PSEUDOPOLYROTAXANES BASED ON POLYANILINE AND CUCURBITURIL

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Polypseudorotaxane structures based on polyaniline as linear polymer and cucurbituril[6] as macrocyclic compound have been synthesized using two methods: by chemical polymerization of aniline in presence of cucurbituril[6] as host and ammonium persulfate as oxidant, and b) by threading of polyaniline chain through cucurbituril[6] cavity, at room temperature. In both cases an aqueous 1M HCl solution has been used as solvent. The inclusion of polyaniline inside cucurbituril[6] cavity is proved by IR and UV-*vis* spectroscopy and solubility behaviour of the pseudorotaxane structures.

INTRODUCTION

Among conducting polymers, polyaniline (PAn) is one of the most studied polymers during the last years due to a combined sum of factors: a cheap and easy to prepare monomer (aniline), is environmental stable, can be doped using a variety of *p* or *n*- dopants or using protonic inorganic or organic acids and its potential in commercial applications.[1-4] However, the low solubility of the doped polymer in most organic solvents is a major drawback for its practical use and many efforts have tried to surpass this dificulty.

Rotaxane and pseudorotaxane architecture in macromolecular chemistry, in which a linear macromolecular chain inserted inside the cavity of many macrocyclic molecules has received much attention in the last years due to their unique and aesthetically structure and potential use as method for improving the polymer solubility.[5-8] As general rule, macromolecular rotaxane structures are obtained mainly by three ways: (a) monomer polymerization or polycondensation in the presence of a macrocyclic compound, (b) threading of a preformed linear polymer chain through macrocycles, and (c) polymerization or polycondensation of a rotaxane monomer. As macrocyclic compounds, crown ethers, cyclophanes and cyclodextrins were successfully used. Maciejewski et al. [9-13] have reported for the first time the synthesis of polyrotaxanes by radical polymerization of various monomers as inclusion adducts with β-cyclodextrin or by their polymerization in presence of these macrocyclic compounds.

Cucurbituril[6], or CB[6], is another macrocyclic compound obtained by acid-catalyzed condensation reaction of glycoluril and formaldehyde.[14-16] Its name is derived from the Latin word for pumpkin (cucurbitaceae) because the structure of the molecule is like an open-ended pumpkin with a hydrophobic cavity having an inner diameter of ~ 0.5 nm, accessible through two polar and identical carbonyl fringed portals. It can form stable complexes with guest molecules, in particular protonated amines.[17] Rotaxane and pseudorotaxane structures containing CB[6], and its higher homologues [n= 7,8] as hosts have been synthesized and studied in the last time.[18-24] However, unlike ciclodextrins (CD) or other macrocylic hosts,

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the CB[n] compounds were less used, probably due to their very low solubility in common organic solvents, they being soluble only in strongly acidic aqueous solutions.

A conducting polymer with rotaxane architecture can be considered as an insulated molecular wire having as core a conjugated macromolecular chain and as shell many macrocyclic compounds. There are only few reports about synthesis of conducting polymers with rotaxane structure. Thus, Lacaze *et al.* [25] have studied the electrochemical polymerization of 2.2'-bithiophene/hydroxypropyl- β -CD inclusion compound in water, when a soluble and low molecular weight polythiophene was obtained. Also, Harada *et al.* [26] have obtained low molecular weight polythiophene (5000 daltons) included in macrocycles as β -CD and 2,6-dimethyl- β -CD by chemical polymerization of inclusion compounds: 2,2'-bithiophene/ β -CD and 2, 2-bithiophene/2,6-dimethyl- β -CD in aqueous solution.   On the other hand, the chemical oxidative polymerization of pyrrole or 3,4-ethylenedioxythiophene/ dimethylated α -, β - or γ –CD adducts, in water, using $K_2S_2O_8$ or $FeCl_3$ as oxidants, reported by Ritter et al., [27] have led to insoluble polymers; during the polymerization reaction the adduct is decomplexed, CDs remain in solution and the net insoluble conjugated polymers are obtained. Also, conducting pseudorotaxanes were obtained by including polythiophene or poly(3-methyl)thiophene in the cavity of β –CD.[28] We also have obtained full aromatic polyazomethines with rotaxane architecture by polycondensation of aromatic diamine/aromatic dialdehyde pairs in the presence of α –and β –CD.[29-31]

