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ORIGINAL CONTRIBUTION

Colloidal aqueous dispersion of polyaniline nanotubes grafted non-covalently with poly(ethylene oxide)-*block*-poly(acrylic acid) copolymer

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Abstract Polyaniline (PANI) nanotubes were prepared by oxidative polymerization of aniline in the presence of two structure-directing agents—salicylic acid (SA) and sodium dodecyl sulfate (SDS). When using only SA, mainly aggregated nanotube dendrites or coral-like structures have been obtained. Addition of a very small amount of the surfactant SDS, much less than the critical micelle concentration, results in substantial reduction of the aggregated nanotube morphology on the account of isolated PANI nanotubes, which is the favorable structure from the point of view of further modification. In order to make the isolated nanotubes water dispersible, their surface was modified by complex formation (non-covalent grafting) with hydrophilic poly(ethylene oxide)-*block*-poly(acrylic acid) copolymer. These water-dispersible PANI nanotubes might be good candidates for some biochemical and biomedical applications.

Keywords Nanotubes · Polyaniline · Water-dispersible

Introduction

Nanotubes research is currently one of the most active areas of nanoscience. Since the discovery of carbon nanotubes [1] and their solubilization in common solvents [2–5], one-dimensional nanoscale materials including nanotubes or nanofibers have attracted considerable attention. Polymeric nanotubes are particularly interesting because of the large number of chemically distinct polymers that can be used for designed preparation of these one-dimensional structures. Consequently, a very broad range of nanomaterials with different surface and/or interior properties that could find application in advanced technologies and materials can be generated [6–9]. One-dimensional nanostructures of conducting polymers are expected to possess the advantage of both low-dimensional systems and organic conductors [10]. They have a great potential in device applications, such as chemical sensors or actuators, light-emitting diodes, gas-separation membranes, etc., as well as in biotechnology (e.g., delivery agents, pharmaceutical agents) [11–13].

Nanomaterials based on conducting polymers are of considerable interest for a variety of biomedical applications [14]. Their response to electrochemical oxidation or reduction can produce a change in conductivity, color, and volume. A change in the electronic charge is accompanied by an equivalent change in the ionic charge, which requires mass transport between the polymer and electrolyte. When counterions enter a polymer, it expands; and when they exit, it contracts. The extent of expansion or contraction depends on the number and size of ions exchanged. Electrochemical actuators using conducting polymers based on this principle have been developed by several investigators. They can be doped with bioactive compounds and can be used in actuators such as microfluidic pumps [14–16]. Among the conducting polymers, polyaniline (PANI) is one of the most promising for technological application because of its controllable chemical and physical properties relating to its oxidation and protonation state, easy synthesis, low cost, and good environmental stability [17]. However, like most conducting polymers, PANI is somewhat intractable and is only slightly soluble in a limited

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number of solvents. The preparation of various colloidal forms has been used to improve the processability of PANI. Typically, aqueous colloidal dispersions of submicrometer PANI particles have been produced by chemical oxidative polymerization of aniline (ANI) in the presence of various polymeric stabilizers such as poly(ethylene oxide) (PEO), poly(vinyl alcohol), poly(*N*-vinyl pyrrolidone), poly(vinyl pyridine), poly(vinyl methyl ether), etc. [18–22]. There are a few reports describing synthesis of stable PANI dispersions by employing amphiphilic block copolymer micelles, such as polystyrene-*block*-poly(ethylene oxide), as the reaction medium [23].

