

Microwave-Assisted Synthesis of Functionalized Polyaniline Nanostructures with Advanced Antioxidant Properties

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Facile and fast microwave- (MW) assisted synthesis of copolymers of aniline and 2-aminobenzoic acid (2ABA) or 2-aminosulfonic acid (2SULFO) was performed by chemical polymerization of several mole ratios of aniline to functionalized aniline (FA). The physicochemical properties of the copolymers thus prepared were compared with the poly(aniline-co-2-aminobenzoic acid) (2ABAPANI) and poly(aniline-co-2-sulfonic acid) (2SULFOPANI) copolymers synthesized by conventional synthesis (CS) at the same temperature. FTIR and UV–vis spectra show the 2ABAPANI or 2SULFOPANI structure in all samples synthesized either conventionally or in the microwave reactor, however the yield was 2.5–3 times higher for nanostructured functionalized copolymers (fPANI) synthesized by MW. The effect of microwave irradiation on the antioxidant properties of the nanostructured 2ABAPANI and 2SULFOPANI copolymers was investigated. These samples showed 2.1–2.4 times better radical scavenger efficacy than their conventionally synthesized counterparts. A formation mechanism of polyaniline nanofibers under MW conditions is tentatively proposed based on thermal and nonpurely thermal effects on the nucleation modes.

Introduction

The discovery of conducting polymers has opened up many possibilities for new polymeric devices that combine unique optical and electrical properties of conducting polymers, and mechanical and processing properties of conventional polymers.¹ The conducting polymer polyaniline (PANI) is an interesting material for incorporation in thermoplastics due to its useful electronic, optical and redox properties. PANI has been extensively studied for its environmental stability in conducting form, ease and low cost of synthesis, unique redox properties, and high conductivity.¹ The commercial exploitation of PANI has been hampered by its intractable nature, as it is normally produced as an insoluble powder.^{2,3} A number of attempts have been made to overcome the poor processability of PANI, including doping with protonic acids such as dodecylbenzene-sulfonic (DBSA) and camphorsulfonic acids (CSA), preparation of PANI composites with thermoplastic polymers, and synthesis of copolymers of aniline and aniline with for example alkyl, carboxylic acid, and sulfonic acid substituents.^{3–8} Self-doping results from the polymerization of a mixture of aniline and an acid group-substituted aniline.⁹ An interesting property of such copolymers is that the presence of an acid group in the polymer backbone can act as a self dopant instead of an external dopant as is the case for PANI.¹⁰

The insolubility of PANI in most common solvents can be circumvented to some extent, by copolymerizing aniline with substituted anilines that impart solubility to the resulting

functionalized PANI copolymers (fPANI). Copolymerization of aniline with aminobenzoic acid (ABA) or aminosulfonic acid (SULFO) gives copolymers that are soluble in aqueous basic media, and in polar solvents such as *N*-methyl-2-pyrrolidone (NMP) and dimethyl sulfoxide (DMSO).^{3,10} The solubility of the copolymer increases with the proportion of ABA or SO₃H in the copolymer chains. Copolymers of aniline and ABA or SULFO have been synthesized by chemical and electrochemical routes, and characterized by spectral, electrical, and thermal studies.^{3,9–14}

PANI and fPANI are efficient radical scavengers for the stable α,α -diphenyl- β -picrylhydrazyl (DPPH) free radical.^{15–21} The radical-scavenging property of PANI and fPANI is beneficial for protection of foodstuffs against deterioration or rubber against oxidative aging and has significant implications for their inclusion as biomaterials in biological media. Wang et al. showed that the antioxidant activity of PANI increased as the nanofibers' surface area increased.²² PANI nanofibers with high surface areas have stronger ability for scavenging free radicals than that of PANI with larger particles and in this respect can have better performance. We recently reported ultrafast and facile synthesis of polyaniline nanofibers using an MW approach at ambient temperature.²³ Under MW irradiation, the nanofibers were produced with high yield (ca. 80%) after only 5 min at room temperature. This approach has paved the way to possible large-scale production of high-quality advanced nanomaterials.