Until now, polyaniline/β –CD pseudorotaxane was synthesized by two ways; by chemical polymerization of inclusion adduct aniline/ β –CD [32] or N-phenyl-1,4-phenylenediamine/ β –CD in aqueous solution using ammonium persulfate,[33] and by inclusion of polyaniline emeraldine base into β –CD in aqueous solution.[33-35]

The aim of this communication is to present our results on synthesis of pseudopolyrotaxane polyaniline/CB[6] by two ways: (a) chemical oxidative polymerization of aniline in presence of CB[6] as host in acidic aqueous solution and using ammonium persulfate as oxidant and (b) by threading of preformed polyaniline chain through inner cavity of CB[6]. To our knowledge there is no reports about synthesis of conducting polymers with rotaxane structure using cucurbiturils as macrocyclic compounds.

EXPERIMENTAL PART

Cucurbituril[6], CB[6] was synthesized from glycoluril and formaldehyde by acid-catalyzed condensation reaction and purified by fractional crystallization and dissolution according to literature method.[16]

Synthesis of polyaniline in presence of CB[6] in 1M HCl solution

2.4072 g (2.4 mmol) CB[6] were dissolved in 30 ml 1M HCl and 0.313 g (2.4 mmol) aniline chlorhydrate were added and the solution was stirred at room temperature for 24 h to allow aniline chlorhydrate to penetrate macrocycle cavity. Then the solution was cooled at 0^oC and 1.654 g (7.2 mmol) ammonium persulfate dissolved in 10 ml water was dropwise. After an induction period the solution becomes blue, blue-dark and then green and an insoluble polymer can be observed. The polymer was filtered after 6 h and washed many times with a 1M solution HCl to remove free CB[6] and then dried. Yield = 0.2144 g.

For comparison, PAn emeraldine salt used as ethalon was synthesized in a similar way by chemical polymerization of aniline in aqueous1M HCl solution but in absence of CB[6].

Encapsulation of polyaniline in CB[6]: 0.8452 g CB[6] were dissolved in 30 ml 1M HCl solution and 0.1544 g polyaniline emeraldine base were added and suspension was stirred at room temperature for two days when a stable suspension is obtained. After two days, the insoluble PAn was filtrated and dried. About 2% from initial polyaniline has dissolved in aq. 1M HCl solution and a blue-green solution was obtained. The same experiment was conducted for 2 days with polyaniline emeraldine base in HCl 1M solution but in absence of CB[6] but in this case no polyaniline amounts has dissolved and a colorless solution is obtained.

Characterization: The FT-Infrared spectra were taken on a DIGILAB-FTS 2000 spectrometer using KBr pellets. UV-vis measurements were carried out on a Specord 200 spectrophotometer.

