Chemical Oxidative Polymerization of β-Cyclodextrin/Aniline Inclusion Complex

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Abstract

A β-cyclodextrin (β-CD)/aniline inclusion complex has been synthesized in aqueous solution and characterized by FT-IR and ^{1}H-NMR spectroscopy, chemical analysis and thermogravimetric method. By elemental analysis and ^{1}H-NMR spectroscopy a complex with stoichiometry 1:1.95 and 1:1.8 (β-CD/aniline) respectively, is found. The complexed aniline was polymerized by chemical oxidative polymerization using ammonium peroxydisulfate in water (pH = 7) and 1M HCl aqueous solution. In both cases, after an induction period, insoluble polyanilines (PANIs) are obtained, however, in water at pH = 7, a polypseudorotaxane architecture containing a β-CD molecule to $\sim$14 aniline units has resulted. In acidic conditions, anilinium cation is highly hydrophilic and inclusion complex has a strong tendency to dissociate to free molecules and emeraldine salt of PANI, free of host molecules is synthesized.

Introduction

Among conducting polymers, polyaniline (PANI) 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, and references therein]. 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 difficulty.

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 aesthetical structure and potential use as method for improving the polymer solubility, in medicine, pharmacology, etc. [5–8]. As general rule, macromolecular rotaxane structures are obtained mainly by three ways: (a) polymerization or polycondensation of a rotaxane monomer, (b) monomer polymerization or polycondensation in the presence of a macrocyclic compound, (c) threading of a preformed linear polymer chain through macrocycles. As macrocyclic compounds, crown ethers, cyclophanes and cyclodextrins (CDs) 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-CD or by their polymerization in presence of macrocyclics.

CDs are cyclic oligosaccharides consisting of six, seven or eight α-(1,4)-linked D-glucopyranose units and a torus-shaped structure having hydrophobic cavities with depths of 0.5 nm and diameters of 0.45 nm for α-CD, 0.7 nm for β-CD and 0.85 nm for γ-CD, respectively [14]. They have the advantage to be soluble in water and some protic polar solvents and form inclusion complexes with a large variety of guests of inorganic and organic nature

A conducting polymer with rotaxane architecture can be considered as an insulated molecular wire having a conjugated macromolecular chain as core and many macrocyclic compounds as shell. There are only few reports about synthesis of conducting polymers with rotaxane structure using (a) or (c) ways. Thus, Lacaze *et al.* [15] 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.* [16] have obtained low molecular weight polythiophene (5000) 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.* [17], have led to insoluble polymers; during the polymerization reaction

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the adduct is decomplexed, CDs remain in solution and the net insoluble conjugated polymers are obtained. Also, conducting pseudorotaxanes were obtained using way (c) by including of polythiophene or poly(3-methyl)thiophene in the cavity of β-CD [18] 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 [19–21].

A polyaniline/β-CD pseudorotaxane was synthesized by two ways; (a) chemical polymerization of inclusion adduct N-phenyl−1,4-phenylenediamine/β-CD in aqueous solution using ammonium persulfate [22], and (b) by inclusion of polyaniline emeraldine base into β-CD in aqueous solution [22–24].

The aim of this communication is to present our results on the chemical oxidative polymerization of β-CD/aniline inclusion complex, in aqueous solution using ammonium peroxydisulfate as oxidant.

Experimental part

β-CD is a commercial product (Aldrich) and was used after drying under vacuum at 50 °C for 24 h.

Preparation of β-CD/aniline inclusion complex

Into an aqueous solution obtained from 0.227 g (0.2 mmol) β-CD in 20 ml distilled water an excess of freshly distilled aniline (5 ml) was added and all mixture was stirred at room temperature for 24 h. Initially, aniline is dispersed as an oil in aqueous solution but later by inclusion in cavity of β-CD a homogeneous solution was obtained, then it became opalescent, and finally a white solid product was separated. The white solid precipitate was filtrated and dried.

Elemental analysis

Calculated nitrogen percent for $C_{42}H_{70}O_{35}$ (β-CD)/ $2(C_6H_7N)$ (aniline). Calculated: 2.12 %, Found: 2.07 %, which corresponds to 1.95 aniline molecules.

