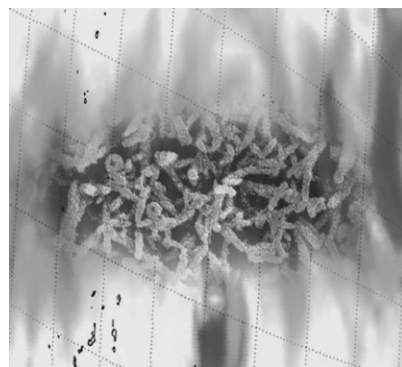


A Rapid and Facile Synthesis of Nanofibrillar Polyaniline Using Microwave Radiation

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We present the first fast and facile microwave assisted synthesis of polyaniline (PANI) nanofibers (“MWA synthesis”). Under conventional synthesis (CS), the polymer was produced with 79.7% yield after 5 h at ambient temperature. However, under microwave irradiation, the nanofibers were produced with yield of 76.2% after only 5 min, i.e., with 78.8% after 20 min at ambient temperature. The FTIR and Raman spectra show the PANI structure in all samples either synthesized conventionally or in the microwave. SEM and TEM confirm the nanofibrillar morphology.



Introduction

The past decade has been a period of exceptionally fast growth in the field of one-dimensional (1D) nanomaterials because of their unique electrical, optical, and magnetic properties as well as their potential applications in sophisticated devices with advanced functions.^[1,2] Such interest emerges from the expectation that the size of electronic circuit components will soon reach the size range of atoms or molecules. Nanofibers of the conducting polymer polyaniline (PANI) in particular have attracted great interest because of their properties which may enable them to find applications as sensors,^[3–5] batteries,^[6,7] molecular electronic devices, corrosion inhibitors,^[8,9] and

separation membranes.^[10,11] While various synthesis methods have been established^[12] preparation of 1D nanostructured PANI with controllable sizes and morphologies on a large scale is still a major challenge. There are different pathways toward the synthesis of PANI nanostructures, but to the best of our knowledge, none of them have used microwave radiation or demonstrated such a fast and efficient fabrication method.

Microwave radiation has been employed in many recent chemical reaction studies (organic and inorganic syntheses, selective sorption, oxidations/reductions, polymerizations, etc.) and has been found to change the kinetics and very often morphology as well.^[13] These reactions are understood to be more environmentally friendly, requiring less energy than conventional processes. A recent American Chemical Society monograph on Green Chemistry^[14] recommends using catalysts or microwave radiation to minimize the energy required for a reaction and consumption of solvents. Microwave heating is also unique in providing scale-up processes with a uniform reaction environment, thus paving the way to large-scale industrial production of high-quality advanced nanomaterials. It has been established that microwave irradiation is becoming an increasingly popular heating method for nanomaterials synthesis.^[15–17]

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In this work we report the first rapid and facile microwave assisted synthesis of PANI nanofibers ("MWA synthesis"). It is a clean, fast, and convenient way to get nanofibers in high yield at ambient temperature. The high yield obtained, short reaction time, and low energy consumption suggest that MWA synthesis could be a favorable alternative for large-scale industrial production compared to conventional synthesis ("CS synthesis").

Experimental Part

Conventional Chemical and Microwave Syntheses

PANI was prepared by aniline oxidation with potassium iodate (KIO_3).^[18–20] To an aqueous solution of 1.25 M hydrochloric acid (12 mL for MW and 240 mL for CS) was added KIO_3 (0.432 g for MW and 8.64 g for CS). Aniline (0.48 mL for MW and 9.6 mL for CS) was added to this solution. Each MW synthesis was carried out for 5, 10, 15, and 20 min and each experiment was repeated three times to verify reproducibility. For conventional synthesis the solution was stirred for 5 h. The reaction mixture was filtered and washed thoroughly with distilled water and acetone to eliminate impurities (e.g., low molecular weight oligomers and other impurities). The retentates were dried in a vacuum oven at 40 °C for 16 h.

Microwave Apparatus

MW irradiation was performed in a single mode focused CEM reactor (Model Discover, CEM Co., Matthew, NC) operating at 2.45 GHz with ability to control output power. Temperature in the system was measured by a fiber optic temperature sensor preventing interaction with MWs and influence on the temperature reading. An external cooling circuit maintained constant temperature of the reaction mixture and constant irradiation power. The absorbed MW power, $P_{\text{abs}} = mC(dT/dt)_i$, was calculated by the calorimetric method measuring temperature increase during the initial heating period $P_{\text{abs}} = mC(dT/dt)_i$. The initial heating period was characterized by a linear temperature increase, during which dissipation of heat by the external thermostat was small. The heat capacity C_p of the solution was approximated as the heat capacity of water. In order to maintain uniform temperature the sample was mixed by magnetic stirring at 400 rpm. All experiments were done under the same conditions by keeping constant irradiation power, temperature, and initial reaction mixture volume (12 mL). Absorbed power was calculated to be 6.6 ± 0.4 W for 93 W emitted power by the instrument. With the experimental design that was used, the temperature was maintained at 24 ± 1 °C in all experiments.

