Studies on the synthesis of low molecular weight, one-dimensional polyanilines prepared by fast emulsion polymerization using (n-dodecylbenzenesulfonic acid)/HCl emulsifiers

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Abstract

Low molecular weight polyaniline nanotubes were prepared by fast emulsion polymerization in the presence of both n-dodecylbenzenesulfonic acid (DBSA) and HCl(aq). The anilinium monomers associated with DBSA emulsifiers were found to self-arrange into strands of associated cylindrical micelles before polymerization, as monitored by their optical activity and optical image. In the presence of some HCl(aq), the monomer-associated cylindrical micelles expanded and the polymerization rate could be speeded up. It was found that the low molecular weight (viscosity-averaged molecular weight) polyaniline obtained can easily lead to the formation of highly conductive, one-dimensional nanotubes or nanofibers monitored by the variation of optical activities and λ_{max} of the UV–visible–near IR spectra during polymerization. The DBSA/HCl ratio played an important role in the eventual properties and morphologies of the one-dimensional polyanilines, which can be illustrated by conductivity, SEM and transmission electron microscopy measurements. The resultant one-dimensional polyaniline nanotubes can be arranged into a layered structure by orientation, illustrated by AFM and wide-angle X-ray diffraction.
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INTRODUCTION

Several approaches have been proposed to obtain polyaniline nanotubes (PANINTs). Kaner and coworkers prepared nanofibrous polyaniline by interfacial polymerization with aniline dissolved in an organic solvent[1] and proposed that homogeneous nucleation led to the nanotube morphology while heterogeneous nucleation led to particles. Levon et al. reported a nanofibrous morphology of n-dodecylbenzenesulfonic acid (DBSA) doped polyaniline originating from the filling of the nanopores of the polyaniline spherical particles into nanorods in the absence of any organic solvent.[2] Chiou and Epstein used the depleted region to illustrate the formation mechanism of PANINTs in dilute solution.[3,4] Zhang et al. suggested that the colorless aggregation present before polymerization resulted in the formation of the tubular morphology of PANINTs. However, this cannot explain how nucleation and growth of the nanotubes evolved.[5] Li et al. used an electrical double layer theory to explain why polymerization occurred only in a one-dimensional helical way, leading to the formation of PANINTs through the balance of attractive and repulsive forces present in the polymerization mixtures.[6] Kinlen issued that the formation of cylindrical of soft template by self-assemble[7–9] and nanofibrous polyaniline can be formed at a dilute aniline solution and the formation of granular particles is in the later-stage polymerization on the formed nanofibers in a concentrated polymerization system.[10] Stejskal et al. proposed the presence of phenazines in the early stage of polymerization when the pH value is high. The phenazines behave as tubular nuclei for the conversion of helical polyanilines into nanofibers in the later stage at lower pH due to the dissociation of persulfate into sulfate ions.[11,12] However, the resultant nanotubules exhibit poor conductivity due to the weak acidic environment (higher pH).

We found that PANINTs form easily through emulsion polymerization in the presence of DBSA and HCl(aq) within a short period of polymerization to obtain a low molecular weight polyaniline

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nanowire. Common emulsion polymerization is carried out with hydrophobic monomers accumulated in the center of micelles with surrounding hydrophobic tails of the emulsifiers, resulting in granular particles made of entangled polymer molecules. It is believed that a long polymerization time (several hours) could lead to the development of polymers with higher molecular weight, which would eventually evolve into more flexible molecules through lots of intramolecular chain folding and intermolecular entanglements.

Therefore, if the reaction time can be reduced to obtain a lower molecular weight polymer to prevent the occurrence of intramolecular folding and intermolecular entanglements, it will be much easier to obtain a one-dimensional, rod-like molecule. In particular, when the monomers are ionic and hydrophilic like anilinium, they will not accumulate in the centers of micelles but will deploy on the micelle surfaces before polymerization. Consequently, more space will be provided for the monomers located on the micelle surfaces, which can reduce the possibility of intramolecular chain folding and intermolecular entanglements during chain growth.[13,14] In the following studies, two important parameters, polymerization time (which is related to molecular weight) and composition of strong mineral protonic acids, are controlled to prepare PANINTs in an emulsion polymerization using DBSA as the emulsifier. The studies try to explain kinetically the formation mechanism of nanotubular polyaniline in emulsion polymerization by measuring the optical activity and UV–visible–near IR spectra during polymerization. The morphologies and structures of the obtained PANINTs are also characterized by SEM, transmission electron microscopy (TEM), AFM and wide-angle X-ray diffraction (WAXD).

EXPERIMENTAL
Preparation of polyaniline
DBSA (Tokyo Kasei Kogyo Co. Japan) (3 g, 0.091 mol, or 0.182 g, 0.273 mol) was dissolved in 50 mL deionized water and the mixture was slowly stirred until a homogeneous solution was formed; then 9 g (0.097 mol) aniline monomer (Tokyo Kasei Kogyo Co. Japan) was added and stirring was maintained for 5 min followed by the addition of 9 mL (0.009 mol) of 1 mol L^{-1} HCl. The mixture then became entirely emulsified after stirring, with the formation of cylindrical micelles. An ammonium persulfate (APS) (Showa Chemicals Instrument Co.) aqueous solution prepared in another beaker by dissolving 7.33 g (0.0323 mol) APS in 30 mL deionized water was kept at low temperature by storing in a freezer for at least 12 h and was taken out to pour directly into the reaction mixture, followed by vigorous stirring with a magnetic stirrer. About 3 min later, the temperature rose very quickly, followed by darkening of the reaction mixture, and the polymerization was allowed to proceed for 30 min before isolation by filtration, followed by washing twice with isopropanol and then water and filtering again; the filter cakes obtained were dried in an oven at 60 °C for 12 h.

Two comparison emulsion polymerizations with reaction times of 30 min and 3 h were carried out with DBSA (35 g) as the only protonic acid present. The polymerization time was controlled at 30 min and 3 h, respectively, after the occurrence of auto-acceleration (darkening). The polyaniline obtained is named PANIDBSA.

Circular optical activity
The circular optical activities of various polyanilines were obtained with a Polax-D type optical meter in which the measured activity (α) was divided by both concentration (c) and thickness of cell (L) to obtain the specific optical activity ($[\alpha] = \alpha/Lc$).

