MODIFICATION OF POLYANILINES PROPERTIES USING MACROCYCLIC COMPOUNDS

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Modification of the polyanilines properties using macrocyclic compounds was studied using two aniline derivatives: aniline and aniline N-propanesulfonic acid. The polymers were obtained by oxidative chemical polymerisation with ammonium peroxidisulfate as oxidant, in the presence of two macrocycles having accessible and hydrophobic cavities: β-cyclodextrin and cucurbit[6]uril. Both monomers have formed inclusion complexes with macrocyle, evidenced by ^{1}H-NMR spectroscopy. Polymerisation of aniline/ β -cyclodextrin adduct led to main-chain pseudorotaxane polyaniline, soluble in polar solvents. The second monomer polymerised in the presence of cucurbit[6]uril, led to a water-insoluble polymer network with macrocycles threaded on the side-chains and/or between two polymer chains as physical crosslinking agent. The physical crosslinking of ionic polyaniline (PANS) with cucurbit[6]uril was also evidenced. Solubility, hydrophilicity and morphology of polymers obtained in the presence of macrocycles are modified.

INTRODUCTION

Polyaniline (PANi) is one of the most promising conducting polymers because has a high electrical conductivity, can be easily synthesized, has well-behaved electrochemistry (the color changes depending on the redox state), and is stable under ambient conditions.[1] However, the low solubility of the polymer in any solvents is an inherent problem that has limited the applications and should be overcome. In this context, great efforts have been made towards the synthesis of the modified structures of the PANi, either from (electro) polymerization of suitable substituted aniline monomers or from the post-modification of the polymer using bulky dopants.[2,3] The purpose of this paper is to present an alternative approach to tune the physical properties of polyanilines using macrocyclic compounds either in the polymer synthesis or processing step (the rotaxane's architecture way). Two polymers are used to evidence this possibility; polyaniline and poly (N-propanesulfonic acid) aniline and two macrocycles, β-cyclodextrin (β –CD) and cucurbit[6]uril (CB[6]). Polyaniline (PANi) is usually synthesized by oxidative polymerization of aniline in aqueous acidic solution when is obtained as emeraldine salt state (ES), green colored and insoluble in any organic solvent.[4] The second polymer (PANS), obtained by a similar procedure, by oxidizing of aniline-N-propane sulfonic acid, is a self-dopable polymer and has an excellent solubility in water.

RESULTS AND DISCUSSION

Two combinations of polymer/macrocycle; *i.e.*, polyaniline/β-cyclodextrin (**P1**) and poly (N-propanesulfonic acid) aniline/ cucurbit[6]uril (**P2**), were chosen to study how the macroscopic properties of the polymers are modified in the presence of the macrocycles. These modifications are evidenced at macroscopic level by change of solubility, hydrophilicity, and other physical

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properties. The two selected polyaniline structures, in emeraldine salt state, have a different behaviour, one polymer (PANi) is insoluble in any solvent and another one (PANS) is soluble in water and polar solvents (DMSO, DMF, NMP). The two macrocycles are one soluble in water (β –CD) and the other one (CB[6]) is insoluble in water but is soluble in aqueous acidic and salt solutions. The chemical structures of the polymers and macrocycles used in this study are presented in the Schemes 1 and 2.

