

Spectroscopic Characterization of Polyaniline Formed by Using Copper(II) in Homogeneous and MCM-41 Molecular Sieve Media

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This work emphasizes the important role of the synthetic parameters in the structure of the polymeric material obtained in the aniline polymerization. The polymers formed by the oxidative polymerization of aniline by copper(II) ions in acidic aqueous solution, acetonitrile/water medium, and also copper(II) acetate complex encapsulated into MCM-41 molecular sieve were characterized by resonance Raman spectroscopy using three exciting laser lines and other techniques such as UV–vis, FTIR, and XANES (Nitrogen K edge). Additionally the products were investigated by thermogravimetric analysis and powder X-ray diffraction. When Cu(II) ions in acidic aqueous medium are used, emeraldine salt (ES–PANI) is formed through the usual head-to-tail polymerization mechanism, while in acetonitrile/water medium a polymer is observed having mainly phenazine-like rings, quinonediimine, and/or phenylenediamine segments in the chains, suggesting that a distinct mechanism is operating. The average molecular weights of the free polymers synthesized in water and in acetonitrile/water were, respectively, ca. 37 300 and 16 900 Da. The encapsulated polymer synthesized in Cu(II)-MCM-41 is a polymeric mixture of (i) ES–PANI and (ii) the polymer obtained when this metal cation was used as oxidant in acetonitrile/water medium. All the characterization data were compared to those ones obtained for standard free polyaniline and also for the encapsulated polymer into mesoporous MCM-41 formed by using persulfate in acidic aqueous medium as oxidant.

Introduction

Polyaniline, PANI, among other conducting polymers, has been extensively investigated due to its relatively high electrical conductivity, simple synthetic route, and good environmental stability.^{1,2} Several properties of conducting polymers such as electrical conductivity, solubility, processability, thermal stability, and mechanical strain are strongly dependent on structural chain defects, departure of ideal structure, polymer conformation, and morphology.^{3,4} Resonance Raman scattering by using exciting laser lines in a wide spectral range is a powerful technique for the structural investigation of self-localized excitations in conducting polymers. Hence, this spectroscopic tool permits the selection of each chromophoric segment present in the polymeric chain by changing the exciting radiation.^{5,6}

The nature of polymeric structure is strongly dependent on the synthetic route employed. In PANI chemical synthesis, persulfate ions ($S_2O_8^{2-}$) in aqueous acid solutions are commonly used as oxidizing agent and the chain structure involves the monomer in a head-to-tail sequence.^{1,2} The isolated green polymer is the well-known PANI in the emeraldine salt form (ES–PANI). Polymerization of aniline can also be done in nonaqueous medium such as acetonitrile and using Cu(II) as oxidant.^{7–9} In these experimental conditions, the structure of the polymer has been recognized to be similar to ES–PANI, with small amount of branched structure (from *ortho* coupling).^{8,9} However, these materials have not been characterized by resonance Raman technique, and its employment can give new insights about the polymer structure and the role of distinct synthetic conditions.

Polyaniline can also be prepared inside inorganic porous materials to control and to enhance the PANI bulk properties due to the organization of the polymeric carbon chains in the confined environment.^{10,11} Thus, PANI has been confined into a variety of host materials such as montmorillonite smectite clay (MMT),¹² FeOCl,¹³ zirconium phosphates,¹⁴ and MCM-41.¹⁵ MCM-41 is a siliceous mesoporous molecular sieve, having a hexagonal array of uniformly sized channels (pore diameters of 1.5–10 nm).¹⁶ This type of inorganic host permits the encapsulation of several PANI chains, leading to conducting polymeric filaments isolated by the inorganic wall. There are many possible synthetic routes to confine PANI in an inorganic porous matrix. Considering some of them, the oxidizing agent can be in liquid solution or fixed inside the host cavities. Confined PANI has been prepared, for example, in Cu(II)-montmorillonite clay,¹⁷ in Cu(II)-zirconium phosphate,¹⁸ and Cu(II)-exchanged tubular aluminosilicate (halloysite).¹⁹ In these systems, the transition metal ion associate to the inorganic structure plays a role of oxidizing agent that promotes the aniline polymerization. Raman and FTIR spectroscopies were employed to characterize the polymer formed by the oxidative polymerization of aniline using Cu(II) in $HFe(SO_4)_2 \cdot 4H_2O$ and $HUO_2 \cdot PO_4 \cdot 4H_2O$ layered compounds, and also in mesoporous aluminosilicate gels.^{20,21} In accordance with these studies, an oligomeric mixture was produced, having segments formed due to the head-to-tail coupling and also due to a head-to-head polymerization, responsible for the presence of hydrazo bonds (N–N).

Our group has used resonance Raman spectroscopy for monitoring the polymerization of aniline in the MMT interlayer region.¹² Although the nanocomposite is green, which could be identified as ES–PANI, the resonance Raman spectroscopic investigation showed that the intercalated polymer also has azo

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bonds (N=N) and phenazine-like units. This result shows that the green color is not a good parameter to state the formation of ES-PANI and also emphasizes that the polymer structure is really dependent on synthetic environment.

In the present work, products formed by oxidative polymerization of aniline using Cu(II) in acidic aqueous and in acetonitrile/water medium (i.e., oxidizing agent in homogeneous medium) and also in Cu(II)-MCM-41 (i.e., oxidizing agent fixed in the nanoporous host) were investigated by resonance Raman, FTIR, UV-vis, and XANES spectroscopic techniques. Elemental and thermogravimetric analyses and XRD patterns of free and confined polymers were also obtained. Gel permeation chromatography (GPC) was used to determine the molecular weight of free polymers. The structures of these macromolecules were compared to those of polymers obtained using persulfate ion as oxidizing agent to promote the polymerization when (i) monomer was dissolved in aqueous acidic solution and (ii) monomer was impregnated in MCM-41 molecular sieve. The set of spectroscopic techniques used in our study permitted the identification of distinct chromophoric segments in PANI chains obtained in the different experimental conditions mentioned above.

Experimental Section

Aniline from Merck was distilled under reduced pressure prior to use. Dyes used as standard in XANES measurements were purchased from Aldrich and other reagents were obtained from Merck.

Polymerization of Aniline in Homogeneous Media. Polymerization of aniline using Cu(II) as oxidant in acidic aqueous solution was performed by adopting the same aniline/oxidant molar ratio and pH that have been employed when persulfate is the oxidizing agent.²² A total of 4.67 g (27 mmol) of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was dissolved in 100 mL of HCl 1 mol·L⁻¹ and added to a solution containing 150 mL of HCl 1 mol·L⁻¹ and 10 mL (108 mmol) of aniline. The reaction mixture was stirred at room temperature for one week. The deep green solid obtained was separated by filtration and washed with 200 mL of HCl 1 mol·L⁻¹ and subsequently with ethanol until the observation of a colorless filtered solution. The polymer was dried under vacuum at room temperature. The sample was characterized by elemental analysis (CHN), and the following data were found: 57.0% C, 4.56% H, and 8.90% N (C/N molar ratio = 6.3). In thermogravimetric analysis (TGA) experiment, the water content was about 9.9 wt % and the residue in air was ca. 1 wt % at 900 °C. Thereafter, this sample will be referred as PANI-Cu/w.

