Aniline Polymerization in Ethanol-water Mixtures

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This study presents new findings of the water/ethanol (ratio) influence on the aniline hydrochloride polymerization process in presence of ammonium persulfate. Water/ethanol mixtures in presence of monomer hydrochloride, as proved by the conductometric, spectrophotometric and refractometric investigations, are far from ideal solutions and promote a partitioned environment , for the polymerization process. By controlling this key parameter (water/ethanol ratio) the polymerization can be shifted from a initial dispersion process to a solution one, followed by precipitation. The associated phenomena revealed modification in terms of conversion, structure (FTIR, UV-VIS), morphology (SEM), thermal stability and doping agent retention (TGA-DTG).

Keywords: conductive polymers, aniline hydrochloride, water/ethanol system, polyaniline

The general interest for conductive polymers and in particular polyaniline (PANI) type or PANI composites is determined by a wide range of synthesis methods and a variety of properties as relatively high conductivities and thermal stabilities, anticorrosive conducting properties, electrorheological, antistatic, suitable for flexible electrodes [1-18]. The fillers used to obtain PANI composites are very different: layered silicates [1,3-5], SiO_2 [2,6-8], TiO_2 [9], carbon nanotubes [10-12], polymers[13-18]. Polysulfone(PS) - PANI membranes obtained by inversion of the immersion-precipitation phase accompanied by chemical reaction were proved particularly interesting composites. Since aniline (ANI) is a good solvent for PS, membranes containing different amounts of ANI are obtained by precipitation with a suitable nonsolvent. This monomer can polymerize by treatment with acid aqueous solutions containing different oxidants [19]. The uniformity of PS-PANI membranes may be improved by the selection of initiatiator in membrane systems for the polymerization of ANI hydrochloride (ANIHCl). The polymerization of 1-naphthylamine in the presence of alcohol-water mixtures showed that short chain co-surfactant changes the polymer morphology and properties [21].

The literature presents some interesting results in case of ANI polymerization (in presence of retinol) with ammonium persufate (APS) involving a certain water/ethanol ratio [22] which enhanced the PANI conductivity. This suggests the existence of a "soft template" effect [22]. However the study do not investigate neither the complete interval, nor the relation with the necesary ammount of water for APS initiating. The PANI particle sizes are smaller at this ratio and the absorption in the UV-VIS (330-400 nm domain due to π -π* transition of aromatic rings) is maximized.

Since the polymerization of aniline in dispersed media involves several particular aspects as a consequence of colloidal system complexity (monomer salt with different polarity (ANIHCl) in the growing process, ethanol/water aggregates, initiator, in terms of interfaces and selective interaction between partners), in this study we investigate how the efficiency of ANIHCl polymerization can be favoured by the initial colloidal state of the polymerization system in relation with different water/ethanol ratios. The colloidal system based on ANIHCl (macroscopically homogeneous in appearance) was investigated by conductometry, spectrophotometry and refractometry to demonstrate the deviation from the ideal solutions and the existence of the nanostructuring. This key feature was discussed in terms of polymerization process (the shift from a dispersion process to a solution one followed by precipitation, according to water/ethanol ratio). The associated phenomena (to the initial state of the polymerization dispersion media) were followed to the final polymer conversion, structure (FTIR, UV-VIS), morphology (SEM), thermal stability and doping agent retention (TGA-DTG).

Experimental part

Materials

Aniline hydrochloride (Sigma-Aldrich, ≥ 99%), ammonium persulfate (Merck-Schuchardt, ≥ 98%), 1 methyl-2-pyrrolidone (Acros-Organics, ≥ 98%), ethanol (Chimreactiv, ≥ 99.2%) were used as received, without additional purification.

PANI preparation

Different water/ethanol mixtures were prepared for the polymerization process. Polymerizations were carried out in glass flasks equipped with magnetic stirrer (350 rpm). The reaction mixture is kept in ice bath (~ 4°C). A typical recipe for polymerization is as follows: in 9.25g of ANIHCl added to a water/ethanol mixture (100g); after solubilization and cooling (about 15 min), 20g of APS were added in ten equal portions (2g) for 90 min long. This procedure was intended to observe how much APS was required (as different water/ethanol ratio were used) for the polymerisation start-up (the reference point was considered the color appearance). After ading the initiator the whole mixture was stirred for another 2 h. After the reaction time end the final product was washed with distilled water. The obtained polymer before drying was additionally filtered and purified by several washings with distilled water and acetone.

