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# Ultrafine nano-colloid of polyaniline

S. Dorey[a,b], C. Vasilev[b], L. Vidal[b], C. Labbe[a,b], N. Gospodinova[a,b,*]

[a]*Laboratoire de Chimie Macromoléculaire, Ecole Nationale Supérieure de Chimie de Mulhouse, 3 rue Alfred Werner, 68093 Mulhouse Cedex, France*
[b]*Institut de Chimie des Surfaces et Interfaces, 15, rue Jean Starcky, BP2488, 68057 Mulhouse Cedex, France*

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## Abstract

We report a synthesis of polyaniline (PANI) suspension of particles with size of about 2–3 nm. This nano-colloid was obtained by aniline oxidative polymerization in dilute and semi-dilute solutions of sodium poly(styrene sulfonate) (PSSNa) with molecular weight equal to 6800 g/mol or higher. The ionic strength of the solution was about $1\times10^{-2}$ mol/l, which corresponds to aniline (and, respectively, PANI) concentration lower than $4.6\times10^{-2}$ mol/l in 5 M solution of formic acid. To the best of our knowledge, it is the first communication dealing with preparation of particles with a molecular scale dimensions, using a rigid backbone polymer with a very strong intermolecular interactions. Important modification of the electronic properties of such dispersed PANI, compared to those of the well-known bulk PANI, was observed.

*Keywords:* Polyaniline; Sodium poly(styrene sulfonate); Nano-colloid

## 1. Introduction

Polyaniline has attracted considerable attention because of its unique electronic, optical, electro-optical properties [1]. One of the key problems related to the potential application of PANI is its non-solubility and non-melting. Preparation of PANI in colloidal form: particles, fibers, thin films, gels is the only way to solve the problem of its processability.

The polymerization of aniline in presence of a water-soluble polymer and surfactants in aqueous or aqueous–organic media is one of the basic approaches for preparation of PANI colloids [2]. This was the goal of our previous investigations. We are pioneers in the preparation of suspension of spherical PANI particles stabilized by poly(vinyl alcohol) [3] and in the control of the particle size (in the range between 100 nm and 2 μm) in uniform PANI suspensions [4]. For the first time we obtained a stable fine PANI dispersion in presence of dodecylbenzenesulfonic acid [5], but under the described reaction conditions, suspension of a very broad particle size distribution (5–50 nm) has been formed.

Utilization of strong polyelectrolytes as poly(styrene sulfonic acid) (PSSA) and its sodium salt for synthesis of as called PANI-PSSA and PANI-PSSNa 'composite' or PANI–PSSNa 'complex' was reported earlier [6–8].

Colloidal dispersions of PANI–PSSNa 'composite' prepared by electro-hydrodynamic polymerization in aqueous (+) or (−) 10-camphor sulfonic acid using PSSNa revealed particles with a mean size of 180 ± 10 nm, although particles dimensions of 1000 nm were also observed [7].

PSSNa have been demonstrated as 'good templates' for enzymatic synthesis of PANI [8]. To this end, both the mechanism of formation and dimensions (morphology) of the complexes, thus obtained, have not been investigated.

PSSNa has been frequently considered as a model of a linear polyelectrolyte and, indeed, many of its properties are typical for ionic polymers including the coil contraction due to the increase of ionic strength of solution. One has to note that this contraction is much more pronounced for low molecular weight PSSNa [9].

For the high molecular weight (MW) PSSNa, the coil–globule transition arising from modification of the solvent

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* Corresponding author. Address: Institut de Chimie des Surfaces et Interfaces, 15, rue Jean Starcky, BP2488, 68057 Mulhouse Cedex, France.
*E-mail address:* n.gospondinova@uha.fr (N. Gospodinova).

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quality from θ-solvent (4.17 M aqueous NaCl at 18 °C) to a poor solvent may proceed through a number of 'molten' globular states. Such smooth and continuous contraction of PPSNa coils (MW = 1,000,000 g/mol) below 18 °C was observed by dynamic light scattering [10].

The collapsed state for high molecular weight PSSNa may also represent a sequence of dense spheres connected by regions of loose polymer. In this case, the radius of the spheres is smaller than either the hydrodynamic radius ($R_h$) or the radius of gyration ($R_g$) [11,12].

The expansion of PSSNa coils due to the decrease in a simple electrolyte concentration (NaCl solution of broad range concentration: $10^{-3}$–0.5 mol/l) has been studied by light scattering and sedimentation velocity of dilute solutions of PSSNa of MW = 1,000,000 g/mol [13].

