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Nanostructured phenomena during the aniline polymerization in water

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Aniline hydrochloride (ANIHCl) polymerization in aqueous phase implies several non-disclosure issues involving polyaniline formation mechanism. New findings emphasized the direct influence between the initial state of the synthesis media (found as a colloidal dispersion) and the polymer formation and structure. The colloidal aggregation occurred by a self-assembling phenomenon (at specific monomer concentrations). This affects the monomer conversions and polymer network structure. This phenomenon was observed by several simple means (refractometry, conductometry, FTIR, UV-VIS, TGA-DTG and SEM analyses). An optimal ANIHCl molar concentration (0.5mol/l) was found for attaining high monomer conversion (over 95%).

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1. Introduction

Polyaniline (PANI) was intensively investigated in many works due to a high interest for conductive polymers. The electrical properties (mainly for the doped emeraldine salt form) were focused on different applications (i.e. conductive, antistatic, anticorrosive coatings, sensors and actuators, conductive fibres, electromagnetic shielding, and flexible electrodes) [1-18].

Aniline hydrochloride (ANIHCl) polymerization in aqueous solutions in presence of ammonium presulfate (APS) is a frequent method for PANI synthesis. But from the best of our knowledge very few information are found involving the formation mechanism. The main part of the publications on materials synthesis (by this method) are reporting restricted conversions for the monomer (around 80%) and do not explain the initial polymerization system and his role on the final polymer. Moreover the influence of the initial ANIHCl concentration is not explored. That is why in this paper we show that in fact the initial state of the polymerization system is fully responsible for the final polymer structure.

In a previous study we verified that polymerization systems such as nanostructured ethanol-water mixtures which can promote the selective solubilization of ANI in the hydrophobic areas as a result of an assembling process [19]. This assembling process is a consequence of the polar monomers nanostructuring [20-22] (i.e. acrylamide [23], vinyl acetate [24] methacrylic acid, acrylic acid [25]).

Therefore, the present study brings new elements on ANIHCl in aqueous medium (which is not an ideal solution), ANIHCl/water ratio influence on the polymer formation (monomer polymerization conducted at high conversion –over 95 %-) and on polymer networks configuration (chains with different oxidation states).

2. Experimental

Polymer synthesis

The polymerizations in water were carried out in reactors equipped with magnetic stirrers (350 rpm) in a ice water bath (~ 4°C).

A typical procedure consists in ANIHCl added in water to obtain different concentrations; ten portions of 2g ammonium persulfate (APS) are added every 10 minutes (20g total amount) in the solution after solubilization and cooling (about 15 minutes). This step was intended to identify how much APS the system require to initiate (as the colour turns dark), indicating the beginning of polymerization. The mixture was continuously stirred for 2 hours, and then washed with HCl 0.1N. The samples are filtered and purified by washing with acetone.

Characterization

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

The ionic conductivity of mixtures was measured with a conductometer Radelkis OK-102-1 at 25°C.

UV spectra were determined on samples diluted in 1 methyl-2-pyrrolidone. It was used a Nicolet Evolution 500 spectrophotometer (Thermo Electron Corp).

FTIR spectra were measured with a Bruker Tensor 37 instrument with ATR diamond crystal.

SEM images were obtained with a FEI Quanta 200 instrument.

Thermal analysis (TGA, DTA, DSC) were performed in nitrogen at a heating rate of 10°C / min using a TA Instrument SDT Q-600 device.

3. Results and discussion

A large domain of ANIHCl molar fractions (0÷0.8) in water was covered by refractive index measurements, UV-VIS absorbance spectra and conductometric analyses. The refractive index dependence on ANIHCl molar fractions seems very similar to ideal solutions (Figure 1a) (almost linear dependence), this result suggesting a good dissociation of the ANIHCl molecules by a fine hydration process.

The linearity seemed clear on the binary solutions 0.07 - 0.7mol/l water- aniline hydrochloride, but the later analyses confirmed the slight deviation tendency, in a more radical manner. In order to verify this aspect, UV-VIS absorptions were measured in the same compositional points investigated by refractometry. In Figure 1b is shown that the molar absorption in UV region (λ≈280nm) do respect the Beer-Lambert law ($A = \varepsilon c l$ where A is the absorbance, ε is the molar extinction coefficient, c is the concentration of the species and l is the pathway). The absorption band at 280nm is related to the n-π* transitions [1]. In this case the linear character is no longer respected, indicating a possible self-assembling as the monomer concentration increases (with a higher degree of association in the most concentrated solution).