β-Cyclodextrin is a carbohydrate-based cyclic compound consisting of seven α-(1,4)-linked D-glucopyranose units and a torus-shaped structure having a hydrophobic cavity with depth of 0.79 nm and diameter of 0.60- 0.78 nm.[5] It has the advantage to be soluble in water and some protic polar solvents leading to inclusion complexes with a large variety of neutral guests of inorganic and organic nature. The cucurbit[n]uril family (abbreviated as CB[n], where n=5-10) comprises macrocyclic compounds obtained by acid-catalyzed condensation of glycoluril and formaldehyde. The most known compound, cucurbit[6]uril, CB[6], was obtained for the first time in 1905[6] and its structure was fully elucidated in 1981.[7] It contains *six* units derived from glycoluril bonded by *twelve* methylene bridges between nitrogen atoms and has a pumpkin-shape structure with high symmetry, high chemical and thermal stability.[8-10] The hydrophobic cavity has a diameter of ~ 0.55 nm that is accessible through two identical carbonyl-fringed portals, the opening of each portal is close to 0.4 nm, through which small molecules or cations can enter the interior.[11] Due to the polar carbonyl groups at the portals and the hydrophobic character of cavity, CB[6] has molecular-recognition properties toward cationic (alkali metal cations) and ammonium ions,[12] and hydrophobic species (amines, amino alcohols, etc.).[13] The main disadvantage of CB[6] is the solubility only in strong acidic solutions that limits very much its use in many studies and applications. Due to their inclusion properties and rigid structure, CDs and CB[n]s have been used for synthesis of main-chain or side-chain polyrotaxanes with polymers as axle.[14] The polyrotaxane structures could be considered as insulated molecular wires and their electro-optical properties are strongly modified versus the parent polymer. The first conducting polyrotaxane with CB[6] as host was synthesized by polymerization of aniline /CB[6] adduct or by encapsulation of polyaniline chain in CB[6] cavity.[15,16]
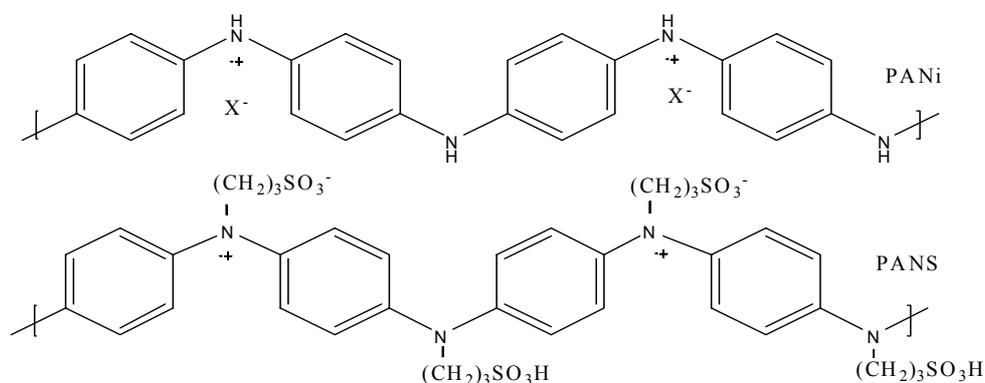
Scheme 1 – The chemical structure of polyaniline (PANi) and poly (N-propanesulfonic acid) aniline (PANS).
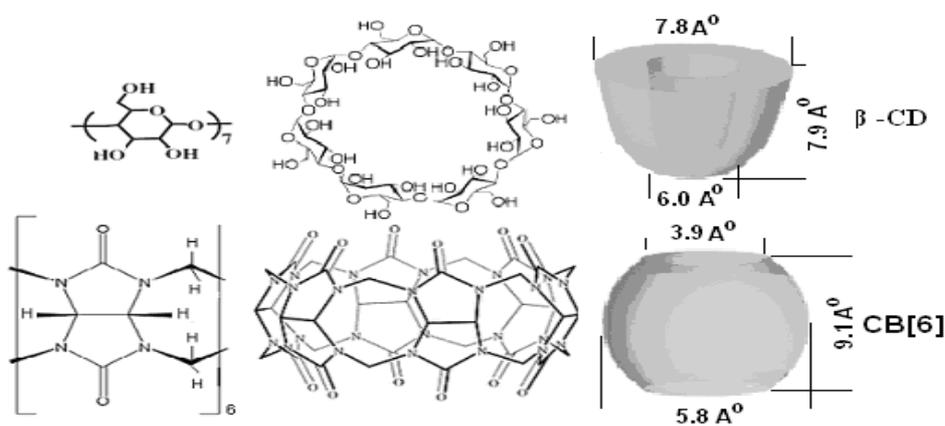
Scheme 2 – Structure of macrocycles and cavity's dimensions.

Inclusion complexes between aniline monomers and macrocycles

The oxidative polymerisation of aniline was carried out in presence of β–CD, while aniline N-propane sulfonic acid was polymerised in the presence of CB[6]. We have observed that both monomers are enclosed into the hydrophobic cavity of the macrocycles as pseudorotaxanes when monomer and macrocycle solutions are mixed and stirred together (Scheme 3). The dimensions of the macrocycle's cavity are sterically compatible with the shape and dimensions of aniline monomers. The hydrophobic interactions of the guest molecule with β-CD and CB[6] and ion-dipole interactions of the ammonium ions with hydroxyl and carbonyl groups of the portals are the driving forces to form the host-guest complexes. Both monomers, in aqueous 1M HCl solution, are in protonated form, as ammonium ions.
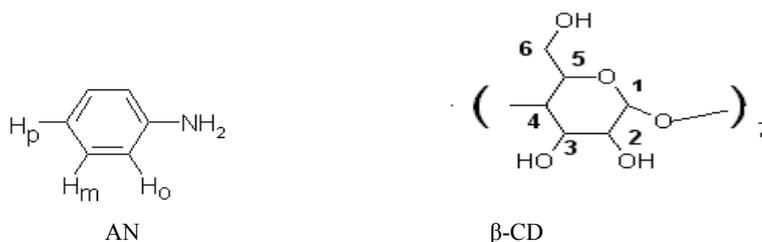
The formation of an inclusion complex between monomer and macrocycle is clearly evidenced from the ^{1}H-NMR spectra of the mixtures of both compounds in aqueous solution.[17] Inclusion of aniline into the hydrophobic cavity of β-CD is clearly observed in NMR spectrum by up-field shifting of the aromatic protons of the monomer, while protons of the host are less affected (Table 1).
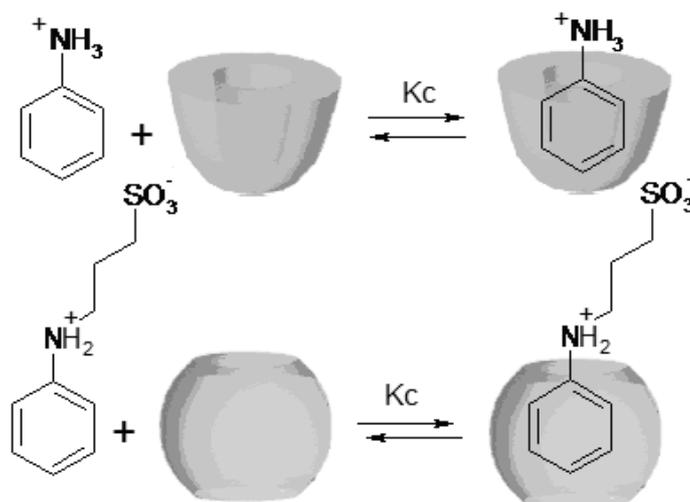
Scheme 3 – Schematic representation of aniline monomers encapsulated into macrocycle cavity.