Intrinsic viscosity [η] and molecular weight
The intrinsic viscosity [η] of emeraldine base (EB) types of various PANINTs was measured in N-methylpyrrolidone (NMP) with a Ubbelohde viscometer in a heating bath controlled at 30 °C.[15]

Electron spectroscopy for chemical analysis (ESCA)
The dedoping level was analyzed with an ESCA instrument Fison (VG)-Escalab 210 using an Al Kα X-ray source at 1486.6 eV, where the binding energies of N$_{1s}$ around 400 eV were recorded.

UV–visible–near IR spectroscopy
The UV–visible–near IR spectra of the sample were obtained with a Hitachi U-2001 and DTS-1700 NIR spectrometer. The wavelength ranged from 190 to 1800 nm.

Conductivity
A four-probe milliohm meter (Lutro MO-2001) was used to measure the conductivity of PANINT powders which were pressed into tablets.

Scanning electronic microscopy (SEM)
Samples for field emission SEM (HR-SEM, Hitachi S-4200; accelerating voltage 15 kV) were powders on carbonic tape and posted on ferric stage.

Transmission electronic microscopy (TEM)
Samples for field emission TEM (HR-AEM, Hitachi FE-2000) were dispersed as a powder in acetone and dropped on carbon-coated copper grids.

Atomic force microscopy (AFM)
Samples for AFM (CSPM 4000) were PANINTs solution cast directly onto a glass plate.

Wide-angle X-ray diffraction (WAXD)
A copper target (Cu Kα) Rigaku X-ray source with a wavelength of 1.54 Å was used for diffraction with scanning angle (2θ) from 2° to 35° with a voltage of 40 kV and a current of 30 mA at a scanning rate of 1° min^{-1}.

RESULTS AND DISCUSSION
Optical microscopy and kinetic formation mechanism of PANINTs
Optical microscopy was used to illustrate the self-assembly of the anilinium monomer of DBSA/HCl salts into cylindrical micelles which were then polymerized into nanotubular polyaniline polymers by the initiators.[13] Before the addition of HCl(aq), the anilinium was associated with DBSA only and demonstrated a thread-like structure with a diameter smaller than 1 μm (Fig. 1(a)),[13] and it is reasonable to assume that the amino group of the anilinium must be pointing toward the center of the cylinder since
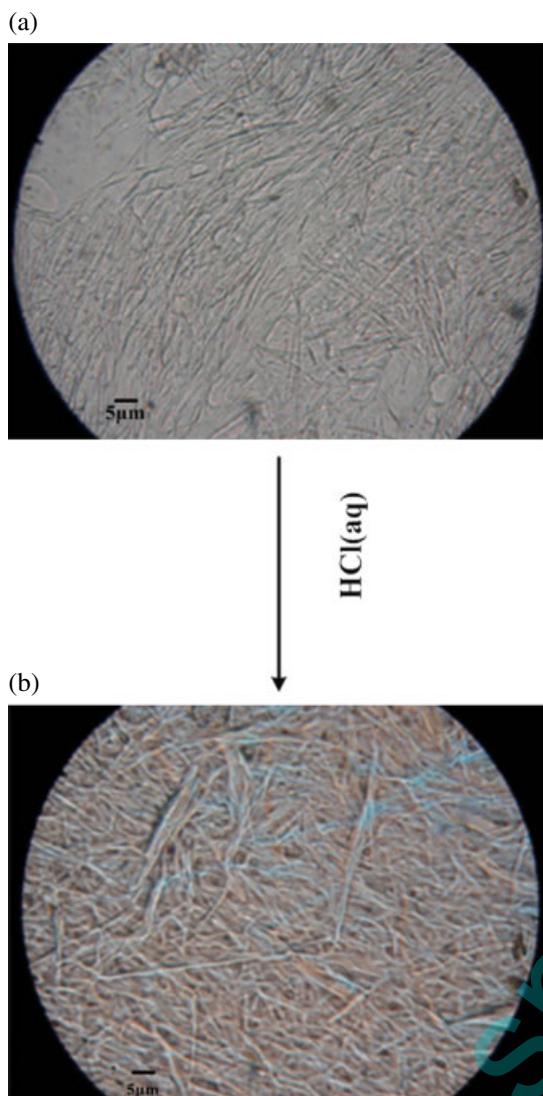
Figure 1. Optical pictures of anilinium salt associated with (a) pure DBSA and (b) mixed protonic acids of DBSA/HCl = 10/1 in molar ratio.

it has to associate with negative sulfonic groups of the DBSA emulsifier.

Interestingly, when some hydrochloric acid was introduced in the system, the diameters of the cylinders expanded up to 1 μm and an overlapping, intertwined fibrous morphology can be clearly seen in Fig. 1(b). Since the number of moles of aniline (0.097) is higher than that of DBSA (0.091), expansion of the cylindrical micelles must come from insertion of additional anilinium monomers created by complexation between free anilines and HCl(aq). Moreover, the highly hydrophilic nature of the formed anilinium chloride salt can turn the amino groups of anilinium from pointing inward to the micelle center to pointing to the outward water medium where a lot of aqueous initiator molecules (APS) are present. Therefore, the amino groups of the anilinium chloride salt are exposed in the water medium and are ready to be attacked by the aqueous initiators as depicted in Scheme 1. If HCl(aq) were not introduced, all the anilinium monomers would point inward to the hydrophobic center of the micelles where lots of long alkyl chains of DBSA emulsifiers are present and the amino group would be covered by its own

hydrophobic phenyl groups to prevent the approach of the aqueous APS initiator, which could only diffuse slowly into the hydrophobic center to initiate the polymerization, similarly to common emulsion polymerization. In other words, initiation can occur in a shorter time and in an easier way when there is some HCl(aq) present in the polymerization mixture. This is why it took only 3 min for the polymerization to proceed into the auto-acceleration polymerization stage to cause a sudden temperature rise and dark color if there were some HCl(aq) present in the system, whereas more than 20 min (22 min) was required to see the temperature rise and dark color when DBSA was the only protonic acid present in the polymerization mixture.

Once polymerization is initiated by the approaching APS, polymerization occurs only at the interface of the water and cylindrical micelles and polyanilines can be formed and placed naturally on the self-assembly cylindrical template to create a conducting jacket on the template (Scheme 1) and become nanotubes or nanofibers associated with both DBSA and Cl⁻ (A⁻) counter ions. The free DBSA molecules that are not complexed with any aniline monomers can be present inside or on the surfaces of the nanorods and can be mostly removed by washing with organic solvents.

