Molecular Composites Obtained by Polyaniline Synthesis in the Presence of *p*-Octasulfonated Calixarene Macrocycle

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ABSTRACT: Polyaniline (PANI) molecular composites were synthesized by chemical oxidative polymerization of the aniline and aniline dimer, *N*-phenyl-1,4-phenylendiamine, in the presence of a macrocycle, calix[8]arene *p*-octasulfonic acid (C8S), using ammonium peroxidisulfate as oxidant. The macrocycle has acted both as acid dopant and surfactant to obtain processable PANI-ES. The PANI/calix[8]arene *p*-octasulfonic acid composite was also obtained by a simple doping of PANI emeraldine base form with calix[8]arene sulfonic acid. The structure of materials was confirmed by Fourier transform infrared, UV–vis and nuclear magnetic resonance spectroscopy. All synthesized composite materials are amorphous and soluble in chloroform, dimethylsulfoxide, NMP, showing excellent solution-processing properties combined with electrical conductivity. Cyclic voltammetry evidenced a good electroactivity for the composite films. Dielectric properties (dielectric constant and dielectric losses) were determined and are comparable with those of other PANI/ionic acid polymer composites. Preliminary studies have evidenced a high dielectric constant (10^4 at 100 Hz) and electrical conductivity of 6×10^{-3} S/cm for PANI composites. From sulfur elemental analysis of the PANI/calixarene, it results that the content in macrocycle is ~30% (weight). © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Among conducting polymers, polyaniline (PANI) is one of the most studied polymers 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 application.[1–4] 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 first attempts have used ring- or nitrogen-substituted aniline derivatives (the covalent way) to obtain modified PANIs. The synthesis of the conducting PANI blends and composites is a very accessible method that combines the processability of the insulated polymers with electrical and redox properties of the PANI.[5,6] An elegant method to obtain processable PANIs is to replace small inorganic acids used in the synthesis step (HCl, H₂SO₄ etc) with long alkyl organic acids (the ionic way), such as *p*-toluenesulfonic acid, dodecylbenzene sulfonic acid, camphorsulfonic acid,[7–9] 4-sulfophthalic acid,[10] or ionic polymers,

i.e., polystyrene sulfonic acid, polyacrylic acid,[1,5,6,11–14] and sulfonated poly(ether sulfone).[15] It was observed that all low molecular or macromolecular organic acids improved the solubility and processability of doped PANI and blends are true molecular composites. Another non-covalent or non-ionic way to solubilize PANI is to thread the PANI backbone through many macrocycles and to disrupt the strong intermolecular forces (the mechanical way). Synthesis of PANIs in presence of macrocycles such as cyclodextrins[16–21] or cucurbiturils[22,23] led to PANIs with pseudorotaxane structure having a better processability and improved optoelectronic properties.[24] Calix[*n*]arenes are another class of macrocyclic compounds (metacyclophanes) very studied in the field of molecular recognition and supramolecular chemistry for their inclusion properties. They have a hydrophobic inner cavity and dimensions comparable with cyclodextrins and cucurbit[6]uril but are sparingly soluble in some organic solvents and insoluble in aqueous solutions.[25] The water-soluble calixarenes are obtained by the appending of ionic (sulfonic acid and carboxylic acid, SO₃H, ─COOH) groups on the upper or lower rim, or cationic ammonium groups on the

upper rim.[26–28] Because sulfonated calixarenes are water-soluble compounds, the synthesis of calix[8]arene functionalized/PANI composites in aqueous solution can be performed. Surprisingly, until now there is only a single report about synthesis of PANI/calixarene salts by protonation of PANI emeraldine base with calix[4]-*p*-tetrasulfonic acid and calix[6]-*p*-hexasulfonic acid in water to give emeraldine salts (ESs).[29] Unlike calix[4]- or calix[6]- derivatives, calix[8]arenes have larger inner cavities, being more able to encapsulate aniline monomers and to form pseudorotaxane structures. The aim of this communication is to present synthesis of composite materials by the chemical oxidative polymerization of aniline or aniline dimer, in aqueous solution using ammonium peroxydisulfate as oxidant in presence of calix[8]-*p*-octasulfonic acid (C8S), as a new attempt for improving of PANI processability. The question that arises is if C8S is host or protonic acid dopant in aniline polymerization? The shape and dimensions of the cavitand makes possible incorporation of PANI backbone into the hydrophobic cavity to obtain rotaxane structures. But the same time, C8S contains eight sulfonic groups, being a strong protonic acid dopant, similar with *p*-toluenesulfonic acid. The doping versus encapsulation of PANI-EB with this macrocycle will be discussed. To the best of our knowledge, this work is the first report on the aniline polymerization in the presence of water-soluble calix[*n*]arenes. The synthesized materials are characterized by Fourier transform infrared (FTIR), ^{1}H-NMR, UV–vis, XRD, and electrochemical methods. Some previous studies have evidenced interesting dielectric properties for PANI blends and composites,[30–32] so dielectric properties of the synthesized composites will be also presented.