Hence, for understanding the process of aniline polymerization in the presence of a such polyelectrolyte as PSSNa, it is necessary to understand the influence of reaction conditions (e.g. concentration of a simple electrolyte and of a polyelectrolytes, temperature) on the shape and dimensions of PSSNa macromolecules. The practical interest of this study is the possibility to control the shape and the size of particles in PANI–PSSNa colloids, thus affecting the design of composites obtained therefrom.

We have studied standard chemical oxidation of aniline in the presence of PSSNa in conditions (e.g. temperature and the ionic strength of the reaction medium, molecular weight of PSSNa, concentration of PSSNa and aniline), which might have an influence on the conformation (and dimension) of the PSSNa coils. The rate of PANI chains growth and competition between the different pathways of PANI chains association can be affected also (e.g. enveloping of a PANI chain in a PSSNa coil or formation of PANI aggregates).

## 2. Experimental section

### 2.1. Materials

PSSNa samples of MW of 208 (monomer), 1440, 6800 g/mol were purchased from Fluka, PSSNa samples of MW of 70,000 and 1,000,000 g/mol were purchased from Aldrich. Reagent-grade aniline, formic acid and ammonium peroxydisulfate were purchased from Aldrich and used as received.

### 2.2. Polymerization

In a typical synthesis of PANI colloid, to a stirred aqueous solution of PSSNa was successively added the corresponding amount of formic acid, aniline and aqueous solution of ammonium peroxydisulfate. The PSSNa concentration in the reaction medium was $1\times10^{-2}$ g/ml. The concentration of aniline was varied between $4\times10^{-5}$ and $8\times10^{-2}$ g/ml at molar ratio aniline/ammonium peroxydisulfate equal to 1. All the syntheses were performed in 5 M solution of formic acid. Polymerization was carried out at 0, 4 and 18 °C for 10 h.

### 2.3. Characterization of colloids

The shape and the dimensions of PANI–PSSNa particles were observed using appropriate microscopic methods. The electronic properties of the species were studied by electronic absorption spectroscopy.

Specimens for the TEM study were prepared by dropping a dialyzed suspension after careful stirring on carbon-coated copper grids. TEM micrographs were obtained using a Philips CM200 instrument working at 200 kV.

TappingMode atomic force microscopy (TM-AFM) was used for recording of topography (or high) and phase (reflecting the viscoelastic properties of the sample) images of the surface of PANI-PSSNa films. These films were spin-coated from the PANI–PSSNa suspensions on Si wafers cleaned by plasma in humid environment. The bombardment of the surface with energetic ions and molecules results in the removal of surface contaminants. In addition, the availability of water molecules saturates the surface with a hydroxyl groups and provides for a highly hydrophilic surface.

For all TM-AFM measurements we used a Digital Instruments MultiMode™ SPM (NanoScope IV controller). We used commercial silicon TM-AFM tips (type NCL-W) with a free resonance frequency in the range from 172 to 191 kHz and spring constants in the range from 33 to 47 N/m. All measurements were conducted in air.

The electronic absorption spectra of the colloids were recorded on a Shimadzu UV-VIS-160A spectrophotometer.

Wide angle X-ray diffraction was collected from dialyzed and lyophilized colloids as well as from of PSSNa of MW 70,000 g/mol after lyophilizing of its solution in 5 M formic acid. For all measurements we used Philips X'Pert-MPD instrument.

## 3. Results and discussion

Summarizing all available data on the influence of concentration of PSSNa, ionic strength and temperature on the shape and dimensions of PSSNa chains, it has to be noted that some observations (for example dependence of $Na^+$ ion activity coefficient on PSSNa concentration at low ionic strength [14]) indicate a core-shell-like structure of partially contracted coils. The hydrophobic phenylene groups tend to cluster together and force the charged groups to stay on the surface of the coil domain.

Hence, it is reasonable to assume that the partially contracted coils (or 'molten' globules) of PSSNa are capable to 'host' the PANI growing chains in the more hydrophobic 'core' as a result of hydrophobic interactions between the PSSNa and PANI chains. The remaining charges of the polyanion prevent the aggregation of as formed particles.

