POLYANILINE SYNTHESIS IN THE PRESENCE OF THREE MACROCYCLIC COMPOUNDS

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Abstract: Oxidative polycondensation of aniline using ammonium peroxidisulfate, in the presence of three macrocyclic compounds having accessible and hydrophobic cavities; β-cyclodextrin, cucurbit[6]uril and sulfonated calix[8]arene was studied. With the first two macrocyclic compounds, polyanilines with pseudorotaxane structure were obtained. The third compound led to the polyaniline doped by the sulfonated calix[8]arene. Encapsulation or doping process of polyaniline as emeraldine base state was also evidenced by spectral methods.

Keywords: polyaniline, macrocyclic compounds, β-cyclodextrin, cucurbit[6]uril, sulfonated calix[8]arene, pseudorotaxane structure

Introduction

Conjugated polymers and their doped forms have attracted tremendous interest due to their interesting scientific aspects and various potential applications in micro- and nano-electronics and optoelectronics.[1,2] Among

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conducting polymers, polyaniline (PANi) and its derivatives stands out due to its outstanding properties being one of the most studied polymers due to a combined sum of factors. The monomer, aniline, is a known and cheap organic compound, its polymerization can be performed by chemical or electrochemical oxidation using water as solvent. The polymer is environmental stable, can be doped using a variety of *p-* or *n-* dopants or using protonic inorganic or organic acids and has many applications.[3-6] However, the low solubility of the doped polymer in most organic solvents, the poor mechanical properties and low processability are major drawbacks for practical use and many efforts have tried to surpass these difficulties. The synthesis of the conducting polyaniline blends and composites is a cheap method that combines the processability of the insulated polymers and electrical and redox properties of the polyaniline.[5] Other methods include: the introducing of the side substituents on the conjugated chain by copolymerization or polymer modification reactions, the doping of PANi emeraldine base form with long alkyl organic acids (i.e.; p-toluenesulfonic acid, dodecylbenzene sulfonic acid, camphorsulfonic acid, polystyrene sulfonic acid, polymethacrylic acid, etc)[1] and synthesis of polyaniline with rotaxane architecture using cyclodextrins[7,8] or cucurbiturils[9] as macrocyclic compounds. Ring- or N-alkyl substituted polyanilines have received far less atention than polyaniline, and their solubility and processability is enhanced but in most cases the electrical conductivities are diminished.[10]

The aim of this communication is to present our recent results on the chemical oxidative polymerisation of aniline, in aqueous solution using ammonium peroxydisulfate as oxidant, in the presence of three macrocyclic compounds, as a new attempt for improving the polymer processability.

Results and discussions

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 (EB).[11]
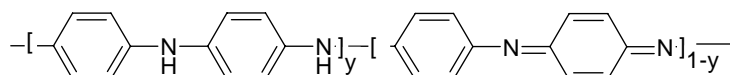
Scheme 1. The chemical structure of polyaniline

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

The following macrocyclic compounds were used in the synthesis of polyaniline: β-cyclodextrin (**1**), cucurbit[6]uril (**2**) and calix[8]arene (**3**) and all three macrocycles have hydrophobic inner cavities able to host aniline molecules (Scheme 2). Moreover, calix[8]arene (**3**) compound contains eight sulfonate groups that confer good water solubility and ability to act as a protonic acid in the synthesis of ES-PANi or the doping of polyaniline emeraldine base.
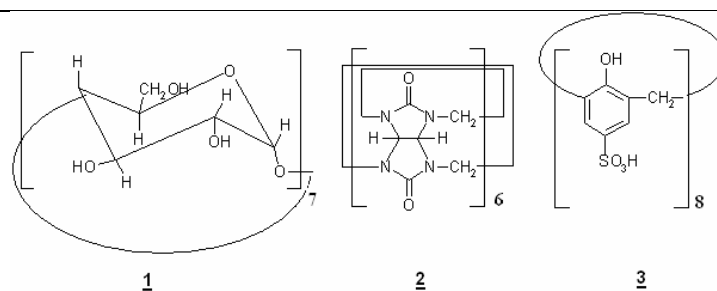
Scheme 2. The structure of macrocyclic compounds

β -Cyclodextrin (CD) (**1**) is a carbohydrate-based cyclic compound consisting of seven alfa-(1,4)-linked D-glucopyranose units and a torus-shaped structure having hydrophobic cavity with depth of 0.5 nm and diameter of 0.7 nm.[12] It has the advantage to be soluble in water and some protic polar solvents leading to inclusion complexes with a large variety of guests of inorganic and organic nature.