With polymerization time close to 30 min (counting from the appearance of the dark color), intramolecular chain folding and intermolecular entanglements can be effectively avoided since the molecular weight is too low to cause long chain coiling and one can obtain polyanilines with more extended chains with longer conjugation chain length (a free carrier tail in the UV–visible–near IR spectrum will thus be seen). Consequently, the presence of additional HCl and polymerization for a short period of time can lead to the formation of polyanilines with either nanotubular or nanofibrous morphologies, avoiding the formation of granular particles of entangled, random-coil molecules.

Basically, the DBSA salts of anilinium can also exhibit a one-dimensional morphology if the polymerization time is adjusted to 52 min (22 + 30 min) to allow more APS to diffuse into the cylindrical micelles. It will take 22 min for APS to diffuse into the cylindrical micelles and then initiation can occur. Initially formed nanofibers will be covered and stuck together by the excess (free) DBSA into bigger bundles and, eventually, into giant, sticky, granular particles (aniline/DBSA = 0.0968/0.915 ≈ 1/10 in molar ratio) when newly formed molecules cover the old ones for a long polymerization time of several hours.[16–19]

Optical activity measured at various polymerization times

Since a cylindrical micelle is made of circularly arranged anilinium moieties which can demonstrate some optical activity, we can measure the specific circular optical activities of the polymerizing mixture at various polymerization times to monitor the degree of circulation of the cylindrical micelles during polymerization and how a tubular or fibrous polyaniline is formed. Before polymerization (before the addition of APS), the specific optical activity of the reaction mixture was as high as 43.5 (Fig. 2). During the initiation stage, this gradually went down to 34.0 after 8 min and recovered to 39.1 after 30 min when the polymerization was stopped by pouring into isopropanol (IPA) non-solvent (Fig. 2). The high optical activity before polymerization indicated the presence of cylindrical micelles seen in the optical pictures in Fig. 1. The decreasing activity in the induction stage (<8 min) revealed the gradual destruction of the cylinders by chain propagation at which stage anilinium monomers were linked together one by one as depicted in Scheme 2. The dissociation of the cylindrical micelles
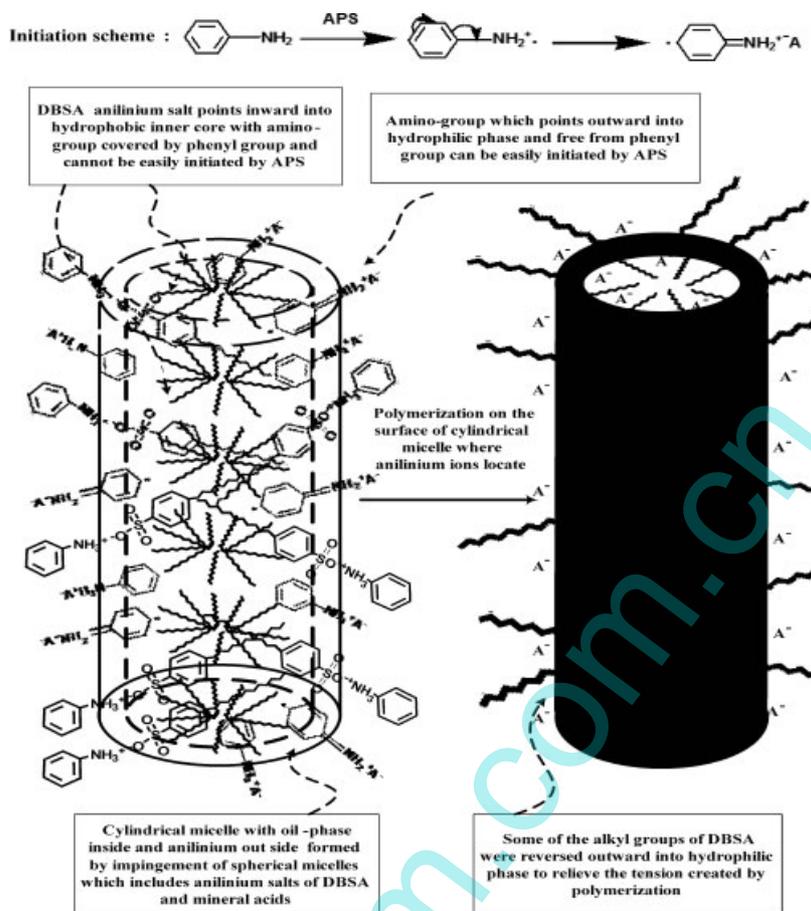
Scheme 1. Mechanism of nanotube formation.

came from the increasing repulsion forces between the long alkyl tails of DBSA-complexed anilinium monomers when their amino ends were linked together by polymerization. The increasing optical activity after 8 min indicated that the polyaniline molecules formed were winding on the cylindrical surfaces, resulting in an increase in circular activity until the polymerization ceased after 30 min (Fig. 2). The growing chains with extended, long alkyl side chains were similar to hairy rods with long, alkyl side chains which can rearrange themselves into a layered structure with interdigitized alkyl side chains after orientation.

Molecular weight determined by viscosimetry

Commonly, the molecular weights of polymers are measured by gel permeation chromatography (GPC) which assumes that all molecules are random-coil, circular particles since the packing materials inside the GPC column have circular pores as well. Therefore, rod-like polyanilines which are not circular or spherical will not easily fit into the circular pores and the obtained molecular weights are usually overestimated, depending on their shapes. In this study, we measured the intrinsic viscosity at constant temperature (30 °C) (Table 1)[15] to calculate the viscosity-averaged molecular weight through the Mark–Houwink relation which has an order equal to 1.36, higher than the maximum value of 0.8 for random-coil polymers. The polyanilines were first dedoped by ammonium water overnight to remove all protonic acids and become EB before dissolving in NMP. The obtained intrinsic viscosities are listed in Table 1 and converted into
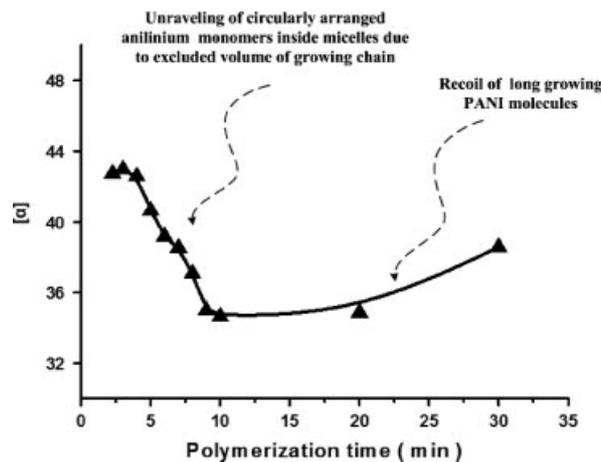
Figure 2. Specific optical activity *versus* polymerization time.