One may expect that the dimensions of PSSNa contracted coils and the amount of remaining charges depend on the molecular weight and concentration of PSSNa as well as on the ionic strength of the solution. Other parameters that should considerably affect the process of PANI–PSSNa particle formation are the concentration and the growth rate of the PANI chains. At a constant monomer/oxidant ratio, the increase in the aniline concentration leads to increase in the chains growth rate.

In order to examine the influence of the molecular weight of PSSNa on the shape and dimensions of PANI–PSSNa colloidal particles, we have performed an aniline polymerization at the same temperature (0 °C) and ionic strength ($1\times10^{-2}$ mol/l) in dilute solution of PSSNa with MW = 1440, 6800, 70,000, 1,000,000 g/mol, respectively, and also in the sodium styrene sulfonate (monomer) solution. In this case, the above-mentioned level of ion concentration was maintained using much lower concentration of aniline (and PANI, respectively) compared to the concentration of formic acid ($4.5\times10^{-2}$ mol/l of aniline compared with 5 mol/l of formic acid).

The influence of temperature on the particle dimensions in the range 0–18 °C, was studied by carrying out the polymerization at the same reaction conditions with respect to ionic strength for a PSSNa sample with MW = 70,000 g/mol.

To test the influence of aniline concentration on particle dimensions, we have performed the PANI synthesis at gradual increasing aniline concentration ($5.6\times10^{-4}$–$8.5\times10^{-1}$ mol/l) in the presence of PSSNa with MW = 70,000 g/mol.

TEM micrographs of PANI–PSSNa suspensions (Fig. 1) revealed three major types of species differing in their shape and dimensions. As shown in Fig. 1a, the basic size of spherical particles of nano-colloids corresponding to the first group of products is ca. 2–3 nm. This size corresponds to the height measured on the AFM topography image (Fig. 2). The presence of particles of larger diameter (ca. 6–8 nm) is