Synthesis of PANI by polymerization of β-CD/aniline adduct in water (pH = 7)

In a 250-ml round bottom flask, 0.8 g adduct β-CD/ aniline and 50 ml distilled water was introduced and the mixture was stirred until a clear solution was obtained. Then 0.4456 g $(NH_4)_2S_2O_8$ were added and in time the solution color changes. After 48 h the black precipitate was filtrated, washed several times with distilled hot water, and dried. Yield: 0.2124 g (26.6% reported to initial adduct).

Synthesis of PANI by polymerization of β-CD/aniline adduct in acidic medium

In a 250-ml round bottom flask, 0.8 g β-CD/aniline adduct was dissolved in 50 ml 1M HCl at room temperature and the mixture was stirred for 2 h. Then 0.4456 g $(NH_4)_2S_2O_8$ was added and in time the solution color changes. After 48 h, the green precipitate was filtrated, washed many times with water, and dried. Yield: 0.3789 g (47.4% reported to initial adduct). A PANI emeraldine salt was synthesized in a similar way by chemical polymerization of aniline in aqueous1M HCl solution but in absence of β-CD.

PANI emeraldine base/β-CD blend

0.2534 g of polyaniline emeraldine base and 0.227 g β-CD (calculated for a β-CD molecule to about 14 units of PANI) were introduced into a mortar. After grinding for 30 min with a glass pestle, the mixture was dropped
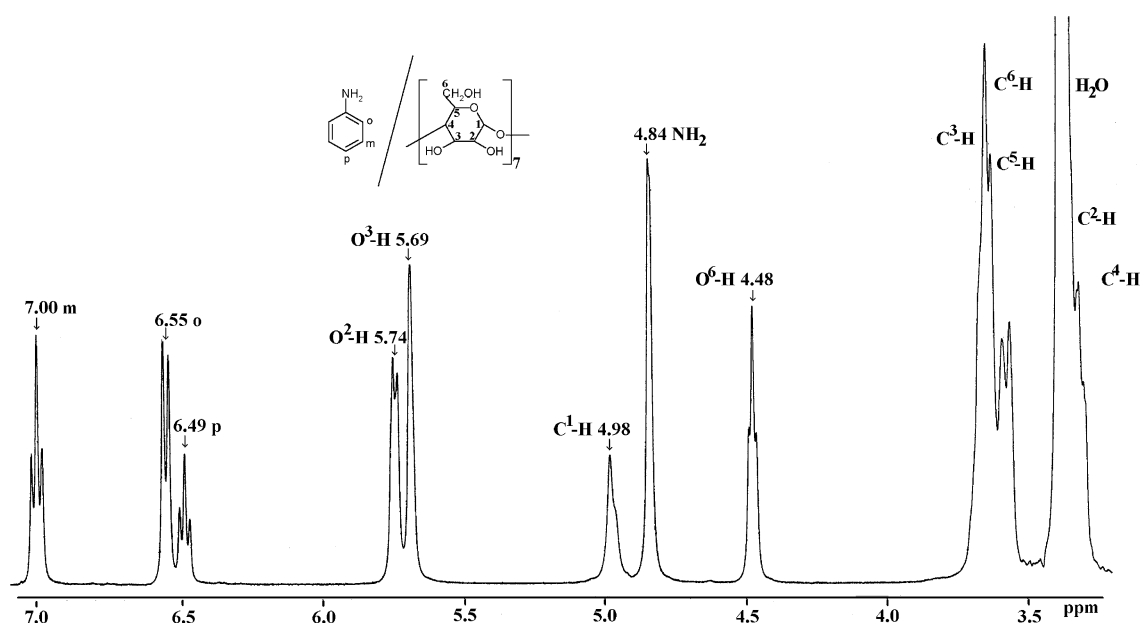

Figure 1. ^{1}H-NMR spectrum (400 MHz, DMSO-d_6, room temperature) of β-CD/aniline complex.

into distilled water (100 ml) and then stirred and warmed at 50 °C for 3 h. The solid polymer (0.2485 g) was collected by filtration, dried and analyzed by FT-IR spectroscopy.