Despite the simplicity of conventional procedures (without MW), the formation mechanisms involved in such processes are quite complex. For example, it is reported that agglomerates are mainly formed when aniline is polymerized under conditions that favor heterogeneous nucleation,²⁴ whereas homogeneous nucleation promoted formation of nanofibers. We believe that revealing the factors that affect the synthesis of regular and

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functionalized polyaniline nanofibers in MW, together with the previous findings based on conventional synthesis, could help to elucidate how polyaniline nanofibers form and to obtain a physicochemical picture about the initial conditions for their genesis. This should help in manipulating and producing polyaniline nanofibers for various applications and facilitate the development of a simple method to synthesize nanofibers of other conducting polymers such as polypyrrole and polythiophene.

In the present work, we have investigated MW-assisted copolymerization of aniline with aminobenzoic and sulfonic acids using potassium iodate (KIO_3). We wish to explore further applications of functionalized polyaniline materials, and to that end we investigated their conditions of formation under MW irradiation and the antioxidant properties of the thus prepared materials.

Experimental Methods

Synthesis. 2ABAPANI and 2SULFOPANI were prepared by aniline oxidation with potassium iodate (KIO_3). To an aqueous solution of 1.25 M hydrochloric acid (12 mL for MW and CS) was added KIO_3 (0.432 g). Polymerization of comonomer mixtures with 1:1 mol ratios of aniline to functionalized aniline (2ABA or 2SULFO) was carried out with aniline and 2ABA or 2SULFO with 0.04 mol in total in the mixture. The synthesis of aniline with 2ABA or 2SULFO with 1:2 and 2:1 aniline: functionalized aniline (FA) mole ratios was carried out employing the same procedure.

Each MW synthesis was carried out for 5, 10, 15, 20, 30, and 40 min (depending on the mole ratio of comonomers), and each experiment was repeated three times to verify reproducibility. To compare morphology with CS synthesis 2ABAPANI samples were synthesized for 20 min (slower synthesis) and 2SULFOPANI for 10 min (faster synthesis) duration time. The reaction mixture was filtered and the retentate 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 overnight.

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. The key part of our experiments is the ability to keep a constant temperature and an irradiation power during the synthesis for a prolonged period of time. This enables a reliable comparison of samples obtained using different reaction times. Such experimental conditions are achieved by carefully balancing the cooling efficiency of the external thermostat and the maximal delivered MW power by the CEM reactor. 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, $P_{\text{abs}} = mC_p(dT/dt)_i$, was calculated by the calorimetric method from the measured temperature increase during the initial heating period $P_{\text{abs}} = mC_p(dT/dt)_i$. 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. 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 $(24 \pm 1)^\circ\text{C}$ in all experiments.

Gel Permeation Chromatography (GPC). Molecular weights were determined with GPC using a 300×7.5 mm Polypore column (Polymer Laboratories, UK). The GPC system consisted of a Waters 515 HPLC pump, a Degassex DG-4400 online 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 mole ratios 2:1, 1:1 and 1:2 of 2ABAPANI (MW) 20 min and 2SULFOPANI (MW) 10 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 Polymer Laboratories 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.

FTIR Spectroscopy. FTIR spectra were recorded with resolution 2 cm^{-1} using a Nicolet 8700 FTIR spectrometer with KBr pellets. 100 scans were averaged for each sample.

SEM. SEM was carried out using a Philips XL30S Field Emission Gun with a SiLi (Lithium drifted) EDS detector with Super Ultrathin 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.

UV–vis Spectroscopy. UV–vis spectra of 2ABAPANI and 2SULFOPANI samples dissolved in a range of solvents with concentration 0.05 g L^{-1} were recorded with a Shimadzu UV-2102PC spectrophotometer over the wavelength range 250–800 nm at ambient temperature.