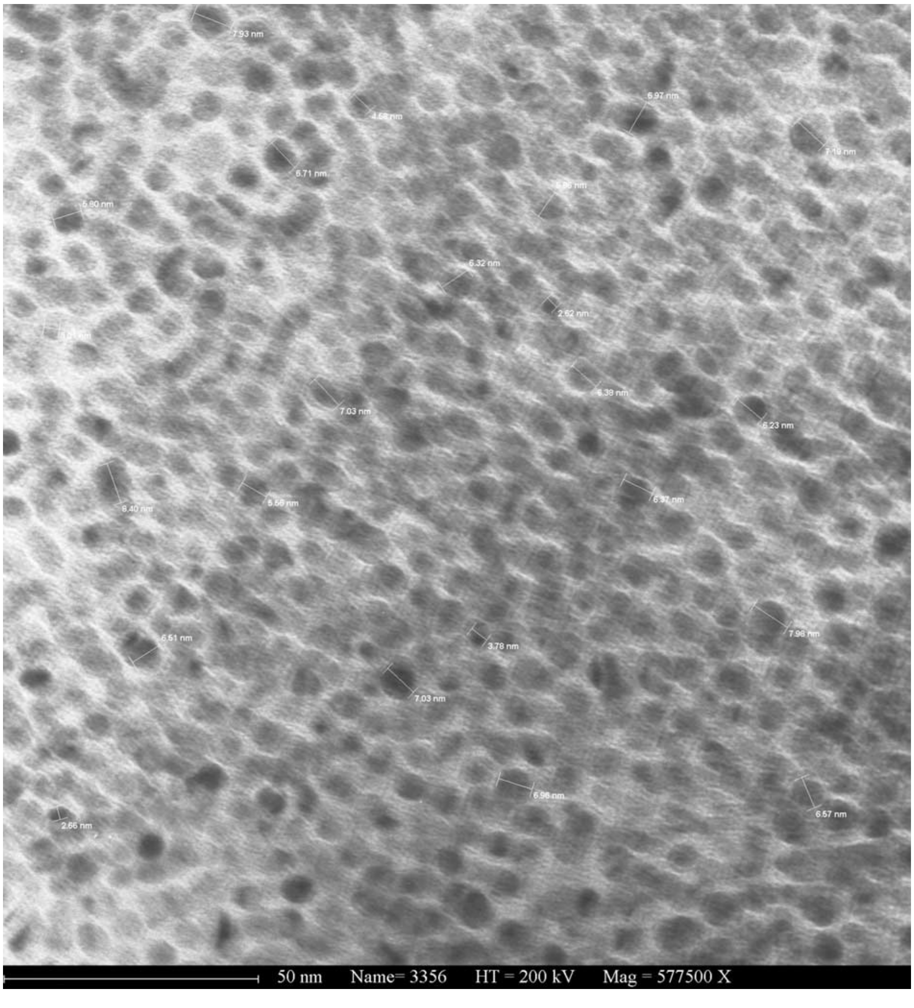

Fig. 1. TEM images of PANI–PSSNa suspension obtained at: (a) $4.5\times10^{-2}$ mol/l aniline concentration in the presence of PSSNa with MW = 70,000 g/mol at 0 °C. (b) The same conditions as (a) by using PSSNa with MW = 1440 g/mol and sodium styrene sulfonate. (c) $8.5\times10^{-1}$ mol/l aniline by using PSSNa with MW = 70,000 g/mol at 0 °C.

related, probably, to possible particle aggregation during the sample preparation. The nano-colloids of particles with such shape and dimensions were obtained for aniline concentration lower than $4.5\times10^{-2}$ mol/l in the presence of PSSNa with MW 6800 g/mol or higher in the whole studied temperature range.

Using a low-molecular-weight PSSNa (MW = 1440 g/mol) as well as sodium styrene sulfonate at the same conditions, leads to formation of aggregates with dimensions of several microns (macroscopic precipitation) consisting of particles with a mean size of 100–130 nm (Fig. 1b).

The suspensions prepared at concentrations higher than the above-mentioned aniline concentration by using of PSSNa with MW = 70,000 g/mol revealed fibrous morphology with a mean diameter of fibrils of 70–90 nm (Fig. 1c).

A comparison between the electronic absorption spectra of PANI–PSSNa suspensions of particles with size of about 2–3 nm and those consisting of particles with diameter of several tens of nanometers indicates an important shift of the absorption maxima towards shorter wavelengths (≈750 nm compared to >800 nm). Moreover, as shown in Fig. 3, for particles with diameter of 2–3 nm, a decrease in the absorption in the range of 700–800 nm due to the transition from 'emeraldine' salt (conducting form) to 'emeraldine' base (non-conducting one) is observed at $pH>8$. The same well known transition for bulk samples or for the suspensions of PANI particles with diameter of several tens of nanometers is typically detected at $pH>4$.

The relationship between the position of the absorption maxima and the MW of PSSNa used (Fig. 4), aniline concentration (Fig. 5) and polymerization temperature (Fig. 6) are similar to the relationship between these reaction conditions and PANI–PSSNa particle dimensions, measured on TEM images.

These results allow us, for the first time, to reveal a relationship between the electronic transport in PANI (and eventually its electrochemical activity) and the level of its dispersion (in our study this corresponds to different size of the particles).

