Nanoobjects of interpolymer complexes of polyaniline and PAMPSA in aqueous solutions

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Abstract. Nanoobjects of interpolymer complex of polyaniline (PAn) and polysulfonic acid have been synthesized. The matrix chemical synthesis of PAn was carried out in aqueous solution at room temperature in the presence of poly-(2-acrylamido-2-methyl-1-propane-sulfonic acid) (PAMPSA) as a matrix. The choice of PAMPSA was determined by its good solubility in water, perfect film-forming properties and high molecular weight (~ 2000000). The polymerization process of aniline on PAMPSA took place at pH ~ 2 on the polymer backbone at high rate, while aniline concentration was sufficiently low. The true solution of PAn-PAMPSA interpolymer complex was coated on mica substrates. We have studied PAn films surfaces using FEMTOSCAN atomic force microscope (AFM) in dependence on the solution concentrations and the presence of strong electrolyte (HCl).

1. Introduction

Polyaniline (PAn) is the most cheap and promising conducting polymer for various applications. From this point of view the preparation of PAn soluble in water and water/organic mixtures is a key technological problem. In this context interpolymer complexes of PAn with various types of polysulfonic acids are of great interest both to theory and practice.

Synthesis of polyaniline in the form of nanotubes, nanocylinders, nanofibers, etc. opens prospects of designing various nanodevices used as high-sensitive detectors and sensors. The following methods are most commonly used for preparation of the above mentioned structures. The first method consists in performing a template-free chemical synthesis in the presence of different sulfonic acids as a dopant [1-7]. In the presence of these dopants in the solution the nanotubes and nanowires of different sizes are formed depending on the polymerization conditions and nature of dopant. In the papers [8-9] oriented PAn nanowires were also prepared electrochemically without using a template. Another method is the chemical polymerization of aniline inside nanoporous templates such as polycarbonate and alumina membranes [10-11]. Polyaniline nanofibers (nanotubes) were also prepared by electrochemical synthesis using cyclodextrin as a molecular anchor [12] and Al₂O₃ as nanoporous templates [13]. The main advantage of these template methods is that one can prepare micro/nanotubes of conducting polymers with controllable length and diameter. Separation of the tubes is achieved by means of dissolution of the supporting plate. However, the removal of the
template often affects PAN nanostructures. In the paper [14] a self-assembly processes were performed in the presence of porous template to prepare highly oriented arrays of PAN nanowires. Biomolecules (DNA) may serve as template for formation of the nano-sized interpolymer complex with PAN [15-16]. Very interesting data on the formation of nano-sized interpolymer complex between polyacrylic acid and PAN were obtained in [17].

2. Experimental
PAN was prepared by oxidative polymerization of aniline in aqueous solution in the presence of poly-(2-acrylamido-2-methyl-1-propane-sulfonic acid) (PAMPSA) used as a matrix, and ammonium persulfate as an oxidant. PAMPSA in the form of a 15-wt % aqueous solution (Aldrich), and ammonium persulfate of reagent grade were used as received. Aniline of reagent grade was distilled at a reduced pressure in a nitrogen atmosphere prior to the synthesis. The synthesis was performed at room temperature while successively mixing solutions of PAMPSA, aniline and ammonium persulfate in water. The ratio of aniline to PAMPSA in the reaction mixture was 1:2 mole/mole-unit, and that of aniline to oxidant was 2:1 mole/mole. The concentration of aniline in the reaction mixture was 4 mM. Spectral measurements in the visible region of spectrum were conducted on a diode-array spectrophotometer Ocean Optics PC 2000. To remove the impurities of oxidant and short oligomers after the end of the synthesis PAN-PAMPSA-complex was deposited from the solution by dioxane and then dissolved in water again. Small volumes of the solution were cast onto a mica substrate and then heated at 50-60°C. After the evaporation of solvent we examined the surface of the prepared samples using a Femtoscan AFM microscope (Advanced Technologies Center, www.nanoscopy.net).