Gel Permeation Chromatography (GPC)

Molecular weights were determined with GPC using a 300×7.5 mm² PolyPore column (Polymer Laboratories, UK). The GPC system consisted of a Waters 515 HPLC pump, a Degasex DG-4400 on-line degasser connected to a series of three GPC columns (a Waters Styrogel HR6 column and two Polymer Laboratories PolyPore columns) with a PolyPore guard, a Rheodyne manual

injector with 200 μL injection loop, and a Waters column oven. The PANI 5 and 20 min samples were dissolved in 5 mL NMP to give 3 mg · mL⁻¹ concentration. The eluent was NMP and the flow rate was 0.3 mL · min⁻¹. All solutions were filtered through 0.45 μm syringe filters before injection onto the column set. The columns and RI detector were maintained at 35 °C. Data acquisition and processing were performed using ASTRA 4 software (Wyatt Technologies Corporation). The Polymerlabs EasyCal PS-1 set of ten Polystyrene standards were dissolved in the same eluent at a concentration of 2 mg · mL⁻¹ and used to obtain a calibration curve under the same conditions.

SEM Characterization

SEM was carried out using a Philips XL30S Field Emission Gun with a SiLi (lithium drifted) EDS detector with Super Ultra Thin Window. The samples were 10 mm in diameter, mounted on aluminum studs using adhesive graphite tape and sputter coated using a Polaron SC7640 Sputter Coater at 5–10 mA and 1.1 kV for 5 min.

TEM Characterization

A JEOL TEM-2010 transmission electron microscope (TEM) was used. The TEM sample was dispersed in hexane by ultrasonication, and then pipetted onto copper coated grids.

FTIR Spectroscopy

Fourier transform infrared (FTIR) spectra were recorded with resolution 2 cm⁻¹ using a Nicolet 8700 FTIR spectrometer with KBr pellets. One hundred scans were averaged for each sample.

Raman Spectroscopy

Raman spectra were recorded at 1 cm⁻¹ resolution using a Renishaw Raman System-Model 1000 spectrometer with 785 nm (red) laser excitation.

Results and Discussion

Yield

Under conventional conditions (CS), the polymer was produced with 79.7% yield after 5 h: if the reaction was continued the yield was 83.4% after 12 h at ambient temperature. By contrast, under microwave irradiation the nanofibers were produced with the remarkable yield 76.2% after only 5 min after the beginning of the reaction, and 78.8% after 20 min at ambient temperature.

SEM and TEM Characterizations

The morphology of the PANI obtained from MWA synthesis (Figure 1a–d) and from conventional synthesis (Figure 1e

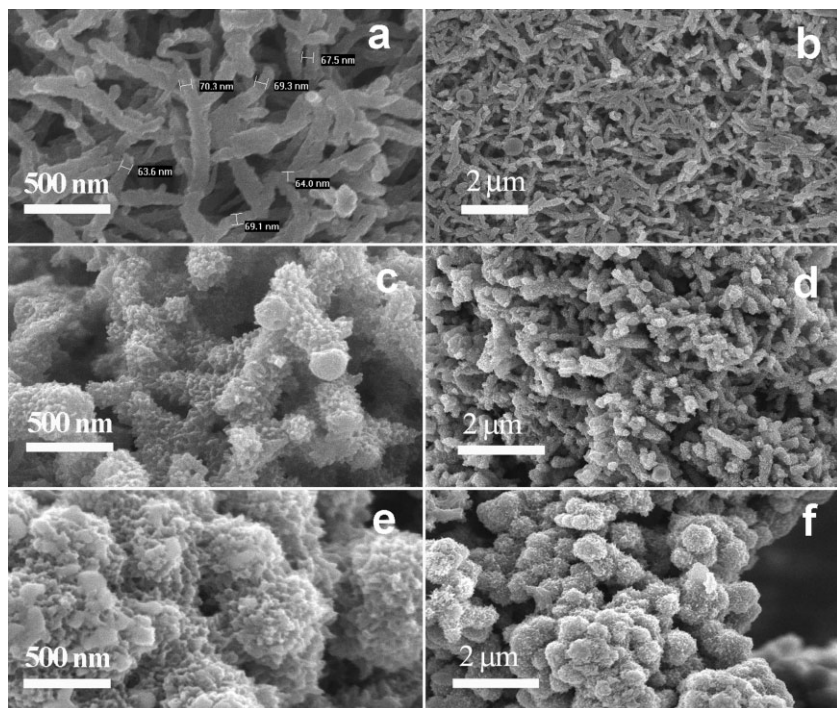


Figure 1. SEM micrographs: sample from a microwave assisted synthesis taken after 5 min (a, b); sample from a microwave assisted synthesis taken after 20 min (c, d); and sample from a chemical synthesis taken after 5 h (e, f).