In order to confirm our hypothesis on the relationship

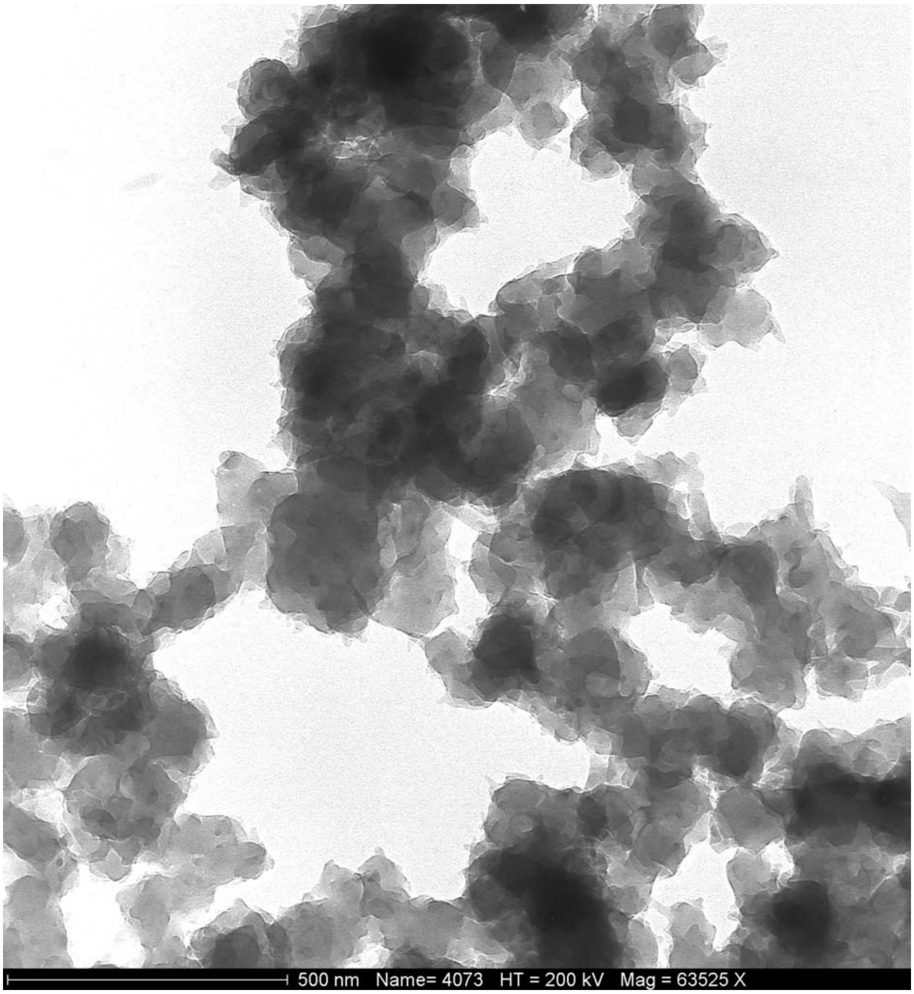

Fig. 1 (*continued*)