EXPERIMENTAL

Materials

Aniline (commercial product) was vacuum distilled just before use. *N*-Phenyl-1,4-phenylendiamine (Aldrich) (aniline dimer) was used as received. Calix[8]-*p*-octasulfonic acid (C8S) was synthesized by a two-step method starting from *p-tert*-butyl phenol. *p-tert*-Butylcalix[8]arene was synthesized from *p-tert*-butyl phenol and paraformaldehyde in presence of a base, in o-xylene as solvent.[25] Calix[8]arene sodium sulfonate salt was obtained from *p-tert*-butyl calix[8] arene by sulfonation with H_2SO_4 98% and debutylation, and precipitation with NaCl.[33] The Na^+ salt (0.5 g), dissolved in 50 mL of deionized water was converted to H^+ form by ion exchange (Ionene cation exchange resins, Merck supplier) and separated by lyophilization. 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 PANI/C8S

One-Step Method. i. A solution obtained from aniline (1.024 g, 0.011 mol) and 0.8412 g (∼0.5 mmol) C8S in 10 mL HCl 1*M* aqueous solution was stirred at room temperature and 3.7 g ammonium peroxidisulfate (aniline/oxidant molar ratio = 1.5) was added in a portion. The blue color of solution developed immediately upon addition of oxidant changed to green within 45 min and after 24 h the green precipitate was filtrated, washed with cold distilled water and dried. Yield = 82.3% (based on aniline and calixarene total amount).

ii. *N*-Phenyl-1,4-phenylendiamine (10 mg, 0.054mmol) and C8S (90 mg, 0.054 mmol) 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 added dropwise 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, washed with distilled water, and finally dried *in vacuo* at 40°C. Yield = 61.5%.

^{1}H-NMR (DMSO, 400 MHz): 7.69, 7.24, 7.10, 6.98, 6.48, 3.9 ppm.

^{13}C-NMR (DMSO, 100 MHz): 152.68, 150.29, 149.77, 148.87, 145.58, 142.00, 138.45, 129.85, 127.15–123.33, 115.72 (aromatic carbons from calixarene and benzenoid carbon atoms of aniline dimer), 39.48 [dimethylsulfoxide (DMSO)], 33.6 ppm (CH_2 from calixarene).

Two-Step Method. A solution obtained from 13 mg (0.036 mmol, on the basis of the tetramer unit) PANI emeraldine base in 10 mL dimethylformamide (DMF) was combined with 60 mg (0.036 mmol) C8S. 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 precipitated and was filtrated and dried. Yield = 55 mg (75.3%).

Characterization

FTIR spectra were recorded on KBr pellets using a DIGILAB-FTS 2000 spectrometer. The UV–vis spectra were measured using an UV–vis SPECORD 200 Analytik Jena spectrometer. ^{1}H- and ^{13}C-NMR spectra were recorded at room temperature on a Bruker Avance DRX-400 spectrometer (400 MHz and 100 MHz) as solutions in DMSO-d_6, and chemical shifts are reported in ppm and referenced to TMS as internal standard. Electrochemical behavior was studied using a Bioanalytical System, Potentiostat–Galvanostat (BAS 100B/W). A conventional three-electrode electrochemical system was used, including a working electrode (platinum disc with Φ = 1.6 mm), an auxiliary electrode (platinum wire), and a reference electrode (consisted of a silver wire coated with AgCl). XRD measurements were performed with a Bruker ADVANCE diffractometer. The X-ray beam was $CuK\alpha_1$ (1.5406Å) radiation operating from a sealed tube operated at 40.0 kV and 30 mA. Data from 3° to 50° (2θ) were obtained using Bragg-Brentano geometry at a scan rate of 1.0 deg/min. Dielectric measurements were performed by a Solartron 1260A impedance/Gain Phase Analyser meter, at room temperature. Measurements of the capacitance (C) over the range of 10^2–10^6 Hz were carried out using pressure compressed (5×10^6 N/m^2) circular pellets of the 16.5-mm diameter and 1.06-mm thickness. Two porous silver electrodes were sputtered on the both sides of the pellet.

RESULTS AND DISCUSSION

It is accepted that PANI can exist in at least three different oxidation states, while the half-oxidized state known as emeraldine base (PANI-EB) is the most important. By doping with protonic acids, PANI-EB is transformed in PANI-ES (Scheme 1).
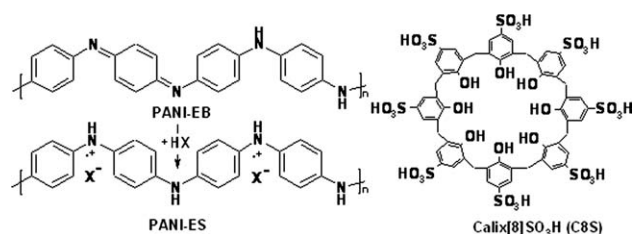
Scheme 1. The chemical structures of PANI-EB, PANI-ES, and sulfonated calix[8]arene (C8S). X$^-$ can be calix[8]SO$_3^-$ and Cl$^-$.

