Preparation of polyaniline nanofibers using the organic solution of aniline as seed

Shuangxi Xing,* Hongwei Zheng

Faculty of Chemistry, Northeast Normal University, Changchun, 130024, P. R. China; e-mail: xingsx737@nenu.edu.cn

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Abstract: Polyaniline (PANI) nanofibers were prepared using an organic solution of aniline as seed in aqueous solution of ammonium persulfate oxidant. Two types of organic solvents were used, which are miscible and immiscible with water to investigate their effect on the properties of the resulting PANI via the aid of SEM, UV-Vis and FT-IR spectra and conductivity measurements. The water dispersity of the polymer was also discussed based on the UV-Vis spectra data. Two possible mechanisms were proposed to explain the formation of the PANI nanofibers during the seed polymerization.

Keywords: polyaniline; nanofibers; organic solvents

Introduction

In recent years, polyaniline (PANI) nanofibers have received much attention owing to their superior properties to the conventional bulk PANI [1-3]. For example, compared to bulk PANI materials, PANI nanofibers show enhanced water processability [4]. Furthermore, PANI nanofibers show improved sensitivity and time response when they are exposed to chemical vapors as they embody porous characteristic resulting in large surface area. Besides, PANI nanofibers also show applications in many fields, including electric devices and flash welding [5]. To obtain PANI nanofibers with high quality, “structural directing agents” are often utilized to guide the formation of nanofibers, such as surfactants, polyelectrolytes, nanowire seeds, and aniline oligomers [6-16]. Under these conditions, the structural directing agents act as templates during the polymerization of aniline in aqueous solutions. A.J. Epstein et al found dilute polymerization of aniline is favourable for production of nanofibrous structures [17, 18]. In the past two years, the preparation of PANI nanofibers received great development owing to the excellent work by J. Huang and R.B. Kaner et al [5, 19-23]. They found that PANI naturally forms nanofibrillar morphology. In order to obtain pure PANI nanofibers, the secondary growth of the initially formed nanofibers must be suppressed. They have developed two effective methods to suppress the secondary growth of the nanofibers, i.e., interfacial polymerization and rapidly mixing reaction. In the former method, aniline is polymerized at the interface between two immiscible liquids, where the newly formed PANI nanofibers diffuse away from the interface to the aqueous solution because of their hydrophilicity. This makes more reaction sites available at the interface and prevents further growth of the PANI nanofibers. During the rapidly mixing reaction, the oxidant is consumed rapidly and depleted after the formation of the nanofibers, which also suppresses the secondary growth of the PANI. Nevertheless, there are still many problems to be solved, such as improving the conductivity and modifying the water dispersity of the...
PANI in order to widen its applications. In our early studies on the synthesis of PANI nanofibers, we found that using PANI/dimethyl sulphoxide (DMSO) solution as seed during the polymerization of aniline led to the formation of uniform PANI nanofibers with relatively high conductivity [24]. The accelerated introduction time and the seeded growth were probably responsible for the formation of the nanofibers. Here, we develop an original seeding polymerization process as an alternative method to obtain relatively uniform PANI nanofibers. In this experiment, aniline monomers were directly dissolved in organic solvent and the solution acting as seed is added into the aqueous solution of the oxidant. Seven kinds of organic solvents were applied for the seed polymerization and two possible mechanisms are proposed.

**Results and discussion**

**Induction time**

Polymerization of aniline is an exothermic reaction where the temperature increases when polymerization begins. Here, we define the period from the addition of oxidant to the beginning of the increase in temperature as induction time to observe the difference of the polymerization of aniline in different systems. The organic solvents can be divided into two classes: DMF, THF, DMSO and NMP are soluble in water to a certain degree; while, toluene, xylene and carbon tetrachloride are immiscible with water.

![Temperature change during the induction time using different kinds of organic solvents for the polymerization](image)

**Fig. 1.** Temperature change during the induction time using different kinds of organic solvents for the polymerization (a-DMF; b-THF; c-DMSO; d-NMP; e- toluene; f- carbon tetrachloride; g- xylene; h-no organic solvent, the vertical line marks a typical induction time of the polymerization without organic solvent).
Therefore, aniline which was dissolved in different organic solvents has different interaction with the oxidant (APS). For the water miscible organic solvents, such as DMSO, the interaction between DMSO and water molecules inhibits the fast dissolution of the aniline into the acid solution to form anilinium ions hence further retards their interaction with the oxidant. Therefore, the induction time is lengthened with ca. 850 s as compared to ca. 490 s for the polymerization of aniline without addition of organic solvents. The induction time for the polymerization of aniline dissolved in DMF, THF and NMP is 520 s, 610 s and 560 s, respectively, as can be seen from Fig. 1. The difference in the induction time may have originated from the different interaction between the organic solvents and the water molecules or hydrogen ions. Stronger interaction resulted in a longer induction time. On the other hand, when toluene, xylene and carbon tetrachloride were used to dissolve aniline, the organic solvents have weak interaction with the water molecules or hydrogen ions. Such seeding polymerization is similar to the interfacial polymerization of aniline carried out in the presence of two immiscible liquids. Under this condition, aniline moves to the interface formed by the two immiscible liquids quickly and reacts with the oxidant in the acid solution to initiate the polymerization. A shorter induction time of ca. 360 s, 390 s and 485 s for toluene, xylene and carbon tetrachloride as organic solvents, respectively, was thereby obtained (Fig. 1e to 1g, respectively).