In comparison with the PANI nanoparticles, which are synthesized by dispersion technique, one-dimensional nano-structured PANI including nanofibers, nanowires, nanorods, nanotubes, nanobelts, and nanoribbons presents several advantages in fabricating nano-devices and in preparing nanoscale electrical connections in highly conducting polymer composites [24]. It has been shown that the tubular and fibrillar morphology of the polyaniline plays an important role for the enhanced charge transport across the electrode/electrolyte interface and conductivity, compared to the conventionally synthesized polyaniline. Recently, various strategies including template synthesis, self-assembly, electrospining, and interfacial polymerization have been developed for the synthesis of one-dimensional nanostructured polyaniline. The soft template synthesis method, also called template-free method or self-assembly method, entails synthesizing the PANI in the presence of structure-directing molecules, such as surfactants or polyelectrolytes. The surfactants include the so-called functionalized protonic acids, such as naphtalenesulfonic acid [25], camphorsulfonic acid [26], 2-acrylamido-2-methyl-1-propanesulfonic acid [27], etc., or their salts, such as sodium dodecylbenzenesulfonate, and sodium dodecyl sulfate (SDS) [28–30]. Another acid, such as salicylic acid (SA; ortho-hydroxybenzenoic acid), has also been used in a self-assembly process during the aniline polymerization leading to one-dimensional PANI nanotubes or to three-dimensional hollow microshperes by simply changing the molar ratio of the dopant SA to monomer ANI [31]. The polyelectrolytes used in the soft template synthesis method include poly (acrylic acid), poly(styrenesulphonic acid), etc. [32, 33].

In this work, we have prepared PANI nanotubes by using simultaneously two structure-directing agents, salicylic acid and sodium dodecyl sulfate, in the oxidative polymerization of aniline. In order to make the isolated nanotubes water dispersible, their surface was modified by complexation with hydrophilic poly(ethylene oxide)-*block*-poly(acrylic acid) copolymer by using the well-known doping reaction of PANI with poly(acrylic acid) [34]. These water-dispersible PANI nanotubes might be good candidates for some biochemical and biomedical applications.

Experimental

Materials

Aniline (99%, Fluka) was distilled under vacuum. Methoxy-PEG (MW 5,000, Fluka) was precipitated in cold methanol (−40 °C), filtered, and dried under vacuum at 40 °C overnight. *tert*-Butyl acrylate (*t*BA) (BASF AG) was stirred overnight on calcium hydride (95%, Merck) with Irganox 1010 inhibitor (CIBA Geigy) and distilled under vacuum. CuBr (98%, Aldrich) was stirred overnight in glacial acetic acid, filtered, and rinsed successively by acetic acid, ethanol, and ether to remove traces of $CuBr_2$. Ammonium peroxidusulfate (98%, Fluka), salicylic acid (99%, Fluka), sodium dodecyl sulfate (99%, Fluka), *N*,*N*,*N*′,*N*′,*N*″-pentamethyl-diethylenetriamine (PMDETA; 98%, Aldrich), 2-bromoisobutyryl bromide (98%, Aldrich), triethylamine (99.5%, Fluka), acetone (99.8%, Merck), SiO_2 (63–200 μm, Merck), tetrahydrofuran (THF; 99.8%, Merck), 1,4-dioxane (99.5%, Merck), and trifluoroacetic acid (CF_3COOH; >99%, Merck) were used as received. Dichloromethane (CH_2Cl_2; 99.8%, Aldrich) was stirred overnight on calcium hydride (95%, Merck) and distilled.

Synthesis of polyaniline

Four millimoles aniline and 0.2 or 0.4 mmol salicylic acid were dissolved in 20 mL either distilled water or 0.35 mM aqueous solution of SDS, with magnetic stirring for 30 min at room temperature. The stirring was stopped, and 4 mmol APS dissolved in 10 mL either distilled water or 0.35 mM aqueous solution of SDS was added. Polymerization was carried out for 16 h at room temperature. The precipitated PANI was filtered and washed repeatedly with water, methanol, and ether. An aliquot of thus obtained "PANI-emeraldine salt" (PANI-ES) was stirred with 1 M NH_4OH for 8 h at room temperature. The precipitate "PANI-emeraldine base" (PANI-EB) was filtered, washed with 1 M NH_4OH, and dried in vacuum at room temperature for 24 h.