viscosity-averaged molecular weight (M_v).[16] The M_v turned out to be about 18 500 and 42 800 g mol^{-1} for EB types of PANINT with 30 min and 3 h polymerization time, respectively. More than 2.5 h polymerization can increase the molecular weight of PANINTs to more than double and causes more chain folding and bending due to the longer backbones.

It was found that PANIDBSA can be easily dedoped into the EB type for 92.1% of dedoping level in ammonium water with
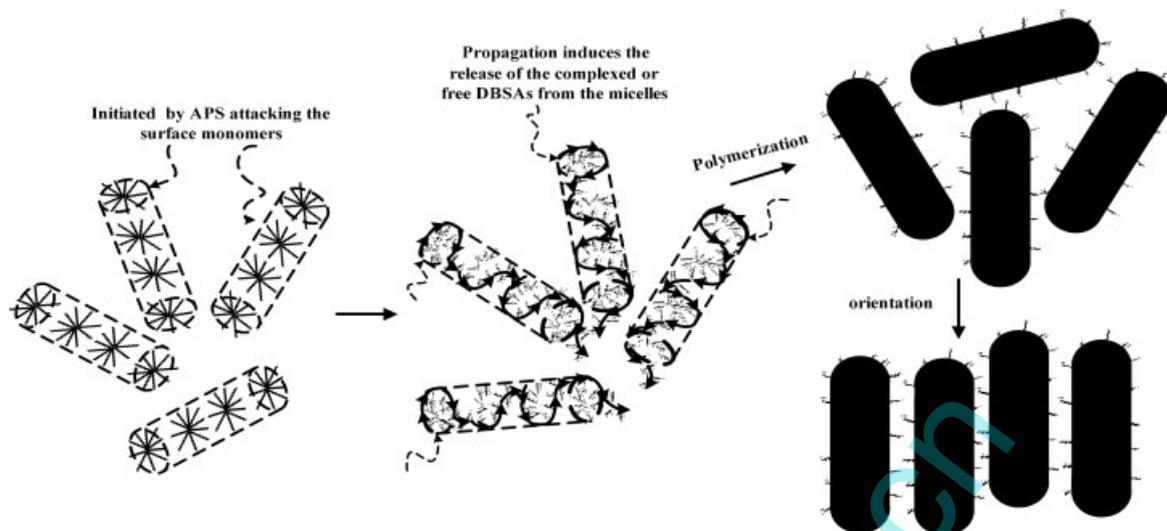
Scheme 2. From cylindrical micelles before polymerization into a layered structure after polymerization.

Table 1. Intrinsic viscosity and molecular weight of EB type polyanilines					
Polymerization time	η_r	$\ln \eta_r$	η_{sp}	$[\eta]^a$	$M_v{}^b$
EB of PANI with 3 h	1.037	0.036	0.037	4.865	42 800
EB of PANINT with 30 min	1.016	0.016	0.016	2.116	18 500

^{a} The intrinsic viscosity was calculated using the equation.[15]

$$[\eta] = \frac{1}{c} \times \sqrt{2 \times (\eta_{sp} - \ln \eta_r)}$$

^{b} M_v was calculated from the Mark–Houwink relation of polyaniline in NMP at 30 °C:[16] $[\eta] = 1.95 \times 10^{-6} M_v{}^{1.36}$.

overnight stirring, but for PANINT it took more than 2 days stirring in ammonium water to obtain only a 77.3% dedoping level, as shown in Table 2 which was constructed for the different states of N_{1s} in the ESCA spectra. The denser structure of PANINTs was able to prevent the loss of protonic acids to ammonium water, which is further evidence that molecules of PANINTs are mostly concentrated and self-assembled into nanotubes and can effectively delay dedoping from the invading

ammonium water molecules. In contrast, the more compact structure of EB of PANINT cannot be redoped to the original doping level, no matter how strong the protonic acids used (concentrated sulfuric acid) and how much time it took (we tried 1 week redoping in concentrated sulfuric acid and we had poorer conductivity than before dedoping). It seems that the walls of the nanotubes can effectively interrupt the mass transfer across the nanowire with a rigid, compact and ordered crystalline structure, demonstrated by its electronic diffraction pattern measured by TEM.

UV–visible–near IR spectroscopy

UV–visible–near IR spectra of various polyanilines are shown in Fig. 3 which illustrates free carrier tails for various polyanilines prepared for 30 min of polymerization. The free carrier tail in the near IR region, which is usually found only when polyaniline is secondarily doped by phenolic derivatives, illustrates that the molecules were changed from the coiled state to a straighter one. The only spectrum without carrier tails is PANIDBSA prepared with a longer polymerization time of 3 h. It reveals that low molecular weight rigid polymers developed using shorter polymerization times can achieve nanotubular or nanofibrous morphologies more easily than high molecular

Table 2. Dedoping percentage of PANINT and PANIDBSA				
	N_{1s} area			
Type	—N= (dedoped quinoid)	—N— (dedoped benzenoid)	—N+— —N= (doped states)	Dedoping level (%)^a
EB of PANINT (30 min)	70.9	408.8	141.1	77.27^b ((70.9 + 408.8)/(70.9 + 408.8 + 141.1))
EB of PANIDBSA (30 min)	101.2	434.8	45.8	92.13^c ((101.2 + 434.8)/(101.2 + 434.8 + 45.8))

^{a} Dedoping level is defined as the percentage of the summation of the dedoped benzenoid and quinoid states measured from ESCA spectra of EB type PANINT and PANIDBSA.
^{b} Dedoping in 1 mol L^{-1} NH_4OH(aq) for 2 days.
^{c} Dedoping in 1 mol L^{-1} NH_4OH(aq) overnight.