Aniline polymerization using Cu(II) as oxidant in acetonitrile/water mixture was performed by adapting the procedure reported by Toshima et al.⁸ A volume of 5.0 mL (54 mmol) of aniline was added into 20 mL of acetonitrile/water mixture (1:1, v/v) containing 0.920 g (5.4 mmol) of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. The reaction mixture was stirred under oxygen bubbling at room temperature for 24 h. The resulting precipitate was isolated by filtration and washed with methanol, HCl 1 mol·L⁻¹ aqueous solution, and distilled water until the filtered solution became colorless. The dark brown solid was dried under vacuum at room temperature. This sample was characterized by elemental analysis (CHN), and the following data were found: 66.3% C, 4.44% H, and 12.6% N. This synthetic procedure was also carried out in air instead of oxygen atmosphere, and a dark brown solid was obtained. This sample showed the following elemental analysis data: 67.3% C, 4.49% H, and 12.9% N (C/N molar ratio = 6.1). FTIR spectra of these two products are the same, indicating

that O₂ atmosphere is not necessary for aniline polymerization. The polymer synthesized in air was used in the studies reported ahead and will be abbreviated as PANI-Cu/ACN.

The polymerization of aniline in aqueous acidic solution using $(\text{NH}_4)_2\text{S}_2\text{O}_8$ was carried out as described.²² PANI was obtained in the emeraldine salt form, ES-PANI. The basic form, EB-PANI, was obtained by treating ES-PANI with an aqueous solution of NH_3 1.0 mol·L⁻¹. The pernigraniline base (PB-PANI) was prepared through oxidation of EB-PANI with *m*-chloroperbenzoic acid, following the procedure described previously.²³ The complex of emeraldine base with Cu(II) (thereafter abbreviated EB-Cu(II)) was prepared adapting the procedure described for the synthesis of the complex PANI-FeCl₃.²⁴ A total of 0.283 g of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (1.65 mmol) was dissolved in 20 mL of nitromethane, and 0.150 g of EB-PANI was added to this solution. The reaction mixture was kept under stirring at room temperature for 15 h. The solid was isolated by filtration and dried under vacuum at room temperature.

The complex $\text{Cu}(\text{an})_2\text{Cl}_2$ (an = aniline) was synthesized using the procedure described previously.²⁵ A total of 0.1705 g of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (1 mmol) was dissolved in 60 mL of ethanol. This solution was added to 40 mL of diethyl ether containing 0.18 mL of aniline (2 mmol). The reaction mixture was kept under stirring at room temperature for 2 h. The olive-green solid was isolated by filtration, washed with ethanol, and dried in a desiccator with silica gel. The complex was characterized by elemental analysis (CNH), and the following data were found: 45.2% C, 4.60% H, and 8.58% N; calculated (considering the formula $\text{C}_{12}\text{H}_{14}\text{N}_2\text{Cl}_2\text{Cu}$), 44.9% C, 4.40% H, and 8.73% N.

Synthesis of MCM-41 and Cu(II)-MCM-41. MCM-41 was prepared following the procedure described previously.²⁶ Tetraethyl orthosilicate (TEOS) was added, under stirring, to an aqueous solution of NH_3 containing hexadecyltrimethylammonium bromide (CTAB). This mixture was kept under stirring at room temperature for 1 h. The molar ratio employed of $\text{H}_2\text{O}/\text{NH}_4\text{-OH}/\text{CTAB}/\text{TEOS}$ was 525:69:125:1. The solid formed was isolated by filtration, washed with distilled water, and dried at room temperature. Afterward, the solid was first calcined in flowing nitrogen at a heating rate of 100 °C/min and subsequently in air at 540 °C for 12 h.

Cu(II) ions were impregnated into MCM-41 as described in the literature.²⁷ A total of 0.25 g of calcined MCM-41 was treated with 25 mL of an ethanol solution of copper acetate monohydrate 5 mmol·L⁻¹. This mixture was stirred at room temperature for 2 h, resulting in a pale blue solid (hereafter Cu(II)-MCM-41). The solid was isolated by filtration and washed with ethanol until the filtered solution was colorless. Cu(II) ions are encapsulated in MCM-41 as the copper acetate compound. This statement is supported by the presence of bands at 2903, 2938, and 2971 cm⁻¹ in the FT-Raman spectrum of Cu(II)-MCM-41 (not shown), assigned to the $\nu\text{C-H}$. When copper chloride was used instead of acetate salt in the impregnation experiment, the metal ion was removed from the molecular sieve in the washing step.

Polymerization of Aniline Encapsulated in MCM-41 and in Cu(II)-MCM-41. The polymerization of aniline in MCM-41 was done following procedure described previously.¹⁵ The host material was exposed to aniline vapor at room temperature for 24 h in a closed chamber. Incorporation of aniline in MCM-41 molecular sieve was confirmed by the presence of characteristic bands of aniline in its Raman spectrum²⁸ (not shown) at 530, 620, 814, 997, 1028, and 1603 cm⁻¹. The amount of aniline in the inorganic solid was estimated through thermogravimetric analysis (ca. 35 wt %). The white solid impregnated

with aniline was added to a recipient, immersed in an ice–water bath, containing an aqueous solution of HCl $0.2 \text{ mol}\cdot\text{L}^{-1}$ and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (aniline/oxidant molar ratio = 1). The suspension was kept under stirring at low temperature for 4 h. The dark green solid (hereafter PANI–MCM-41) was isolated by filtration, washed with water, and dried under vacuum at room temperature. This sample was characterized by elemental analysis, and the following data were found: 19.2% C, 3.70% H, and 3.74% N (C/N molar ratio = 6.0).

Polymerization of aniline in Cu(II)-MCM-41 was carried out exposing the host to aniline vapor for 2 days at room temperature in a closed chamber. The pale blue solid became brown after this time. Afterward, the sample was kept in a desiccator under dynamic vacuum for about 12 h. The solid was characterized by elemental analysis, and the following data were found: 13.1% C, 2.40% H, and 2.22% N (C/N molar ratio = 6.9).

Instrumentation. Elemental chemical analyses (CHN) were carried out in a Perkin-Elmer model 2400 analyzer at Chemistry Institute (Universidade de São Paulo-USP). FTIR spectra of samples dispersed in KBr pellets were recorded on a Bomem MB100 spectrometer with a resolution of 4 cm^{-1} . A Shimadzu UV3101PC spectrophotometer equipped with an integrating sphere was employed to record the diffuse reflectance spectra. BaSO_4 (Waco Pure Chemicals) was used as reference (100% reflectance). The Kubelka–Munk method was used to convert the diffuse reflectance spectra to the absorbance mode through the software supplied with the spectrophotometer. Powder X-ray diffraction (XRD) patterns were recorded on a Philips diffractometer model PW1710 using $\text{Cu K}\alpha$ radiation. Thermogravimetric analyses (TGA) were carried out using a Shimadzu TGA-50 instrument, under synthetic air (flow rate = 50 mL/min) and a heating rate of $10 \text{ }^\circ\text{C/min}$ up to $900 \text{ }^\circ\text{C}$.