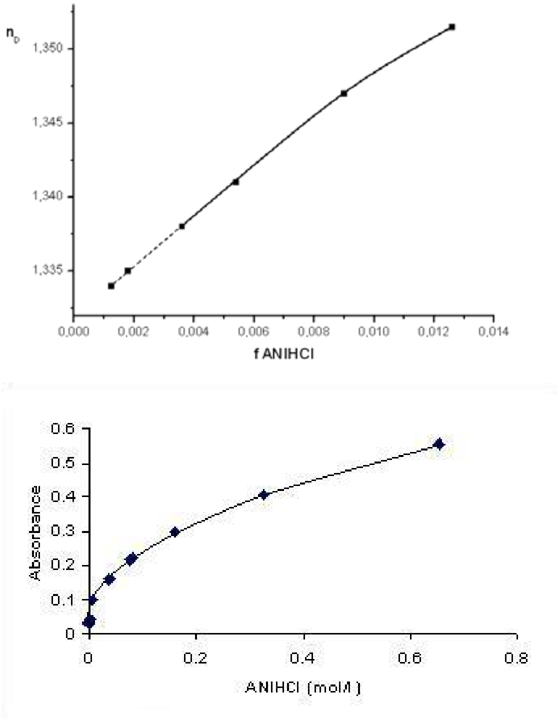

Fig. 1a. Change of refractive index for the mixtures ANIHCl – water. b. The change of absorbance of n-π transitions in UV-VIS spectra for the ANIHCl-water mixtures related to the molar concentration of aniline hydrochloride.*

As indicated to this point so far, the self-assembling could be present, but should be verified also in another property direct involvement. In this context a supplementary investigation was followed, with the following assumption: If the ANIHCl assembles, the dissociation in the water phase should be lower, which in terms of conductivity, would be translated as poorer electrolyte character (which is not the case of ANIHCl ionic nature). It is well known that good electrolytes possess also a linear dependence between conductivity and molar fraction. The conductometric results revealed particular changes in the conductivity of the mixtures ANIHCl – water (Figure 2). The domain up to 0.3 ANIHCl/water, is almost linear indicating a good dissociation of the ANIHCl ions with good mobility (in good agreement with his ionic nature). After this ratio the dependence is no longer linear and the electrolyte character is suddenly altered. The conductivity is also restricted by a lower dissociation of the ions as the ANIHCl/water ratio increases, and the self assembling is again confirmed.

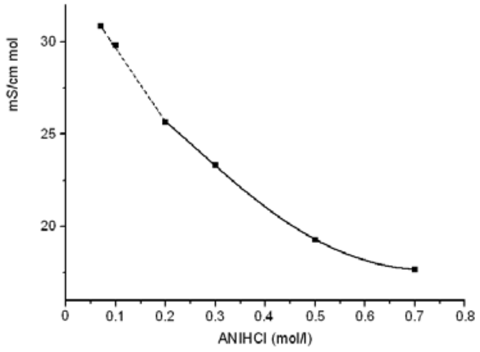

Fig. 2. Changes in the conductivity of the mixtures ANIHCl – water. ● - solution conductivity; ■ - molar conductvity of ANIHCl.

As we described in the experimental section the APS adding was done in small portion to evaluate the necessary amount for polymerization start. It was considered that the amount of APS added (proportional to the time of the polymerization) could be correlated with the access of either the dissociated phase or to the self-assembled phase. The dependence (Figure 3) between the APS amount required for starting the polymerization and the ANIHCl molar fraction clear indicates the favourable cases of self-assembled phases. The mixtures colouring with less ANIHCl dissolved occurs after a long time. This is in good agreement with polymerization theory because of a lower probability for the initiators molecules to meet the high dissociated ANIHCl. The effect of the opposite phenomenon (at higher ANIHCl concentration) is drastically increased also by the pseudo-bulk polymerization occurred in the assembled phase (well known in dispersion polymerization techniques)