Cucurbit[n]urils (**2**), abbreviated as CB[n], are macrocyclic compounds obtained by acid-catalyzed condensation of glycoluril and formaldehyde. The most known compound is CB[6] obtained for the first time in 1905.[13] It contains *6* units derived from glycoluril linked by *12* methylene groups derived from formaldehyde and has a pumpkin-shape but its structure was fully elucidated in 1981.[14] Other lower or higher homologues were synthesized by Day et al.[15] CB[6] has a cavity of ~0.55 nm diameter accessible by two portals of ~4 nm diameter. The dimensions of other CB[n] are: CB[5]; 0.44 nm/0.24 nm; CB[7]; 0.73 nm/0.54 nm; CB[8]; 0.88 nm/0.69 nm.[16] The main disadvantage of CB[n] is their solubility only in strong acidic solutions that limits very much their use in many studies and applications. Cucurbit[6]uril is soluble only in strong acids, conditions favourable for aniline polymerisation. Unlike **1** that preferentially binds neutral guest molecules, **2** preferentially binds guests

with positive charges and in the aniline polymerisation, anilinium cations are responsible species in the growing step. We have observed the polymerisation of aniline in acidic solution and presence of **2** have led to emeraldine salt form with pseudorotaxane architecture.[9]

Calix[n]arenas are cyclic oligomers synthesized by the base-catalyzed condensation of *p*-substituted phenols and formaldehyde and they are sparingly soluble in some organic solvents and insoluble in aqueous solutions.[17] By introduction of anionic (sulfonate) groups on the upper rim or lower rim or cationic (ammonium) groups on the upper rim, water soluble calixarenes are obtained.[18] Calixarenes possess a similar architecture to CDs but they are able to undergo conformational changes that involve flips (between cone, partial cone and 1,2 or 1,3-alternate conformers) for cyclic tetramers. The inner cavity of calix[6]arene has an opening between 0.2-0.29 nm while calix[8]arene in its most expanded conformation has an opening of 0.45 nm or more in diameter. Therefore, calixarenes are able to form inclusion complexes with alkali ions but only superior homologues can include also organic molecules to form pseudorotaxane compounds, precursors for rotaxanes and polyrotaxanes. Only calix[8]arenes possess an annulus large enough to allow an guest to cross the two rims. However, until now a conducting polymer hosted by calixarenes has not been reported. There is only a report about the use of calix[6]arene for synthesis of a rotaxane.[19]

Polymerisation of aniline or aniline dimer in aqueous solution using ammonium persulfate as oxidant and in the presence of β –CD led to pseudorotaxane polyaniline/ β –CD.[20] The same structure was obtained by inclusion of polyaniline emeraldine base as N-methyl pyrrolidone or DMSO solution into β –CD dissolved in water and mixing the two solutions.[7,21,23]

By mixing of aniline (or aniline dimer) with an aqueous solution of β-CD, after some hours a white solid precipitate separated. This compound was identified as adduct of ~ 1:2 composition (β-CD /aniline) as result of aniline inclusion in the hydrophobic cavity of macrocyclic compound. The formation of the pseudorotaxane structure was checked by NMR spectroscopy and confirmed by elemental analysis, IR and TGA measurements.[8] The oxidative polymerisation of the inclusion adduct can lead to a polymer having a pseudorotaxane structure if the reaction is carried out in neutral media while in acidic conditions the dissociation of inclusion complex in free partners is favourezed and aniline is polymerised to its emeraldine salt form.

FTIR spectra of polymers synthesized in presence of β-CD (Figure 1) 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} (v C-H out of plane bending of 1,4 rings) and 611 (aromatic ring deformation).[5,6,11] 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 [15]. The last bands assigned to β-CD are clear evidenced for PANi synthesized in neutral media and suggests a higher content of β–CD threaded onto the polymer chain. 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

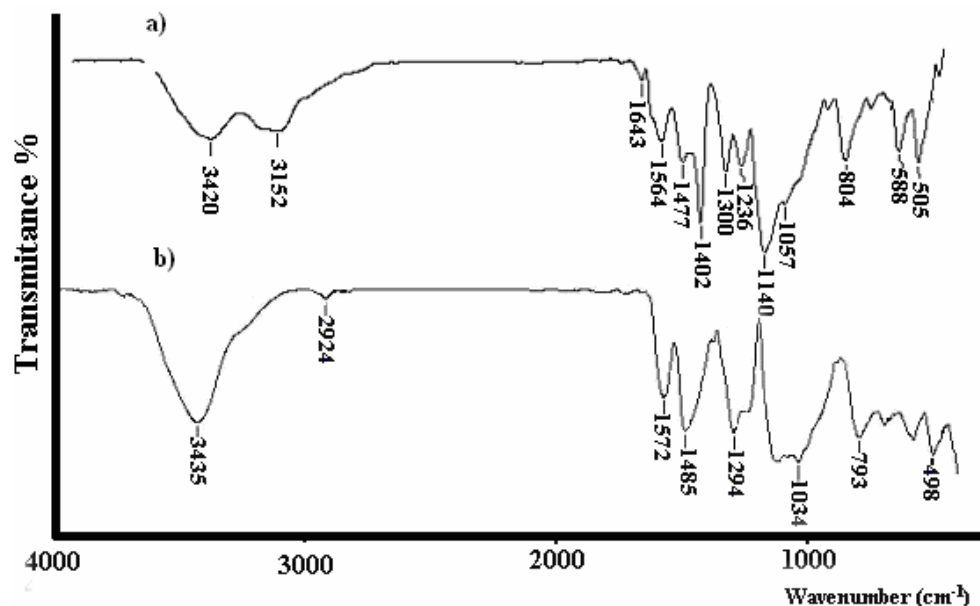pseudorotaxane PANi during polymerization and/or separation processes of polymers.