RESULTS AND DISCUSSION

The solubility of cucurbiturils, CBs[n], mainly in acidic media and on the other hand the possibility to obtain polyaniline by chemical oxidation of aniline in aqueous acidic solution opens up the strategy to synthesize polyanilines with rotaxane structures by threading the macrocyclic compound onto polymer chain in one or two step processes. In Scheme 1 is represented chemical structure and dimensions of CB[6] macrocycle. The compound is a macrocycle cavitand obtained by acid-catalyzed condensation of glycoluril with formaldehyde, has a rigid structure and a hydrophobic cavity of ~0.55 nm in diameter that is accessible through two identical fringed portals, each containing six carbonyl groups.[15, 36] The polar nature of two portals of ~ 0.4 nm allows this macrocycle to host various neutral molecules and cations whose dimensions are able to fit inside the cavity.[17] Thus, CB[6] form very stable complexes with protonated diaminoalkanes $(k > 10^5 \text{ mol}^{-1})$ and moderate stable complexes with protonated aromatic amines, benzene or tetrahydrofuran $(k \sim 10^2 \text{ mol}^{-1})^{17}$ by their inclusion inside its hydrophobic cavity. Protonated 4-methyl benzylamine was found to be the largest cation that can be included in the cavity of CB[6].[37] Aniline molecule and also polyaniline chain have small molecular volumes with cross sectional diameter of about 0.4 nm and it fits closer in the cavity of CB[6]. The ability of CB[6] to form inclusion complexes with organic molecules can be used to synthesize various rotaxane, pseudorotaxane and catenane supramolecular structures.[17] In terms of cavity size, CB[6] is analogous to α-CD where only one molecule of aniline can be included, while β-CD having a higher inner diameter, can accommodate even two aniline molecules.[32, 38] Moreover, unlike CDs which preferentially bind neutral guest molecules, CBs[n] bind preferentially guests with positive charges and in the aniline polymerization, anilinium cations are responsible species in the growing step. Therefore, CB[6] can form more stable complexes with aniline than β-CD and IR spectrum of PAn synthesized in presence of CB[6} shows the presence of a higher quantity of macrocycle remained after many washings with diluted aq.HCl solution.
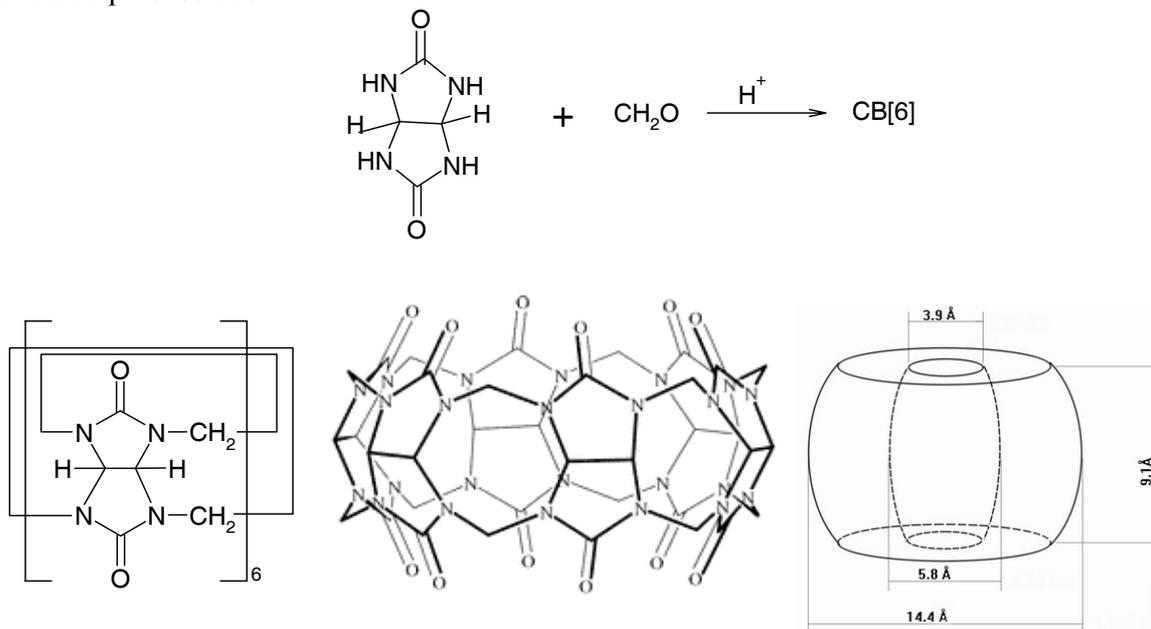
Scheme 1: Chemical structure and dimensions of cucurbit[6]uril macrocycle

Polyaniline can exist in three different oxidation states (Scheme 2), in which y can vary from y=0, fully oxidized form (pernigraniline base) to y=1, fully reduced form (leucoemeraldine base). The intermediary oxidized state having y=0.5 is known as emeraldine base.[1-4]
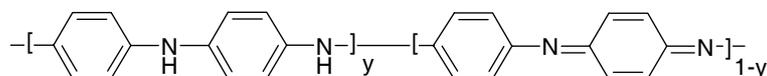
Scheme 2: The chemical structure of polyaniline

In neutral medium, polyaniline is obtained as emeraldine base, is black colored and soluble only in strong polar solvents while in acidic conditions, emeraldine salt form, green colored and insoluble in any organic solvents, is synthesized.