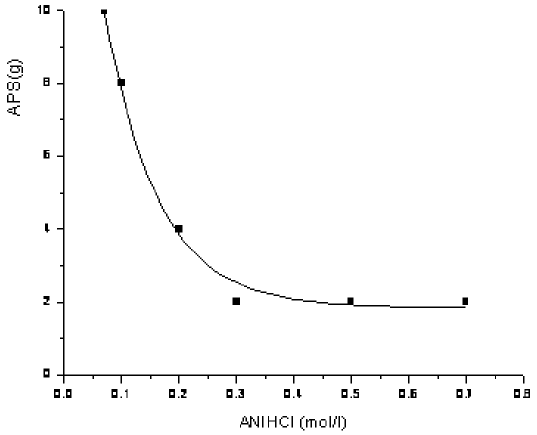

Fig. 3. The variation of the amount of APS needed for starting the polymerization with the molar concentration of ANIHCl.

The observed enhancement in terms of polymerization kinetic is in good agreement with the monomer conversions (larger amounts of polymer as ANIHCl concentration increases).

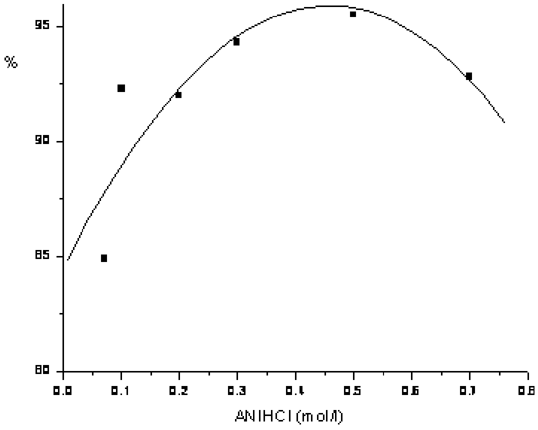

Fig. 4. The variation of amount of polymer formed according to the different concentration of ANIHCl.

The results obtained for ANIHCl ratio around 0.5 showed a final conversion over 95%. The polymerization process can be driven at high conversions by tuning the ANIHCl concentration.

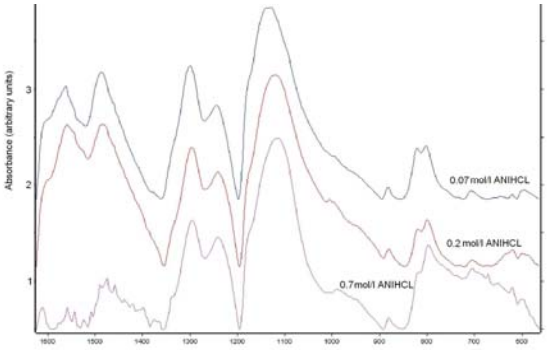

Fig. 5. FTIR spectra of polyaniline samples obtained at different concentrations of ANIHCl.

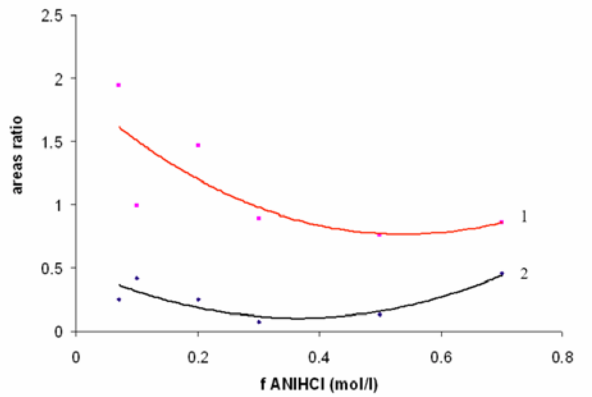

Fig. 6. Area ratios of 1300cm^{-1} / 1245 cm^{-1} peaks (1) and 1477 cm^{-1} / 1560 cm^{-1} (2) in FTIR spectra of polyaniline samples obtained at different concentrations of ANIHCl.