PANI-EB, is blue-black colored and soluble only in strong polar solvents (DMF, NMP, DMSO, HMPTA) while in acidic conditions, PANI is synthesized as ES, green colored and insoluble in any organic solvent. The organic acid C8S used in this study has a macrocyclic structure and a hydrophobic inner cavity with dimensions compatible with those of aniline and PANI backbone, being able to host them as pseudorotaxane structures. Moreover, C8S contains eight sulfonic acid groups and eight phenolic acid groups that confer solubility and can act as dopant of PANI-EB. The eight sulfonic acid groups all have a same and very low pK_a value (pK_a $\sim$1)[34] while the eight phenolic protons have different pK_a due to the intramolecular hydrogen bonds. For instance, in hexasulfonic acid calix[6]arene only two phenolic groups have ionizable protons with pK_a values of 4.76 and 3.44 and also C8S has only two ionizable OH groups. The polymerization of aniline was carried out at low pH ($<$2) and in these experimental conditions C8S is expected to act only as an octa-anionic species. Thus, unlike cyclodextrin and cucurbituril macrocycles, sulfonated calix[8]arene compound is a bifunctional one and could play a double role: as host by hydrophobic cavity or as protonic acid in the synthesis of ES-PANI or the doping imine nitrogens of PANI-EB leading to the mixing at molecular level of the two components. Therefore, it is interesting to study the polymerization of aniline in the presence of this macrocycle and to see the role of the macrocycle.

Synthesis of PANI Composites with Calix[8] Arene Sulfonic Acid

In the one-step method, PANI composites were synthesized by chemical polymerization of aniline and aniline dimer, N-phenyl-1,4-phenylendiamine, in an aqueous solution containing C8S and $(NH_4)_2S_2O_8$ as oxidant. The polymerization was carried out in 1M HCl aqueous solution or only in water because even in absence of HCl the pH of the C8S solution in bidistilled water (1M concentration) is acid (pH = 1.96–2.0). In both cases, a green polymer, insoluble in water, was separated by filtration and characterized. The C8S/PANI material is soluble in DMF, DMSO and other polar solvents (NMP, HMPA) and can be processed as thin films on diverse electrodes or supports.

In the two-step method, PANI composites were obtained by mixing of PANI emeraldine base as solution in DMF, with C8S. PANI-EB was obtained from HCl-doped PANI (synthesized by a classic method), by neutralizing with 1M NH$_4$OH at room temperature. The protonation of PANI-EB with C8S in solution is observed by in time changing of the color (from blue characteristic for PANI-EB to green for PANI-ES) and precipitation of the PANI–C8S complex.
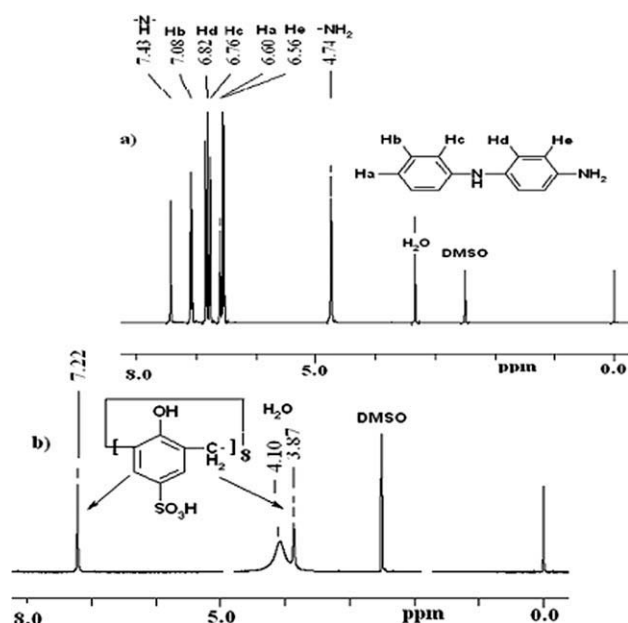

Figure 1. ^{1}H-NMR spectra (DMSO-d_6) of: (a) N-phenyl 1,4-phenylenediamine, (b) C8S.

The nuclear magnetic resonance (NMR) spectroscopy is a very useful method to discriminate between doping versus rotaxane formation. The inclusion of aniline monomers inside of the hydrophobic cavity should be accompanied by upfield shifting of the aromatic protons signal due to the shielding effect of macrocycle while doping reaction has a major effect on the amine group. The ^{1}H-NMR spectra of the N-phenyl 1,4-phenylenediamine and C8S with signals assignments are presented in Figure 1 and they confirm the structures of two partners.