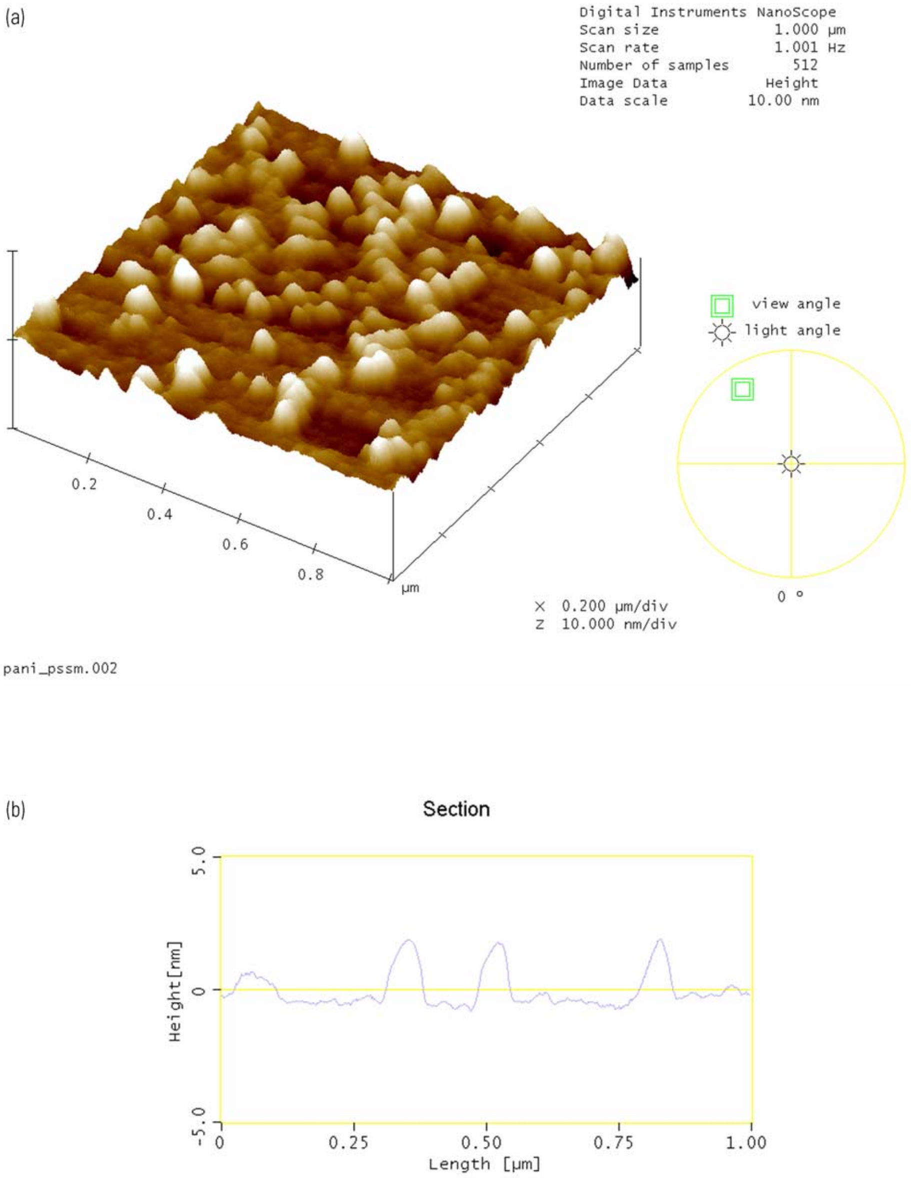

Fig. 2. Topographic AFM image (a) of a thin film obtained by deposition of PANI–PSSNa suspension. A cross-section of the image (b) shows that the height of PANI–PSSNa particles is about 3 nm. The size of the image is $1\times1\ \mu m^2$ and the $Z$-range is 10 nm.

between the dimensions of PSSNa coils and those of PANI–PSSNa particles, we have calculated the dimensions of PSSNa coils (hydrodynamic radius, $R_h$, radius of gyration, $R_g$, and end-to-end-length, $h$) by using of well-known empirical and theoretical relations.

At θ-conditions (4.17 M NaCl solution at 18 °C), the value of the characteristic constant is given as $R_{g_\theta}/M = 3\times10^{-3}$ for a completely sulfonated PSSNa, where $M$ is the molecular weight of PSSNa [9]. This corresponds to a constant value $R_{h_\theta}/M = 1.3\times10^{-4}$, if one considers the following Akcasu–Han relation $R_{h_\theta}/R_{g_\theta} = 0.664$ [15].

The values for $R_{h_T}$ and $R_{g_T}$ corresponding to an ionic strength of $1\times10^{-2}$ mol/l and 18 °C (θ-temperature) were calculated using the relation $\alpha_\eta^2 = R_h^2/R_{h_\theta}^2$ [16] and $R_h/R_g = 0.6$ at low salt concentration [13], where $\alpha_\eta^2$ is an expansion factor calculated according to empirical relation [17]:

$$\alpha_\eta^2 = 6.4\times10^{-2}M^{1/4}I^{-1/3} + 1.1$$

where $I$ is the ionic strength.

The values for $R_{h_0}$ and $R_{g_0}$ corresponding to an ionic strength of $1\times10^{-2}$ mol/l and 0 °C were calculated using a factor $\alpha_T = R_{h_0}/R_{h_T}$, experimentally determined by Serhatly et al. [10] at low salt concentration ($\alpha_T = 0.45$), and $R_{h_0}/R_{g_0} = 0.6$.

Finally, the values for $h$ and $C$ were calculated using $R_{g_0}$ and the following relations:

$$h^2 = R_{g_0}^2/0.166$$

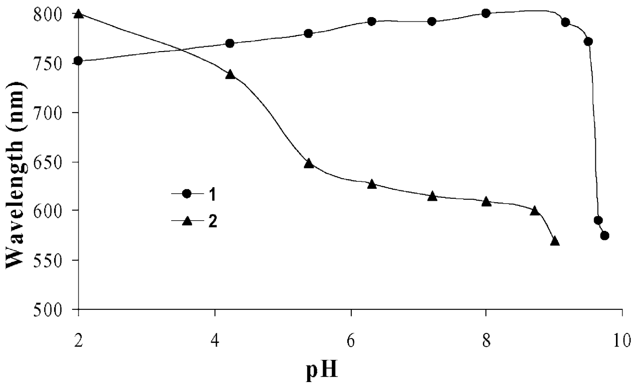

Fig. 3. Dependence of the absorption maxima in the visible range of the electronic spectrum of PANI versus pH of the medium: (1) PANI–PSSNa suspension (particle diameter is 2–3 nm). (2) Bulk PANI (widely published data).

and [13]

$$C = M/R_g^3 N_{av}(2)^2(5/3)^{3/2}$$

where $N_{av}$ is Avogadro's number, $R_g$ is in cm and $C$ is concentration in g/ml (the concentration range lower than $C$ corresponds to dilute solution).

The calculated values are given in Table 1. It is worth mentioning that the calculated value of $R_{g_T}$ for PSSNa with MW = 1,000,000 g/mol is in agreement with the experimental data of Takahashi et al. [18] and Borokhov et al. [13]. At this temperature (18 °C), the PSSNa concentration ($1\times10^{-2}$ g/ml) is higher than the critical value for high molecular weigh PSSNa. At 0 °C, for both MW = 70,000 and 1,000,000 g/mol samples, PSSNa concentration corresponds to dilute solution.