Form the FTIR spectra of polyaniline samples obtained for each compositional fraction (Figure 5) all the specific bands absorption were found: at 1300cm^{-1} corresponds to C-N stretching vibration of the leucomeraldine component and the band at 1245 cm^{-1} attributed to the protonated C-N groups; the intense peak at 1140cm^{-1} assigned to C-H vibrations in plane of pernigraniline, typical for delocalized electrons. The bands at 1477 cm^{-1} and 1560 cm^{-1} are assigned to stretching vibrations of C=C in benzenic and quinoid rings respectively. C-H out of plane vibrations in the ring 1,4 are indicated by a low intensity band around 800cm^{-1}. [5,6,7,12,16,18,20,22,26,27]. As shown above the obtained structure corresponds to emeraldine. The emeraldine structure can be controlled towards a more delocalized state (by favouring the quinoid segments) as a function of ANIHCl concentration. This is key factor for controlling the polymer formation mechanism, by the initial synthesis parameters and the state of the dissociated monomer.

The ratio between specific peak areas of C-N from leucomeraldine oxidation state and of protonated C-N groups was calculated for each compositional point used in the synthesis process (Figure 6); and in the same manner the ratio between specific peak area of benzenoid and quinoid rings. The pernigraniline state has a higher concentration towards leucomeraldine at 0.3 mol/l ANIHCl initial concentration. Having these parameters the emeraldine segments share can be chosen by adjusting the monomer molar fraction.

In agreement with the literature the UV-VIS spectrum of polyaniline in solution (n-methylpyrolidone), presents two bands with a maximum absorption around 325nm and 620nm, specific for the conductive state[16,21]. The maximum observed at 325nm is assigned to π-π* transition in benzenoid units, and the maximum of 620nm is attributed to exciton transition (conductive form) found in the diimino-quinoide units. The area ratios of π-π* transitions bands over the exciton transitions bands are shown in Fig. 7. The conductive form of polyaniline is not dependent on the concentration of molar fraction of monomer. We can find an increase of non-conductive polyaniline at small concentration of ANIHCl as we have seen in Fig. 6.

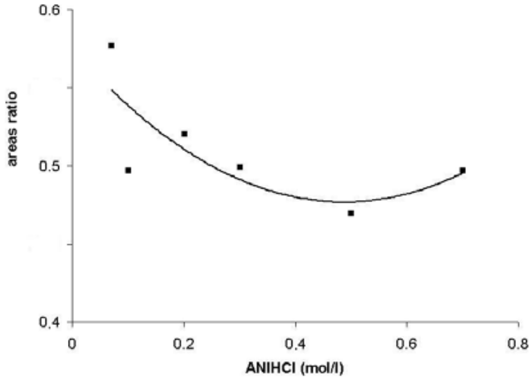

Fig. 7. Area ratios of π-π transitions bands over the exciton transitions bands ($A\lambda_{620nm}/A\lambda_{325nm}$) at different mole concentration of ANIHCl in UV-VIS spectra.*

SEM images of synthesized polyaniline were obtained from various ratios of anilinium chloride / water (Figure 8). The aggregation tendency is very strong for all investigated samples, However, the polyaniline elementary particles were found in the sub-micron domain. In case of lower ANIHCl the aggregation tendency is a smaller, well-shaped particle predominate. The morphology suggests associated diameters smaller then 50nm. This involves a high specific surface area of the final powders. Several generations of particles (from tens of nanometers to 1µ) are obtained by the increasing of the concentration of monomer. Thus we obtain polyaniline particles with a crystal-like morphology. This can be explained by an increased degree of association of active centers.