The ^{1}H-NMR spectrum of 1: 1 dimer/C8S mixture (Figure 2) is significantly different from the spectra of the pure components and has evidenced that an acid/base adduct was formed by mixing of the two partners. The resonances arising from —NH—
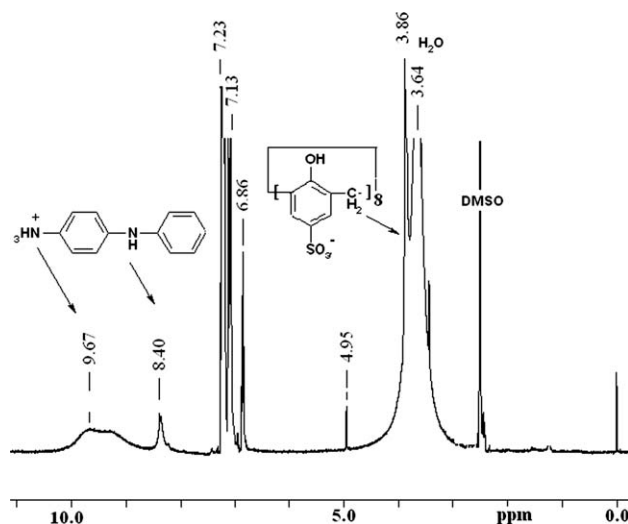
Figure 2. ^{1}H-NMR spectrum (DMSO-d_6) of 1: 1 molar ratio, N-phenyl 1,4-phenylenediamine/C8S mixture.
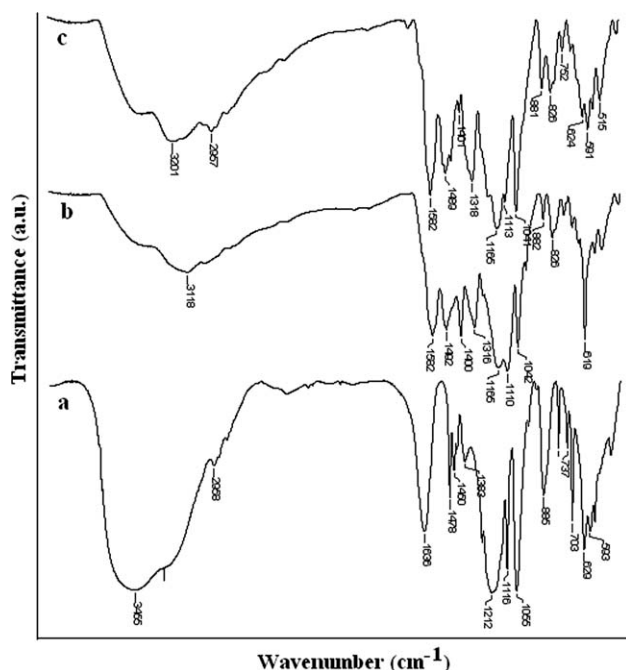
Figure 3. FTIR spectra of: (a) C8S, (b) PANI/C8S obtained by one-step method, and (c) PANI/C8S obtained by two-step method.

and —NH_2 of the dimer changes from 7.43 ppm and 4.74 ppm, in absence of C8S, to 8.40 ppm and 9-10 ppm (broad signal), respectively, in the presence of C8S. 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 by 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 C8S. Therefore, N-phenyl 1,4-phenylenediamine and aniline, in solution with C8S forms an acid–base type complex that by oxidative polymerization occurs to C8S doped PANI, where the dopant anions are sulfonate calix[8]arene groups. The ^{13}C-NMR spectrum of the N-phenyl 1,4-phenylenediamine/C8S mixture presents signals assigned for carbon atoms of both partners, without a clear shifting of signals.

FTIR and ^{1}H-NMR Spectroscopy

The FTIR spectra of polymers obtained by polymerization or by doping of PANI emeraldine base with C8S in DMF solution are very similar and confirm the incorporation of sulfonated calix[8]arene in the final polymer (Figure 3). Sulfonated calixarene being water-soluble compound, aniline polymers were washed with a plenty of water to remove the unbonded calixarene. 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 C8S, are present in the polymers spectra suggesting the presence of the macrocycle. The characteristic bands of PANI-ES; 1582 (N=Q=N, quinoid ring), 1499 cm^{-1} (N=B=N, benzenoid ring), 1400 (C—N stretching of QBQ),

1310 cm^{-1} (C—N stretching of QBC, QBB, BBQ), are also present in the IR spectra.

If we compare the polymerization of aniline in the presence of other two macrocycles; β-CD[16–21]and CB[6][22,23] some conclusions can be drawn. From the dimensional analysis, it results that all three macrocycles, β-cyclodextrin, cucurbit[6]uril, and calix[6]arene are able to encapsulate aniline monomers because their shapes and dimensions are compatible and by polymerization of cycloadducts pseudorotaxane structures should be obtained. However, PANI 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. The differences between these three hosts is that β-CD and CB[6] have a rigid and hydrophobic cavity and aniline monomers can be encapsulated from aqueous solution due to hydrophobic and H bonds interactions. Calix[8]arene has also a hydrophobic cavity able to hosts aniline monomers. However, it is conformationally more flexible in solution as observed on the ^{1}H-NMR time scale. ^{1}H-NMR spectrum (in CDCl$_3$ at 400 MHz) of calix[8]arene shows signals at 9.61 (d, OH), 7.18 (s, 2H from aromatic ring), 4.37(d, 1H, from —CH$_2$—), 3.50 (d, 1H from —CH$_2$—) and 1.26 ppm (9H, s, from tert-butyl). The appearance of two signals assigned for —OH and methylene protons of Ar—CH$_2$—Ar unit shows that p-tert-butyl calix[8]arene is in a non-"pleated-loop" conformation. By treatment with sulfuric acid and debutylation, calix[8] p-octasulfonic acid (C8S) shows in NMR spectrum methylene protons only a single sharp signal at 3.87 ppm (Figure 2) specific for a "pleated-loop" conformation stabilized by intramolecular hydrogen bonds.[35] Moreover, this macrocycle contains strong acid sulfonic groups (to introduce water solubility) more able to interact with aniline monomer to form an acid–base adduct. Thus, by polymerization of adduct, PANI-ES protonated by sulfonic acid groups of C8S was obtained (Scheme 2).