Values for $h$ of PSSNa coils (dilute PSSNa solution of ionic strength $1\times10^{-2}$ mol/l and 0 °C) versus MW of PSSNa are shown in Fig. 7. As one can see, $h$ values higher than ≈2–3 nm, which corresponds to PSSNa with MW of 6800 g/mol or higher, allow obtaining an ultrafine nano-colloid of PANI with particle size of the same order.

These results allow us to propose a mechanism for PANI–PSSNa nano-particles formation considering that a PANI chain can grow inside the 'molten' globule of PSSNa. This is only possible in case of sufficient 'host' volume and strong and regular intermolecular interactions between the two types of macromolecules involved and an appropriate concentration and growth rate of the PANI chains.

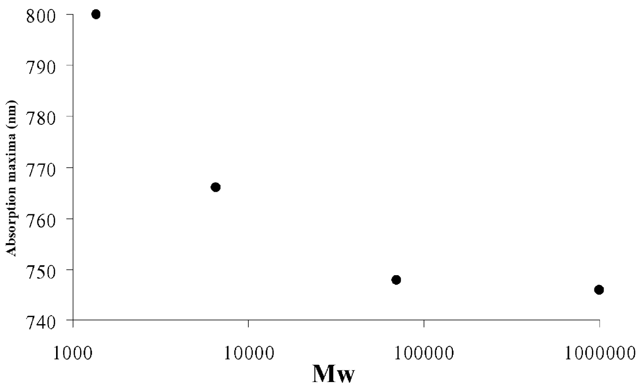

Fig. 4. Dependence of the absorption maxima in the visible range of the electronic spectrum of PANI–PSSNa suspension versus MW of PSSNa.

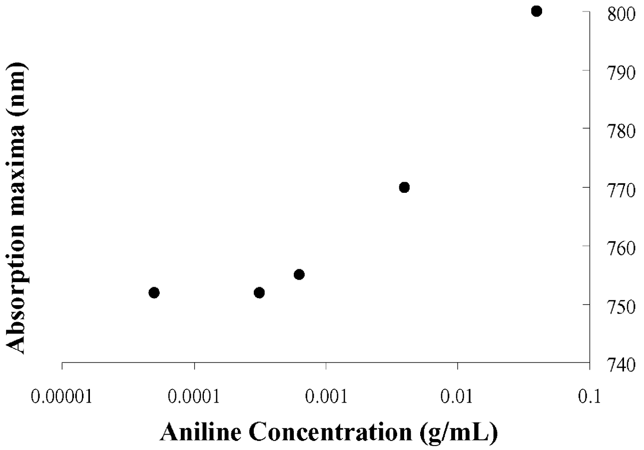

Fig. 5. Dependence of the absorption maxima in the visible range of the electronic spectrum of PANI–PSSNa suspension versus aniline concentration.

A comparison between the positions of the principal Bragg peaks in the X-ray profiles of PANI (2$\theta$ = 16, 22, 26) and PSSNa (2$\theta$ = 17.5, 22.5, 25.5) (not presented here), allow us to consider that these macromolecules are able to establish sufficiently regular intermolecular interactions.

In the dilute solution, with respect to PSSNa and aniline concentrations, both 'molten' globule conformation of PSSNa macromolecules and low rate of PANI growth occurred. In this case, only the 'host' volume of PSSNa determined by its molecular weight controls the nanoparticles formation. If the volume of the PSSNa molten is not sufficiently high, the growing PANI chains are not completely enveloped and hence, formation of aggregates is possible. It is reasonable to suppose that in the presence of

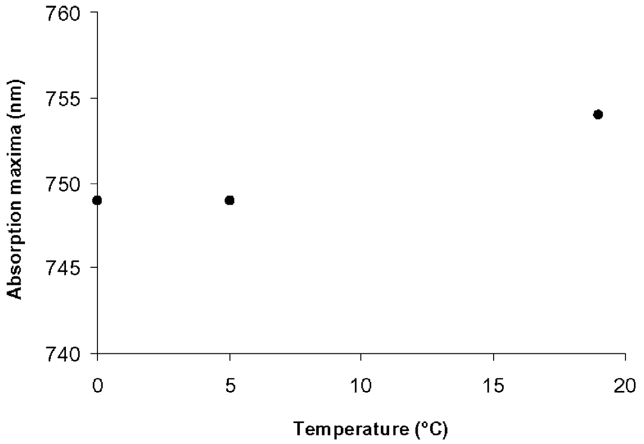

Fig. 6. Dependence of the absorption maxima in the visible range of the electronic spectrum of PANI–PSSNa suspension versus polymerisation temperature.