Raman spectra at 632.8 nm (He–Ne laser, Spectra Physics model 127) and at 514.5 nm (Ar^+ laser, OmNichrome model 543-AP) exciting wavelength were recorded in a Renishaw Raman imaging microscope (system 3000) containing an Olympus metallurgical microscope and a CCD detector. The laser beam was focused on the sample in a ca. $1 \text{ }\mu\text{m}$ spot by a $50\times$ lens. Laser power has always been kept below 0.7 mW at the sample to avoid its degradation. FT-Raman spectra were recorded in a FT-Raman Bruker FRS-100/S spectrometer using 1064 nm exciting radiation (Nd:YAG laser Coherent Compass 1064-500N) and a InGaAs detector.

Molecular weight of polymers was measured through gel permeation chromatography (GPC). The deprotonated polymers were dissolved in *N*-methyl-2-pyrrolidinone (NMP), and the carrier solvent was NMP containing 0.1% LiCl. The GPC columns were Supelco Progel TSK G4000, TSK G5000, and TSK G3000, kept at $60 \text{ }^\circ\text{C}$, and the carrier solvent flow rate was 0.5 mL/min . UV detector set at 330 nm was used to monitor the polymer elution. A calibration curve was obtained with standard polystyrene of molecular weight 50 000, 30 000, 17 500, 9000, 5000, and 2500 Da.

XANES spectra were recorded using the facilities of the National Synchrotron Light Laboratory (LNLS), Brazil. SGM beam line has a focused beam of roughly a 0.5 mm^2 spot. The spectra were recorded in total electron yield detection with the sample compartment pressure at 10^{-8} mbar . All energy values in the nitrogen K edge spectra were calibrated using the first resonant peak of nitrogen K edge XANES spectrum of potassium nitrate.²⁹

Results and Discussion

Polymerization of Aniline in Homogeneous Media. Figure 1 shows the FTIR spectra of polymers formed from the oxidation

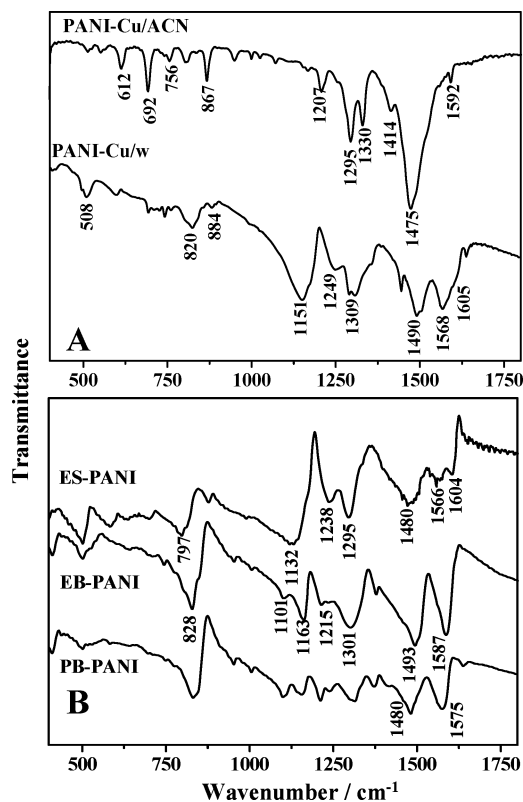


Figure 1. FTIR spectra of (A) PANI prepared using Cu(II) in homogeneous media and (B) standard PANI.

of aniline by Cu(II) in acidic aqueous medium (PANI–Cu/w) and in acetonitrile/water medium (PANI–Cu/ACN). For comparison, the spectra of the standard PANI polymers ES, EB, and PB–PANI are also shown, prepared as described in the Experimental Section. The spectra of standard PANI are in agreement with those reported in the literature.^{23,30,31} As it can be seen, the PANI–Cu/w spectrum is similar to that of ES–PANI synthesized using persulfate in acidic aqueous medium, but it does not present the sharp negative bands observed in the ES–PANI spectrum. These features are named as Evans holes. The Evans holes have been shown to be more pronounced and sharper in samples with high conductivity.³¹ The absence of these holes in the PANI–Cu/w spectrum suggests that this polymer presents lower electrical conductivity than ES–PANI. The PANI–Cu/ACN spectrum has the same spectral profile as the one reported in ref 8, where the authors considered that the isolated polymer has an ES–PANI-like structure with a small amount of branched segments.

The resonance Raman spectra of PANI–Cu/w, PANI–Cu/ACN, and also of standard PANI polymers for different exciting radiation are presented in Figure 2. The ES–PANI spectrum excited at 632.8 nm radiation presents bands characteristic of ES–PANI radical cation (at 1163 , 1320 , 1336 , and 1625 cm^{-1}) and bands due to dication (at 1489 and 1581 cm^{-1}). When going to EB or PB–PANI spectra excited at 632.8 nm , the characteristic $\nu\text{C}=\text{N}^{+}$ stretching at 1320 and 1336 cm^{-1} of the radical cation segments disappears. In addition, the $\nu\text{C}=\text{N}$ stretching at 1489 cm^{-1} (due to dication segments in the ES–PANI spectrum) shifts and increases its relative intensity in EB and PB–PANI spectra. It is possible to observe that PANI–Cu/w spectra show the same spectral profile as that of ES–PANI when considering the same exciting wavelength. This result indicates that the structure of PANI–Cu/w is similar to ES–PANI, in concordance with FTIR data. The great difference in PANI–

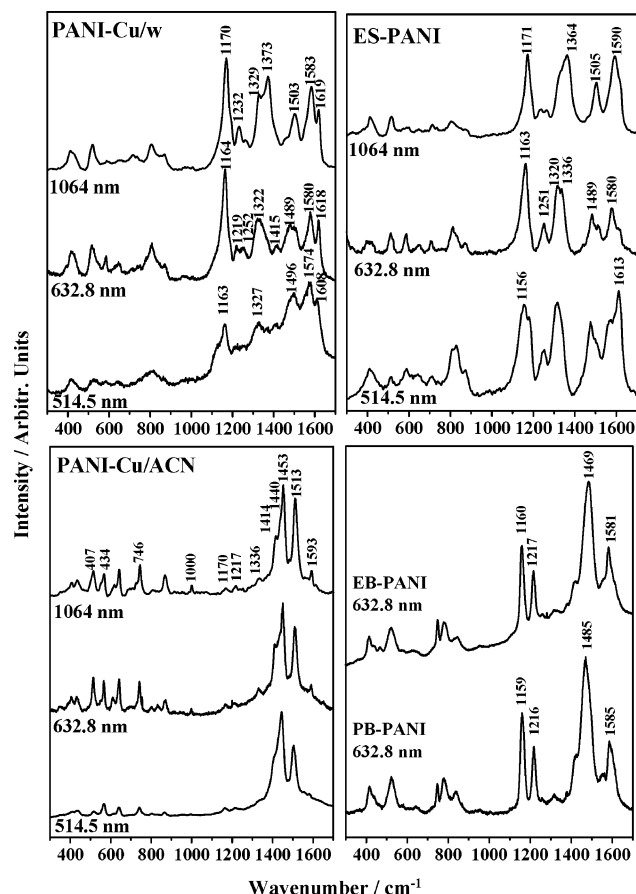


Figure 2. Resonance Raman spectra of PANI–Cu/w, PANI–Cu/ACN, ES–PANI, EB–PANI, and PB–PANI.