Table 1

400 MHz ^{1}H-NMR (DMSO-d_6) chemical shifts (in Hz) of aniline and β-CD protons in free and complexed state

Protons	AN	β-CD	AN/ β-CD	Δδ, Hz AN/ β-CD
Ho	2644		2616	+28
Hm	2805		2797	+8
Hp	2613		2585	+28
C^1-H		1933	1932	-1
C^2-H		1345	1345	0
C^3-H		1449	1454	-5
C^4-H		1325	1326	-1
C^5-H		1425	1425	0
C^6-H		1449	1454	-5
O^2-H		2288	2292	-4
O^3-H		2268	2267	+1
O^6H		1779	1778	+1

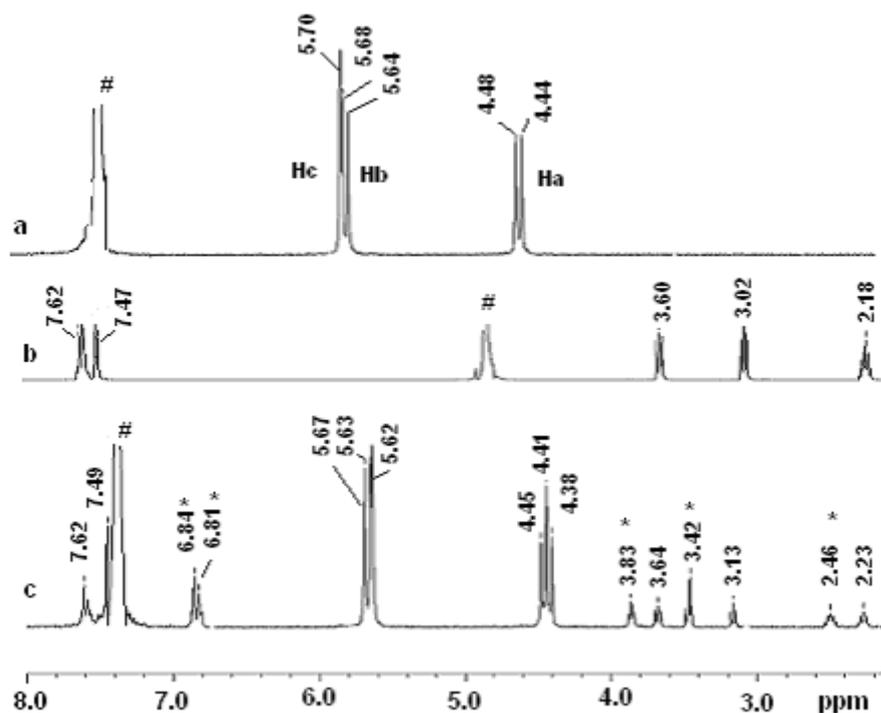+ shielding, – deshielding shift. Chemical shifts are expressed in Hz with reference to DMSO-d_6 signal.

Fig. 1 – ^{1}H-NMR spectra (D$_2$O-20%DCl) of: (a) CB[6], (b) ANS, (c) CB[6]/ANS.
Peaks marked with (#) is due to D2O/DCl and (*) represents ANS encapsulated in the cavity of CB[6].

Table 2

400 MHz ^{1}H-NMR (D$_2$O/DCl (20%) chemical shifts (in Hz)
of aniline N-propane sulfonic acid (ANS) and CB[6] protons, in free and complexed state
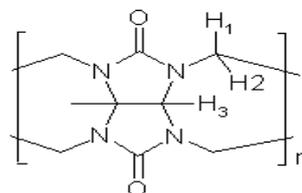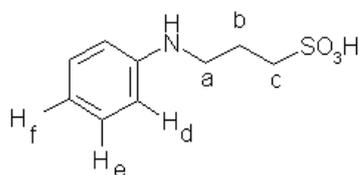
	ANS		CB[6]	

Protons	ANS	CB[6]	CB[6]/ANS complex	Δδ CB[6]/CB[6]
Ha	1447		1531	-84
Hb	1212		1374	-162
Hc	879		984	-105
Hd	2991		2721	+270
He	3024		2741	+283
Hf	3038		2741	+297
H1		1808	1765	+43
H2		2264	2259	+5
H3		2292	2246	+46

+ shielding, - deshielding shift. Chemical shifts are expressed in Hz with reference to DPS signal.

Aniline N-propanesulfonic acid forms also a pseudorotaxane with CB[6] and its formation can be monitored by ^{1}H-NMR spectroscopy. Fig. 1 shows the NMR spectra of both individual partners and their mixture. The spectra of pure components show signals for ANS at 2.20 (m, 2H, -CH$_2$-SO$_3$-), 3.13 (t, 2H, N-C-CH$_2$-), 3.64 (t, 2H, -N-CH$_2$-), 7.49 (2H, m, *m*- aromatic protons) and 7.62 ppm (3H, *o*- and *p*- aromatic protons) while CB[6] shows signals at 4.46 ppm (d, 12H, J$_{HH}$=15.6 Hz), 5.66 ppm (d, 12H, J$_{HH}$=15.6 Hz) and 5.70 ppm (s, 12H). As can be seen in Fig. 1c upon the addition of ANS to the CB[6] solution (in NMR tube), aromatic protons signals of the encapsulated ANS