Characterization:

The FT-IR spectra were taken on a DIGILAB-FTS 2000 spectrometer (KBr pellets). ^{1}H-NMR spectral analyses were performed on a Bruker Avance DRX-400 spectrometer as solutions in DMSO-d_6 for monomers and polymers and chemical shifts are reported in ppm and referenced to DMSO-d_6 signal (2.5 ppm). Thermal gravimetric analysis (TGA) measurements were performed on MOM (Budapest, Hungary) thermobalance apparatus, in air and at a heating rate of 10 °C/min.

Results and discussion

β-CD/aniline inclusion complex

Aniline is poorly soluble in water, mixing aniline with water an emulsion is obtained. In presence of β-CD, this emulsion is transformed into a solution that in time becomes turbid and finally a white solid separates. NMR spectroscopy is the most reliable technique available to characterize inclusion adducts of CDs [25]. In the ^{1}H-NMR spectrum (in DMSO-d_6) of the aniline, aromatic protons from *ortho* position appear as a doublet signal at 6.69 ppm, while *meta* and *para* protons appear as triplets at 7.10 and 6.60 ppm, respectively. Amine protons appear as a singlet situated at 4.98 ppm. ^{1}H-NMR spectrum of the β-CD/aniline adduct (Figure 1) shows aromatic protons from *ortho* position of

aniline as a doublet at 6.55 ppm, and *meta* and *para* protons as triplets at 7.00 and 6.49 ppm, respectively. All aromatic and amine (4.84 ppm) protons of aniline are shifted upfield due to the inclusion aniline inside of β-CD cavity.

The chemical shifts of β-CD and aniline protons in the uncomplexed and in the complexed forms in DMSO-d_6 solution have been assigned and tabulated in Table 1.

Demarco and Thakkar [25] have investigated cyclodextrin inclusion complexes formation by NMR spectroscopy and they observed that if the guest is incorporated inside of the host molecule then the protons located in the interior of the cavity (C^3–H, C^5–H

Table 1. 400 MHz ^{1}H-NMR chemical shifts of aniline and β-CD protons in free and complexed state[a]

Protons	Aniline	β-CD	β-CD/aniline complex	Δδ
H-*ortho*	2675		2621.2	53.8
H-*meta*	2840		2802	38
H-*para*	2642		2594.8	47.2
–NH$_2$	1993.2		1937.2	56
C$_1$–H		1933.6	1992	−58.4
C$_2$–H		1342.4	1342.4	0
C$_3$–H		1464.4	1457.6	6.8
C$_4$–H		1324.4	1326.4	−2
C$_5$–H		1432	1430	2
C$_6$–H		1451	1450.8	0.2
O$_2$–H		2295.8	2297.2	−1.4
O$_3$–H		2274.6	2275.2	−0.6
O$_6$–H		1792.8	1790.4	2.4

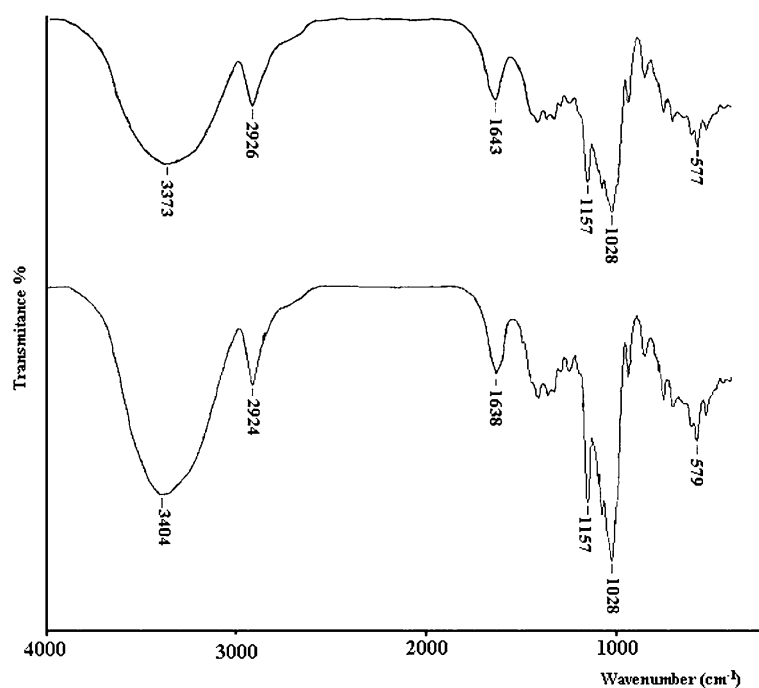[a]Chemical shifts are expressed in hertz with reference to DMSO-d_6 signal, solvent, DMSO-d_6, 20 °C.