The ^{1}H-NMR spectrum is presented in Figure 4 and shows signals assigned to protons of both macrocycle (7.24 ppm and 4.0 ppm) and PANI chain: 6.49 ppm (NH), 6.98, 7.10 ppm (aromatic protons). The presence of C8S in composite is evidenced
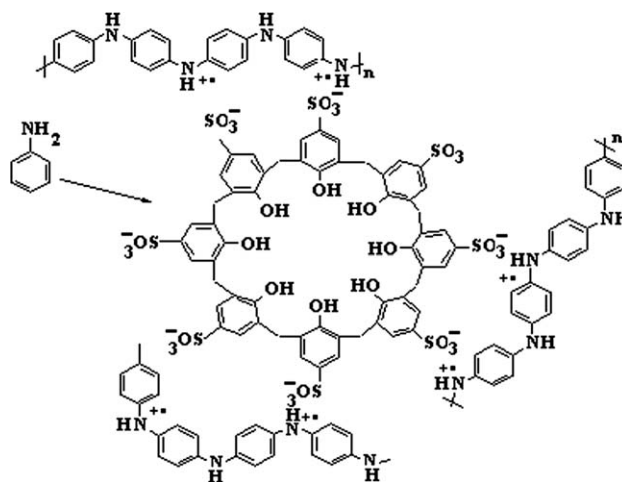

Scheme 2. Doping of PANI with C8S.
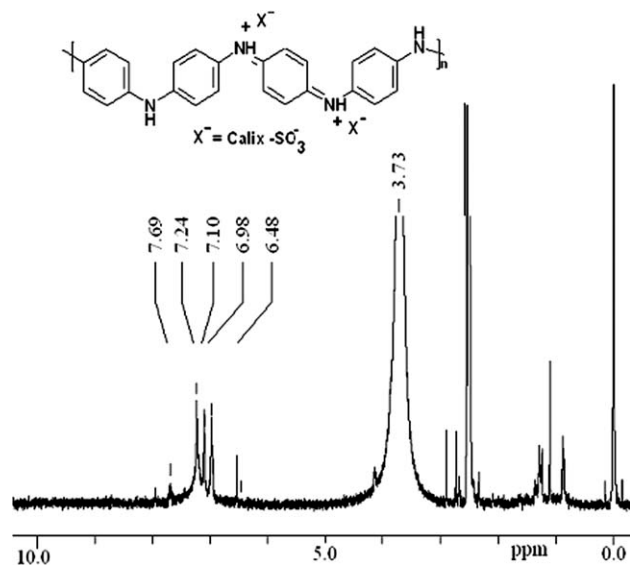
Figure 4. ^{1}H-NMR spectrum of the PANI/C8S in DMSO-d_6 solution. Signals at 2.5 and 3.73 ppm arise from DMSO-d_5 and water.

also by sulfur elemental analysis that indicates ~6% S corresponding to about 0.13 macrocycles for every structural unit of PANI (or ~30% mass of C8S).

Electronic Absorption Spectra of PANI Composites
The electronic absorption spectrum of PANI/calixarene in DMF is presented in Figure 5 (curve a) and shows three broad absorptions at 296 nm, 430 nm and 560 nm and increasing absorption after 800 nm indicating the presence of PANI in the doped state. If the solution is neutralized with NH$_4$OH aqueous the peaks associated with doped form disappear and spectrum is characteristic for PANI-EB form (Curve b).
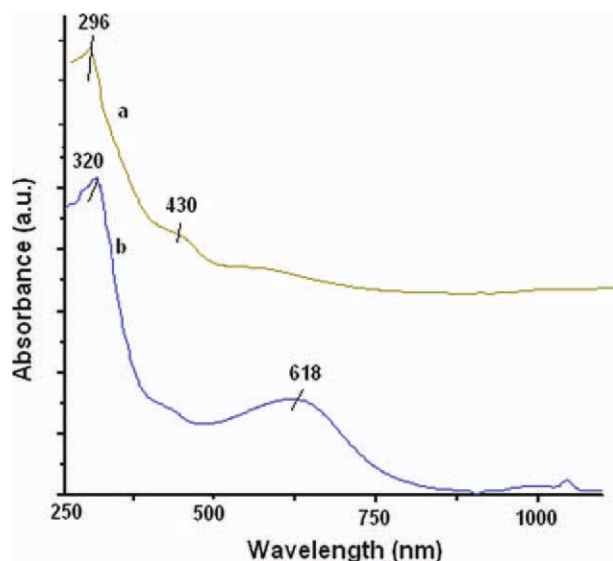
Figure 5. UV spectra (DMF) of PANI/C8S in ES state (a) and after treating with a base (Curve b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
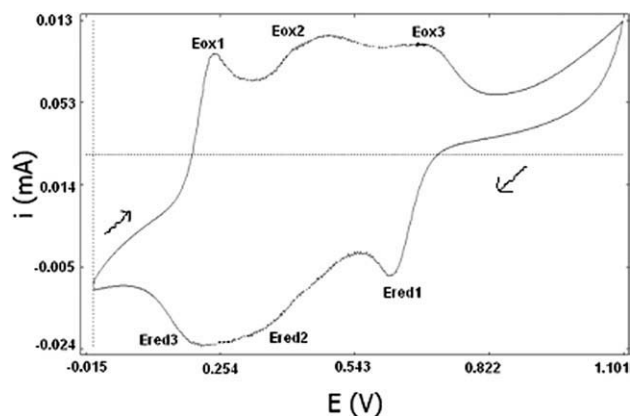
Figure 6. Cyclic voltammogram of PANI/C8S film on Pt disc electrode in H$_2$SO$_4$ 1M solution, at a scan rate of 50 mV/s.