Characterization

Refractive indices were measured at 25°C with an Abbe type refractometer.

Conductivity of mixtures were measured with a conductometer Radelkis OK-102-1 at 25°C.

UV spectra were determined in the 250-800cm spectral range on diluted samples with appropriate mixtures water/ethanol. It was used a Nicolet Evolution 500 spectro-photometer (Thermo Electron Corp).

FTIR spectra were measured with a Bruker Tensor 37 instrument with Golden Gate ATR system, on powder samples.

SEM images were obtained with a FEI Quanta 200 instrument. The powder samples were deposited on a metal stub using a carbon tape.

Thermal analyses (TGA, DTA, DSC) were performed in nitrogen with a heating rate of 10°C/min with a TA Instruments SDT Q-600 system. The PANI samples were dried in vacuum at 60°C before analyses.

Results and discussions

In previous studies [23] it was shown that the solubility of monomers in a water/ethanol mixture shows a significant increase at the molar ratio higher than 1/5. These results confirm previously published data [24, 25] which highlights the ability of C_1-C_4 alcohols to self associate in water with a pronounced change in the physico-chemical properties at different molar ratio. Around this molar ratio (1/5 ethanol/water) the obtained PANI presents a maximum or a minimum in the measured properties [22].

To elucidate these nanostructuring phenomena of mixtures in which ANI can be polymerized, we begin this study with the physico-chemical analysis of water/ethanol mixtures containing ANIHCl 2%wt. It covers all range of EtOH molar fractions (0÷1) where the same amounts of ANIHCl was disolved – the protonated active monomer in ANI polymerization.

The changes of refractive index and conductivity of these mixtures are given in figure 1a. One can notice a nonlinear dependence, demonstrating that such mixtures are not ideal mixtures. Both properties exhibit a major discontinuity at f_{H2O} = 0.833 corresponding to a molar ratio water/EtOH = 5/1.

The water/ethanol mixtures are nanostructured after the induction of different neighborhoods depending on the ratio between components. In the case of ANIHCl these changes are highlighted by the λ_{max} change of ANIHCl of UV-VIS spectra (fig. 2). The maximum value of wave number deviation is observed exactly at f_{H2O}=0,833 - the best combination. The same phenomenon was observed too in the styrene solutions, [27].

An important objective of this paper is ANIHCl polymerization in these nanostructured systems. APS was added in 10 increments as solids during the polymerization. It was noticed its very low solubility in EtOH-rich mixtures. We considered necessary to correlate the amount of APS added (proportional to the time of the early polymerization), when the mixture is colored mostly with the initial ethanol/water fraction.

In figure 3 are represented the changes of APS amount required for starting polymerization. If the system contains only ANIHCl and water (f_{H2O}=1) the colouring appears immediately after the first 2g of APS were introduced. In case of no water mixtures (f_{H2O}=0) the colouring does not appear after the addition of all amounts of APS. It appears after another hour. The initiator is not soluble in EtOH. Figure 1b shows that ANIHCl is ionized under these conditions. A key feature was the major deviation (of the refractive index and conductivity) from linear dependence (on water/ethanol ratio) at $f_{H2O} \geq 0.833$. This deviation may be correlated with the higher degree of ANIHCl associations. In figure 2, λ is maximum in this domain.
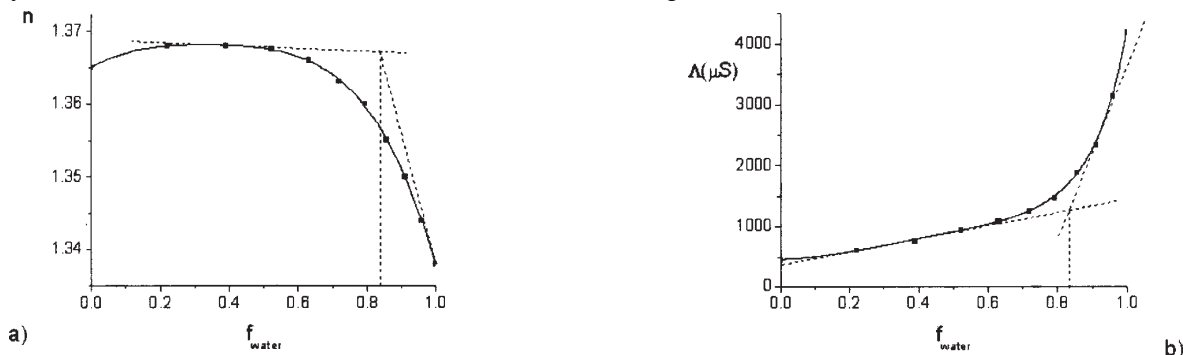