The DPPH free radical scavenging activity of each sample was determined according to the method described previously¹⁶ but using a higher strength DPPH solution adapted for use with CP powders. 1.5 mL of freshly prepared 610 $\mu\text{mol L}^{-1}$ DPPH solution (containing $n = 1.22 \times 10^{-5}$ mol of DPPH radicals) in MeOH was reacted with 100 μL of MeOH solutions of 2ABAPANI and SULFOPANI samples. 0.3 mg of each sample added to 1.6 mL of total reaction mixture was tested. The reaction mixtures were stirred for 30 s and UV–vis spectra were recorded at 516 nm after 30 min.

Results and Discussion

The yields of 2ABAPANI and 2SULFOPANI samples synthesized under conventional (CS) and MW conditions are shown in Table 1. Under conventional synthesis 2SULFOPANI copolymers were produced with 24.6, 21.4, and 16.8 wt % yields for 2:1, 1:1, and 1:2 mol ratios respectively after 10 min. However, using MW this was significantly improved, resulting in 59.7, 54.1, and 39.6 wt % yields, respectively. In the case of 2ABAPANI, the improvement was even more significant. The yields under CS after 20 min were 14.6, 11.0, and 8.1 wt % for various mole ratios, whereas under MW radiation these values significantly increased (~ 3 times) to 39.8, 31.6, and 23.2 wt %, respectively. The 2ABAPANI copolymers have been synthesized by inverse emulsion polymerization with yields 78.8, 84.0, and 36.1% obtained with the ratios 2:1, 1:1 and 1:2 of aniline to *o*-amino benzoic acid respectively after 24 h.³ The yield decreases with the increase in the amount of 2ABA in the reaction, in accordance with the proposed mechanism where

TABLE 1: Yield of the fPANI Samples Obtained under Conventional (CS) and Microwave (MW) Synthesis

sample	mole ratio A:FA	5 min.(wt %) MW	10 min (wt %) CS	10 min (wt %) MW	15 min (wt %) MW	20 min (wt %) CS	20 min (wt %) MW	30 min (wt %) MW	40 min (wt %) MW
2SULFO PANI	2:1	55.9	24.6	59.7	60.3		61.0		
	1:1	49.5	21.4	54.1	56.2		58.4		
	1:2		16.8	39.6			42.8	44.7	
2ABA PANI	2:1	34.5		36.1	37.4	14.6	39.8		
	1:1					11.0	31.6	34.0	
	1:2					8.1	23.2		25.1

TABLE 2: Molecular Weight of the fPANI Samples Obtained under Microwave (MW) Synthesis

sample	mole ratio A:FA	10 min (5 min) (g mol ⁻¹)	20 min (5 min) (g mol ⁻¹)
2SULFOPANI	2:1	16 174 (15 963)	
	1:1	14 105	
	1:2	11 372	
2ABAPANI	2:1		15 046 (14 678)
	1:1		12 751
	1:2		10 103