Figure 1. FTIR spectra (KBr pellets) of: PANi emeraldine salt synthesized in presence of β-CD, in acidic (a) or neutral (b) media

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[23]. 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 cavity of CD. 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. Unlike CDs which preferentially bind neutral guest molecules, CBs[n] bind preferentially

guests with positive charges. 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. We have synthesized pseudopolyrotaxane polyaniline/CB[6] by two ways: (i) chemical oxidative polymerization of aniline in presence of CB[6] as host in acidic aqueous solution and using ammonium persulfate as oxidant and (ii) by threading of preformed polyaniline chain through inner cavity of CB[6] (Scheme 3).
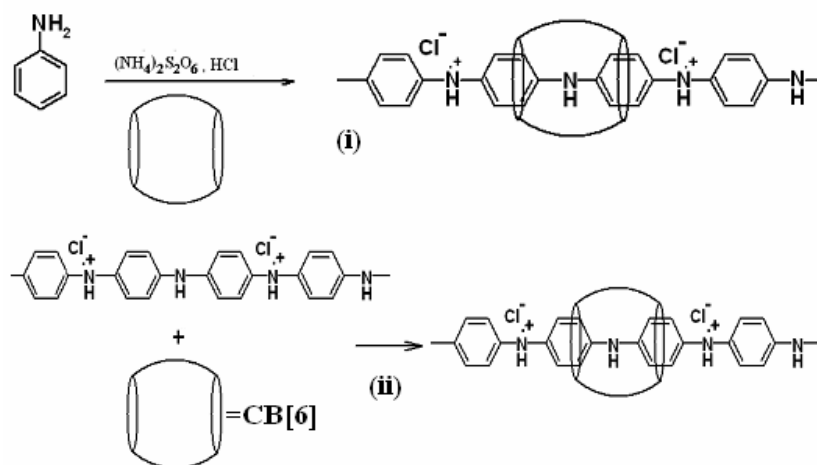
Scheme 3. Synthesis of polyaniline/CB[6] by (i) chemical polymerisation of aniline/CB[6] inclusion adduct and (ii) encapsulation of polyaniline emeraldine salt in CB[6]
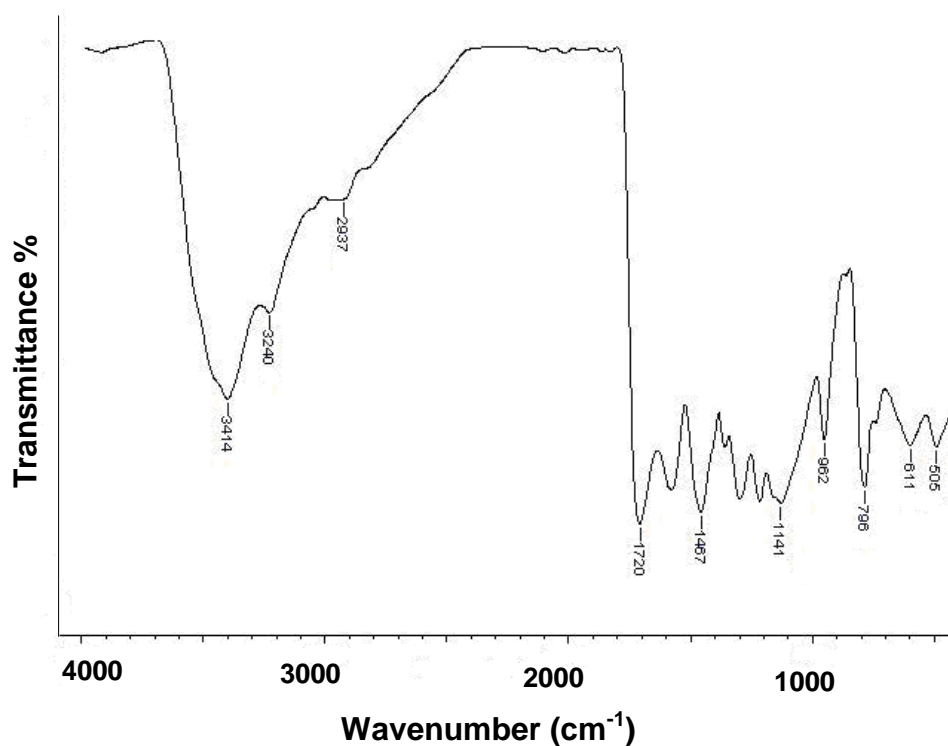
Figure 2. FTIR spectrum (KBr pellets) of: PANi/CB[6]

The way (b) is entropically unfavorable but is enthalpically favourized by noncovalent interactions. Polyaniline was the first conducting polymer with rotaxane structure synthesized using cucurbiturils as macrocyclic compounds.[9]

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 PANi synthesized in presence of CB[6] presents 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}) (Figure 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.