Figure 2. FT-IR spectra (KBr pellets) of β-CD (top) and β-CD/aniline complex (bottom).

and C^6–H) would be shielded by the guest. As can be seen in Table 1, these protons are shielded at high magnetic fields while the other ones are unaffected or are deshielded (they are situated on the outer surface of β-CD). Therefore, our conclusion is that aniline is incorporated inside of the β-CD cavity as a pseudorotaxane.

Calculation of adduct stoichiometry was performed by ^{1}H-NMR using the intensity ratio of the peaks at 4.98 ppm assigned to C_1H of the β-CD and at 7.00 ppm assigned to *meta* aromatic protons of aniline and proved by elemental analysis. The number of aniline molecules included in the β-CD cavity was found to be 1.8 by ^{1}H-NMR and 1.95 by elemental analysis. Cramer and Henglein [26] have found that inclusion adducts of CD/aniline have composition of 1:2 for β-CD and 1:1.1 for α-CD. The geometry of CDs gives a doughnut shaped hydrophobic cavity having an internal diameter of ca. 5.7 Å for α-CD and ca. 7.8 Å for β-CD [14]. Aniline molecule has a small molecular volume with cross sectional diameter of about 4.0 Å and it fits closer in the cavity of α-CD, while in β-CD more than one molecule can be included and the adduct is less stable due to a higher difference between the partner dimensions.

Figure 2 shows FTIR spectra of β-CD and β-CD/aniline adduct. β-CD presents strong absorption bands at 3373 (OH-stretching, H-bonded), 2926 (CH stretching), 1643 (OH bending), 1157 (CO stretching glucosidic bond, OH bending/CO stretching of C–OH group), 1080 (CO/CC stretching) and 1028 cm^{-1} (CO/CC stretching) [14]. There is no differences between FTIR spectrum of β-CD and β-CD/aniline adduct (both spectra show the same strong bands and their intensities ratio is preserved) and this one can be explained by presence of only 12–14% weight percent aniline in adduct and therefore, aniline characteristic peaks are covered by β-CD absorption bands. However, the inclusion of aniline in solid adduct can be very easy proved by H-NMR spectrum and by its behavior in chemical oxidative polymerization of the adduct (with ammonium peroxydisulfate), when the same characteristic color sequence as in polymerization of free aniline is developed.

TGA of β-CD/aniline complex (Figure 3), in air (10 °C/min) evidences two endothermic processes between 80 and 180 °C assigned to removing of water retained by β-CD in the first step and then due to the evaporation of aniline included in macrocycle's cavity. The melting of β-CD is accompanied by decomposition and culminates at 300 °C.