The typical absorption spectrum of PANI-EB[36,37] generally shows two absorption bands between 315–345 nm and 590–650 nm, their position depending on the synthesis and processing methods. The first band is associated to the π–$\pi^\star$ transition and the second one to the excitation of the amine segment of the polymer chain. The electronic spectrum of PANI-ES shows three absorption bands at 325–360 nm, 400–430 nm, and 780–825 nm,[36,38] the first peak being associated with π–$\pi^\star$ electron transition within benzenoid rings, while the second is due to polaron to $\pi^\star$ transition and the third peak is for π-to-polaron transition.

Electrochemical Behavior of PANI Composites
Figure 6 shows the cyclic voltammetry of the synthesized composite deposited on a Pt disc (Φ = 1.6 mm) electrode obtained in H$_2$SO$_4$ 1M solution. The composite was dissolved in DMF and the solution was cast on the platinum working electrode and evaporated to form a thin solid film. The CV experiments were carried out with scan rates of 50 mVs^{-1} and the potential was scanned between 0 and 1.10 V. The cyclic voltammogram showed three pairs of oxidation/reduction peaks, E_{ox1} = 0.249 V, E_{ox2} = 0.480 V, E_{ox3} = 0.672, and E_{red1} = 0.621 V, E_{red2} = 0.335 V, E_{red3} = 0.225 V. The first peak (0.249 V) can be ascribed to the oxidation from leucoemeraldine to emeraldine base being accompanied by the exchange of anions between the PANI film and the solution while the third peak (0.672 V) is assigned to the oxidation the emeraldine state to the pernigraniline state being accompanied by the exchange of protons between PANI film and the solution.[39] The second redox couple (0.48/0.335 V) could be assigned to quinone intermediates.[40] All process is reversible and accompanied by reversible modification of the film color, from green to blue and brown.

DIELECTRIC PROPERTIES
Measurements of the dielectric properties up to 100 MHz and room temperature were carried out with pressure compressed pellets of PAN doped with calix[8]arene. The real part of complex permittivity ε' (dielectric constant), the imaginary part of complex permittivity ε'' (dielectric loss factor) and tan δ as function of frequency are shown in Figure 7. It is observed that both ε' and ε'' decrease with the increase of frequency between
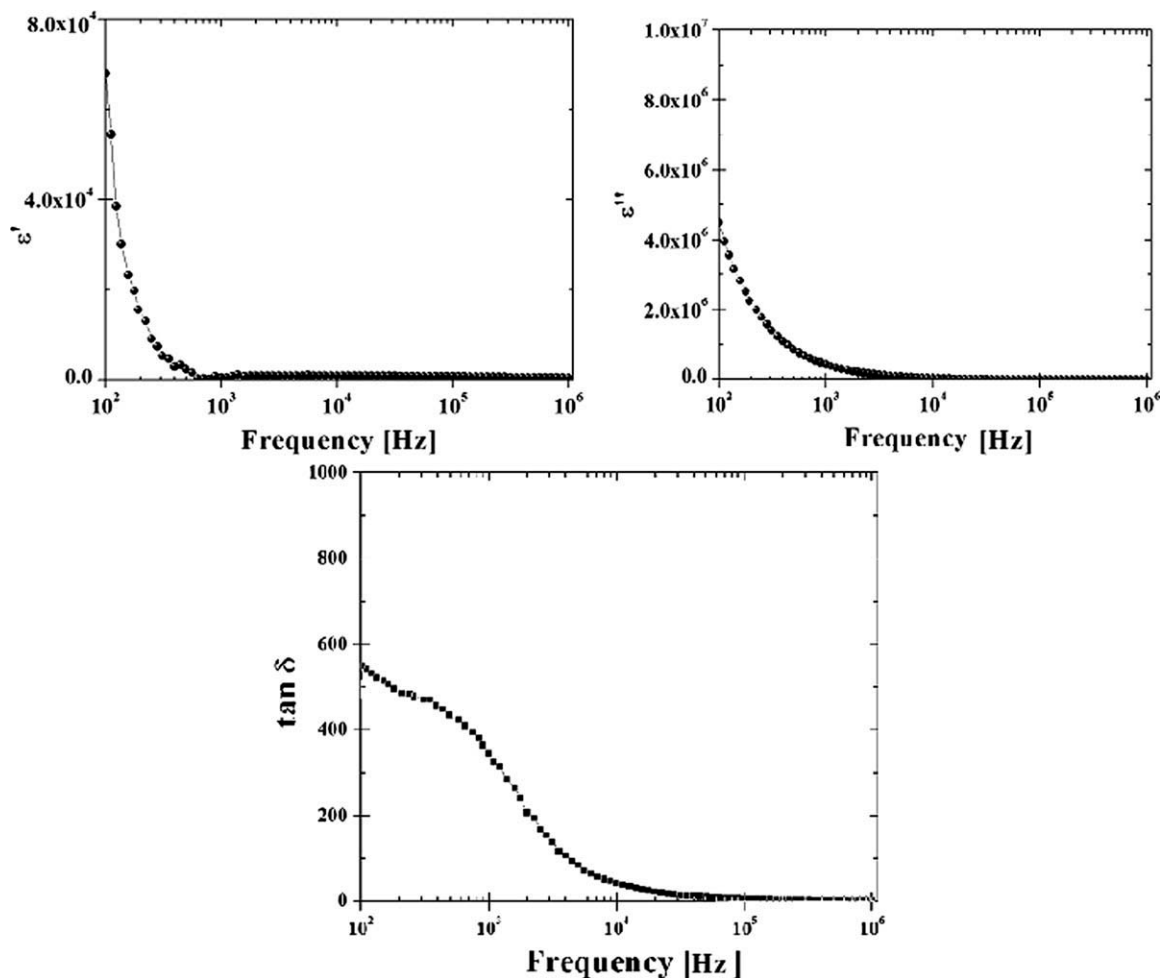
Figure 7. Frequency dependence of: dielectric constant, dielectric loss and tan δ for PANI/C8S.