Fig. 1. (a) Change of refractive index for mixtures water/ethanol with 2% dissolved ANIHCl;
(b) Changes in the conductivity of mixtures water/ethanol with 2% dissolved ANIHCl.

| Exp.n° | EtOH | | H₂O | | | Polymer (g) | The amount of APS used for solution colouring (g) |
	g mol	f EtOH	g mol	vol. % H₂O	f H2O		
4077	--	0	100 100	100	1	7,89	2
4078	26,56 0,576	0,136	66 3.66	66,0	0,864	7,32	4
4079	50 1.087	0,282	50 2,77	43,8	0,718	6,93	8
4080	20 0.435	0,0899	80 4,44	75,75	0,910	8.86	2
4081	80 1,739	0,610	20 1,11	16,3	0,39	7,25	14
4082	100 2,174	1,0	--	0	0	6,08	--
4083	65 1.413	0,42	35 1,94	29,6	0,58	7,91	10
4084	44 0.956	0.235	56 3,111	50	0,156	8,4	18
4085	34 0.739	0,167	66 3,66	60,2	0,833	7,72	6
4090	90 1,156	0.771	10 0,55	8,06	0,219	8,7	9

Table 1
POLYMERIZATION CONDITIONS FOR ANIHCl IN EtOH/H₂O mixtures 9.25g ANIHCl + 100g (EtOH + H₂O) + 20g APS 4h (2x10 portions of APS)
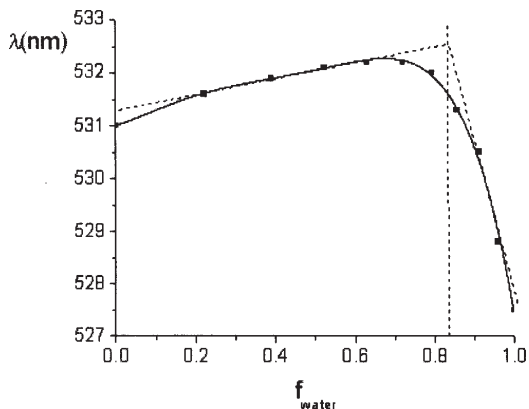
Fig. 2. λ_{max} variation to corresponding to ANIHCl dissolved in mixtures water/ethanol .
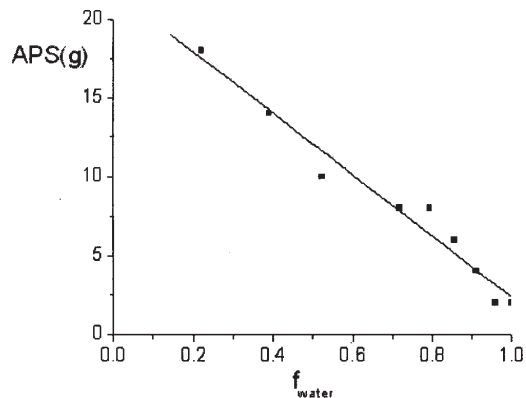

Fig. 3. The variation of the amount of the necessary APS for starting the polymerization according to mole fraction of water in the initial mixture.
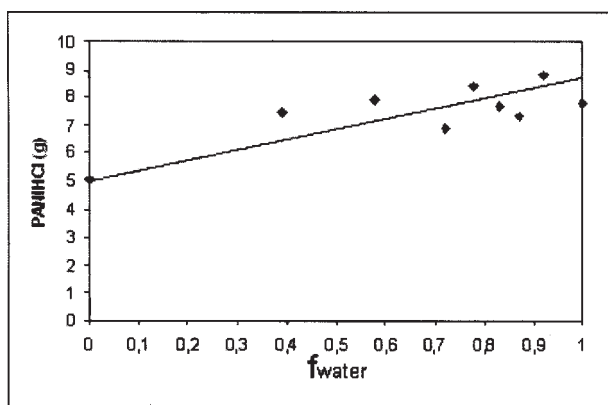

