Millipore Inc.) containing 0.1 M lithium perchlorate (Acros) as supporting salt.

Polymer mass measurements were performed on platinum-coated glass. Polymer samples were rinsed with water, then dried at 50 °C to constant mass, which was obtained by *ex situ* determination, using a Mettler AE 163 balance with a precision of 10^{-5} g. Reproducibility was checked by three consecutive polymerizations.

Elemental analyses were performed by the CNRS Analysis Centre, Vernaison, France.

Chemicals

β-Cyclodextrin (βCD) and hydroxypropyl-β-cyclodextrin (HPβCD) were provided by Aldrich and used as received. All details concerning monomer synthesis are given in ref. 8.

The βCD–dipyrrolyl complexes were obtained by precipitation under argon by the following general procedure: a 16.3 mM βCD and 16.3 mM monomer solution in water was heated to reflux with vigorous stirring for 2 h, then allowed to cool at room temperature. The inclusion complex separated from the solution by precipitation, and was isolated by filtration, washed with water then with ether, and dried under vacuum (2×10^{-2} torr) for 4 h at room temperature.

βCD–**1**: Yield: 33%. Anal. Calcd for **1**:2(HPβCD):$5H_2O$ ($C_{98}H_{170}N_2O_{77}$): C, 45.13; H, 6.52; N, 1.07; O, 47.27. Found: C, 45.12; H, 6.79; N, 1.27; O, 46.82%.

βCD–**2**: Yield: 33%. Anal. Calcd for **2**:2(HPβCD):$5H_2O$ ($C_{98}H_{170}N_2O_{75}$): C, 45.69; H, 6.60; N, 1.09; O, 46.62. Found: C, 45.29; H, 6.78; N, 1.17; O, 46.76%.

βCD–**3**: Yield: 30%. Anal. Calcd for **3**:2(HPβCD):$6H_2O$ ($C_{100}H_{176}N_2O_{76}$): C, 45.80; H, 6.72; N, 1.07; O, 46.41. Found: C, 45.95; H, 6.90; N, 1.10; O, 46.04%.

βCD–**4**: Yield: 21%. Anal. Calcd for **4**:2(HPβCD):$6H_2O$ ($C_{102}H_{180}N_2O_{76}$): C, 46.22; H, 6.80; N, 1.06; O, 45.92. Found: C, 46.34; H, 6.82; N, 1.08; O, 45.75%.

Two of the monomers presented in this study were polymerized chemically in water (magnetically stirred for two hours and purged of dissolved oxygen by bubbling argon) in the presence of Fe^{3+} under conditions given in Table 6. The polymers were repeatedly washed with water and then dried under vacuum.

Acknowledgements

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Paper 9/00177H