yields. It is well known that PANI can form different supramolecular structures (nanofibers, nanotubes, nanospheres, nanosheets, etc.) depending on the conditions (such as concentrations, temperature, pH, etc.).^[21,22] At this point we cannot definitely say why there are some morphological differences in the samples after 5 and 20 min. The sample was exposed to a prolonged microwave irradiation from 5 up to 20 min, and this obviously affected the morphology, while the structure remained relatively similar (confirmed by FTIR, Raman, and MW).

The SEM micrographs of the samples obtained by conventional synthesis after 5 h are shown in Figure 1e and f. The PANI shows granular structure with no obvious entangled nanostructures (i.e., nanofibers). This granular morphology is the common characteristic of conventionally synthesized PANI material.

A representative TEM micrograph of a sample after 20 min MWA synthesis is shown in Figure 2. The elongated morphology seen in the SEM micrographs is

clearly visible, and the presence of nanofibers can be confirmed. At this point there is no evidence of nanotubular morphologies and it seems that rod-like structures prevail in this sample.

To probe the possible structural differences involved in the formation of the various assemblies, FTIR and Raman spectroscopies for each of the structures obtained from MW and conventional synthesis were carried out and the spectra were compared.

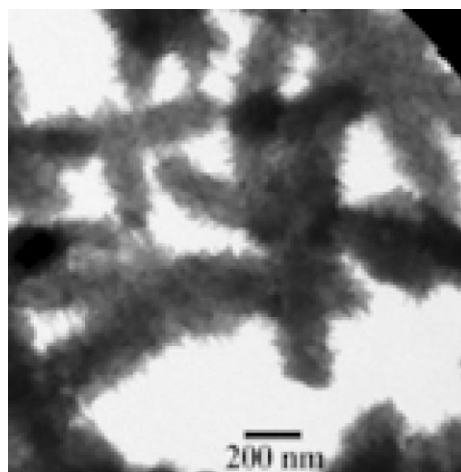


Figure 2. TEM micrograph of the sample from a microwave assisted synthesis taken after 20 min.

and f) was determined by SEM. After 5 min from the beginning of the MWA synthesis PANI shows a nanofibrillar structure. Remarkably, this product was obtained with 76.2% yield. The fibers are relatively uniform and entangled with diameter between 60 and 70 nm and length around 1 μm . In addition to the nanofibers spherical nanostructures are noticeable, and some of them are hollow. This indicates partial morphological heterogeneity of the sample. Because porous materials have larger specific surface area, this material may act as a promising catalyst or chemical sensor carrier. Furthermore, the sample obtained after 20 min still exhibits nanostructured morphology (partly elongated structures). However, the nanofibrillar morphology is not as evident as the structures become covered with small particles: the surface of the nanofibers is not as smooth as in the sample after 5 min probably due to further PANI polymerization.^[21,22] The nanofibers become thicker and shorter which could imply a different polymerization mechanism at a later stage of reaction. The molecular weights for the samples obtained after 5 and 20 min were 17 473 and 18 689 $\text{g} \cdot \text{mol}^{-1}$, respectively, corresponding to average repeat unit numbers of 195 and 205. This is in line with the FTIR and Raman results which suggest the presence of very similar structures in both cases. Also, this means that the polymerization was substantially completed after 5 min and this is again in line with the values obtained for the