Chemical oxidative polymerization

To obtain polyaniline with pseudorotaxane architecture, the chemical oxidative polymerization of β-CD/aniline inclusion complex was carried out in aqueous solution at room temperature, using ammonium peroxydisulfate as oxidant, in acidic or neutral medium. After an induction period, a sequence of color changes took place, as in
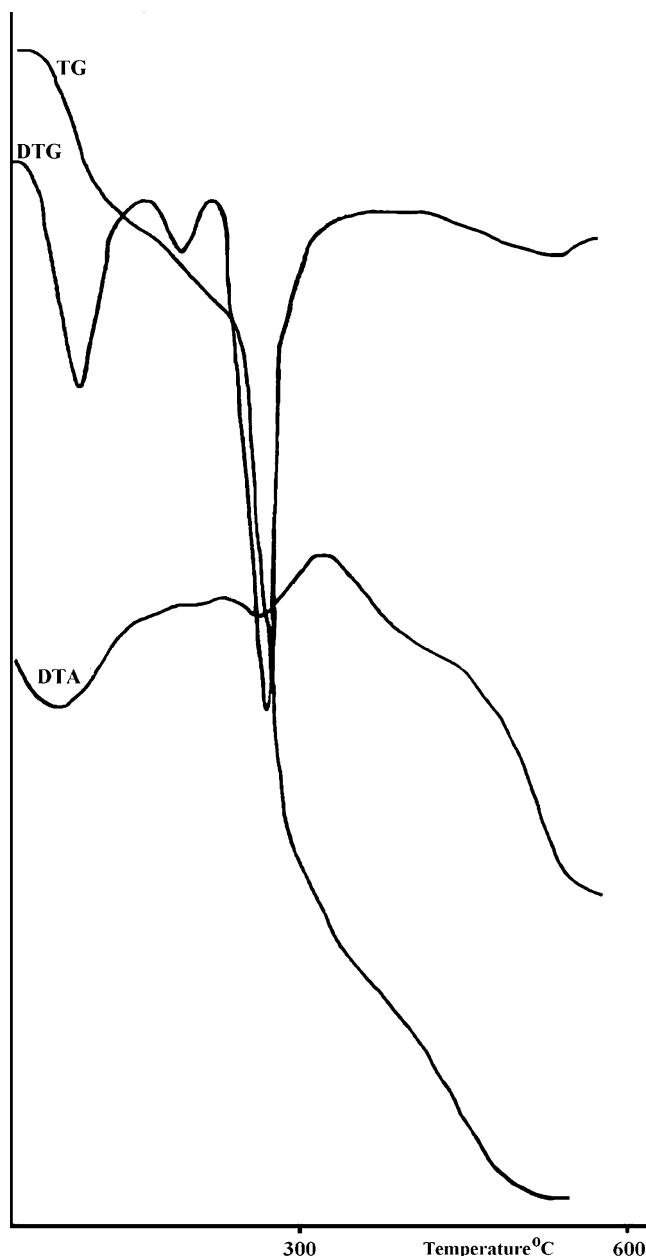

Figure 3. TG, DTG and DTA curves for β-cyclodextrin/aniline inclusion complex.

aniline polymerization and water-insoluble polymers were obtained, their color being black (at pH = 7) or green (pH acid). The polymers were washed with hot water to remove residual oxidant, aniline and uncomplexed β-CD. The structure of the polymers was studied by FT-IR and H-NMR spectroscopy.

Polyaniline can exist in three different oxidation states (Scheme 1), 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].
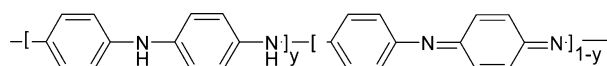
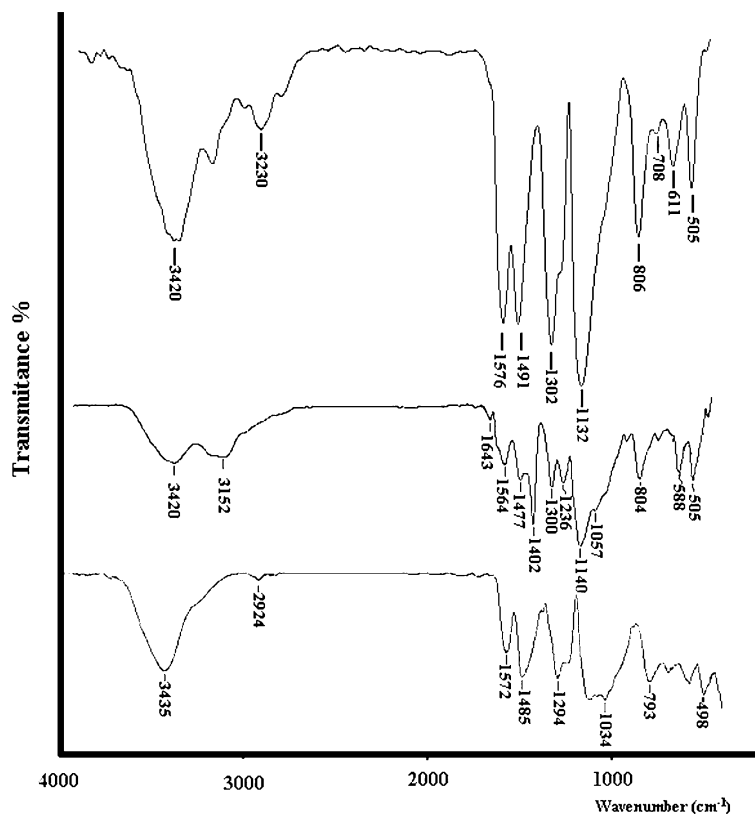*Scheme 1.* The chemical structure of polyaniline.