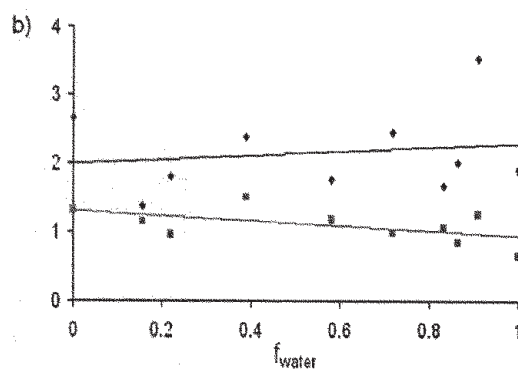Fig. 4. The variation of the amount of the polymer formed according to the mole fraction of water
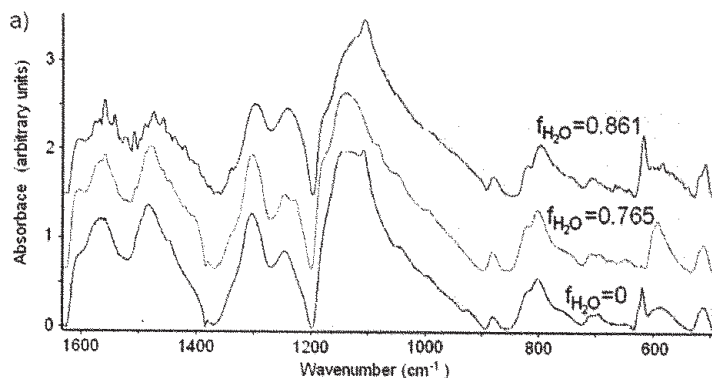

Fig. 5. (a)FTIR spectra of polyaniline samples obtained at different mixtures EtOH/H$_2$O; (b). Area ratios of 1300cm^{-1} / 1245 cm^{-1} bands (■) and 1477 cm^{-1} / 1560 cm^{-1} (♦) in FTIR spectra of polyaniline samples obtained at different mixtures EtOH/H$_2$O

We believe that these results are very important. They are supported by the amount of polymer obtained by polymerization in all ranges of compositions. The variation of amount of polymer is represented in figure 4. It should be noted that in EtOH we obtain the minimum amount of polymer. In the presence of EtOH, ANIHCl has a smaller conductivity (fig.1b) and APS is not soluble.

Reduced amount of polymer suggests that ANIHCl must be dissociated and ionized in solution of initiator for an efficient polymerization.

For this reason all polymerization systems of ANI contain water, if not totally, in a large part [1-22].

The influence of nanostructuration of initial water/ ethanol mixtures induces a structural change of the obtained polymer. The way the state of solubility of the monomer affects the final polymer structure is exemplified by IR spectra modification (fig. 5a). Absorption band at 1300cm^{-1} corresponds to C-N stretching vibration of the leucomeraldine component and the band at 1245 cm^{-1} is

attributed to protonated C-N groups [12, 16, 20, 22]. The intense band at 1140cm^{-1} is assigned to C-H bending vibrations of pernigraniline and is considered to be a measure of delocalized electrons specific to the quinoid units [12, 16, 22]. The bands at 1477 cm^{-1} and 1560 cm^{-1} are assigned to stretching vibrations of C=C in benzenic and quinoid rings respectively. Finally the 1,4-C-H aromatic out of plane vibrations are showing a low intensity band around 800cm^{-1}. In conclusion the polyaniline synthesized in this work consist in emeraldine salt.

Figure 5b shows that by increasing the water/ethanol ratio, the leucomeraldine state is promoted and the development of pernigraniline state is disfavoured.

SEM images of synthesized polyaniline in EtOH/H$_2$O mixture were obtained (fig. 6). At high magnifications PANI presents nanostructures dependent on EtOH/H$_2$O fraction.