585
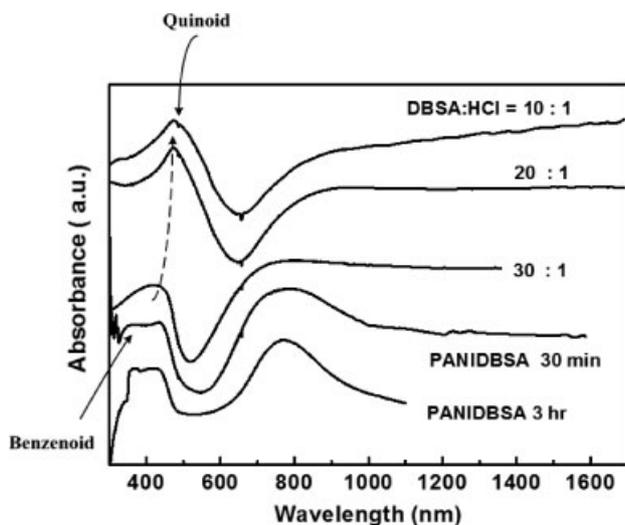
Figure 3. UV–visible–near IR spectra of various PANINTs and PANIDBSAs.

Figure 4. UV–visible–near IR spectra of (a) PANINT with DBSA/HCl = 30/1 and (b) PANIDBSA prepared for different polymerization times.

weight polymers. Furthermore, the absorption in the near IR region became flat (DBSA/HCl = 20/1 molarwise) and even rose (DBSA/HCl = 10/1 molarwise) with higher content of HCl (Fig. 3), indicating that the conductivity of the obtained polyanilines can be significantly improved simultaneously through highly conjugated backbones. In particular, the UV–visible–near IR spectra red shifted with HCl(aq) composition and covered almost the entire near IR region, corresponding to more extended one-dimensional polyaniline nanotubes or nanofibers. Furthermore the carrier tail was not found in the UV–visible–near IR spectrum of PANIDBSA[17–20] (Fig. 3), where only λ_{max} around 780 nm can be seen, corresponding to the presence of a poorly conjugated, coiled polyaniline chain. These nanotubular or nanofibrous molecules are similar to hairy rod molecules which have a tendency to arrange into an ordered, layered structure[21,22] and give a well-defined layered structure after orientation, as illustrated in the WAXD patterns and AFM micrographs.

When DBSA was the only dopant and polymerization was carried out for only 30 min after the induction period (total 52 min including 22 min of induction), the PANINTs demonstrated an insignificant free carrier tail in the near IR region as shown in Fig. 3. However, a peak at 780 nm similar to that of the PANIDBSA of 3 h still exists, illustrating that some of the molecules were not extended but still in the coiled state due to the presence of an excess of free DBSA which can also cause the re-coiling of the polyaniline through the so-called anti-secondary doping effect.[17–20] Additionally, λ_{max} in the UV range can reveal the doping level of polyaniline by the relative absorbance of π to π^* transition peaks of benzenoid and quinoid moieties, which are assigned to 355 nm and 475 nm, respectively. When more HCl(aq) was present in the polymerization mixture, the λ_{max} of quinoid (475 nm) red shifted and became sharper, and was attributed to the increasing doping level and better conjugation with the formation of nanotubes or nanofibers. There was no significant absorption for benzenoid (355 nm) of PANIDBSA whether it is prepared with 30 min of polymerization or not (Fig. 3).

The variation in optical activity during polymerization discussed in the previous section can also be related to the UV–visible–near IR spectra which can reveal the degree of conjugation from the absorption wavelength of λ_{max}. UV–visible–near IR spectra taken at various polymerization times (less than 30 min) were used to
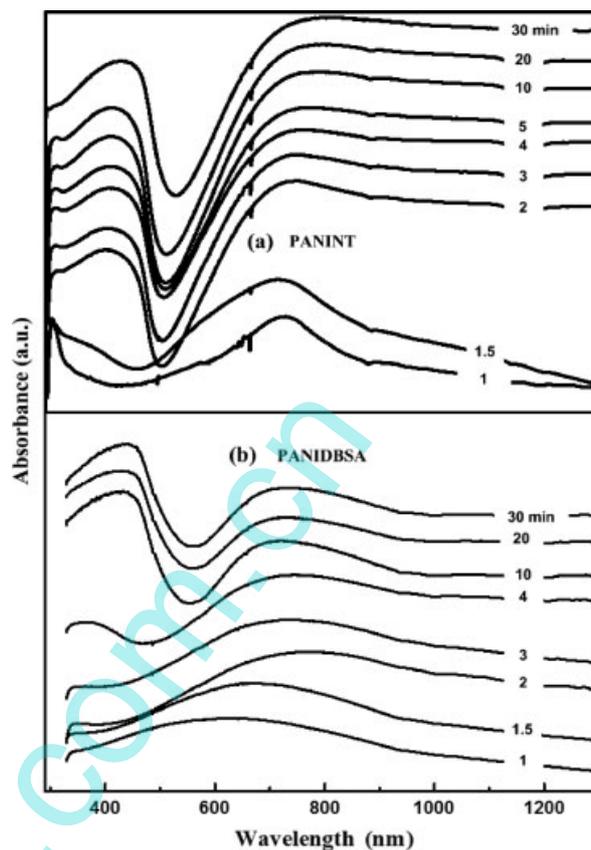
kinetically study the growth of polyaniline chains for PANINT with DBSA/HCl = 30/1 molarwise and PANIDBSA, respectively. The UV–visible–near IR spectra showed a single absorption peak located at 600–700 nm without any carrier tail in the initial stage below 2 min for both PANINT with DBSA/HCl = 30/1 molarwise and PANIDBSA (Fig. 4). After 2 min, the PANINT started to demonstrate two λ_{max} values at 420–440 and 760 nm, respectively. A free carrier tail in the near IR region developed also at this stage; the absorbance never decreased and maintained a high absorption level in the near IR range as shown in Fig. 4(a), indicating the presence of highly conjugated, extended molecules in the nanotube. In addition, both λ_{max} values red shifted with the process of polymerization until the polymerization ceased at 30 min, revealing a gradual extension of molecular chains during polymerization.