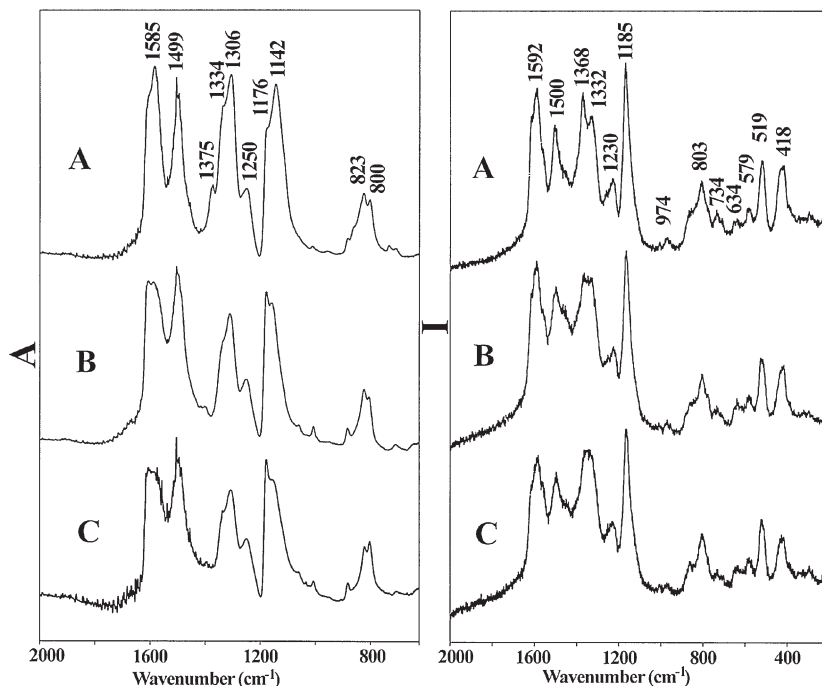


Figure 3. FTIR spectra (right) and Raman spectra (left) of the samples: (A) microwave assisted synthesis sample taken after 5 min; (B) microwave assisted synthesis sample taken after 20 min; and (C) chemical synthesis sample taken after 5 h.

FTIR Spectroscopy

Representative FTIR spectra of the samples are shown in Figure 3 (left). The intense bands at 1585 and at 1499 cm^{-1} are attributed to C=C stretching in the quinoid and benzenoid rings, respectively.^[24] The low intensity band at 1375 and the shoulder at 1176 cm^{-1} are attributed to C=N stretching.^[23,24] For standard PANI the strong band at $\approx 1140 \text{ cm}^{-1}$ is referred to as an “electronic band” and often related to the doped structure. A band at 823 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 the type of substituted benzene.^[23,24] According to the FTIR spectra shown in Figure 3 which all have similar features, the PANI structure is retained even in the sample obtained by MW after 5 min.

Raman Spectroscopy

Raman spectra of the samples obtained by MW after 5 and 20 min and for the conventional synthesis are shown in Figure 3 (right). The bands at 1592 and 1500 cm^{-1} are characteristic for C–C stretching in-plane of the benzenoid ring and C=N stretching band of the quinoid diimine units, respectively. The band at 1332 cm^{-1} is assigned to C–N stretching of the cation radical species, while the band at 1230 cm^{-1} belongs to C–N of benzenoid units.^[23,24] The bands at 1185, 803, and 734 cm^{-1} are attributed to C–H

bending of the quinoid rigs, C–H wag out-of-plane of the benzenoid ring (para), and C–H wag out-of-plane of the benzenoid ring. The band at 634 cm^{-1} is due to a benzenoid ring deformation in-plane of the benzenoid ring while the band at 520 cm^{-1} is assigned to a quinoid deformation in-plane of the benzenoid ring. The band at 419 cm^{-1} is attributed to a ring deformation out-of-plane of the benzenoid ring.^[23,24] The FTIR and Raman spectra show the PANI structure in all samples either synthesized conventionally or in the microwave.

Conclusion

In summary, a novel method for fast and facile, room-temperature synthesis of PANI 1D structures is demonstrated in this communication. Nanofibers of PANI are successfully obtained for the first time under microwave radiation in relatively high yield (76.2%) and $\bar{M}_w = 17\,473 \text{ g} \cdot \text{mol}^{-1}$ after 5 min. Further polymerization

for 20 min gave 78.8% yield and $\bar{M}_w = 18\,689 \text{ g} \cdot \text{mol}^{-1}$, which means that the polymerization was substantially completed after 5 min. The morphology was confirmed by SEM and the PANI structure by FTIR and Raman. This method provides a convenient and environmentally friendly way to produce PANI nanostructures. Because of the high penetration depth of microwave radiation and specific heating mechanisms the effects resulted in enhanced reaction kinetics. We hypothesize that both non-thermal and thermal effects could be responsible for the fast kinetics and effects on morphology. The effect of microwave irradiation on chemical processes is still debatable. Some research groups have mentioned the existence of so-called non-thermal microwave effects, which cannot be easily estimated by temperature measurements. They lead to a sudden acceleration of reaction rates.^[25,26] Regardless of the type of activation (thermal) or kind of microwave effects (non-thermal), microwave energy has its own advantages which are still waiting to be fully understood and applied to chemical processes. To reveal the formation mechanism and to obtain optimum conditions for MWA synthesis further experiments will be carried out by our research group and will be reported in a subsequent paper.

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