**Morphology**

The SEM images of the PANI obtained from aniline dissolved in the first class of organic solvents as seed are shown in Fig. 2. Nanofibers with length of 300 to 400 nm and width ranging from 50 to 60 nm are observed. In our former experiment where PANI powder was dissolved in DMSO as seed to obtain PANI nanofibers, we found that the accelerated induction time was responsible for the formation of uniform nanofibers because of the suppression of the secondary growth of the PANI [24].

![Fig. 2. SEM images of the samples using different kinds of organic solvents for the polymerization (a-DMF; b-THF; c-DMSO; d-NMP).](#)
However, in this experiment, the induction time for the polymerization of aniline by using aniline/organic solvents as seed is shorter than that for the conventional polymerization of aniline. Here, we consider the organic solvents act as dispersant during the whole polymerization owing to their interaction with water molecules or hydrogen ions. The initially formed PANI nanofibers are dispersed by the organic solvents and the secondary growth of the nanofibers in conventional polymerization of aniline is thereby inhibited. Finally, the PANI nanofibers are obtained.

When aniline dissolved in the second class of organic solvents as seed were used, the process of formation of the nanofibers was similar to that of the interfacial polymerization. The polymerization of aniline was carried out at the interface formed by the two immiscible liquids. Because it is the intrinsic characteristic for the aniline to form nanofibers after polymerization [22], PANI nanofibers were generated after a period of induction time when aniline seed was added into the aqueous solution containing oxidant. The migration of the newly formed hydrophilic PANI nanofibers to the water phase suppresses the secondary growth of the nanofibers thereby no apparent aggregation was observed (see Fig. 3).

![Fig. 3. SEM images of the samples using different kinds of organic solvents for the polymerization (a- toluene; b- carbon tetrachloride; c- xylene; d-no organic solvent).](image)

**FT-IR spectra**

The FT-IR spectra of the different samples are shown in Fig. 4. The presence of the characteristic peaks of PANI doped with HCl indicates the successful polymerization of aniline [24]. The peaks at ca. 1560 and 1490 cm\(^{-1}\) are assigned to C=C stretching of the quinoid and benzenoid rings, respectively, and the peak at ca. 1140 cm\(^{-1}\) represents the C-H aromatic in-plane bending. The peak observed at 1292 cm\(^{-1}\) is
related to the C-N stretching vibration of the benzenoid ring. The band falling in the range 800-860 cm\(^{-1}\) is identified with the out-of-plane bending of C-H bond in the 1,4-disubstituted ring, which has been used as a key to identify this type of substituted benzene. The peak at about 1140 cm\(^{-1}\) is often related to the doped structure; therefore, the results suggest that the PANI obtained by using aniline seed dissolved in organic solvents is more protonated than that from the conventional polymerization, as can be seen from Fig. 4. The peak normally observed at 1136 cm\(^{-1}\) has red-shifted to about 1128 cm\(^{-1}\) when using the seed polymerization with aniline/DMF seed. The other samples also exhibited different degrees of red-shifts, indicating that a slightly higher doping level was obtained when the aniline is polymerization by using this seed method.

![FT-IR spectra of the samples using different kinds of organic solvents for the polymerization](image)

**Fig. 4.** FT-IR spectra of the samples using different kinds of organic solvents for the polymerization (a-DMF; b-THF; c-DMSO; d-NMP; e- toluene; f- carbon tetrachloride; g- xylene; h-no organic solvent).

**UV-Vis spectra and water dispersity**

A typical absorption spectrum of PANI doped with HCl has two absorption peaks at about 330 nm and 420 nm and one absorption peak maximum (\(\lambda_{\text{max}}\)) at about 850 nm (see Fig. 5). The first two peaks often combine to emerge as a platform. The peak at 330 nm arises from \(\pi-\pi^*\) electron transition within benzenoid segments and the peak at 420 nm, accompanied by the absorption with 850 nm as the maximum peak is related to the doping level and formation of polaron [8].

The water dispersity of the different samples can be observed from their corresponding UV-Vis spectra based on the absorption intensity because the measurement is conducted quantitatively. From Fig. 5, we can find most of the samples prepared from seed polymerization have better water dispersity than that obtained from conventional method except Samples b and c which uses THF and DMSO as organic solvents, respectively. This may have resulted from that the more
uniform the PANI is, the better dispersity it has [4]. However, as for Samples b and c, poorer water dispersity may have originated from their longer induction time than the conventional one. Under these conditions, the interaction between aniline and THF or DMSO is stronger than those between aniline and other organic solvents, leading to the corresponding PANI having weaker interaction with water.