Synthesis of poly(ethylene oxide)-*block*-poly(acrylic acid) copolymer

Synthesis of PEO macroinitiator

Methoxy poly(ethylene glycol), $MPEG_{113}$, was reacted with 3 mol eq. of 2-bromoisobutyryl bromide in dry CH_2Cl_2 in the presence of triethylamine (3 mol eq.) for 24 h at 20 °C. The reaction mixture was filtered to remove the insoluble hydrobromide salt, and then CH_2Cl_2 was evaporated. The product was dissolved in THF, and the macroinitiator was precipitated in cold CH_3OH (−40 °C). It was recovered by filtration and dried in vacuum at 50 °C. The degree of

esterification (98%) was calculated from the ^{1}H NMR spectrum.

Synthesis of PEO_{113}-block-$PtBA_{19}$ diblock copolymer

$PEO_{113}Br$ macroinitiator (1.5 g, 0.3 mmol) was dissolved in acetone (1.2 mL) and degassed using dry nitrogen with stirring for 45 min. Then the catalyst CuBr (0.042 g, 0.3 mmol), PMDETA ligand (0.061 mL, 0.3 mmol), and the freshly distilled and degassed monomer *t*BA (0.85 mL, 5.8 mmol) were added. The polymerization was carried out at 50 °C for 8 h. Purification was achieved by precipitation of the reaction mixture in cold CH_3OH (−40 °C) and filtration. The copolymer was redissolved in THF and passed through a silica column to remove the Cu(II) catalyst. Finally, THF was evaporated under vacuum; the copolymer was dissolved in dioxane and freeze dried. The composition, calculated by ^{1}H NMR analysis, corresponds to a degree of polymerization of P*t*BA=19. THF-gel permeation chromatography (GPC) showed a monomodal molecular weight distribution (MWD) and M_w/M_n=1.08 (see Figs. S1 and S2 in the supporting information).

Synthesis of PEO_{113}-block-PAA_{19} diblock copolymer

PEO_{113}-*block*-$PtBA_{19}$ diblock copolymer was dissolved in dry freshly-distilled CH_2Cl_2, and then a 5-fold molar excess of CF_3COOH (with respect to the amount of the *tert*-butyl group) was added. The reaction mixture was stirred at room temperature for 24 h and then dialyzed against $CHCl_3$ for 3 days (membrane cutoff 2K). Finally, the solvent was removed by rotating evaporation.

Mixing of PANI-EB nanotubes with PEO_{113}-*block*-PAA_{19} diblock copolymer

Firstly, PANI-EB nanotubes were dispersed in water (0.025 mg/mL) by ultrasonication for 2 min. Then, a 0.5-mL solution of $PEO_{113}PAA_{19}$ in THF was added to 20-mL dispersion of PANI-EB in water under ultrasound in 30 s. The weight ratio of copolymer to PANI was 20:1. The copolymer excess was removed by filtration of the dispersion (membrane pores size 1.2 μm), and the collected nanotubes were washed repeatedly with water.

Nuclear magnetic resonance

^{1}H NMR spectra were recorded in $CDCl_3$ using a 250-MHz Bruker AC-spectrometer. The number-average DP of P*t*BA was calculated by comparing the peak integral assigned to the PEO protons (O–CH_2) at 3.63 ppm to the P*t*BA protons (δ=2.21 ppm (1H, CH_2–C(C=O)*H*) and the signals between 1.2 and 1.7 ppm (2H, CH_2–C(C=O)H; 9H, O–C(CH_3)$_3$)).

Gel permeation chromatography

Gel permeation chromatography measurement was performed with PSS SDV-gel columns (5 μm, 60 cm, 1×linear (10^2–10^5 Å), 1×100 Å) with THF as eluent (flow rate= 1.0 mL/min) at room temperature and using refractometry for detection. The MWD was determined using polystyrene calibration.

Ultrasonication

Ultrasound was generated by a sonication bath operating at 35 kHz and 20 °C.

UV–Vis spectroscopy

UV–Vis absorption spectra of aqueous dispersions were recorded in the 200–900-nm range using a Perkin-Elmer UV–Vis spectrophotometer at 25 °C.