Figure 1 shows FTIR spectra of CB[6], polyaniline emeraldine salt and polyaniline synthesized in presence of CB[6]. FTIR spectrum of PAn shows characteristic absorption bands at 3400-3550, 3231, 3048, 2953, 2839 cm^{-1} (which can be assigned to NH$_2$ and NH asymmetric stretching vibrations), 1576 cm^{-1} (stretching of quinoid, –N=Q=N-) units, 1491 cm^{-1} (stretching of benzenoid, –N-B-N-) units, 1302 cm^{-1} assigned to –C-N- stretching vibrations in QBQ, QBB and BBQ units, 1225 cm^{-1} (–C-N-stretching in BBB units), 1132 cm^{-1} (a mode of –Q=N(+)H-B- or -B-NH-B- units, 806 cm^{-1} (v –C-H out of plane bending of 1,4 rings) and 611 cm^{-1} (aromatic ring deformation).[2] FTIR spectrum of CB[6] presents peaks at 3420 cm^{-1} (-N-H), 1734 cm^{-1} (carbonyl absorption), 1479,1379, 1327,1236, 1190, 966, 802 and 756 cm^{-1} while spectrum of PAn synthesized in presence of CB[6] is a sum of the two spectra, with peaks characteristic both polyaniline (3414, 3240, 2941, 2849, 1591, 1468 cm^{-1}) and CB[6] (3414, 3240, 1720, 1371, 1312, 1229, 1142, 962 cm^{-1}). After many washings with acidic aqueous1M HCl solution the intensity of these signals is unchanged, therefore, CB[6] remains in the insoluble polymer suggesting that partial encapsulation of the polymer chains during polymerization occurs and a polypseudorotaxane architecture is formed (Scheme 3). The number of macrocycles threaded onto polymer chain could not be estimated by elemental analysis or IR and NMR spectroscopy.
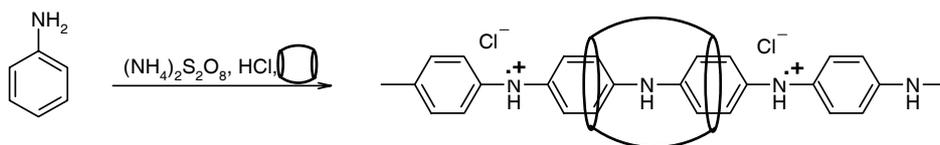
Scheme 3: The chemical structure of PANI emeraldine salt/ CB[6] with a pseudorotaxane architecture

It is well known that polyaniline emeraldine salt is insoluble in water and organic solvents due its rigid and conjugated structure. However, threading of a preformed linear polymer chain through macrocycles encapsulation of PAn in CB[6] allowed it to be dissolved in aqueous1M HCl solution. When we introduced a small amount of polyaniline emeraldine base into an aqueous acidic solution of CB[6] (molar ratio between aniline units/macrocyle =1) and stirred the suspension at room temperature all polymer was finely dispersed in the solution and after two days the solid was separated by filtration and a blue-green aqueous solution was obtained. The solid was recovered in ~98 % yield, the rest of polymer was dissolved in aqueous acidic solution. The inclusion reaction of polyaniline in CB[6] cavity was checked by UV-vis spectroscopy. The as-formed inclusion product was soluble in 1M HCl solution, while polyaniline in absence of CB[6] is completely insoluble in acidic solution and no absorption is observed in UV-vis region.

The electronic absorption spectrum of polyaniline encapsulated in CB[6] shows two absorptions located between 350-430 nm (assigned to π-π * transitions in phenyl groups) and 640-830 nm assigned to emeraldine salt form, while the slight absorption between 500-580 nm is from emeraldine base forms (protonation of emeraldine base to emeraldine salt was not completely) and can be assigned to the excitation of the imine segment of the polymer chain (Fig. 2).
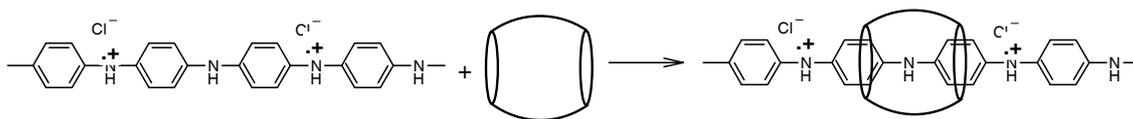
Scheme 4: Encapsulation of polyaniline emeraldine salt in CB6