TABLE 1: Weight-Average and Number-Average Molecular Weights and Polydispersity for Some Samples of Polyaniline

sample	weight average molecular weight (\bar{M}_w)	number average molecular weight (\bar{M}_n)	polydispersity (\bar{M}_w/\bar{M}_n)
PANI–Cu/w	37260	21670	1.7
PANI–Cu/ACN	16900	11230	1.5
ES–PANI	91960	64330	1.4

Cu/w spectra to those of PANI–Cu/ACN for all exciting wavelengths leads us to conclude that these two polymers do not have the same structure. For all exciting radiations, PANI–Cu/ACN spectra present bands (at 1414, 1440, 1453, and 1513 cm^{-1}) that are not observed in ES–PANI spectra. This result is in disagreement with the polymeric structure proposed by Toshima et al.⁸ for PANI–Cu/ACN. If the polymer has ES–PANI-like chains with a small amount of branched structure, the PANI–Cu/ACN spectrum should be very similar to the ES–PANI at the 1064 nm exciting radiation (where the resonance Raman bands of ES radical cation are very intense). However, this is not observed when the spectra shown in Figure 2 are evaluated.

One of the questions that arise about the nature of the PANI–Cu/ACN sample is if it is an oligomer or a polymer. Table 1 presents the weight average (\bar{M}_w), number average molecular weights (\bar{M}_n), and polydispersity of PANI–Cu/ACN, PANI–Cu/w, and ES–PANI. The \bar{M}_w of ES–PANI is similar to the value reported using a comparable synthetic procedure.³² The \bar{M}_w of PANI–Cu/w is ca. 2.5 times lower than that of ES–PANI but is in agreement with the value reported for the

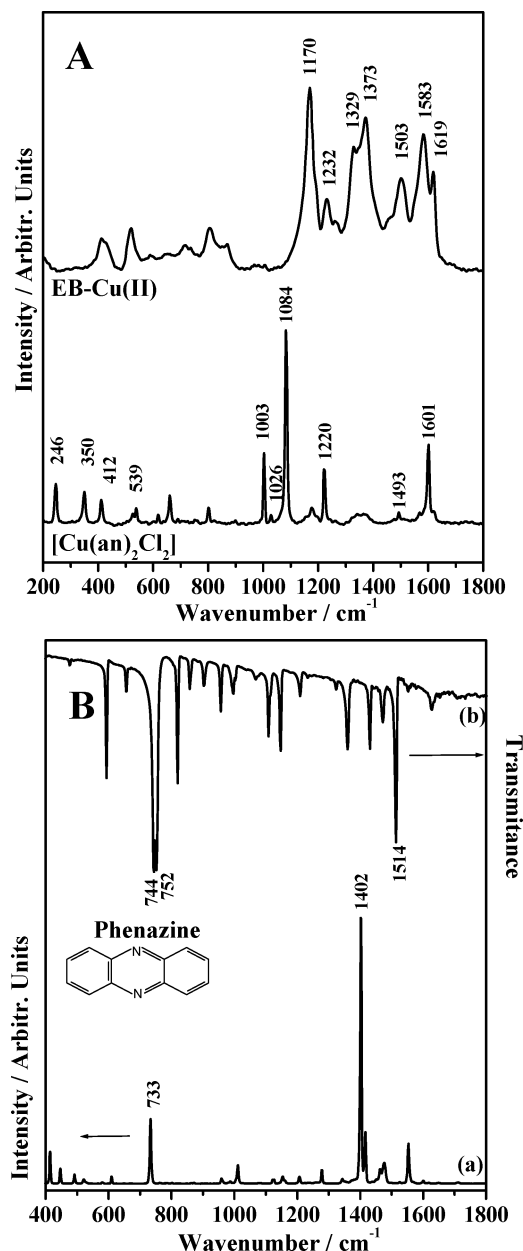
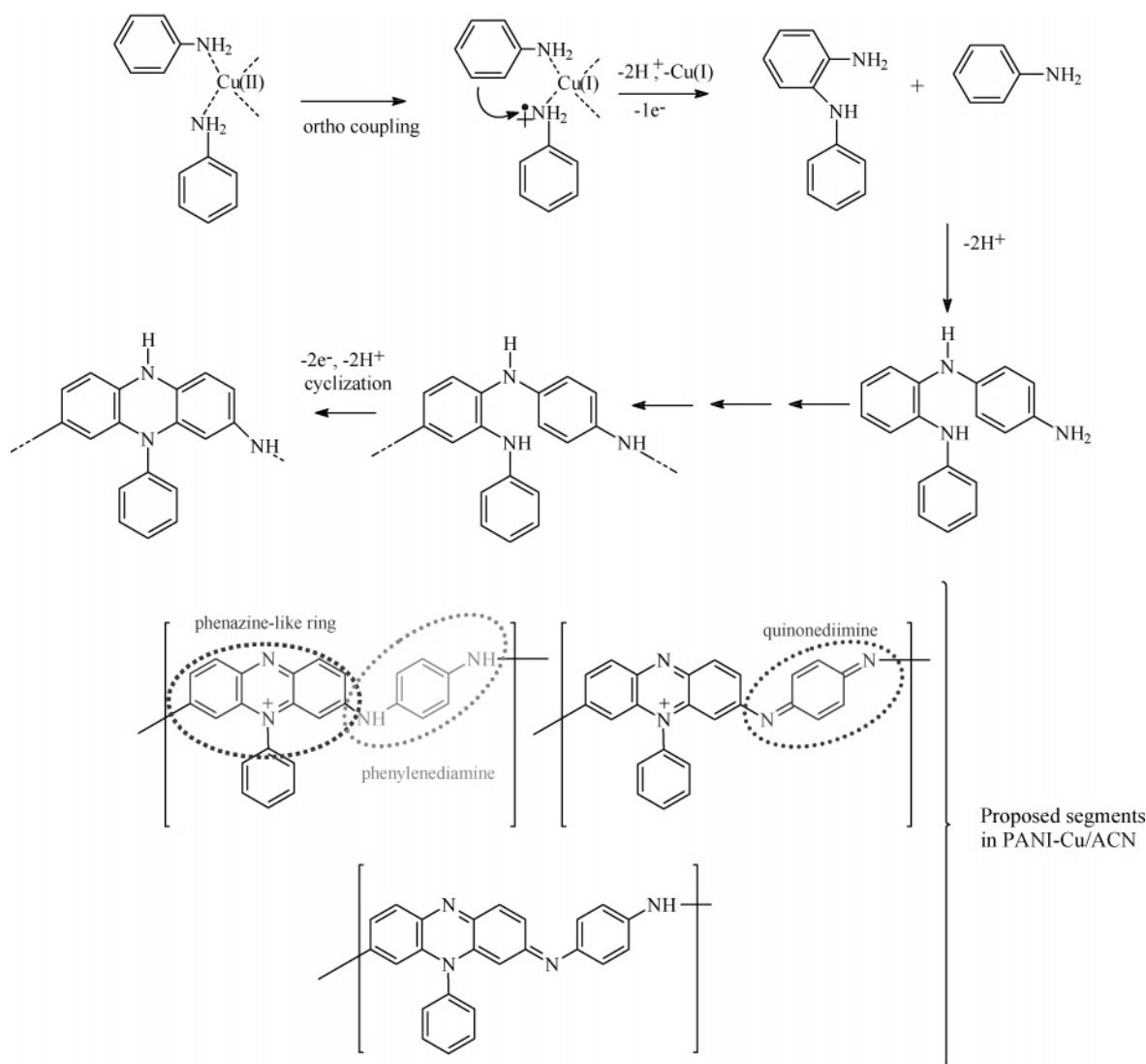


Figure 3. (A) FT-Raman spectra of possible products formed during the aniline polymerization using Cu(II) and (B) FT-Raman (a) and FTIR spectra (b) of Phenazine.

polymer synthesized using Cu(II) perchlorate in acetonitrile medium.⁷ The \bar{M}_w value of PANI–Cu/ACN is 16 900, considering aniline as a mero, the polymer chain has ca. 180 repeating units.