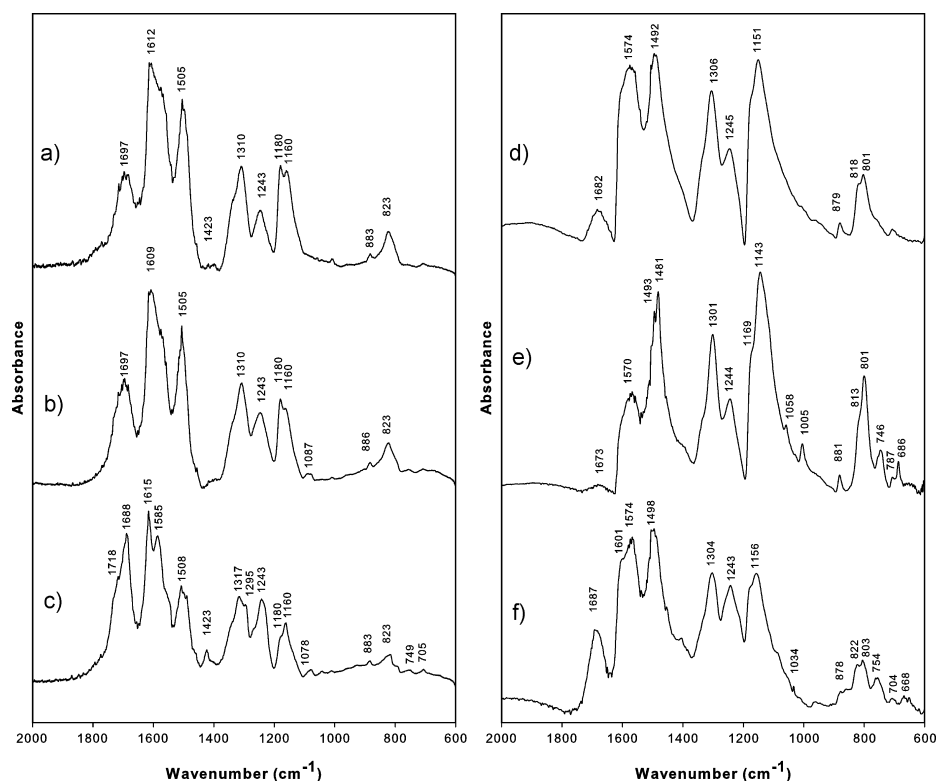
the electron-withdrawing carboxylic group deactivates the aromatic system, slowing down the polymerization of 2ABA in comparison to that of aniline.⁹

GPC Studies. Molecular weights (M_w) of 2ABAPANI and 2SULFOPANI samples obtained by MW irradiation after 20 and 10 min respectively are shown in Table 2. The values are between 10 000 and 16 000 g mol⁻¹ for all samples. This means that all samples typically contained 100–200 monomer units.

FTIR Spectroscopy. FTIR spectra of 2ABAPANI samples obtained in MW and CS synthesis using 2ABA are shown in Figure 1. There are strong bands at 1697 and 1688 cm⁻¹, a shoulder at 1718 cm⁻¹, and peaks at 1609–1615 cm⁻¹, all of which can be assigned to a stretching vibration of C=O from carboxylic group^{10,12} (MW synthesis, parts a–c of Figure 1). The intensity of these bands increases when the proportion of

2ABA increases, which is expected. However, the relative intensities for these bands are not the same for CS synthesis where the peak for the 1:1 ratio (part e of Figure 1) exhibits a lower intensity compared with corresponding bands obtained for 2:1 ratios (part d of Figure 1). This could mean that the 2ABA is not incorporated as efficiently for this specific molar ratio. The intense bands and shoulders at around 1580 cm⁻¹ and the bands at 1500 cm⁻¹ are present in all spectra (Figure 1) and can be attributed to C=C stretching in the quinoid and benzenoid rings, respectively.^{10,12}

The bands at about 1310, 1174, and 1150 cm⁻¹ are attributed to C=N stretching.^{25,26} For CS synthesis, bands at ca. 1150 cm⁻¹ (sometimes referred as an electronic band)^{25–27} are significantly stronger than their MW counterparts. This means that samples obtained by CS should be more conductive and implies increasing occurrence of linear structures and head-to-tail coupling. This is in line with the postulate that the steric effect of substituted groups increases the torsion angle between the close phenyl rings and obstructs charge delocalization, resulting eventually in a decrease in the conductivity.^{8,27} Moreover, the extended conjugation is disrupted by the electron withdrawing effects of the –COOH group (electronic effect).²⁷ The bands at around 700 cm⁻¹ are usually associated with out of plane C–C deformation vibrations and out of plane C–H bending respectively in monosubstituted aromatic rings.^{25,26} Since mono-

**Figure 1.** FTIR spectra of 2ABAPANI after 20 min under MW a) 2:1, b) 1:1, c) 1:2; and CS d) 2:1, e) 1:1, and f) 1:2 mol ratios.