are shifted at higher field while aliphatic protons signals exhibit a downfield shift. By adding more monomer the signals intensity assigned to free ANS increases while their position is slight modified. From signals integral ratio of the complexed monomer with CB[6] it results a 1:1 stoichiometry for ANS/CB[6] complex. The signals of free, non-encapsulated ANS are also present because aniline derivative was used in excess. Since signals for complexed and free ANS are observed as distinct and sharp peaks, any exchange between complexed and free ANS is slow on the NMR time scale and complexation constant (Kc) can be determined. Thus, using NMR spectroscopy, Kc was determined for ANS/CB[6], being $2.97.10^4$ M^{-1}. The structure of the AN/ β-CD and ANS/CB[6] complexes can be envisioned as in Scheme 3, with ammonium ions encircled by ion-dipole interactions with hydroxyls or carbonyls groups of β-CD and CB[6], respectively. ANS has a hydrophobic part (aromatic moiety) and a hydrophilic rest (propane sulfonate group). In the cavity of CB[6] the aromatic ring is more probable included by hydrophobic interactions and dipole-ion interactions between carbonyl groups of the host and NH$^{(+)}$ ions from monomer. The shielding of aromatic protons by CB[6] (Table 2) proves this assumption. The up-field shifting of signals is significant higher than for An/ β–CD system that is a weak complex, suggesting that ANS formed with CB[6] a tight complex. Aliphatic protons of propane sulfonate groups are deshielded because they are held outside the portals of the macrocycle, in the deshielding region.

Oxidative polymerization of inclusion adducts

The chemical oxidative polymerization of aniline/ β-CD inclusion complex led to an encapsulated polyaniline chain in many macrocycles as is represented in Scheme 4. The hydrophilicity is enhanced due the mantle, the polymer became soluble in polar organic solvents (DMF, DMSO) and even in water.

The IR and NMR spectroscopy proved the presence of the macrocycle by characteristic signals in spectra of polymers (Figs. 2 and 3). FTIR spectra of polyaniline synthesized in presence of β-CD (Fig. 2) show that all characteristic peaks of PANi were present: 1559 cm^{-1} (assigned as C=C stretching of the quinoid rings), 1473 cm^{-1} (C=C stretching of benzenoid rings), and 798 cm^{-1} (ν C-H out of plane bending of 1,4 rings).[4] Wide absorption bands at 3443, 2900 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), 2921 cm^{-1} (CH stretching of β-CD) and 1128 cm^{-1} (CO and CC stretching in β-CD) are also evidenced.

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 PANS synthesized in presence of CB[6] presents peaks characteristic both of polyaniline (3443, 3008, 2930, 2853, 1479 cm^{-1}) and CB[6] (3414, 3240, 1734, 1376, 1327, 1236, 1148, 964 cm^{-1}) (Fig. 2). After many washings with acidic aqueous 1M 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. The product obtained by post-modification of PANS with CB[6] has a similar FTIR spectrum with peaks characteristic both for PANS and CB[6].

The ^{1}H-NMR spectra have evidenced the presence of macrocycles in the polymers: signals at 3.77, 3.92, 4.14 ppm assigned to β-CD, or 4.33, 5.45 and 5.61 ppm for CB[6] and also signals in aromatic region assigned protons from benzene rings of polyaniline backbone. Signals of propane sultone side chain are hidden by wide signals from water (3.4 ppm) and DMSO-d$_5$ (2.5 ppm).
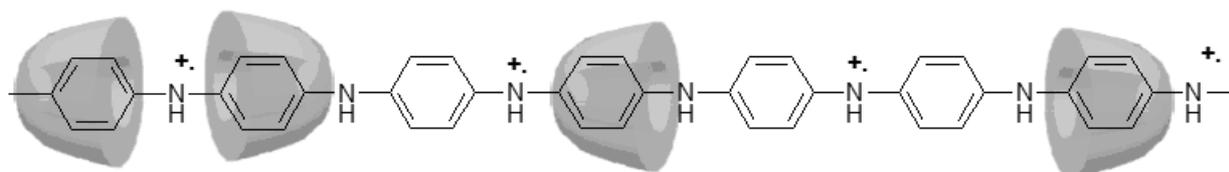
Scheme 4 – Structure of PANi encapsulated in many β –cyclodextrins.

Unlike PANi, polyaniline N-propanesulfonic acid is a water-soluble polyaniline derivative, self-dopable by sulfonic acid group. The polymer synthesized in the presence of CB[6] became insoluble in water and was separated in a DMSO-soluble fraction and an insoluble one. Sterically, the CB[6] macrocycle can't be threaded on the PANS backbone because the distance between two adiacent N-propane sulfonate groups is smaller than the length of the macrocycle (9.1A°). Therefore, it is possible as during the polymerization step the macrocycle to be dethreaded in solution or slipped on the propane sulfonic side chain, complexing the ammonium ion by the other portal. We have observed that the oxidative polymerization of both inclusion complexes takes place with a long induction period comparing with free aniline monomers because the oxidation of the amine group and N-C couplings in the initiation step are hindered.