Scanning electron microscopy

A drop of PANI nanotubes dispersion in water was deposited on a glass substrate, dried, and coated with gold for 60 s. The morphology was studied by using a JEOL JSM-5510 scanning electron microscope (SEM) operating at 10 kV.

Transmission electron microscopy

A drop of PANI-EB dispersion in water was deposited on a transmission electron microscopy (TEM) copper grid (3.05 mm, 200 mesh) coated with a Formvar film, and the solvent was allowed to evaporate. A Zeiss CEM902 apparatus, equipped with a CCD camera for digital imaging, was used at an accelerating voltage of 80 kV.

Results and discussion

It has been recently shown [31] that, in oxidative polymerization of ANI in the presence of salicylic acid, changing synthesis conditions, especially the molar ratio SA to ANI, the morphology of the PANI obtained can be changed from one-dimensional nanotubes to three-dimensional hollow spheres. When the SA to ANI molar ratio is equal or lower than 0.1, the formation of PANI nanotubes reaches 90%. In a further work, Zhang et al. [35], using a series of carboxylic acids, have demonstrated that the nanotubes aggregated to form nanotube dendrites when the carboxylic acids contain OH group. It has been proposed that the micelles formed by carboxylic acid act as a template in the formation of the nanotubes, while the hydrogen bonds

between the polymer chain of PANI and the OH group of the acid supply as a driving force to form aggregated nanotube dendrites. On the other hand, rodlike PANI nanoparticles have been prepared by oxidative polymerization of aniline hydrochloride (ACH) in SDS micelles at higher molar ratios of ACH to SDS [36]. It has been suggested that changing the molar ratio of ACH to SDS from 0.2 to 1.0 induces growth of micelles from spheres to long rods because of the screening of electrostatic interactions and consequent changes in the surfactant packing parameters.

We have obtained PANI nanotubes using the two structure-directing agents—SA and SDS. When using only SA, mainly aggregated nanotube dendrites (Fig. 1a) or coral-like structures (Fig. 1b) have been obtained irrespective of the molar ratio of SA to ANI=0.1 or 0.05. At both SA concentrations used, addition of a very small amount of the surfactant SDS (0.35 mM) much less than the critical micelle concentration and ACH to SDS molar ratios much higher as compared to the above cited work of Hassan et al. [36] results in substantial reduction of the aggregated nanotube morphology on the account of isolated PANI nanotubes (Fig. 1c), which is the favorable structure from the point of view of further modification. It can be supposed that SDS, even in a low concentration, affects the hydrogen-bonding interactions between the amine nitrogen of the PANI chain and the OH group of SA, which is responsible for the formation of aggregated nanotube dendrites. As a result of reduction of hydrogen-bonding interactions, increasing amount of isolated nanotubes was obtained by simultaneous use of the two structure-directing agents. Generally, PANI nanotubes coexist with some other PANI nanoparticles; however, it was established that, at synthesis conditions used, PANI nanotubes are the dominant volume fraction. Moreover, mainly PANI nanotubes were recovered by an additional filtration (membrane pore size 1.2 μm) of PANI aqueous dispersion sonicated for 2 min. Figure 1d is a typical SEM micrograph of PANI nanotubes obtained after filtration. The tubes are straight and uniform in diameter (outer diameter ca. 180± 20 nm), and the length is in the range of several microns. Specifically, the surface of the tubes is rather rough. The tubular morphology was further proved by TEM analysis (Fig. 2). Most of the nanotubes are hollow along the whole length, and their inner diameter is about 30–60 nm. It was found that the treatment of as-prepared PANI-ES with NH_4OH(aq) in order to obtain PANI-EB (described in the "Experimental" section) did not change the morphology of the polymer, as stated above.