3. Results and discussion
Spectral changes during the chemical synthesis of polyaniline in the presence of PAMPSA are demonstrated in Figure 1. At the first stage absorbance simultaneously increases at 320 nm and 650 nm, which corresponds to the accumulation of amine and quinoid forms of aniline, respectively [18]. This process has typical autocatalytic nature. In the second stage we observed fast shift of the absorption maximum at ~ 600 nm to the red area near ~730 nm reflecting the formation of localized polarons and rise of absorbance at 435 nm (cation-radicals) [18].

![Figure 1. Optical absorption spectra of the reaction solution during chemical synthesis of PAN in the presence of PAMPSA. 1 – 120 s, 2 – 370 s, 3 – 470 s, 4 – 570 s, 5 – 590 s, 6 – 610 s, 7 – 700 s.](image-url)
of the oxidized units reaches some critical point, a rapid polymerization occurs, during which green semi-oxidized form of polyaniline appears [19-20].

It should be noted that the system remains phase-homogeneous on all stages of conversions and PAn-PAMPSA interpolymer complex is soluble in water and water/organic mixers in contrast to ordinary chemical synthesis of PAn in inorganic acids. The polyaniline synthesis in the presence of PAMPSA proceeds at a high rate and at small concentrations of reagents as compared with the ordinary chemical synthesis. This is owing to a high degree of association of aniline on PAMPSA, which ensures a high local concentration of aniline and hydrogen ions.

After the end of the synthesis PAn-PAMPSA complex was deposited from the solution and then dissolved in water to obtain the following concentrations: 0.4 and 0.024 mM. AFM-images of PAn-PAMPSA interpolymer complexes on mica substrates are presented in Figure 2. We can see that at higher concentrations interpolymer complexes of PAn-PAMPSA form labile associates that easily dissociate at low concentrations. The principal feature of PAn-PAMPSA solutions is the existence of separated nanoobjects of PAn-PAMPSA complexes in sufficiently dilute solutions. These solutions are very stable.

![AFM images of PAn-PAMPSA nanoobjects on mica substrates coated from aqueous solutions of PAn-PAMPSA interpolymer complexes of different concentrations: a) 0.4 mM and b) 0.024 mM.](image)

AFM data of PAn-PAMPSA nanoobjects at various scales are presented in Figure 3. Rod like nanoobjects were observed over the substrate. Their sizes range within 2-10 nm (height), 20-40 nm (diameter) and 50-300 nm (length). These values are characteristic of the polymer molecules of PAMPSA used in our experiments. It indicates that we have obtained true solutions of the interpolymer complexes PAn:PAMPSA in water. Nevertheless in dilute solutions the association of these complexes takes place to some extent.

![AFM image of PAn-PAMPSA nanoobjects (0.012 mM) coated on the mica substrate from solution containing low-molecular-weight strong electrolyte (0.5 M HCl) is presented in Figure 4. Earlier it was found [21-22] that in these conditions polymer electrolytes may have more compact globular form. The geometrical sizes of globules in Figure 4 are as follows: height– 5-10 nm, diameter – 200-300 nm.](image)
4. Conclusions
The matrix chemical polymerization of aniline on the polymer backbone of PAMPSA proceeds at high rates although aniline concentration is very low. PAn-PAMPSA interpolymer complex formed is easily soluble in water and water/organic mixers. Solutions with low ionic strength are homogeneous molecular dispersed systems. They are very stable at long storage in contrast to well-known PEDOT (poly(ethylenedioxythiophene)) water dispersions. Well separated rod-like PAn-PAMPSA nanoobjects sediment from the low-ionic-strength solutions. Transition to the compact ball-like forms takes place in solutions with high ionic strength. Simplicity of synthesis of the interpolymer complexes of such
composition, as well as easy procedure of preparing their true solutions and coating onto substrates, open great opportunities for designing nanodevices for various applications.

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