By mixing the aqueous solution of PANS with CB[6], the polymer became insoluble in aqueous solution and partially soluble in DMSO. A priori, the interaction between PANS and CB[6] could proceed by two modes of interaction (Fig. 4). We can assume two processes that could take place: (i) the propane sulfonate group is encapsulated inside CB[6]' cavity and hydrophilicity of propane sulfonate group is diminished, and (ii) CB[6] has the role of a physical crosslinking agent for anionic polymers. The encapsulation of the PANS main chain inside of many CB[6] macrocycles is not possible due to the side substituents. We have also checked the cross-linking of other ionic polymers (*i.e.*, polystyrene sulfonic acid, methacrylic acid or their salts) in presence of CB[6] by mixing their aqueous solutions with 0.2M NaCl CB[6] solution when a solid product precipitated. The precipitate is insoluble in aqueous solution or organic solvents. The role of physical crosslinking agent of CB[6] is based on the fact that the carbonyl groups from the two portals of CB[6] can bind metal ions, especially, alkali metal ions, such as Na^+ or K^+ or protons with high affinity and selectivity by ionic-dipole and electrostatic forces. The intermolecular linking of PANS chains by CB[6] as bis functional agent, led to a physically crosslinked network that should be reversible in presence of stronger additives.
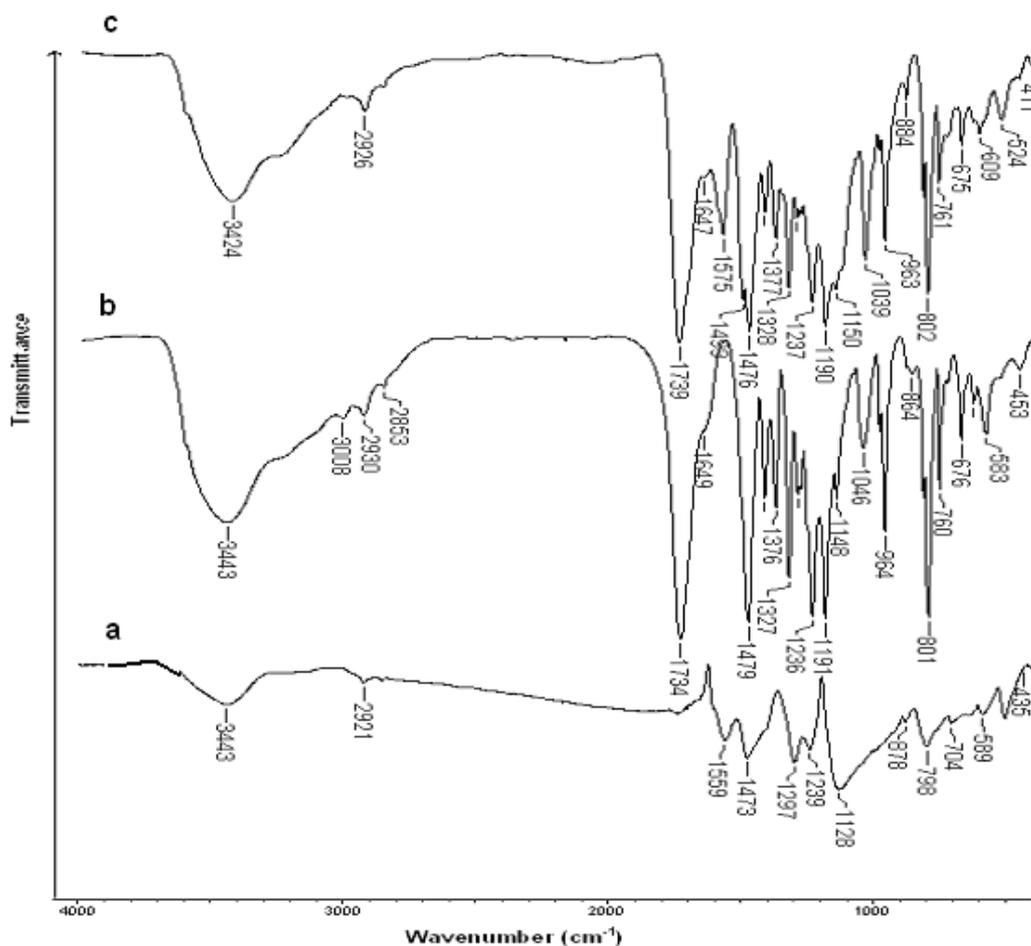

Fig. 2 – FTIR spectra (KBr pellet) of: (a) **P1**, polyaniline synthesized in presence of β -CD,
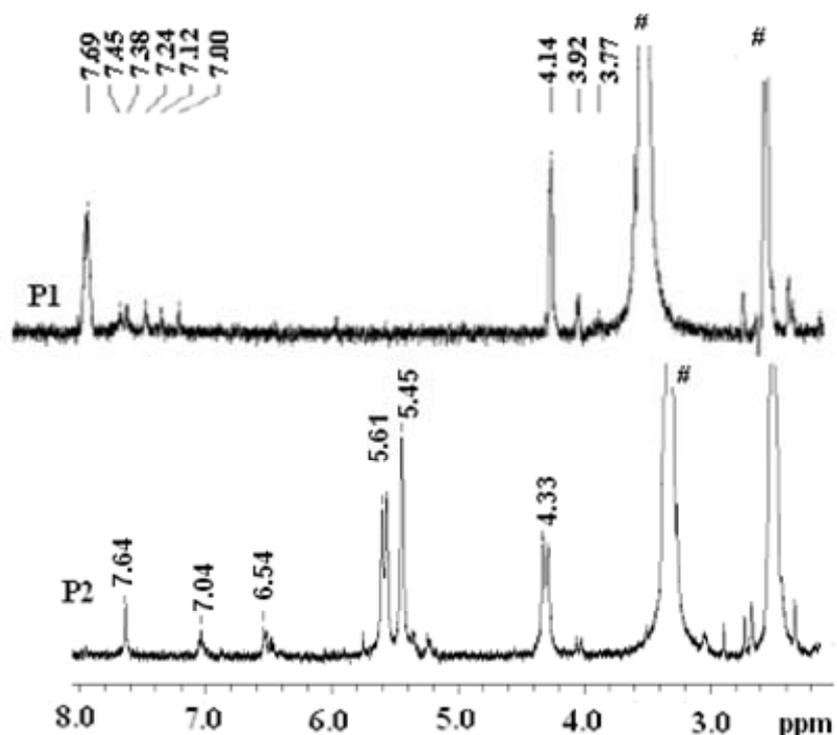(b) **P2**, polyANS synthesized in presence of CB[6], and (c) physically crosslinked PANS with CB[6].