It took 2 min more (totally 4 min) for PANIDBSA prepared for 30 min with the single protonic acid DBSA to develop a free carrier tail in the near IR region as shown in Fig. 4(b) which also illustrates an additional λ_{max} at around 780 nm after polymerization similar to that of PANIDBSA prepared for 3 h. Two λ_{max} values were found for PANIDBSA 4 min later and both peaks red shifted at this stage but the red shift disappeared after 4 min. The λ_{max} at 780 nm is more significant and the free carrier is not significant compared with that of PANINT with DBSA/HCl = 30/1 molarwise in Fig. 4(b), resulting from the less extended structure caused by the anti-secondary effect.[17–20] The free carrier in the near IR region eventually disappeared for PANIDBSA when the polymerization time was prolonged to 3 h, as shown in Fig. 3.

Conductivity

The conductivity of various PANINTs prepared with different molar ratios of DBSA/HCl are listed in Table 3 which reveals that the presence of HCl(aq) does not just speed up the polymerization by providing more available anilinium monomers for the APS initiator (Scheme 1) but also significantly increases the conductivity of the resulting PANINTs. In other words, their conductivity decreases with increasing proportions of DBSA, which can effectively decrease the conductivity of polyanilines through the anti-secondary doping effect.

SEM micrographs

SEM micrographs of polyaniline nanorods prepared in the presence of various ratios of DBSA/HCl and washed with IPA are shown in Fig. 5. When the mole ratio of DBSA/HCl was 10/1 as shown in Fig. 5(a), we find randomly distributed nanorods of polyaniline. When DBSA/HCl ratios are increased to 20/1 and 30/1, the nanorods come closer and become ordered, as shown in Figs 5(b) and 5(c). Clearly, the rods are gradually being stuck together by the freer DBSA molecules which are not washed out by IPA and stay outside the nanorods, acting as adhesives. In particular, when DBSA/HCl reaches 30/1, these nanorods become parallel to become bundles when a higher portion of DBSA is present. Figures 5(a)–5(c) illustrate that nanofibers were actually formed very rapidly in the early stage of polymerization (within 30 min) in the presence of both DBSA and HCl.

The nanofiber products are embedded in free DBSA clusters before washing with IPA when DBSA was the only protonic acid (PANIDBSA), as shown in Fig. 5(d). A morphology with mixed granules and nanowires emerged after washing with IPA as seen
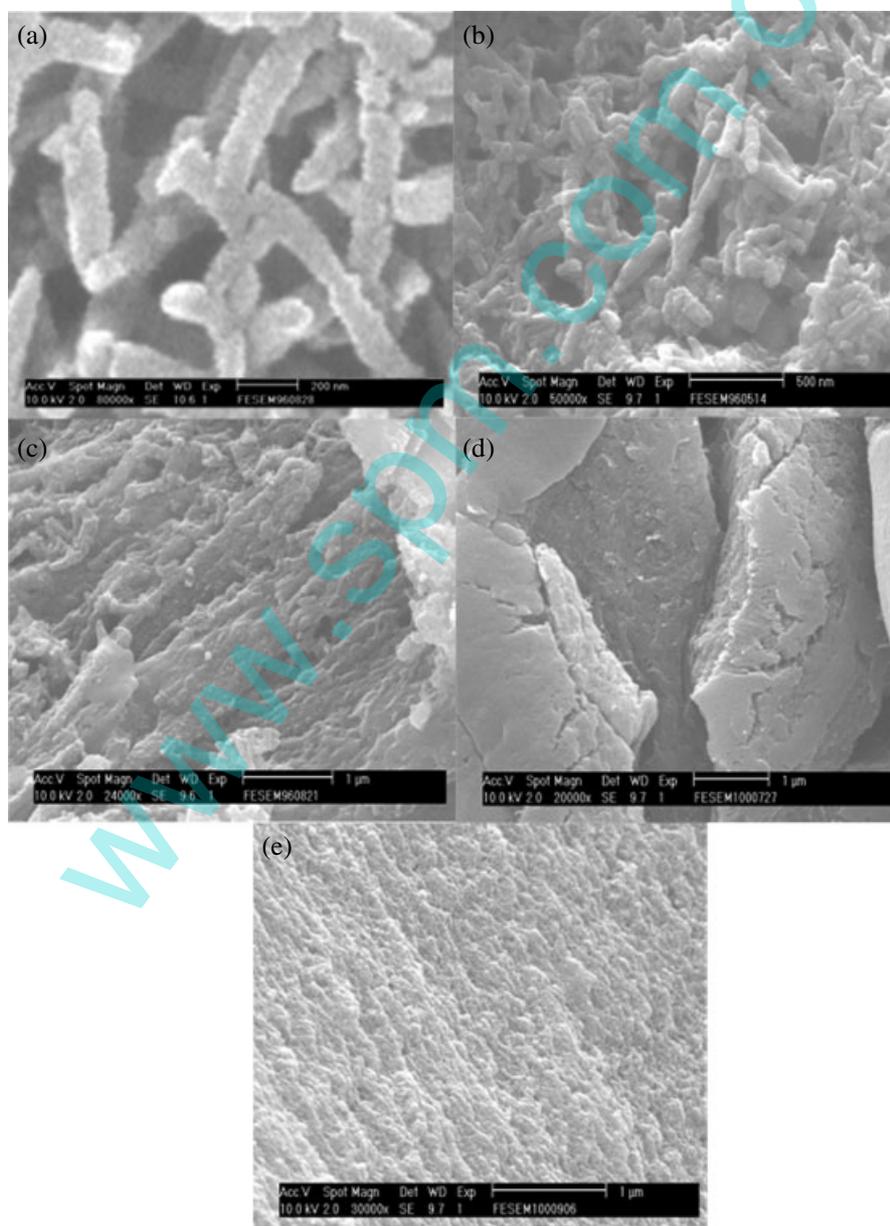
Figure 5. SEM pictures of PANINTs with molar ratios of (a) DBSA/HCl = 10/1, (b) DBSA/HCl = 20/1, (c) DBSA/HCl = 30/1 washed with IPA, (d) neat PANIDBSA prepared for a polymerization time of 3 h and (e) PANIDBSA washed with IPA.

Table 3. Conductivity σ of various polyanilines	
DBSA/HCl ratio (washed by IPA)	σ (S cm^{-1})
10/1	5.9
20/1	3.2
30/1	1.1
Pure DBSA	0.8
Pure DBSA (not washed)	0.025

in Fig. 5(e), indicating that there are still some nanowires present, buried in the free DBSA ocean. However, these nanowires are not as well aligned and straight like those prepared in the presence of DBSA and HCl(aq) but become curved, as seen in the TEM micrograph.