PANI-ES sample, obtained in the presence of the two structure-directing agents at SA to ANI molar ratio=0.1 and SDS concentration 0.35 mM, was selected for surface modification by non-covalent grafting of a poly(ethylene

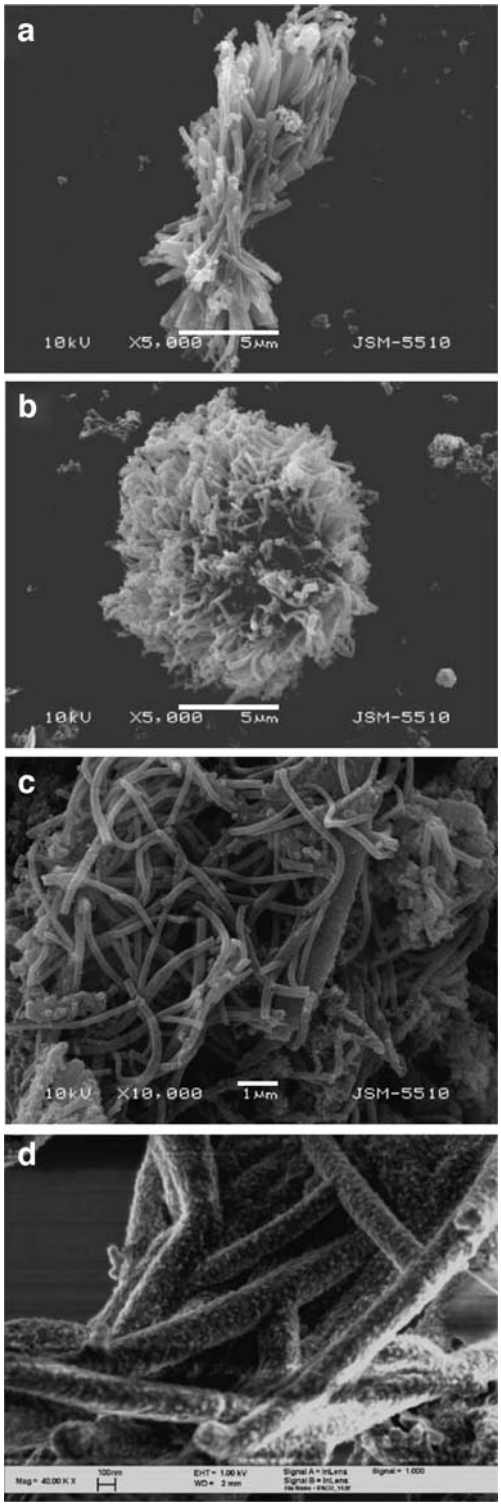

Fig. 1 SEM images of PANI nanotubes synthesized under different conditions: [ANI]=0.13 M; [ANI]/[APS]=1; [SA]/[ANI]=0.1. **a** Dendrite-like morphology; [SDS]=0. **b** Coral-like morphology; [SDS]=0. **c** Isolated nanotubes; [SDS]=0.35 mM. **d** Isolated nanotubes recovered by additional ultrafiltration; [SDS]=0.35 mM

oxide)-*b*-poly(acrylic acid) ($PEO_{113}PAA_{19}$) AB diblock copolymer. PEO is one of the most preferred polymers for various bio-related applications because of its biocompatibility, non-toxicity, non-immunogenicity, protein resistance, and good solubility under various physiological conditions [37]. On the other hand, a complex formation between the strong basic imine/amine centers of PANI and acidic groups can result in the attachment of PAA blocks onto the PANI nanotubes surface. The $PEO_{113}PAA_{19}$ diblock copolymer was synthesized by atom transfer radical polymerization employing the macroinitiator technique. Firstly, PEO-Br macroinitiator was synthesized by reacting methoxy-PEG (MW 5,000) with 2-bromoisobutyryl bromide as described elsewhere [38]. The polymerization of *tert*-butyl acrylate, initiated by PEO-Br, was carried out in the presence of the CuBr/PMDETA catalyst system in acetone at 50 °C. Finally, P*t*BA was acidolyzed to poly (acrylic acid) by treatment with trifluoroacetic acid following a procedure described elsewhere [39].