Figure 4. FT-IR spectra (KBr pellets) of: PANI emeraldine salt synthesized in absence (top) or presence of β-CD, in acidic (middle) or neutral (bottom) media.

In neutral medium, polyaniline is obtained as emeraldine base (black colored and soluble in strong polar solvents) while in acidic conditions emeraldine salt form (green colored and insoluble) is synthesized (Figure 4).

FT-IR spectra of polymers synthesized in presence of β-CD (Figure 3) show that all characteristic peaks of PANI were present: 1564–1571 cm^{-1} (assigned as C=C stretching of the quinoid rings), 1485–1477 cm^{-1} (C=C stretching of benzenoid rings), 1294–1300 cm^{-1} (C–N stretching vibrations) and 1140 cm^{-1} (–N=Q=N–), 800–830 cm^{-1} (ν $_{C–H}$ out of plane bending of 1,4 rings)

and 611 (aromatic ring deformation). Wide absorption bands at 3400–3550, 2924 cm^{-1} (which can be assigned to NH$_2$ and NH asymmetric stretching vibrations from aniline units but also to OH-stretching from β-CD), 2924 cm^{-1} (CH stretching of β-CD) and 1000–1100 cm^{-1} (CO and CC stretching in β-CD are also evidenced [2]. These last bands are clear evidence for PANI synthesized in neutral media and suggests a higher content of β-CD threaded onto the polymer chain.

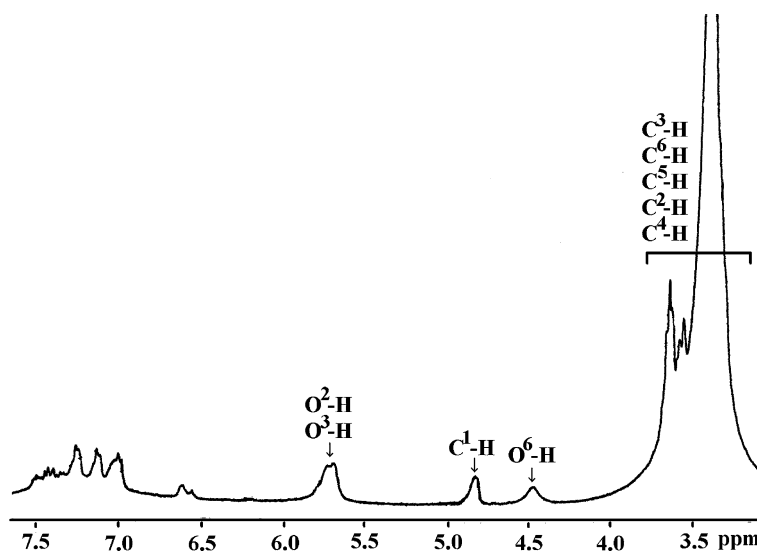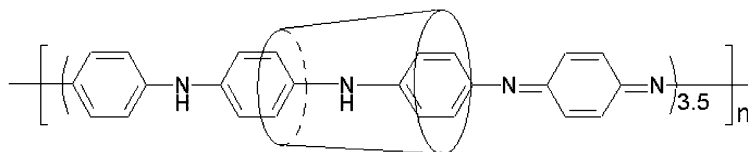The ^{1}H-NMR spectrum of PANI (synthesized in neutral medium) is presented in Figure 5 the polymer

Figure 5. ^{1}H-NMR (400 MHz, DMSO-d$_6$, room temperature) of PANI synthesized from β-CD/aniline complex in neutral medium.
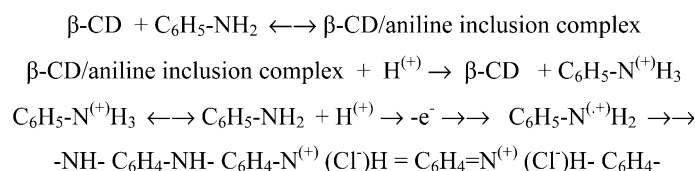
shows multiplet signal at 6.9–7.5 ppm that can be assigned to aromatic and –NH– protons of emeraldine base structure. The signals positioned at 5.65–5.8 ppm (O^2–H, O^3–H), 4.45–4.55 ppm (O^6–H) and 3.0–4.0 ppm (C^3–H, C^6–H, C^5–H, C^2–H and C^4–H) are from β-CD. Therefore, β-CD remains in the insoluble polymer suggesting that partial encapsulation of the polymer chains occurs and a polypseudorotaxane architecture is formed.