It seems the presence of HCl(aq) in the polymerization mixture can not just result in the straighter nanorods of the obtained polymers but also shorten the induction time of initiation step of polymerization and improving their conductivity. In other words, both DBSA emulsifier and HCl play important roles in building up a one-dimensional polyaniline beside the low molecular weight, resulting from fast polymerization.

TEM and electronic diffraction

Likewise, TEM micrographs of the PANINTs prepared with various amounts of DBSA with constant HCl concentration are shown in Fig. 6 to indicate whether they are solid or hollow. In Fig. 6(a), when less DBSA was used the PANINTs are not glued together by free DBSA and therefore they can be separated from each other and become numerous single solid nanofibers. When the DBSA/HCl ratio is below 20/1, the prepared polyanilines are solid nanofibers even after washing with IPA. These nanofibers (before washing) aggregated together by free DBSA when the composition of DBSA was increased from 20/1 to 30/1, as shown in Fig. 6(c). What is more surprising is that the solid nanofibers in Fig. 6(c) became hollow (nanotubes), as shown in Fig. 6(d), after washing with IPA, indicating that some free DBSA molecules were staying inside the nanotubes before IPA washing. In other words, the nanofibers seen in Fig. 6(c) are actually nanotubes filled with free DBSA molecules whose disappearance left more empty space inside and solid nanofibers turned into nanotubes. The electron diffraction patterns of the outer layer and inside of the IPA-washed PANINTs are shown in Figs 6(e) and 6(f) which were used to confirm the almost empty hollow core and the higher crystallinity of the tube layer. From the electron diffraction pattern of a single nanotube, we understand that the nanotube outer layer is made of ordered crystallized polyaniline molecules, which demonstrated a diffraction pattern of high crystallinity with some tiny dots appearing on the concentric circles due to either high crystallinity or the formation of helix-like crystals. Neither dots nor a significant diffracted circle can be found for the tube core which was once occupied by free DBSA before IPA washing.

The TEM micrograph of PANIDBSA prepared with 3 h of polymerization demonstrates a granular morphology (Fig. 6(g)), whose free, covering DBSA can be partly removed by organic solvents and shows a micrograph of intercepted, curved nanowires (Fig. 6(h)). However, these curved nanowires were not hollow but exhibited solid structures with a highly ordered diffraction pattern as shown in Fig. 6(i) which also shows a lot of tiny dots at the

outer diffracted circles. It is possible that the vast number of free DBSA molecules inside the PANIDBSA tubes cannot be entirely washed out by IPA, which stopped themselves to demonstrate a tubular structure like PANINTs. In addition, the curved morphology can hamper the inside, free DBSA molecules from being washed by IPA.

Thus, the use of some small HCl molecules to replace huge DBSA ones in the micelle can avoid the steric hindrance of overcrowded DBSA molecules inside micelles and stabilize the tubular template formed to polymerize into nanotubes.

WAXD and AFM

When outnumbered (DBSA/HCl $>$ 10/1 in molar ratio) anilinium monomers of DBSA salts which were arranged in a cylindrical micelle are polymerized and connected with each other during chain propagation, the bulky long alkyl chains of the anilinium DBSA salts become side chains of the resultant one-dimensional polymers and a strong, repulsive tension will be built up if they are still arranged inside the cylindrical micelles, as depicted in Scheme 2. It is reasonable to assume that the growing chains will undergo uncoiling during propagation. Some of the linked DBSA tails of the growing chains inside the cylindrical micelles will be gradually released from inside the cylinders with the process of polymerization (Scheme 2) and some long, alkyl chains will be reversely directed into the water medium. Eventually, the growing chains will be straightened up by the repulsion force between the DBSA tails and the length of conjugation along the backbone, and conductivity will be increased at the same time. Therefore, the extended polyaniline chains will be able to line up with each other into a so-called layered structure[17–20] after orientation, and to present the X-ray diffraction pattern shown in Fig. 7 which demonstrates an additional, significant absorption peak at lower angle. The layered structure has a low angle peak at about $2\theta = 3°$, representing the (002) plane and the d-spacing of the c-axis which was the interdigitization length of the extended long, alkyl side chains.

Another way to confirm the layered structure of the nanorods is by taking AFM micrographs of PANINTs, shown in the upper part of Fig. 7. Interestingly, the AFM micrograph clearly exhibits parallel arranged nanofibers of PANINTs, indicating that most of the PANINTs are laying on the glass plate with interdigitized long alkyl chains of complexed DBSA after orientation, thus demonstrating the layered structure described in Fig. 7 and Scheme 2.

CONCLUSIONS

A simple emulsion polymerization method can be used to prepare highly conjugated one-dimensional nanotubular or nanofibrous polyanilines in the presence of both DBSA and hydrochloric acid.

The optical pictures of micelles before polymerization exhibited the presence of cylindrical micelles covered with DBSA-complexed anilinium; these were not easily initiated by APS with their amine groups covered by its phenyl group. The cylinders were expanded significantly with additional aqueous HCl(aq) which provided aqueous anilinium monomers not covered by phenyl groups and can be easily initiated by the APS in water.