Fig. 3 – ^{1}H-NMR spectra (DMSO-d_6) of: (a) **P1**, PANi synthesized in presence of β-CD,
and (b) **P2**, PANS synthesized in presence of CB[6]. Peaks marked with (#) are due to DMSO-d_5 and water.
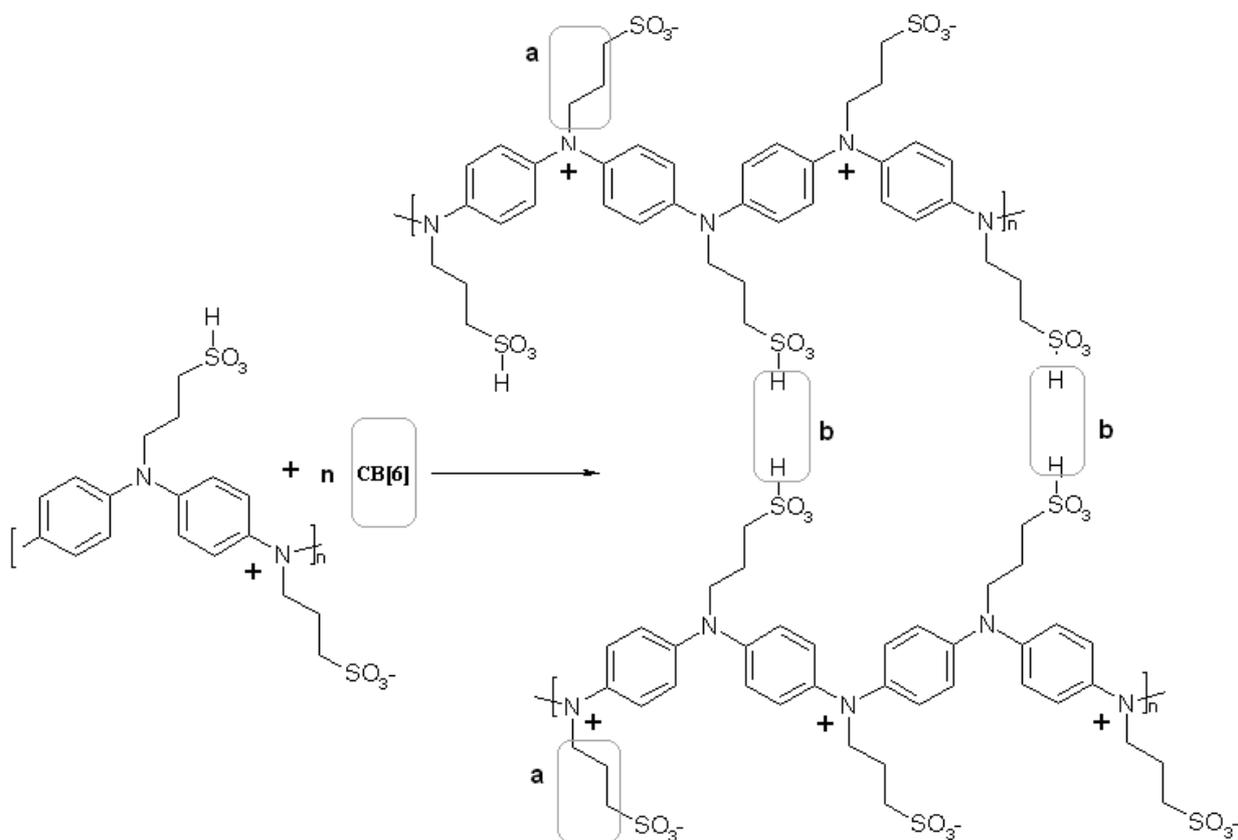

Fig. 4 – Possible interactions between PANS and CB[6]:
a) threading on side chain, and b) physical crosslinking of two polymer chains.

X-ray diffraction

The X-ray diffraction patterns of three PANS samples, are presented in Fig. 5. The patterns showed crystalline peaks for homopolymer indicating a high degree of crystallinity. The development of the highly ordered structures for poly(aniline-N alkanesulfonate)s was evidenced by Rhee *et al.*[18] The aqueous polymer solutions formed highly liquid crystalline phases with high orientational and positional order associated with ionic interactions between alkylsulfonates groups and polyaniline main chain. The high structural order is maintained also in the polymer synthesized in the presence of CB[6] but the PANS cross-linked with CB[6] is amorphous.