The PANI–Cu/ACN sample could be a pure polymer or contaminated by secondary products. One possible byproduct could be a coordination compound containing aniline bound to Cu(II). Although it would be decomposed in very acidic aqueous solution due to the formation of anilinium ions, a copper–aniline complex could be formed in acetonitrile solution. The strong and medium Raman bands of $[\text{Cu}(\text{an})_2\text{Cl}_2]$ complex at 1003, 1084, and 1601 cm^{-1} (Figure 3A) are not observed in PANI–Cu/ACN spectra (Figure 2), excluding the possibility that PANI–Cu/ACN is contaminated by the copper–aniline complex. Another possibility is the formation of EB–PANI having the nitrogen atoms of the polymeric chain coordinated to Cu(II). The resonance Raman spectrum of the EB–Cu(II) polymer (Figure 3A) is very different from that observed for PANI–

SCHEME 1: Schematic Proposed Mechanism for Formation of Phenazine-like Segments in PANI–Cu/ACN

Cu/ACN at 1064 nm (Figure 2), discarding the possibility of this polymer being responsible for the unexpected Raman profile of PANI–Cu/ACN.

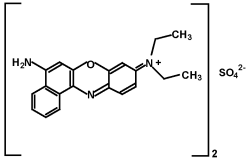
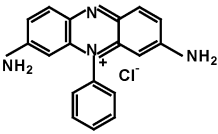
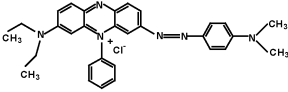
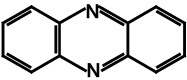
It is reported in the literature³³ that Cu(II) complexes promote the ortho coupling of aromatic compounds. In addition, there are some examples showing that after an ortho (N–C) coupling, a cyclization reaction frequently occurs.³⁴ If these processes are occurring during the synthesis of PANI–Cu/ACN, phenazine-like rings could be present in its polymeric chain. The Raman bands at 1414 and 746 cm^{-1} in the spectra of PANI–Cu/ACN (Figure 2) can be correlated with the bands at 1402 and 733 cm^{-1} in the Raman spectrum of phenazine (Figure 3B). The polymer band at 1513 cm^{-1} does not have a counterpart in the phenazine Raman spectrum, but it is observed in the FTIR spectrum of this compound. These correlations suggest that the phenazinic unit is present in the structure of PANI–Cu/ACN. Nevertheless, the strong band at 1453 cm^{-1} in the polymer spectra (Figure 2) is not observed in the phenazine Raman spectrum. After being soaked in D_2O and dried under dynamic vacuum, the PANI–Cu/ACN polymer decreases the relative intensity of the 1453 cm^{-1} band and a new one is observed at 1433 cm^{-1} . No change is noticed in the intensity of the bands at 1513 and 1414 cm^{-1} . These results indicate that an NH bending vibration mode contributes to the band at 1453 cm^{-1}

and also suggest that, besides phenazine-like rings in the repeating unit of the polymer, there are 1,4-phenylenediamine segments.

Considering that radical cations and dications segments of ES–PANI have high Raman signal when using 1064 and 633 nm exciting radiations, we conclude that these segments do not participate in the repeating unit of the polymer and that the polymeric chain has high proportion of cyclic units. The possible segments formed in the polymerization of aniline when using acetonitrile/water medium and copper ions are shown in Scheme 1. Cu(I) produced in the reaction should be reoxidized to Cu(II) by atmospheric oxygen molecule. The electronic paramagnetic resonance spectrum of PANI–Cu/ACN (not shown) displays signal of Cu(II) (copper(I) is EPR-silent).

The structure of PANI–Cu/ACN was also characterized using XANES spectroscopy. This technique was successfully used for the investigation of the oxidation states of nitrogen in polyaniline³⁵ and in the PANI–MMT clay nanocomposites.¹² The spectra of several compounds containing nitrogen in different oxidation states and environment were recorded to obtain a XANES spectra library. Table 2 shows the structure and the tentative assignment of the bands of Nile blue (structure having amine, oxazine-like, and positive imine nitrogen), Phenosafranine (amine, phenazine-like, and positive imine nitrogen), Janus

TABLE 2: Tentative Assignment of N1s \rightarrow 2p π^* Resonance Energies of Nitrogen K XANES for Standard Compounds

Compound/ Structure	Energy (eV)						
	-N=	-N= phenazinic or oxazinic ring	-N=N- Azo bond	+• -N=	-N ⁺ = 	=N [≡]	-NH-
 Nile blue		398.2			399.6		401.9
 Phenosafranin		398.4			399.4	400.7	
 Janus green B		398.4	398.7		399.7	400.6	
 Phenazine		398.2				400.6	
ES-PANI				399.1			402.7
EB-PANI	397.7					400.6	402.7
PB-PANI	397.7					400.6	

green B (amine, phenazine-like, positive imine nitrogen, and azo bond), Phenazine (phenazine-like nitrogen), and EB, ES, and PB-PANI.

Figure 4 shows the XANES spectra of PANI-Cu/ACN together with the standard compounds that have similar spectral profiles. The spectrum of PANI-Cu/ACN shows a strong and broad absorption centered at 398.2 eV. This band could be assigned to the sum of peaks at 397.7 eV (imine nitrogen), 398.2 eV (phenazine-like nitrogen), 399.7 eV (positive imine nitrogen), and 401.7 eV (amine nitrogen). XANES data reinforce the presence of acyclic amine and imine groups together with phenazine-like rings in the structure of PANI-Cu/ACN. As it was stressed in the discussion about the resonance Raman results, there are no ES-PANI radical cation segments, but there are NH groups that lead us to propose the repeating units shown in Scheme 1. The observation in XANES spectrum of an imine nitrogen leads us to propose an alternative assignment for the strong Raman band at 1513 cm⁻¹: instead of a phenazine band it could be attributed to a ν CN of the quinonediimine segments,

or this band can be associated to these two segments of polymeric chain.

Polymerization of Aniline Encapsulated in Cu(II)-MCM-41. For characterizing the polymer encapsulated into Cu(II)-MCM-41, its structure and spectroscopic behavior were compared to that of PANI-MCM-41 formed by the oxidative polymerization of aniline using persulfate as oxidant. The spectroscopic properties of the polymers synthesized in homogeneous media using aniline and Cu(II) ions will also be considered in this section for comparison purposes.