Polyaniline/sulfonated calix[8]arene was synthesized also by two methods. In the *one - step method*, chemical polymerization of aniline dimer, N-phenyl-1,4-phenylendiamine, in an aqueous solution containing calix [8]arene sulfonic acid using $(NH_4)_2S_2O_8$ as oxidant was carried out. A green polymer, insoluble in water, was separated by filtration and characterized. The ^{1}H-NMR spectra (DMSO-d_6) of the dimer, sulfonated calix[8]arene and their 1:1 mixture (Figure 3) have evidenced that an acid/base adduct was formed by mixing of the two partners. The ^{1}H-NMR spectra of the *N*-phenyl-1,4-phenylenediamine and sulfonate calix[8]arene with signals assignments are presented in Figure 3,a and b.
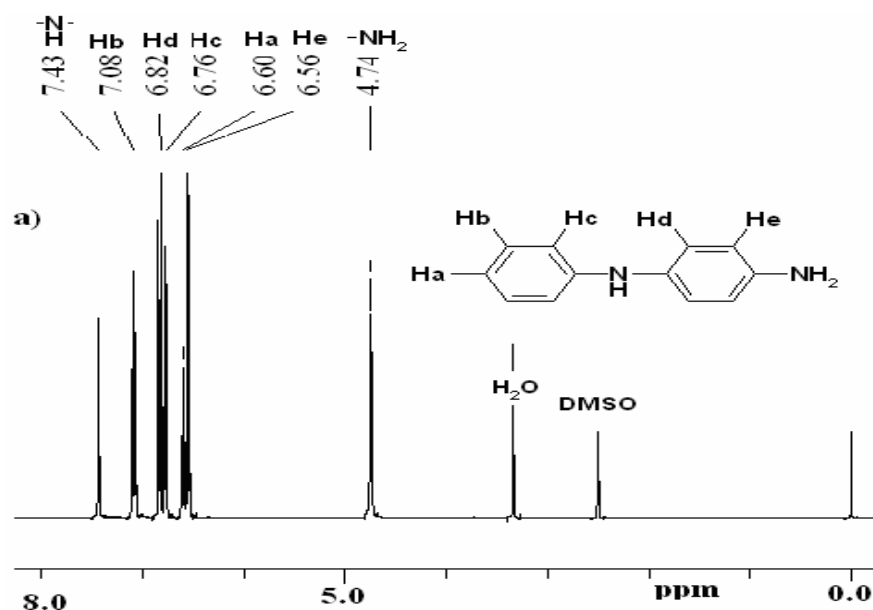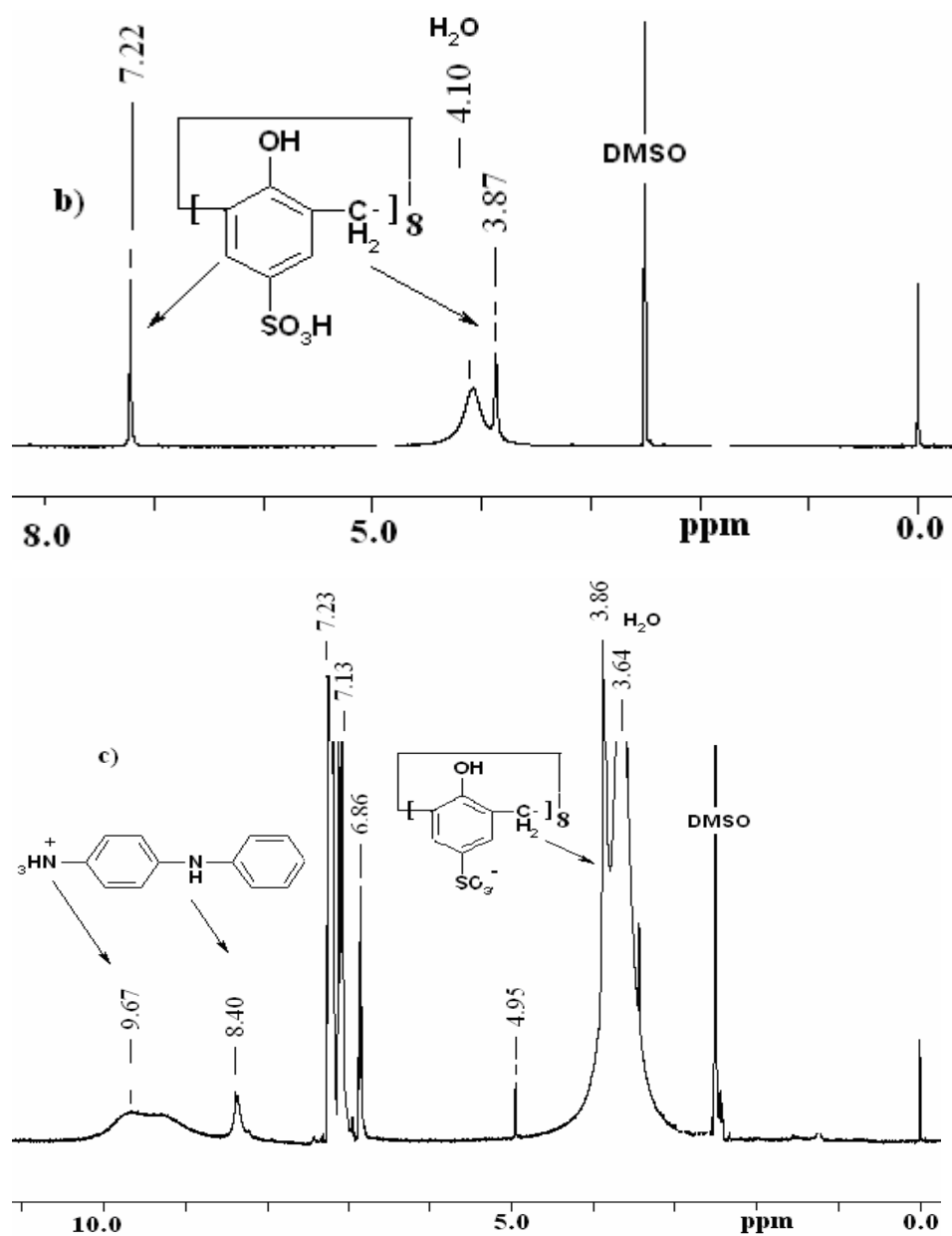
Figure 3. ^{1}H-NMR spectra (DMSO-d$_6$) of: (a) N-phenyl 1,4-phenylenediamine, (b) sulfonic acid calix[8]arene, and (c) 1:1 molar ratio, N-phenyl 1,4-phenylenediamine/sulfonic acid calix[8]arene mixture