In conclusion, polyaniline with pseudorotaxane structure has been synthesized by chemical oxidative polymerization of aniline chlorohydrate in presence of a macrocyclic compound having a rigid and hydrophobic cavity, cucurbit[6]uril, and by encapsulation of macromolecular linear chain inside of macrocycle cavity.
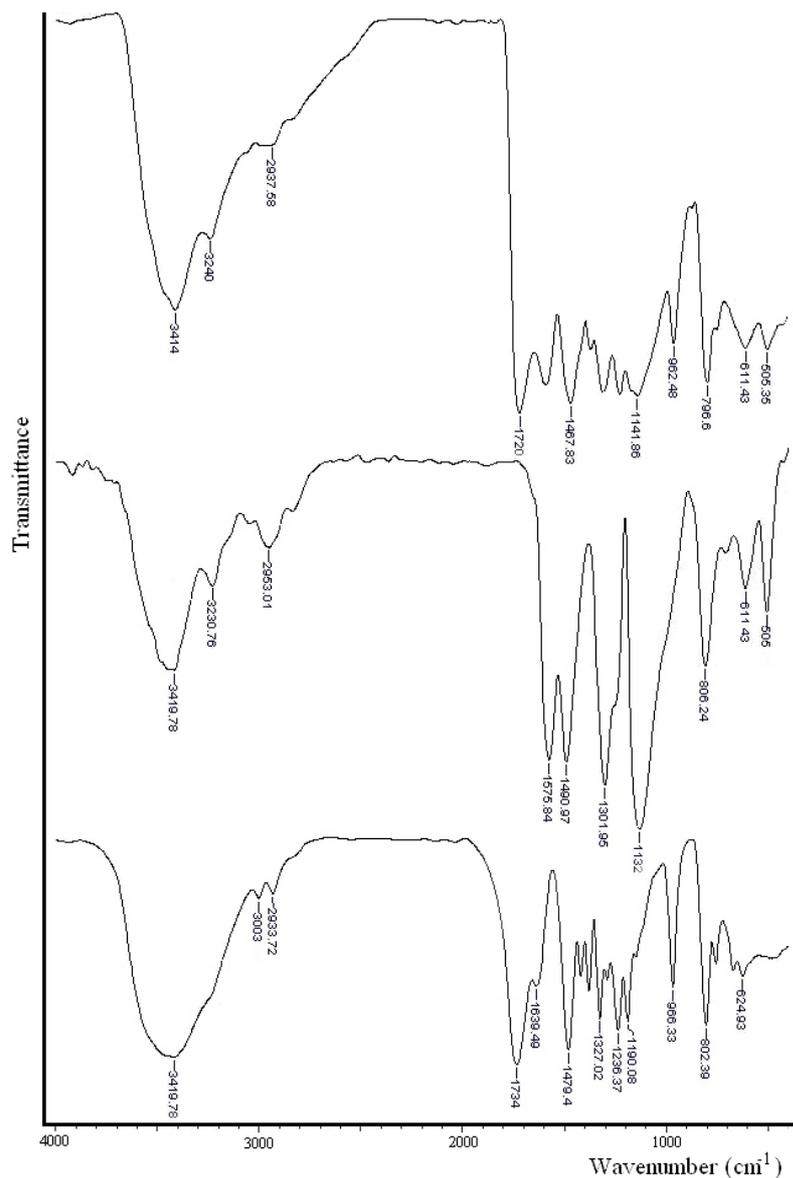
Fig. 1– FTIR spectra KBr pellets) of: PAn/CB[6] (top), PAn (middle) and CB[6] (bottom)
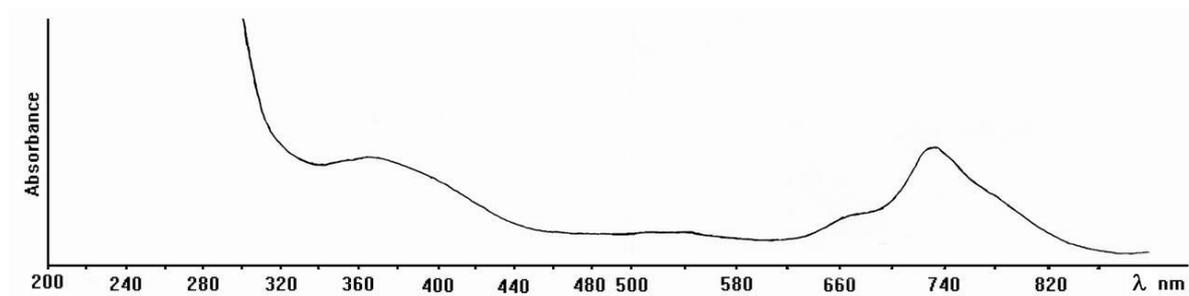

Fig. 2 – UV-vis spectrum (1M HCl aq. solution) of polyaniline included in cavity of CB[6].

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