When the $PEO_{113}PAA_{19}$ copolymer was added to the aqueous dispersion of PANI-EB, its color immediately changed to green, obviously because of the doping of PANI chains with the carboxylic acid groups of the copolymer. However, the content of AAc constitutional units in the copolymer is quite low, and the carboxylic acid groups are confined on the copolymer chains. Thus, some of these groups are unable to participate in the doping [34], and the respective effect is relatively weak, distinctive polaron band at wavelengths beyond 800 nm in the electronic absorption spectrum [40] being hardly visible (Fig. 3). Nevertheless, comparing the spectra of PANI-EB and PANI-$PEO_{113}PAA_{19}$ shown in Fig. 3a, some obvious differences can be noted: (a) a shoulder at ca. 440 nm is visible for PANI-$PEO_{113}PAA_{19}$, while it is absent in PANI-EB spectrum; and (b) the absorbance at wavelengths beyond 750 nm is higher for PANI-$PEO_{113}PAA_{19}$ as compared to PANI-EB. These two bands are related to the doped protonated form (polaron structure) of PANI [40, 41]. It can be concluded that, on mixing PANI-EB with $PEO_{113}PAA_{19}$, complex formation between the strong basic imine/amine centers of PANI and carboxylic acid groups of $PEO_{113}PAA_{19}$ occurs. The attached copolymer chains improve the stability of the sonicated PANI dispersion as seen from Fig. 4. While the PANI-EB dispersion has been completely separated in a 24-h period, the sonicated dispersion of PANI-$PEO_{113}PAA_{19}$ is still stable. This was also confirmed by the UV–

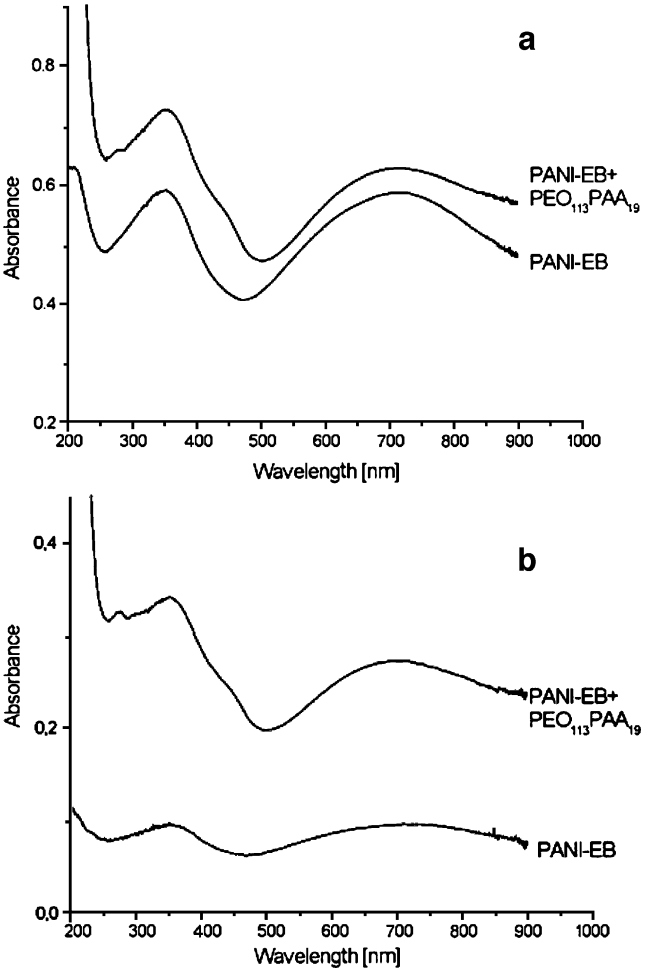

Fig. 3 UV–Vis absorption spectra of aqueous dispersions of PANI-EB (pH=5) and PANI-$PEO_{113}PAA_{19}$ (pH=3) immediately after preparation **a**; and next to twenty-four-hour storage **b**