10^2–10^6 Hz. At 1 Hz, the dielectric constant and dielectric loss factor have values of 5×10^6 and 1×10^7, respectively, while the dc electrical conductivity at room temperature is 6×10^{-3} S/cm.
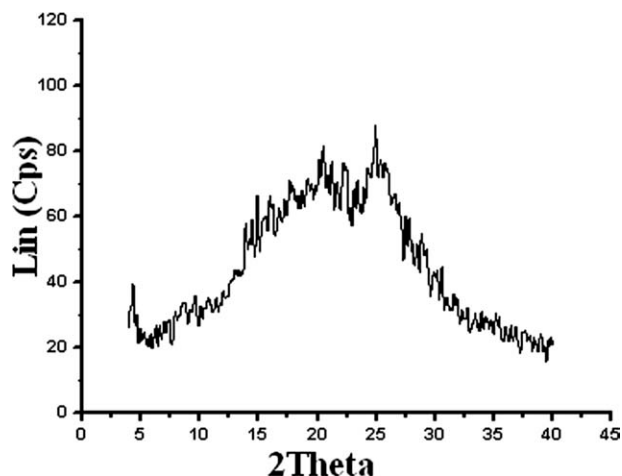

Figure 8. XRD pattern of PANI/C8S.

These composites have high dielectric properties, comparable with those of other PANI/ionic polymers blends[30] and make them very interesting materials for dielectric applications.

XRD pattern of PANI/C8S powder synthesized by one step method is presented in Figure 8 and is characteristic for a material with low crystallinity degree, having small broad peaks at 2θ = 20.2 and 25.5°. The doping of PANI chains with the bulky octaanion of the macrocycle led to an amorphous composite. The XRD pattern of PANI synthesized in standard conditions and undoped state showed an amorphous polymer with a crystallinity degree about 33%, with three peaks at 2θ = 15.1, 20.4, and 25.5°, respectively.[41–43] The first peak was assigned to periodicity parallel to the polymer chain and the third peak was attributed to the periodicity perpendicular to the polymer chain. These peaks can be also observed in PANI/C8S composites

CONCLUSIONS

PANI/p-octasulfonated calix[8]arene composite materials have been prepared by *in situ* oxidative polymerization of aniline in presence of calixarene macrocycle or by protonation of PANI emeraldine base with the macrocycle, in solution. Elemental

analysis and spectral methods have evidenced the presence of the macrocycle as acid dopant (about 30% weight) and all spectral features characteristic of PANI in the protonated state. Even if calix[8]arene derivative has a hydrophobic cavity with shape and dimensions able to encapsulate PANI backbone, the formation of pseudorotaxane structures has not emerged because interactions of acid/base type between sulfonic acid groups of macrocycle and amine or imine nitrogens of PANI are stronger than hydrophobic interactions between the two partners. By polymerization of this acid–base adduct, a protonated PANI with interesting dielectric properties has resulted.