To bring a supplementary proof about pseudorotaxane structure of the PANI obtained by polymerization of inclusion adduct in neutral medium, a physical mixture obtained by grinding of polyaniline emeraldine base with β-CD, in the same composition, was prepared. The FT-IR spectrum of the blend is identical with the bottom spectrum from Figure 4. However, by washing of this blend with warm water all β-CD was very easily removed and pure PANI emeraldine base is obtained.

The relative integrated intensities of the aromatic protons signals (6.9–7.5 ppm) and that of the O^2–H and O^3–H allow the estimation of the content of β-CD in PANI. The integral lines give 1.0 for aromatic and NH protons (5H) and 0.25 for O^2–H and O^3–H (14 H) and the calculation leads to a value around one macrocycle to 14 aniline units (Scheme 2).

cavity of CD (Scheme 3). Thus, the oxidation with $(NH_4)_2S_2O_8$ of the anilinium cations involves only the free molecules and it could explain the differences between the polyanilines synthesized in acidic and neutral conditions.

Such a behavior has been also observed by Mirzoian and Kaifer [28]. They have investigated the complexation in aqueous solutions of viologen derivatives with β-CD and have found that dication forms are not bonded, the cation-radical forms are weakly bonded, while the neutral forms of guests are strongly bound by hydrophobic forces.

Conclusions

Inclusion of aniline monomer in hydrophobic cavity of β-CD was studied by ^{1}H-NMR and FT-IR spectroscopy and checked by chemical analysis and thermogravimetry. It is observed that about two aniline molecules are encapsulated by hydrophobic cavity of β-CD in aqueous solution. The oxidative polymerization of inclusion adduct can lead to a pseudopolyrotaxane structure if the reaction is carried out in neutral media. In acidic conditions, the dissociation of β-CD/aniline inclusion com-

Scheme 2. The chemical structure of PANI emeraldine base/β-CD with a pseudorotaxane architecture.

$$\beta\text{-CD} + C_6H_5\text{-}NH_2 \longleftrightarrow \beta\text{-CD/aniline inclusion complex}$$

$$\beta\text{-CD/aniline inclusion complex} + H^{(+)} \rightarrow \beta\text{-CD} + C_6H_5\text{-}N^{(+)}H_3$$

$$C_6H_5\text{-}N^{(+)}H_3 \longleftrightarrow C_6H_5\text{-}NH_2 + H^{(+)} \rightarrow -e^- \rightarrow\rightarrow C_6H_5\text{-}N^{(\cdot+)}H_2 \rightarrow\rightarrow$$

$$\text{-NH- } C_6H_4\text{-NH- } C_6H_4\text{-}N^{(+)} (Cl^-)H = C_6H_4{=}N^{(+)} (Cl^-)H\text{- } C_6H_4\text{-}$$

Scheme 3. Polymerization mechanism of β-CD/aniline inclusion complex in 1M HCl solution.

However, PANI formed in 1M HCl media contains constitutive β-CD only as traces and it means that (a) the inclusion complex is subject to dissociation phenomena during polymerization step, or (b) less probable β-CD is dethreaded from pseudorotaxane PANI during polymerization and/or separation processes of polymers (Scheme 3).

CDs have ability to form stable inclusion complexes with hydrophobic molecules in aqueous solution, the OH groups encircling the cavity entrances can contribute to guest binding through hydrogen bonds. Also, their inner surface of the cavity is almost neutral and they bind preferentially neutral guest molecules [27]. In aqueous acidic media, aniline exists predominantly as the aniline cation and because of its highly hydrophilic NH_3^+ group it has the tendency to come out of the

plex in free partners is favourized and aniline is polymerized to its emeraldine salt form.

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