If we use only water as solvent, ovoid particles with the length over 150nm are obtained. As the alcohol concentration increases up to 50% molar, the particles
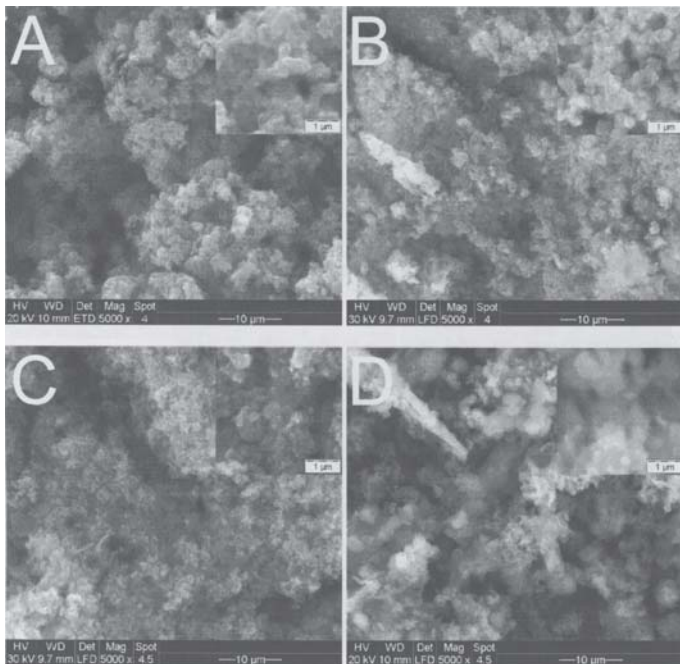
Fig. 6. SEM images of synthesized polyaniline
obtained at different molar fractions of water:
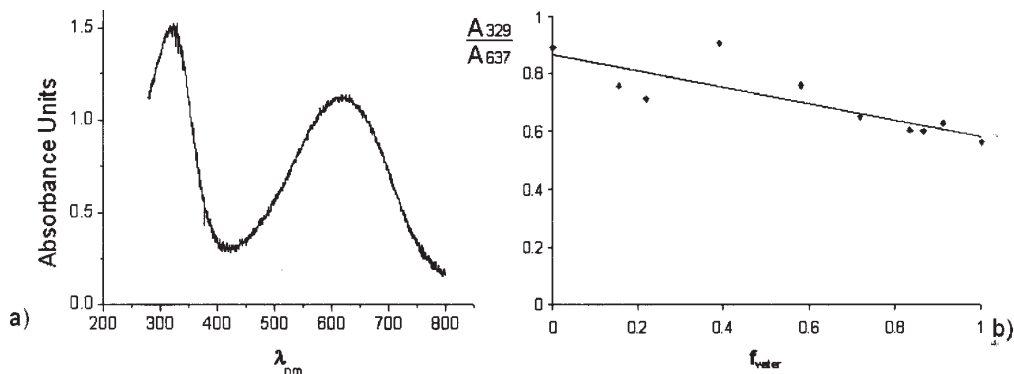A) 1;
B) 0.833; C) 0.58; D) 0

Fig.7.(a) UV-vis spectra of polyaniline; (b) Area ratios of π-π^* transitions bands to the exciton transitions bands
at different mole fraction of water

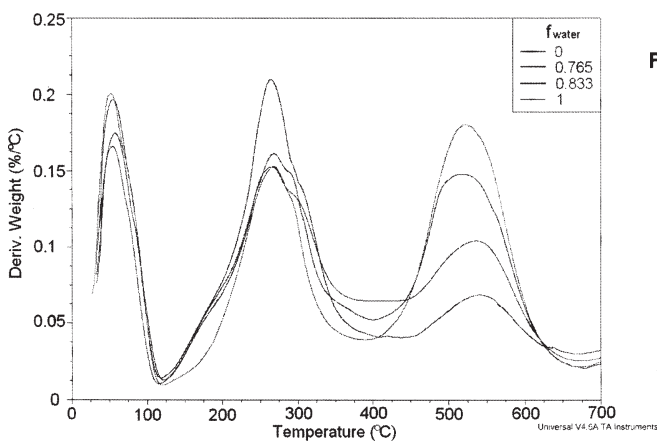Fig. 8. The DTG analysis - derived weight loss for PANI obtained
from ANIHCl in ethanol/water mixtures and APS, synthesized in
conditions of table 1

Fig. 9. Water molar fraction (F) contained by polyaniline samples at
different molar fractions of water