The XRD pattern of PANi synthesized in standard conditions and undoped state is characteristic of amorphous polymer with a crystallinity degree about 33%, showing three peaks at 2θ =15.1, 20.4 and 25.5 $^\circ$, respectively.[19] The first peak is assigned to periodicity parallel to the polymer chain and the third peak is attributed to the periodicity perpendicular to the polymer chain. The polymer synthesized in presence of β - CD kept the all peaks characteristic for PANi but they are more sharply and a new peak at 8.5^0, assigned to β –CD, was observed.
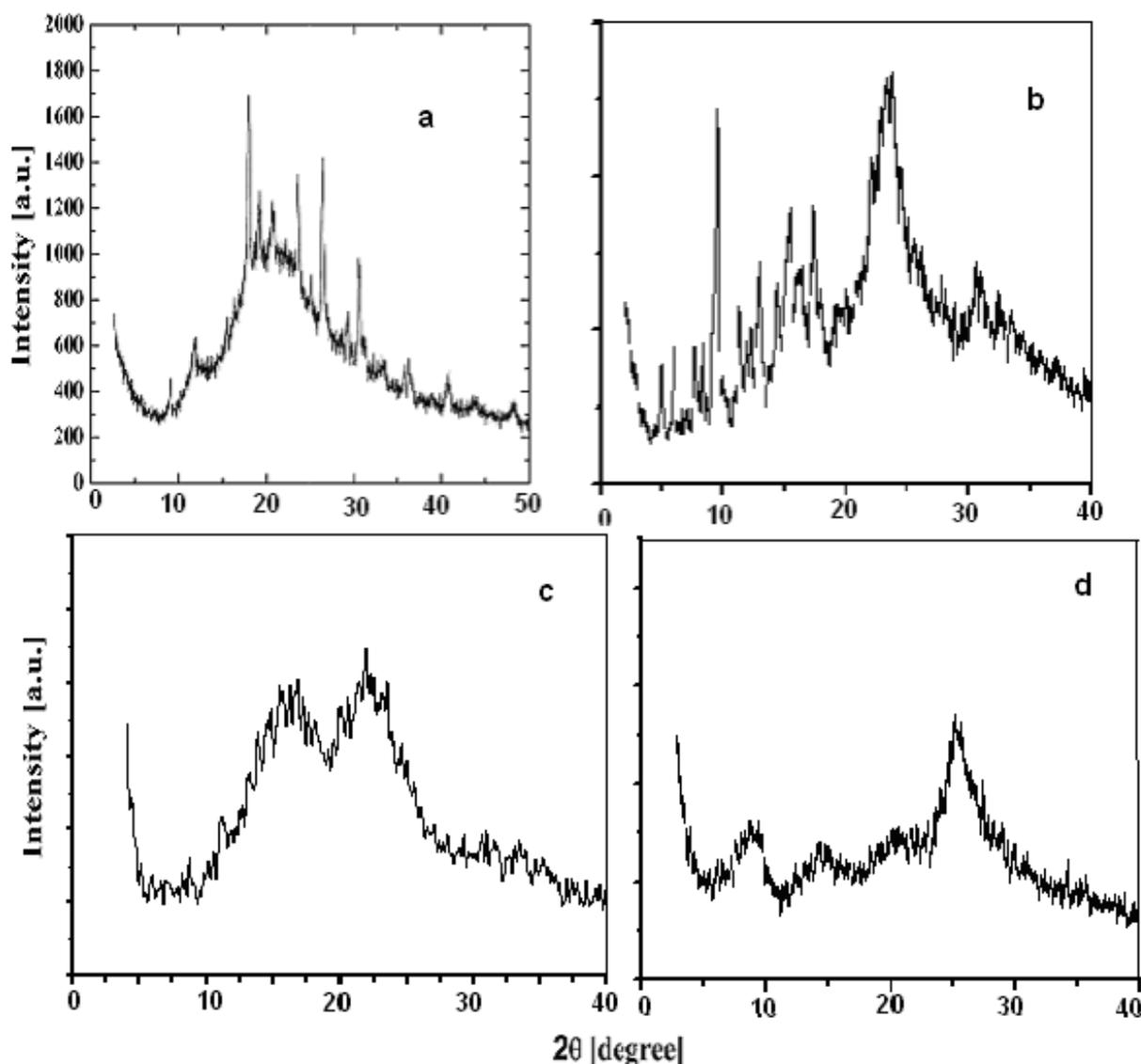

Fig. 5 – XRD spectra of: (a) PANS, as reference polymer, (b) **P2**, PANS synthesized in presence of CB[6], and (c) physically crosslinked PANS with CB[6], and d) **P1**, PANi synthesized in presence of β-CD.
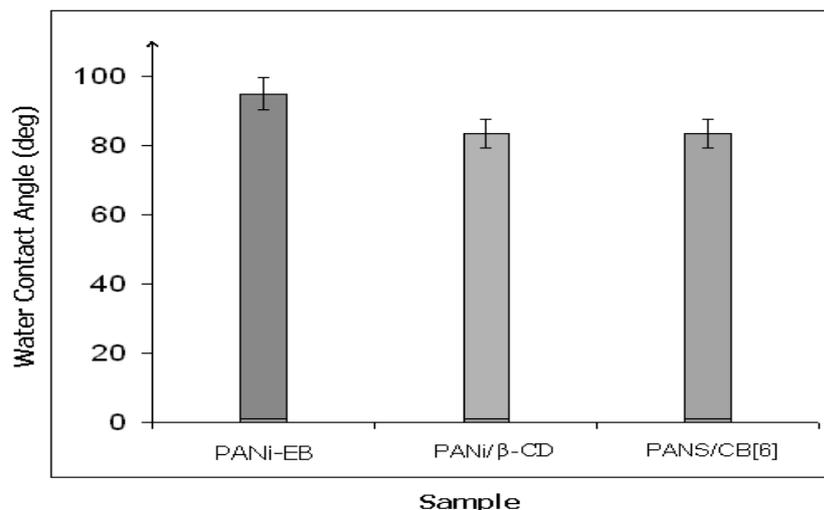
FIig. 5 – Water contact angles of the polymers.