XRD pattern at small angle is a useful data to characterize long-range ordered mesoporous materials. The XRD patterns of MCM-41, Cu(II)-MCM-41, PANI-Cu-MCM, and PANI-MCM-41 are shown in Figure 5. All diffraction patterns present peaks which could be indexed as $hk0$ reflections of the hexagonally arranged pore of this molecular sieve, indicating that even after the aniline polymerization the characteristic structure of MCM-41 is maintained. The impregnation of Cu(II) acetate compound in MCM-41 leads to a decrease in the

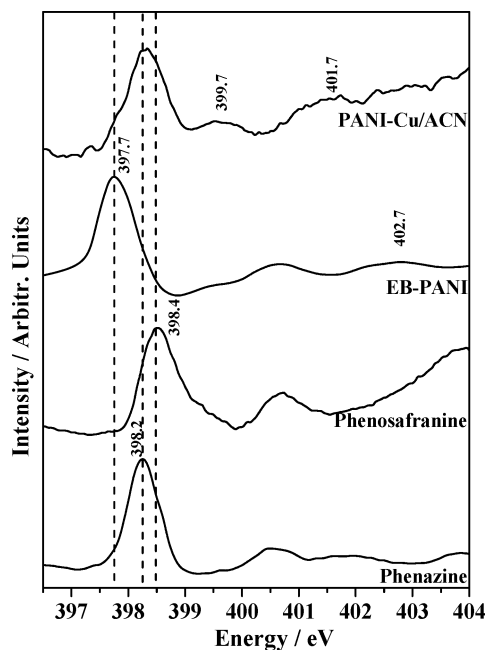


Figure 4. XANES spectra at the nitrogen K edge of Phenazine, Phenosafranine, EB-PANI, and PANI-Cu/ACN.

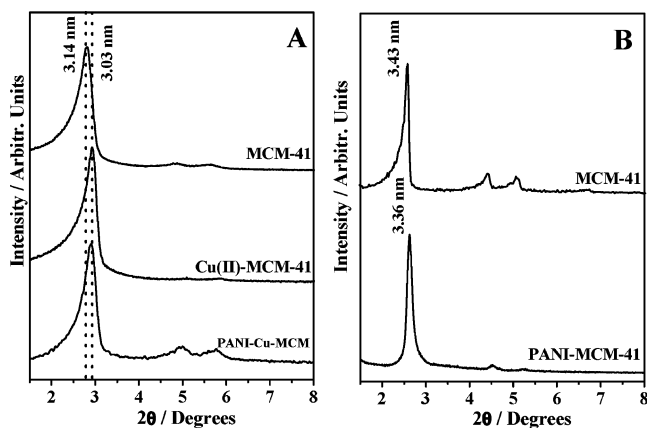


Figure 5. X-ray diffraction patterns of (A) MCM-41, Cu(II)-MCM-41, and PANI-Cu-MCM; and (B) MCM-41 and PANI-MCM-41.

interplanar distance d_{100} from 3.14 to 3.03 nm. This change can be attributed to the hydrolysis of some Si-O-Si bonds of MCM-41. A similar change has been observed when MCM-41 is treated with water vapor and acidic and basic solutions.^{36,37} The interplanar distance d_{100} was maintained after polymerization of aniline vapor into Cu(II)-MCM-41. The variation in interplanar distance d_{100} for PANI-MCM-41 observed in Figure 5B could also be attributed to the hydrolysis of MCM-41 walls.

Figure 6 presents FTIR spectra of MCM-41 and the polymers encapsulated into MCM-41 and Cu(II)-MCM-41. The bands of inorganic host dominate the FTIR spectra. According to the literature,^{36,38} the following bands are due to the MCM-41 framework: 459 (rocking of Si-O-Si group), 802 (Si-O symmetric stretching), 956 (Si-O-H stretching), and 1080 and 1240 cm^{-1} (anti-symmetric stretching of Si-O-Si). The band at 1627 cm^{-1} was assigned to O-H bending of adsorbed water molecules. The weak and medium bands at 884, 1229, 1304, 1490, 1580, and 1605 cm^{-1} in the FTIR spectrum of the polymer formed inside MCM-41 using persulfate as oxidant are characteristic of ES-PANI (Figure 1), indicating a head-to-tail polymerization of aniline. This result is similar to a previous one reported for the polymerization of aniline in aluminosilicate

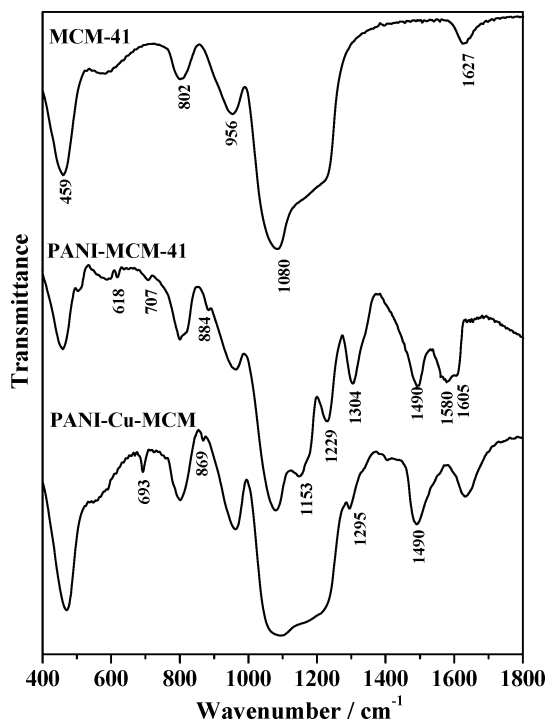


Figure 6. FTIR spectra of MCM-41, PANI-MCM-41 and PANI-Cu-MCM.

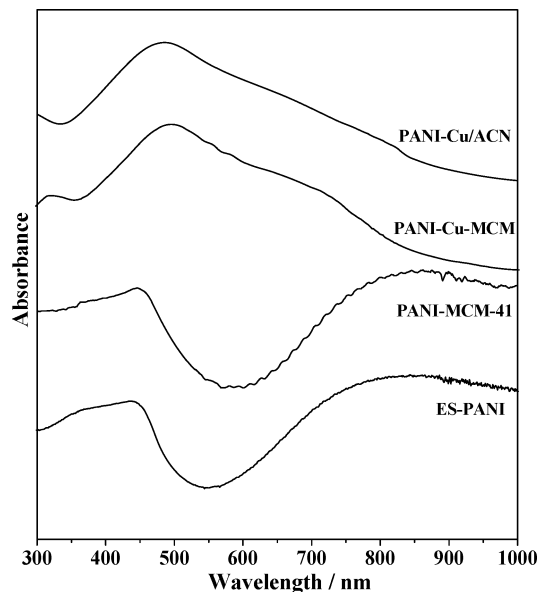


Figure 7. UV-vis-NIR electronic absorption spectra of solid samples: PANI-Cu/ACN, PANI-Cu-MCM, PANI-MCM-41, and ES-PANI.