The ^{1}H-NMR spectrum of the 1:1 dimer/**3** mixture is significantly different from the spectra of the pure compounds (Figure 3c). The resonances arising from –NH- and –NH$_2$ of the dimer changes from 7.43 ppm and 4.74 ppm, in absence of **3**, to 8.40 ppm and 9-10 ppm respectively, in the presence of **3**. The strong downfield shifting of the signals assigned to –NH- and –NH$_2$ protons could be explained only by protonation of amine group by sulfonic acid groups (or less probable, phenolic hydroxyls). Moreover, amine protons signal becomes appreciably broadened, suggesting that the exchange with protons of sulfonic groups occurs at a rate that is within the NMR time scale. Similarly, a mixture of dimer and an excess of HCl showed a NMR pattern very similar to that of dimer in presence of **3**. Therefore, N-phenyl 1,4-phenylenediamine in solution with **3** forms an acid-base type complex and its oxidative polymerization occurs to polyaniline in doped state, where the dopant anions are sulfonate calix[8]arene groups. The polymerization was carried out in 1M HCl solution or only in water. Even in absence of HCl, the pH of the aqueous solution of sulfonate calix[8]arene is acid. The acidity of the **3** measured in bidistilled water (1M concentration) is pH=1.96-2.0.

The sulfonated calix[8]arene/polyaniline is soluble in DMF, DMSO and other polar solvents (NMP, HMPA). The ^{1}H-NMR spectrum presented in Figure 4 shows signals assigned to protons of macrocycle and polyaniline chain.