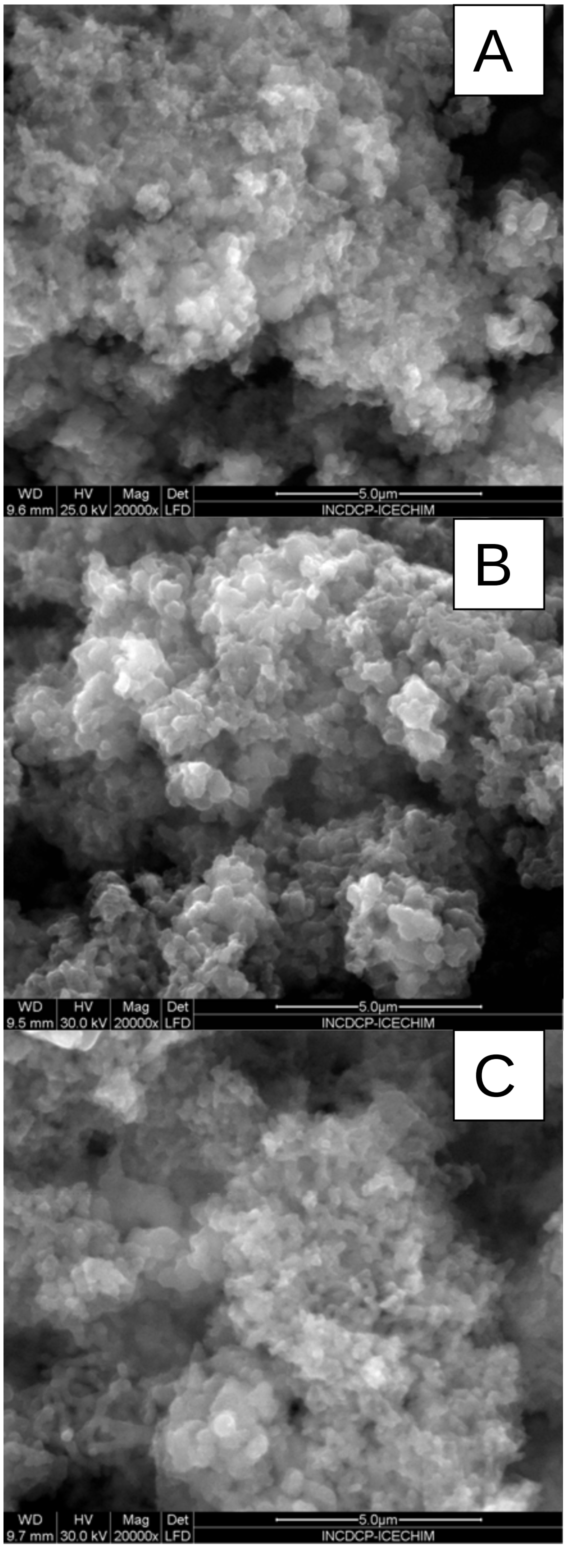

Fig. 8. SEM images of synthesized polyaniline obtained at different molar concentrations of ANIHCl: A) 0.07 mol/l; B) 0.3 mol/l; C) 0.7mol/l

TGA curves (Fig. 9) showed three steps of weight loss. The first step, up to 120ºC is attributed to the loss of water molecules. The second area in the range of 120-300°C, is related to the elimination of the dopant. The weight loss in the area of 300-700ºC corresponds to polymer chain degradation [6,12,28].

The doping degree slightly increases and the absorbed water slightly decreases with the concentration of monomer. We can find the same thermal stability in all samples; the residue left after the degradation of polymer is not dependent on the initial synthesis conditions.

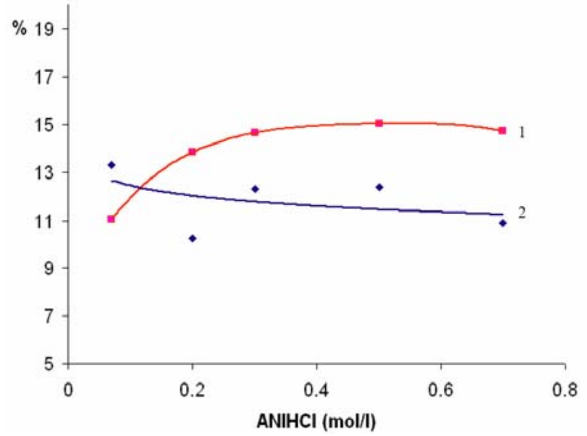

Fig. 9. Gravimetric loss fraction of water (1), and dopant (2) contained by polyaniline samples at different concentrations of ANIHCl.

4. Conclusions

The synthesis system for obtaining PANI, starting from ANIHCl monomer in aqueous phase is far from a solution polymerization. The ANIHCl/water mixture at high monomer concentration promotes the self-assembling of the organic molecules. The amount of initiator (APS) necessary for the synthesis start is lower on high ANIHCl loads. There is an optimal monomer molar ratio (0.5 to water) for which high conversions are attained (over95%). The PANI formation mechanism can be controlled by the monomer molar ratio adjustment. By regulation of the ANIHCl/water ratio the PANI structure can be designed by controlling the network segments found in different oxidation states (leucomeraldine/pernigraniline). To the best of our knowledge, this is the first time we demonstrate the real state of the initial polymerization system and his key role on the polymer synthesis and structure.

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