MCM-41.¹⁵ The FTIR spectrum of the polymer confined in Cu(II)-MCM-41 is not different from PANI-MCM-41, though it also presents very weak bands at 693, 869, and 1295 cm^{-1} , which are observed in the spectrum of PANI-Cu/ACN (Figure 1).

The absorption spectra of the solid samples PANI-Cu-MCM, PANI-MCM-41, PANI-Cu/ACN, and ES-PANI are shown in Figure 7. Characteristic bands of ES-PANI at 370, 440, and 800 nm are observed in the PANI-MCM-41 spectrum, corroborating the FTIR data. On the other hand, the reflectance spectrum of the product immobilized in Cu(II)-MCM-41 shows absorption at 500 nm and a shoulder at 700 nm. The band at 500 nm is also observed in the PANI-Cu/ACN spectrum, which

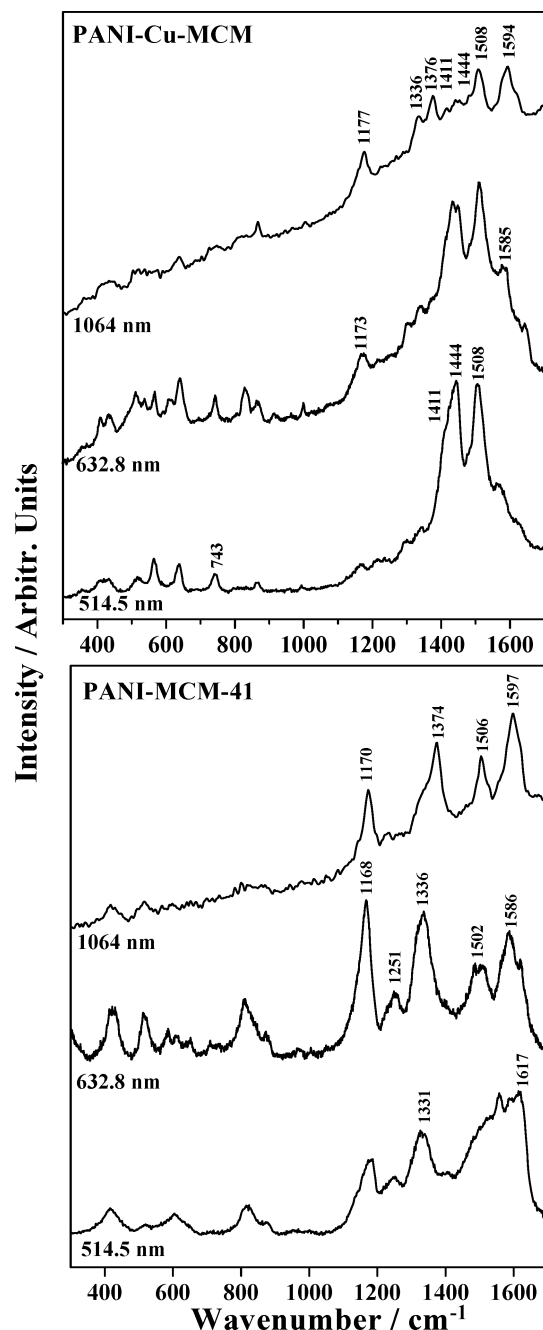


Figure 8. Resonance Raman spectra of PANI-Cu-MCM and PANI-MCM-41.

reinforce the FTIR results about the formation of similar polymeric segments in PANI-Cu/ACN and Cu(II)-MCM-41.

Figure 8 shows the resonance Raman spectra of PANI-Cu-MCM and PANI-MCM-41 at 514.5, 632.8, and 1064 nm exciting wavelengths. For all exciting radiations, the resonance Raman spectra of PANI-MCM-41 are similar to ES-PANI spectra (Figure 2), confirming that the head-to-tail polymerization of aniline occurs inside MCM-41, when persulfate is used as oxidant. In contrast, the Raman spectra of PANI-Cu-MCM are similar to PANI-Cu/ACN spectra (Figure 2), but the bands at 1177, 1336, 1376, and 1594 cm^{-1} , that are characteristic of radical cation segments of ES-PANI, appear in the spectra at 1064 nm. At this exciting radiation, the resonance Raman condition for the radical cation is fulfilled, so its bands are enhanced while there is a decrease of the relative intensities of the bands of phenazine-like ring at 1411 and 1444 cm^{-1} , since

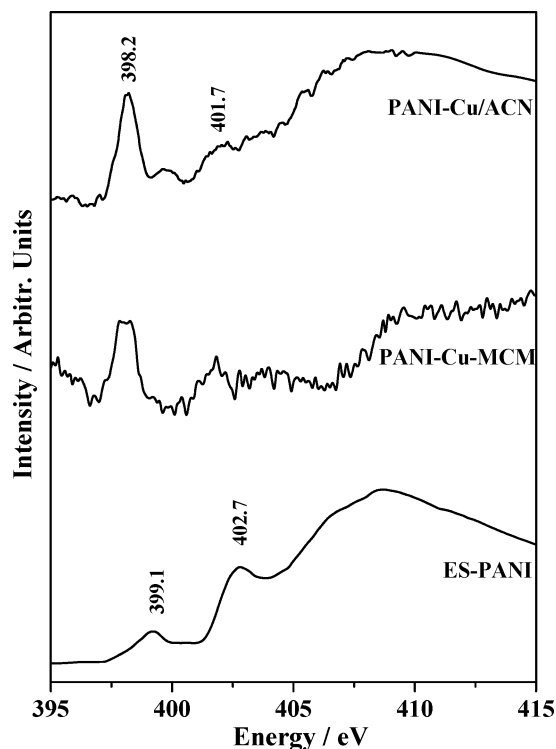


Figure 9. XANES spectra in the nitrogen K edge of PANI-Cu/ACN, PANI-Cu-MCM, and ES-PANI.

at this radiation phenazine bands are out of resonance. This result shows that together with a polymer of the same structure of PANI-Cu/ACN, ES-PANI is also formed during in situ polymerization of aniline in Cu(II)-MCM-41.

Figure 9 presents the XANES spectra of PANI-Cu-MCM, PANI-Cu/ACN, and ES-PANI. The spectrum of PANI-Cu-MCM has low signal/noise ratio but it was possible to see the spectral profile presented by PANI-Cu/ACN. Nevertheless, characteristic peaks of ES-PANI suggested by resonance Raman data were not observed. The reason of this apparent disagreement can be accounted by (i) the high noise in the XANES spectrum, due to the low concentration of polymer in the nanocomposite and (ii) the very high signal when using Raman technique since the resonance condition is fulfilled.

The thermal behaviors of PANI-MCM-41 and PANI-Cu-MCM were investigated using TGA and were compared to those of the inorganic hosts and of the free polymers. TGA curves of these samples are shown in Figure 10. The TGA curve of ES-PANI presents three major steps of weight loss (DTG peaks at 67, 234, and 504 $^{\circ}\text{C}$) attributed to the release of moisture (about 19 wt %), HCl, and to the polymer decomposition, respectively.³⁹ The main weight loss of MCM-41 and Cu(II)-MCM-41 (about 20 wt %) occurs up to 100 $^{\circ}\text{C}$ (DTG peak at 61 $^{\circ}\text{C}$) and it is ascribed to the liberation of adsorbed water molecules. For the Cu(II)-MCM-41 sample, a loss of about 1.6 wt % observed at ca. 290 $^{\circ}\text{C}$ can be related to the acetate thermal decomposition. When this sample is heated to 350 $^{\circ}\text{C}$ under air, the bands attributed to νCH in the Raman spectrum disappeared, confirming the decomposition of acetate around 290 $^{\circ}\text{C}$.