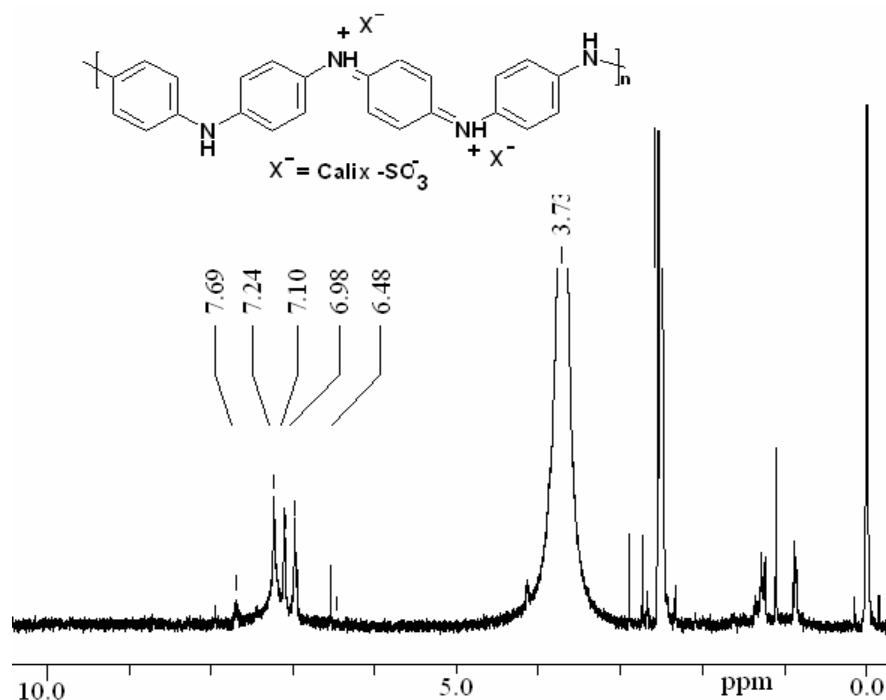
Figure 4. ^{1}H-NMR spectrum of the sulfonated
calix[8]arene/polyaniline in DMSO-d_6 solution.

b) In the *two-step method*, PANi/**3** was obtained by mixing of polyaniline emeraldine base (solution in DMF) with calix[8]arene sulfonic acid. Emeraldine base PANi was obtained from HCl-doped PANi (synthesized by a classic method), by neutralizing with 1M NH$_4$OH at room temperature. The doping of EB-PANi with **3** in solution is observed by in time changing of the colour (from blue to green) and precipitation of the PANi-**3** complex. Because the dopant has a bulky structure, the doping process is kinetically limited. The FTIR spectra of polymers obtained by polymerization of N-phenyl 1,4-phenylenediamine in presence of **3**, or by doping of polyaniline emeraldine base with **3** in DMF solution are very similar and confirms the incorporation of sulfonated calix[8]arene in the final polymer (Figure 5).

The peaks at 3201-3118 cm^{-1}, assigned to –OH stretching vibrations, 1318-1316, 1113-1111 cm^{-1}, assigned to S=O band and the peaks at 1040, 800 and 620 cm^{-1} assigned to S-O-S stretching from **3**[24], are also present in the polymers spectra suggesting the presence of the macrocycle.
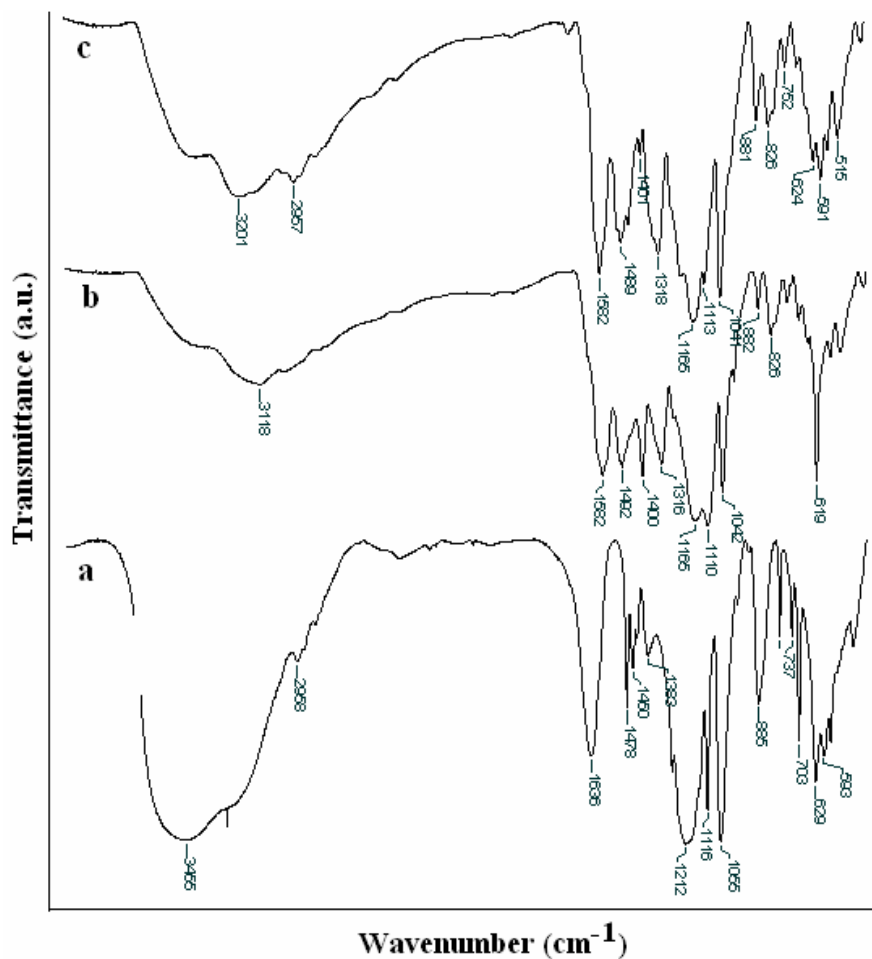

Figure 5. FTIR spectra of sulfonated calix[8]arene (a), sulfonated calix[8]arene/polyaniline obtained by *one-step method* (b), and sulfonated calix[8]arene/polyaniline obtained by *two-step method* (c).