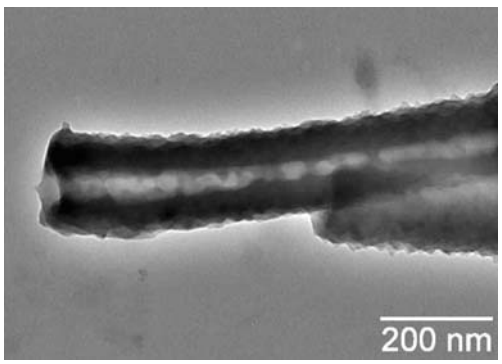

Fig. 2 TEM image of PANI nanotube: [ANI]=0.13 M; [ANI]/[APS]=1; [SA]/[ANI]=0.1; [SDS]=0.35 mM

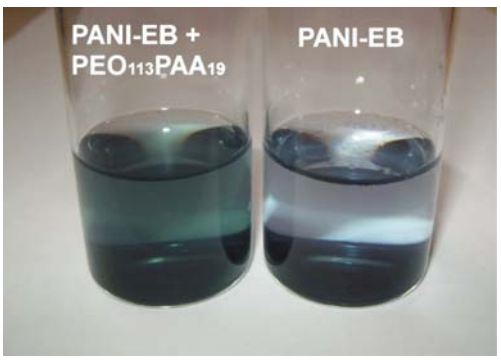

Fig. 4 Visual observation of aqueous dispersions of PANI-$PEO_{113}PAA_{19}$ and PANI-EB next to 24-h storage

Vis spectra shown in Fig. 3b. Next to the 2-day storage, the absorbance of the dispersion of PANI-$PEO_{113}PAA_{19}$ is much higher as compared to the PANI-EB dispersion. The modified PANI nanotubes were recovered by filtration (membrane pore size 1.2 μm) and washed with water in order to eliminate the copolymer excess. Analyses by SEM and TEM did not show any difference in the PANI nanotubes morphology before and after modification. The clear visualization of $PEO_{113}PAA_{19}$ layer on the PANI nanotubes' surface was impossible because of several factors like rough nanotube surface, large difference between the diameter of PANI nanotubes and the thickness of $PEO_{113}PAA_{19}$ layer, and much higher electron density of PANI nanotubes compared to the copolymer (see Figs. S3 and S4 in the supporting information).

In order to confirm that the dispersion stability results from the non-covalent grafting of PAA chains onto PANI surface and the PEO block provides a steric stabilization, PANI-EB dispersion was prepared under the same experimental conditions, except that $PEO_{113}PAA_{19}$ was replaced by PEO_{113}. Color change from blue to green was not observed, and the stability of this dispersion was identical to the stability of pristine PANI-EB nanotubes dispersion in water. Evidently, the surface modification of PANI nanotubes by $PEO_{113}PAA_{19}$ improves their dispersability in water. More detailed studies about the effect of the copolymer composition and molecular weight as well as determination of the grafting ratio are subject of future investigation.

It can be noted that an alternative approach for preparation of similar aqueous dispersion of PANI-$PEO_{113}PAA_{19}$ would be the direct synthesis of PANI by oxidative polymerization of aniline in the presence of $PEO_{113}PAA_{19}$. However, the acrylic acid is a weak acid (pK=4.25), and the protonation of PANI will be achieved rather with the help of the strong sulfuric acid produced by the formation of protons and sulfate anions during the polymerization of aniline and decomposition of the oxidant, ammonium peroxydisulfate, than by the carboxylic acid groups [42]. Thus, the surface modification of PANI nanotubes possibly obtained by non-covalent grafting of a poly(ethylene oxide)-*b*-poly(acrylic acid) ($PEO_{113}PAA_{19}$) AB diblock copolymer would be impossible.

Conclusions

Polyaniline nanotubes were obtained by oxidative polymerization of aniline in the presence simultaneously of two structure-directing agents—salicylic acid and sodium dodecyl sulfate. In order to make the isolated nanotubes water dispersible, their surface was modified by complex formation (non-covalent grafting) with hydrophilic poly (ethylene oxide)-*block*-poly(acrylic acid) copolymer. These water-dispersible PANI nanotubes might be good candidates for some biochemical and biomedical applications.

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