The TGA curve of PANI-MCM-41 shows the release of adsorbed water (ca. 19.5 wt %; DTG peak at 61 $^{\circ}\text{C}$), HCl molecules (DTG peak at about 215 $^{\circ}\text{C}$), and the polymer decomposition above 360 $^{\circ}\text{C}$ (DTG peaks at 457 and 555 $^{\circ}\text{C}$). The pyrolysis of the encapsulated polymer occurs over a higher temperature range (ca. 360–600 $^{\circ}\text{C}$) than that observed for ES-

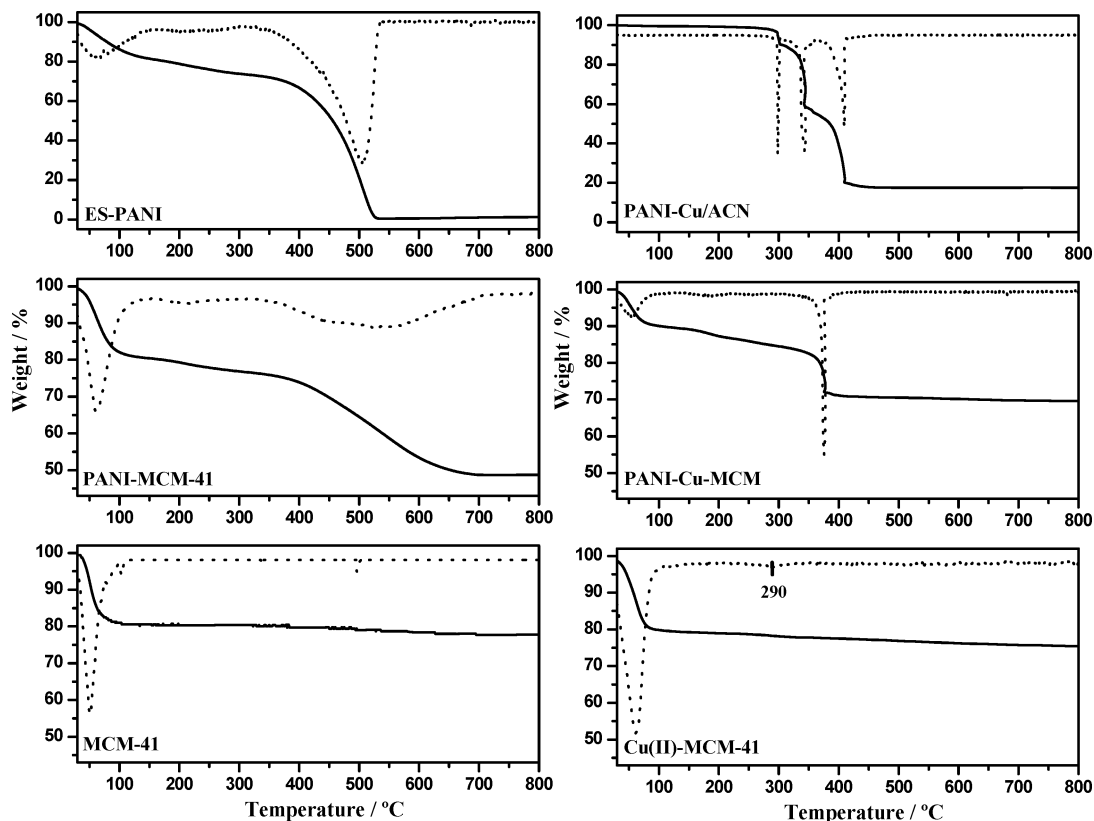


Figure 10. TGA (—) and DTG (---) curves under air atmosphere of PANI–MCM-41, PANI–Cu–MCM, MCM-41, Cu(II)-MCM-41, PANI–Cu/ACN, and ES–PANI.

PANI (ca. 360–520 °C; DTG peak at 504 °C). The different thermal behavior between free and encapsulated polymer is due to diffusional constraints in the molecular sieve channel system. No difference was observed in the TGA curves for PANI–MCM-41 (Figure 10) and PANI encapsulated in the aluminosilicate MCM-41 reported in ref 11.

According to TGA data, PANI–Cu/ACN is an anhydrous solid and presents three weight-loss steps in the range of 290–410 °C (DTG peaks at 298, 342, and 409 °C), which attribution is out of the scope of this study. The residue obtained at 900 °C (ca. 17.7 wt %) is a gray solid characterized as CuO by Raman spectroscopy (bands at 298, 344, and 630 cm^{-1}), indicating that this polymer has considerable amount of Cu(II) ions. This result corroborates the proposal that in acetonitrile/water solution the organic structure is tightly bound to the metal cation (nitrogen atoms coordinated to copper), which is not possible in water acidic media where aniline is protonated (no coordinated to Cu^{2+}). As it was reported in Experimental Section, PANI–Cu/w sample has only 1 wt % of residue when heated at 900 °C, reinforcing the statement that in HCl 1 $\text{mol}\cdot\text{L}^{-1}$ solution the polymer is protonated and not bound to the transition metal. The proposal shown in Scheme 1 seems really plausible: the presence of aniline monomer molecules in the copper coordination sphere changes the polymerization pathway in relation to the process observed in acidic water solution.

PANI–Cu–MCM sample loses about 3 wt % in the 100–200 °C range (DTG peak at ca. 178 °C) and ca. 13 wt % between 300 and 450 °C (DTG peak at 370 °C). The event at 178 °C can be ascribed to the release of aniline molecules encapsulated in the molecular sieve since before evacuation this sample showed this weight loss of 35 wt % and presents a FTIR band at 1604 cm^{-1} (assigned to aniline) that decreased significantly after evacuation for about 12 h. The step observed

at about 370 °C is due the polymer thermolysis. A modest event was also noticed at about 250 °C that can be related to the acetate decomposition.

Conclusions

The data obtained in this study show the essential contribution of spectroscopic techniques (resonance Raman in particular) for the conducting polymers characterization. The characterization results of the polymers formed by the oxidative polymerization of aniline by Cu(II) ions emphasize the important role of the environment in the nature of final product. We can conclude that *ortho* coupling and cyclization are the predominant synthetic route in a medium where aniline molecules are coordinated to Cu(II) (i.e., the metal cation plays a role of *structure-directing agent*). In contrast, the aniline protonation in acidic medium hinders the coordination to Cu(II), and the usual head-to-tail polymerization mechanism is favored. The polymer formed in Cu(II)-MCM-41 has segments with phenazine-like ring plus 1,4-phenylenediamine and/or 1,4-quinonediimine and segments with ES–PANI structure. The former structure can be explained by the presence of Cu(II) inside the MCM-41 molecular sieve. The knowledge of the influence of synthetic parameters in the final polymeric structure makes it possible to choose the better experimental conditions (solvent, oxidizing agent, inorganic environment, etc.) to get the desired macromolecule structure and related properties.

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