Experimental

N-phenyl-1,4-phenylendiamine (Aldrich) (aniline dimer), was used as received. Aniline (commercial product) was vacuum distilled just before use. β –Cyclodextrin (β-CD) (Aldrich) was used after drying under vacuum at 50 ^{0}C for 24 h. Cucurbit [6]uril, (CB[6]) was synthesized from glycoluril and formaldehyde by acid-catalyzed condensation reaction and purified by fractional crystallization and dissolution according to literature methods[15]. *p-tert-* Butylcalix[8]arene was synthesized by a one step method from *p-tert* butyl phenol and paraformaldehyde in presence of a base, in *o*-xylene as solvent.[17] The water soluble calixarene sulfonate was synthesized from *p-tert* butyl calix[8] arene by sulfonation with H_2SO_4 98%, when the labile *tert* butyl group was replaced with sulfonate one.[25] Commercial ammonium peroxidisulfate, hydrochloric acid and other organic reagents were used without purification. Freshly bidistilled water was used to prepare all aqueous solutions.

Synthesis of polyanilines

Polyaniline/β-CD and polyaniline/CB[6] were synthesized by chemical oxidation of equimolar mixtures of aniline/macrocyclic compound in 1M HCl solution using $(NH_4)_2S_2O_8$ as oxidant, molar ratio oxidant/aniline = 1.5, 0°C and inert atmosphere. The reaction mixture was stirred 24 hours and the polymer was separated by filtration, washed with diluted HCl and water to remove unreacted monomer and oxidant and then dried. Polyaniline/ β-CD was synthesized also in neutral solution. For comparison, PANi emeraldine salt, used as ethalon, was synthesized in a

similar way by chemical polymerization of aniline in aqueous 1M HCl solution but in absence of macrocycles.

Synthesis of polyaniline in presence of sulfonated calix[8]arene

a) one-step method

10 mg (0.054mmol) *N*-phenyl-1,4-phenylendiamine and 90 mg (0.054 mmol) sulfonated calix[8]arene were dissolved in 5 mL distilled water. The solution was stirred for 3 h at room temperature and then 19 mg (0.081 mmol) ammonium peroxidisulfate in 3 mL distilled water was dropped over a period of 10 min. The color of solution becomes gradual green. The mixture was stirred for 48 h at room temperature under a nitrogen atmosphere. The polymer was filtered and dried in vacuo at 40°C. Yield = 61.5 %.

b) two-step method

A PANi emeraldine base (synthesized in a previous step) solution obtained from 13 mg (0.036 mmol, on the basis of the tetramer unit) in 10 mL DMF was combined with 60 mg (0.036 mmol) sulfonated calix[8]arene. The initial homogeneous mixture was stirred for 96 h at room temperature under a nitrogen atmosphere and in time, once the doping process took place an insoluble green product separated which was filtrated and dried. Yield = 75.2 %.

Characterization

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.

Conclusions

From the dimensional analysis it results that all three macrocycles used in polyaniline synthesis, β-cyclodextrin (**1**), cucurbit[6]uril (**2**) and calix[8]arene (**3**) are able to encapsulate aniline monomers because their dimensions are compatible and by polymerization of cycloadducts (pseudo)rotaxane structures should be obtained. The cavity dimensions of **1** (0.7 nm), **2** (0.4 nm) and **3** (~0.45 nm) allow them to host aniline or aniline dimer in the inner cavity as a pseudorotaxane compound. However, polyaniline with pseudorotaxane structure has been synthesized only by chemical oxidative polymerization of aniline and aniline dimer in presence of β-cyclodextrin and cucurbit[6]uril. These macrocycles have a rigid and hydrophobic cavity and encapsulate aniline monomers from aqueous solution due to hydrophobic interactions and hydrogen bonds. Calix[8]arene **3** has also a hydrophobic cavity able to hosts aniline monomers. However it has a very flexible cavity with openings varying between 0.2-0.45 nm, too small to thread aniline molecules. This macrocycle interacts with aniline monomers by sulfonic acid groups to form an acid-base adduct. When polymerisation of aniline was carried out in the presence of this macrocycle only a green solution of polyaniline emeraldine salt doped with sulfonic acid groups of **3** was obtained.