The optical activity and UV–visible–near IR spectra taken at various polymerization times prove that it is easier to prepare a highly conductive, one-dimensional polyaniline if the polymerization time is limited to about 30 min, counting from initiation, in the presence of some strong HCl protonic acid.
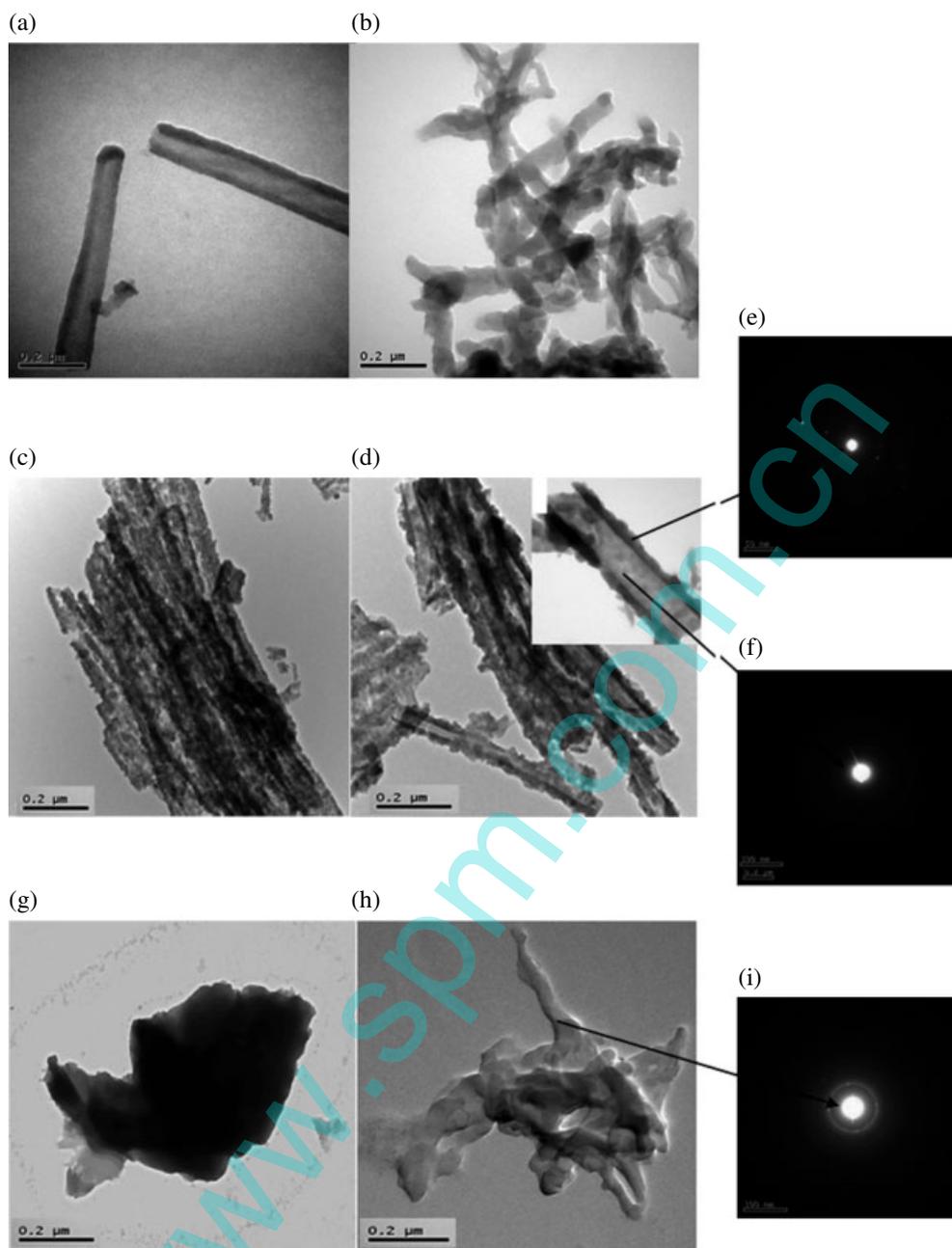
Figure 6. TEM pictures of PANINTs prepared with (a) DBSA/HCl = 10/1, (b) DBSA/HCl = 20/1, (c) DBSA/HCl = 30/1 and (d) DBSA/HCl = 30/1 washed with IPA. Electron diffraction patterns of (e) the outer layer and (f) the inside of a single PANINT of (d). (g) Neat PANIDBSA with 3 h of polymerization time, (h) PANIDBSA washed with IPA. (i) Electron diffraction pattern of (h).

Both SEM and TEM micrographs illustrated the nanofibrous or nanotubular structure of PANINT with mole ratios of DBSA/HCl ranging from 10/1 to 30/1. The micrographs of PANIDBSA which only has DBSA in it exhibited only a granular morphology. The solid PANINTs can become hollow after removing the free DBSA by IPA. UV–visible–near IR spectra demonstrated free carrier tails in the near IR region, resulting from the highly conjugated structure of the PANINT molecules.

The polymerization of the cylindrical micelles caused an excluded volume effect that induced the reversion of some alkyl ends of complexed DBSA molecules. The reversed DBSA became long hairy side chains of the resultant PANINTs, which then associated into a layered structure after orientation, as characterized by WAXD and AFM.

Future work will include finding the relationships between the formation of nanotubules with different types and ratios of strong mineral protonic acids etc.

589
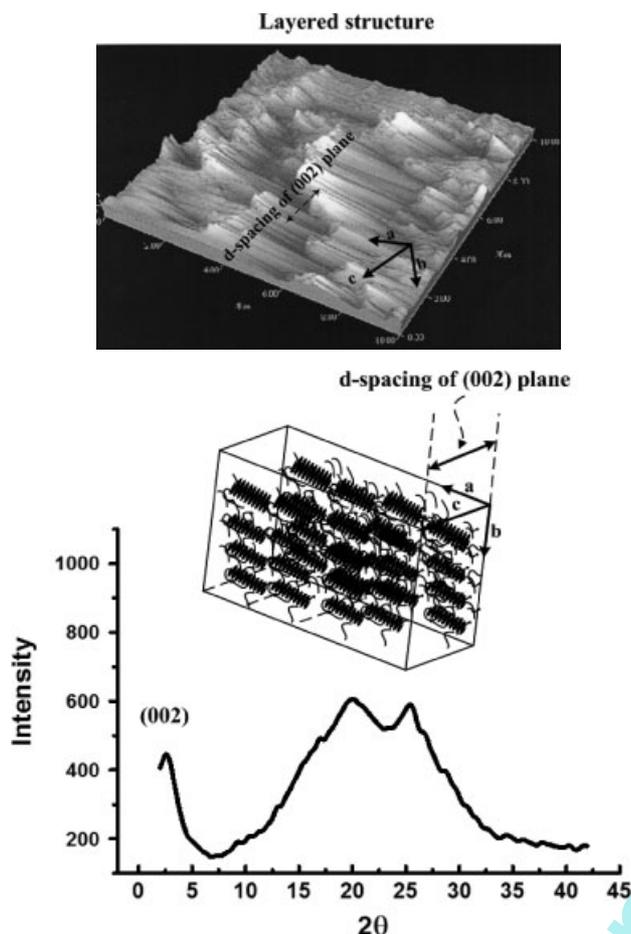
Figure 7. WAXD and AFM picture of oriented, solvent-cast PANINTs prepared with DBSA/HCl = 30/1 molarwise.

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