![Fig. 5. UV-Vis spectra of the samples using different kinds of organic solvents for the polymerization (a-DMF; b-THF; c-DMSO; d-NMP; e-toluene; f-carbon tetrachloride; g-xylene; h-no organic solvent).](image)

Conductivity

The conductivity values of different samples with reaction time of 6 h and 12 h are listed in Table 1. The polymerization of aniline might be incomplete when the reaction time is below 6 h; however, aggregation becomes significant when reaction time is longer than 12 h. As deduced from the FT-IR spectra data, nearly all the samples obtained from seed polymerization show higher conductivity than that from conventional method. This may result from that a higher doping level can lead to a higher conductivity value. Apart from that, the uniform morphology of the samples from seed polymerization contributes to the relatively high conductivity [25]. On the other hand, we found that the conductivity of the samples using the first class of organic solvents increases with reaction time (Table 1), which is similar to that without organic solvent, because a longer reaction time induces a relatively complete polymerization and a longer conjugation chain length is then obtained. However, the conductivity of the samples using the second class of organic solvents showed a slight decrease with reaction time. Because the polymerization of the aniline using interfacial method can lead to a fast reaction process, the resulting PANI reaches its maximum conductivity in a relatively short time. The existing organic solvents that are immiscible with water may disturb the polymerization when the reaction time is prolonged, which results in the decrease of the conductivity.
**Tab. 1.** Preparation conditions for different samples and their corresponding conductivity obtained from 6 h and 12 h, respectively.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Organic solvent</th>
<th>Conductivity (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>6 h</td>
</tr>
<tr>
<td>a</td>
<td>DMF</td>
<td>7.96</td>
</tr>
<tr>
<td>b</td>
<td>THF</td>
<td>5.64</td>
</tr>
<tr>
<td>c</td>
<td>DMSO</td>
<td>7.94</td>
</tr>
<tr>
<td>d</td>
<td>NMP</td>
<td>1.80</td>
</tr>
<tr>
<td>e</td>
<td>toluene</td>
<td>7.98</td>
</tr>
<tr>
<td>f</td>
<td>carbon tetrachloride</td>
<td>8.10</td>
</tr>
<tr>
<td>g</td>
<td>xylene</td>
<td>7.66</td>
</tr>
<tr>
<td>h</td>
<td>-</td>
<td>1.80</td>
</tr>
</tbody>
</table>

**Conclusions**

Different kinds of organic solvents including DMSO, DMF, THF, NMP, toluene, xylene and carbon tetrachloride were used to dissolve aniline and the corresponding solutions acting as seed was dropped into the aqueous solutions of APS to initiate the polymerization of aniline. The resulting PANI showed relatively uniform nanofiber morphology with high conductivity. The interaction between the organic solvents and the PANI might play an important role in forming and dispersing the PANI nanofibers when using solvents that are miscible with water. However, the last three solvents that are immiscible with water can be used to explain the formation of the nanofibers via the interfacial polymerization method. The interaction between the solvents and the monomers had effect on the formation, structure, conductivity and water dispersity of the resulting PANI to different extents. The stronger the interaction is, poorer the water dispersity shown by the polymer. This seed polymerization method allows the synthesis of nanostructured PANI with higher conductivity and varying levels of water dispersity thereby widening the scope of applications for this material.

**Experimental part**

**Materials**

Aniline was distilled under vacuum before use and other regents were used as received.

**Synthesis of PANI**

A typical experiment was carried out as follows: 0.47 g of aniline was dissolved in 1 mL of organic solvent (dimethyl formamide (DMF), tetrahydrofuran (THF), dimethyl sulphoxide (DMSO), N-methyl-2-pyrrolidinone (NMP), toluene, xylene and carbon tetrachloride). Then the resulting solution was added dropwise into the hydrochloride solution (ca. 99 mL) containing 1.14 g of ammonium persulfate (APS) under stirring. The mixture was stirred at room temperature for 6 h and 12 h, respectively. The resulting precipitate was collected by filtration. After the product was then repetitively washed by deionized water and ethanol, the product was dried under vacuum at...
room temperature for 48 h. The total volume of the mixture was 100 mL and the molar ratio of the aniline and APS was kept at 1:1. The detailed preparation conditions are listed in Table 1. For the conventional polymerization of aniline, no organic solvent was added into the system while the other conditions remained the same as above.

Characterization

The morphology of the resulting PANI was observed using a scanning electron microscopy (SEM, JEOL FESEM JEM-6700F) with gold coating.

Optical spectra of the samples were recorded on a UV-2550 UV-Vis spectrometer. The dispersity of the product in water was measured based on their corresponding UV-Vis spectra and the measurement was conducted quantitatively as follows: 0.0100 g of sample was dispersed in 50.00 mL of deionized water under ultrasonic treatment for 3 min. Deionized water was used as background for this measurement.

FT-IR spectra of the different samples were measured on an FTIR-8400s (Shimadzu) spectrometer in the transmission mode. Standard KBr technique was applied. Resolution of the measurements was 4 cm⁻¹.

The conductivity of powder pellets at room temperature was measured by a typical four-probe method (SDY-5). For each value reported, at least three measurements were averaged.

References