REFERENCES

1. Skotheim, T.A.; Reynolds, J.R.eds., Handbook of Conducting Polymers, 3rd ed.; CRC Press: New York, **2007.**

2. Lux, F. *Polymer* **1994,** *35*, 2915.

3. Kang, E.T.; Neoh, K.G.; Tan, K.L. *Prog. Polym. Sci.* **1998,** *23*, 277.

4. Gospodinova, N.; Terlemezyan, L. *Prog. Polym. Sci.* **1998,** *23*, 1443.

5. Pud, A.; Ogurtsov, N.; Korzhenko, A.; Shapoval, G. *Prog. Polym. Sci.* **2003,** *28*, 1701.

6. Anand, J.; Palaniappan, S.A.; Sathyanarayana, D.N. *Prog. Polym. Sci.* **1998,** *23*, 993.

7. Heeger, A.J. *Synth. Met.* **1993,** *55*, 3471.

8. Sariciftci, N.S.; Smilowitz, L.; Cao, Y.; Heeger, A.J. *Synth. Met.* **1993,** *22*, 188.

9. Taka, T.; Laakso, J.; Levon, J.K. *Solid State. Commun.* **1994,** *92*, 296.

10. Palaniappan, S.; Ajit, S.J. *Appl. Polym. Sci.* **2010,** *118*, 2704.

11. Huang, J.H.; Yang, S.C. *Synth. Met.* **1989,** *29*, E271.

12. Chen, S.A.; Lee, H.T. *Macromolecules* **1995,** *28*, 2858.

13. Liu, J.M.; Yang, S.C. *J. Chem. Soc. Chem. Commun.* **1991, 1529.**

14. Liao, Y.H.; Levon, K. *Polym. Adv. Technol.* **1993,** *6*, 47.

15. Kanhegaokar, S.A.; Chunji, G.; Choi, E.Y.; Kwon, O.P.; Lee, S.H. *J. Appl. Polym. Sci.* **2011,** *120*, 1138.

16. Yuan, G.L.; Kuramoto, N.; Takeishi, M. *Polym. Adv. Technol.* **2003,** *14*, 428.

17. Shimomura, T.; Akai, T.; Fujimori, M.; Heike, S.; Hashizume, T.; Ito, K. *Synth. Met.* **2005,** *153*, 497.

18. Shimomura, T.; Yoshida, K.; Ito, K.; Hayakawa, R. *Polym. Adv. Technol.* **2000,** *11*, 837.

19. Yoshida, K.; Shimomura, T.; Ito, K.; Hayakawa, R. *Langmuir* **1999,** *15*, 910.

20. Yuan, G.L.; Zhou, F.; Yin, S.; Kuramoto, K. *Polym. Bull.* **2008,** *61*, 705.

21. Grigoras, M.; Conduruta, D.G. *J. Incl. Phenom. Macrocyclic. Chem.* **2006,** *54*, 101.

22. Grigoras, M.; Conduruta, D.G. *Rev. Roum. Chim.* **2006,** *51*, 987.

23. Liu, Y.; Shi, J.; Chen, Y.; Ke, C.G. *Angew. Chem. Int. Ed.* **2008,** *47*, 1.

24. Grigoras, M.; Vacareanu, L. *Supramol. Chem.* **2010,** *22*, 237.

25. Gutsche, C.D.; Dhawan, B.; No, K.H.; Muthukrishnan, R.J. *Am. Chem. Soc.* **1981,** *103*, 3782.

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

27. Shinkai, S.; Araki, K.; Tsubaki, T.; Arimura, T.; Manabe, O. *J. Chem. Soc. Perkin. Trans. I* **1987, 2297.**

28. Shinkai, S.; Tsubaki, T.; Sone, T.; Manabe, O. *Tetrahedron Lett.* **1984,** *25*, 5315.

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

30. Ho, C.H.; Liu, C.D.; Hsieh, C.H.; Hsieh, K.H.; Lee, S.N. *Synth. Met.* **2008,** *158*, 630.

31. Soares, B.G.; Leyva, M.E.; Barra, G.M. *O.; Khastgir, D. Eur. Polym. J.* **2006,** *42*, 676.

32. Chwang, C.P.; Liu, C.D.; Huang, S.W.; Chao, D.Y.; Lee, S.N. *Synth. Met.* **2004,** *142*, 275.

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

34. Atwood, J.L.; Clark, D.L.; Juneja, R.K.; Orr, G.W.; Robinson, K.D.; Vincent, R.L. *J. Am. Chem. Soc.* **1992,** *114*, 7558.

35. Gutsche, D.C. *J. Am. Chem. Soc.* **1999,** *121*, 4136.

36. Inoue, M.; Navarro, R.E.; Inoue, M.B. *Synth. Met.* **1989,** *30*, 199.

37. Sai Ram, M.; Palaniappan, S.J. *Mater. Sci.* **2004,** *39*, 3069.

38. Cao, Y.; Smith, P.; Yang, C. *Synth. Met.* **1995,** *69*, 191.

39. Orata, D.; Buttry, D.A. *J. Am. Chem. Soc.* **1987,** *109*, 3574.

40. Zhang, J.; Shan, D.; Mu, S. *Polymer* **2007,** *48*, 1269.

41. Seshadri, D.Y.; Bhat, N.V. *J. Polym. Sci. B* **2007,** *45*, 1127.

42. Anilkumar, P.; Jayakannan, M. *Langmuir* **2006,** *22*, 5952.

43. Pouget, J.M.; Jozefowicz, M.E.; Epstein, A.J.; Tang, X.; MacDiarmid, A.G. *Macromolecules* **1991,** *24*, 779.