Solubility and Surface hydrophilicity

The solubility of the conducting polymers is one of the important factors to the processability and has importance practical applications. PANi in emeraldine base state can be only dissolved in strong polar solvents such as NMP, HMPTA, DMF, DMSO, DMAc but PANi in emeraldine salt state is insoluble in any solvent. β-CD is soluble in water, aqueous solutions and DMF, DMSO, etc, while CB[6] is soluble in concentrated acids or aqueous salts solutions. We have observed that PANi/ β-CD synthesized in acidic conditions is soluble even in water due to the β-CD.

The surface hydrophilicity of the PANi's was characterized by static water contact angle. It is know that the surface hydrophilicity (0-90°) is an important feature of polymeric materials. Polyaniline-emeraldine base is a relatively hydrophobic material, its water contact angle of 94° has reported by Shishkonova et al.[20] Water contact angle of PANi/ β-CD and PANS/CB[6] were determined and the results are shown in Fig. 6.

The water contact angles of PANi/ β-CD and PANS/CB[6] were 82.44°, respectively 82.37°. Both polymers have a lower water contact angles than PANi-EB and therefore a higher hydrophilicity. This is due to the hydrophilic structure of the polymer/macrocycle complex which contains polar carboxyl groups and respectively hydroxyl groups.

EXPERIMENTAL PART

Cucurbit[6]uril, CB[6], was synthesized according to the reported methods[6,7] and subsequent modifications.[21,22] β-Cyclodextrin, β-CD, a commercial product (Aldrich) was used as received. All other chemicals were reagents grade and used without purification. Polyaniline (PANi) and poly (N-propanesulfonic acid) aniline (PANS), as reference polymers were synthesized by chemical oxidative polymerization of aniline and aniline N-propane sulfonate, respectively. The FTIR 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) or TMS. Water contact angle measurements of the compounds films were measured using a contact angle and surface tension meter (KSV instruments CAM 200). A drop of Milli-Q water was placed on the surface of the sample and the images of the water drop was recordered by a digital camera. The images were then analyzed with KSV software to give the contact angles data. The contact angle of each sample was taken as the average of five measurements at different points. XRD measurements were performed with a Bruker AD8 ADVANCE diffractometer. The X-ray beam was CuKα₁ (1.5406 Å) radiation operating from a sealed tube operated at 40.0 kV and 30 mA. Data from 3° to 40° (2θ) were obtained using Bragg-Brentano geometry at a scan rate 1.0 deg/min.

Polymerization of aniline derivatives in presence of macrocycles

a) **P1**. β-CD (0.3 g 0.26 mmol) was dissolved in 6.4 mL HCl 1M and 0.0343 g (0.26 mmol) aniline clorhydrate was added to obtain a clear solution that was stirred at room temperature for 24 h under nitrogen for inclusion of aniline in macrocycle cavity. Then, 0.09 g (0.39 mmol) ammonium persulfate was added to start oxidative polymerisation. After an induction period a color was developed that turns on violet-blue and finally green. The green precipitate was filtrated after 24 h, washed with water, methanol and acetone and dried. Yield= 125.4 % (calculated on the basis of aniline) or 12.86% (calculated on the basis of aniline + β CD).

b) **P2**. 0.2 g (0.2 mmol) CB[6] and 0.043g (0.2 mmol) aniline N-propanesulfonic acid were introduced in 8 ml aqueous solution of 0.2M NaCl and the solution was stirred at room temperature for 24 h. When ammonium persulfate 0.068 g, 0.3 mmol) was added to start polymerisation an insoluble

product becomes out of solution but the reaction was carried out in heterogeneous conditions and after 24 h the solid product was separated by filtration. Yield = 433.95% (based on ANS) or 76.83%. The product was separated in two fractions, a soluble or insoluble fraction in NaCl 0.2M aqueous solution. The soluble fraction is formed mainly from free CB[6] and PANS components. It was observed that in time the soluble fraction (1-2 h) became insoluble in any solvent and has spectral characteristics similar with the crosslinked polymer obtained by postmodification reaction.

Post-modification of PANS using CB[6]

PANS, 0.0613 g dissolved in 10 mL NaCl 0.2M aqueous solution was mixed with another solution of 0.285 g CB[6] in 10 mL NaCl 0.2M. The molar ratio between macrocycle and structural unit of the polymer was ~ 1:1. The mixture was stirred at room temperature for 6 h and the green precipitate was filtrated and washed with NaCl 0.2M solution to remove the free components and finally with distilled water. The product was dried in oven at 40 $^{\circ}$C. Yield = 30%.

CONCLUSIONS

A strategy for modification of polyanilines properties, based on the formation of supramolecular structures by host-guest interactions between polyanilines and macrocycles, was studied in this paper. The recognition abilities of cyclodextrins and cucurbiturils were used to obtain main-chain or side-chain pseudorotaxanes having properties different of pure partners. PANS with CB[6] formed a physically network and macrocycle by the two portals complexed the-SO$_3$H by hydrogen bonds.

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