Acknowledgments

References

1.   Skotheim, T. A., and Reynolds, J. R., eds., *Handbook of Conducting Polymers*, 3-rd edition CRC Press, New York, 2007.

2.   Pud, A., Ogurtsov, N., Korzhenko, A., and Shapoval, G., *Prog. Polym. Sci.,* **28**, 1701 (2003).

3.   Lux F., *Polymer,* **35**, 2915 (1994).

4.   Kang, E. T., Neoh K. G., and Tan, K. L., *Prog. Polym. Sci.,* **23**, 277 (1998).

5.   Anand, J., Palaniappan S. A., and Sathyanarayana, D. N., *Prog. Polym. Sci.,* **23**, 993 (1998).

6.   Gospodinova, N., and Terlemezyan, L., *Prog. Polym. Sci.,* **23**,1443 (1998).

7.   Yuan, G. L., Kuramoto, N., and Takeishi, M., *Polym. Adv. Technol.,* **14**, 428 (2003).

8.   Grigoras, M., and Conduruta, D. G., *J. Incl. Phenom. Macrocylic Chem.,* **54**, 101 (2006).

9.   Grigoras, M., and Conduruta, D. G., *Rev. Roum. Chim.,* **51**, 987 (2006).

10.   Leclerc, M., Guay, J., and Dao, L. H., *Macromolecules,* **22**, 649 (989); Wei, Y., Focke W. W., Wnek, G. E., Ray, A., and MacDiarmid, A. G., *J. Phys. Chem.,* **93**, 495 (1989); Watanabe, A., Mori, K., Iwabuchi, Y.,

Iwasaki, Y., Nakamura, Y., and Ito, O., *Macromolecules,* **22**, 3521 (1989); Chevalier, J. W., Bergeron, J. Y., and Dao, L. H., *Macromolecules,* **25**, 3325 (1992); Manohar, S. K., MacDiarmid, A. G., Cromack, K. R., Ginder, J. M., and Epstein, A. J., *Synth. Met.,* **29**, E349 (1989); MacInnes, D., and Funt, .L., *Synth. Met.,* **25**, 235 (1988).

11.   Grigoras, M., Catargiu, M. A., and Bendrea, A. D., *Polianiline*, editura Tehnopress, 205 pag. (2010).

12.   Szejtli, J., *Cyclodextrins and Their Inclusion Complexes*, Akademiai Kiado, Budapest, (1982).

13.   Behrend, R., Meyer, E., and Rusche, F., *Liebigs. Ann. Chem.*, **339,** 137, (1905).

14.   Freeman, W. A., Mock, W. L., and Shih, N. Y., *J. Am. Chem. Soc.*, **103**, 7367, (1981).

15.   Day, A., Arnold, P., Blanch, .J. and Snushall, B, *J. Org. Chem.*, **66,** 8094, (2001), Kim, J., Jung, I. S., Kim, S. Y., Lee, E., Kang, J. K., Sakamoto, S., Yamaguchi, K., and Kim, K., *J. Am. Chem. Soc.*, **122**, 540, (2000).

16.   Lee, J. W., Samal, S., Selvapalam, N., Kim H. J., and Kim, K., *Acc. Chem. Res.*, **36**, 621, (2003).

17.   Gutsche, C. D., Dhawan, B., No K. H., and Muthukrishnan, R., *J Am. Chem. Soc.*, **103**, 3782, (1981).

18.   Shinkai, S., Arimura, T., Araki, K., Kawabata, H., Satoh, H., Tsubaki, T., Manabe, O., and Sunamoto, J., *J. Chem. Soc. Perkin Trans.*, **I**, 2039, (1989).

19.   Arduini, A., *Angew. Chem. Int*. Ed., **39**, 3453, (2000).

20.   Grigoras, M., and Vacareanu, L., *Supramol. Chem.*, **22**, 237, (2010).

21.   Shimomura, T., Yoshida, K., Ito, K., and Hayakawa, R., *Polym. Adv. Technol.*, **11**, 837, (2000).

22.   Yoshida, K., Shimomura, T., Ito, K., and Hayakawa, R., *Langmuir*, **15**, 910, (1999).

23.   Lee, J. W., Samal, S., Selvapalam, N., Kim, H. J., and Kim, K., *Acc. Chem. Res*., **36**, 621, (2003).

24.   Davey, J. M., Too, C. O., Ralph, S. F., Kane-Maguire, L. A. P., and Wallace, G. G., *Macromolecules*, **33**, 7044, (2000).

25.   Steed, J. W., Johnson, C. P., Barnes, C. L., Juneja, R. K., Atwood, J. L., Reilly, S., Hollis, R. L., Smith, P. H., and Clark, D. L., *J. Am. Chem. Soc.,* **117**, 11426 (1995).