become smaller (50-60nm). Also, we can see the appearance of large conglomerates, with the concentration of ethanol exceeding the molar fraction 1/5. This can be explained by the increasing of environment hydrophobicity and related to the solution conductivity. Thus, new centers of nucleation occur during synthesis, and the polymerization takes place both on the particles already formed, as well in solution.
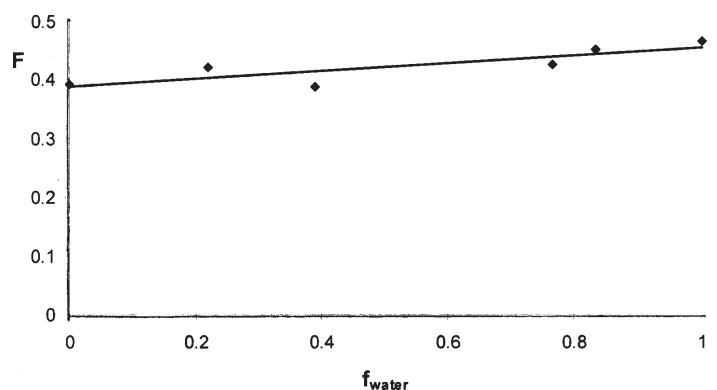
The UV-VIS polyaniline spectrum (fig. 7a) in a solution of n-methylpyrolidone presents two bands with maximum absorption at 329nm and 637nm, indicating its conductive state. Maximum observed at 329nm is assigned to π-π^* transitions in benzoic units, and the maximum of 637nm is attributed to exciton transition (conductive form) in the units diimino-quinoide [16, 21]. It is shown in figure 7b that a linear decrease of area ratios of π-π^* transitions bands to the exciton transitions bands occurs. It is very well correlated with figure 5b. This fact reinforces the idea that the conductivity is increasing with the molar fraction of water of synthesis conditions.
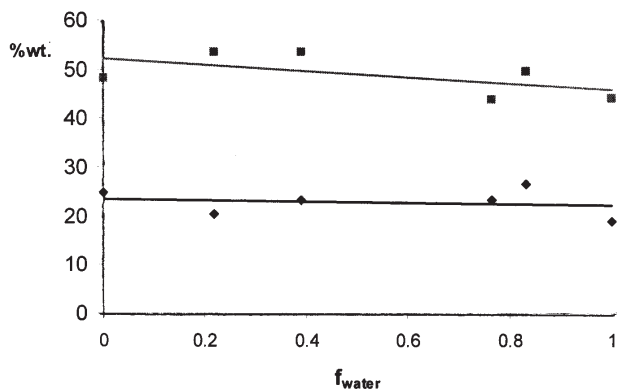
Fig. 10. Gravimetric residue (■) and doping (♦) of polyaniline samples at different molar fractions of water.

The thermal degradation was followed by TGA-DTG using a heating rate of 10°C/min and inert atmosphere (nitrogen). DTG curves showed three specific intervals for the weight loss (fig.8). The first interval up to 120°C is assessed to the loss of water molecules. For the second interval between 120-300°C, we assume to the elimination of dopant (the hydrochloric acid from ANIHCl). The weight loss on 300-700°C interval corresponds to polymer chain degradation [6, 12, 20].

The molar fraction of water contained by PANI samples for the different water/ethanol ratios used in synthesis is shown in figurte 9, where a direct proportional dependence can be observed. The DSC analysis (not shown here) did not reveal the water of crystallization. This fact could be explained by the bonded water nature. The residue at 700°C (fig. 10) and dopant weight loss in polyaniline samples at different molar fractions of water are very slightly influenced by the reaction medium. This indicates that the initial water/ethanol ratio affects more the conformation of the chains (as above described FTIR, UV-VIS, morphology) and not the polymer chain nature (network grafted or cross-linking effects) .

Conclusions

Water/ethanol mixtures in presence of monomer hydrochloride as proved by the conductometric, spectrophotometric and refractometric investigations are far from ideal solutions and promote a partitioned system, for the polymerization process. By controlling this key parameter (water/ethanol ratio) the polymerization can be shifted from a dispersion process to a solution one followed by precipitation. In the final stage of the polymerization the precipitation (and aggregation) occurs in both cases, that is why is difficult to assess the particles dimension in the dispersion media. However the water/ ethanol ratio acts on two major domains (as shown on FTIR, UV-VIS and conversion results: i) one represented by domains over 0.8 molar fraction of water which favours the monomer conversion (ANIHCl mobility is high in the initial polymerization stage) and ii) bellow 0.8 molar fraction of water when the conversion is slightly restricted (at the same reaction time), but since a higher amount of ethanol is present in the polymerization system, the secondary phase of the polymerization process is influenced (large polymer chains growing with more pronounced hydrophobic character). This second domain (rich in ethanol), as demonstrated by the FTIR and UV-VIS results, ,promotes the pernigranilne conformational state with higher delocalization of the electrons. From the best of our knowledge this is for the first time when is demonstrated,

that this key factor (water/ethanol ratio) can adjust by one hand the monomer conversion and the emeraldine segmental chain nature. Since the ammonium persulfate is not soluble in organic media (i.e. only EtOH), the state of ionization of partners is reduced. That is why the conversion is reduced and the quinoid forms (pernigraniline) are also favored. The structural properties of PANI are affected by the initial structure of polymerization media. The associated morphology (of the final product) sustained all the aspects described above by indicating smaller dimensions of the elementary particles (found in the aggregates) for the samples obtained with large amount of water (because of a higher number of initiating centers)

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