Table 1
Calculated values for $R_h$, $R_g$, $h$ and $C$ for PSSNa with different molecular weight at θ-conditions (4.17 M NaCl solution, 18 °C), at low ionic strength ($10^{-2}$ mol/l, 18 °C), at low ionic strength and low temperature ($10^{-2}$ mol/l, 0 °C), respectively

| MW (g/mol) | DP[a] | $R^2_{h_\theta}$ (nm$^2$) | $\alpha^2_\eta$ | $R^2_{h_T}$ (nm$^2$) | $R_{h_\theta}$ (nm) | $R_{h_T}$ (nm) | $R_{g_\theta}$ (nm) | $R_{g_T}$ (nm) | $R_{h_0}$ (nm) | $R_{g_0}$ (nm) | $h$ (nm) | $C_0$[b] (g/ml) | $C_T$[c] (g/ml) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1440 | 7 | 0.19 | 2.93 | 0.56 | 0.44 | 0.75 | 0.61 | 1.25 | 0.34 | 0.57 | 1.40 | | |
| 6800 | 33 | 0.90 | 3.80 | 3.42 | 0.95 | 1.85 | 1.43 | 3.08 | 0.64 | 1.07 | 2.63 | | |
| 70,000 | 340 | 9.10 | 5.93 | 53.96 | 3.02 | 7.35 | 4.55 | 12.25 | 2.05 | 3.42 | 8.39 | $1.7\times10^{-1}$ | $1\times10^{-3}$ |
| 1,000,000 | 4854 | 130 | 10.48 | 1362.4 | 11.4 | 36.91 | 17.17 | 61.52 | 7.72 | 12.86 | 31.56 | $4.5\times10^{-2}$ | $4.5\times10^{-4}$ |

[a] Degree of polymerisation.
[b] Critical PSSNa concentration at 0 °C.
[c] Critical PSSNa concentration at 18 °C.

sodium styrene sulfonate the mechanism of particles formation is different compared to the mechanism in presence of PSSNa.

It is worth mentioning that the mechanism of fibril formation at high aniline concentration is not clear. There are many parameters, which could affect the formation of such ordered structures. Higher concentrations of growing rigid PANI chains can probably lead to a formation of structures consisting of aligned, extended chains. To this end, it is not clear what conformation of PSSNa one could observe at these conditions and what is the role of PSSNa chains in the alignment of PANI chains.

## 4. Conclusions

The nano-colloid of PANI particles of size 2–3 nm were obtained by aniline oxidative polymerization in dilute and semi-dilute solutions of sodium poly(styrene sulfonate) (PSSNa) with molecular weight of 6800 g/mol or higher. The ionic strength of the solution was about $1\times10^{-2}$ mol/l, which corresponds to aniline concentration lower than $1\times10^{-2}$ mol/l in 5 M solution of formic acid. To the best of our knowledge it is the first communication dealing with preparation of particles with a molecular scale dimensions by using a rigid backbone polymer with very strong intermolecular interactions. Important modification of the electronic properties of such dispersed PANI compared to those of the well-known bulk PANI was observed.

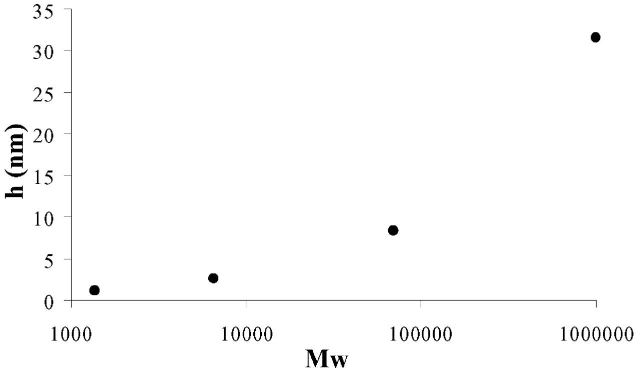

Fig. 7. Dependence of the ‘end-to-end-length’ of PSSNa coils (ionic strength $1\times10^{-2}$ mol/l and 0 °C) versus MW of PSSNa.

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