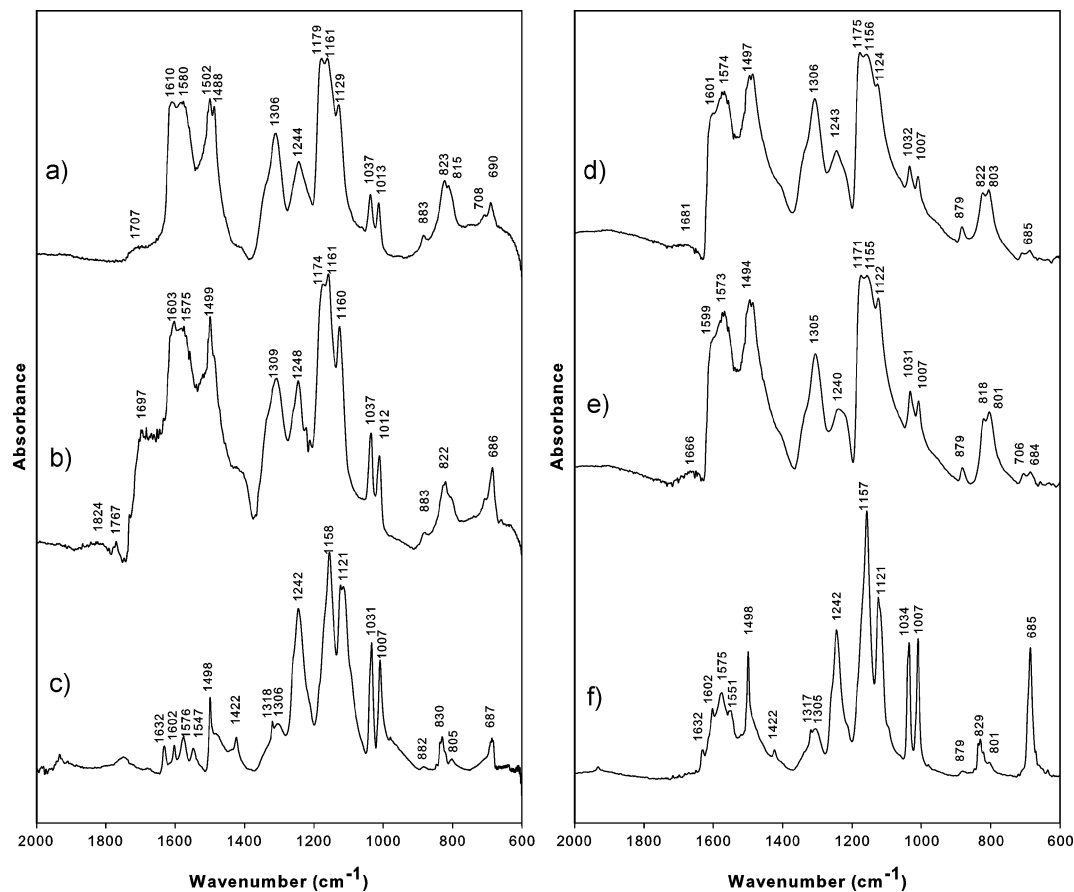


Figure 2. FTIR spectra of SULFOPANI after 10 min under MW a) 2:1, b) 1:1, c) 1:2; and CS d) 2:1, e) 1:1, and f) 1:2 mol ratios.

substituted rings are always terminal in the chain, the bands associated with them are clearly visible only in spectra of short-chain oligoanilines, which show low intensity for both syntheses, in accordance with the aforementioned GPC measurements. In addition, there is a very low intensity band at around 880 cm^{-1} that probably originates from the branched 1,2,4-trisubstituted ortho-coupled benzene rings. However, the main peak is at 820 cm^{-1} , which originates from C–H out of plane bending in 1,4-disubstituted ring structures (*para*-coupling), and is an indicator that head-to-tail coupling of aniline occurs, and this is especially evident in CS synthesis.^{25,28}

The bands at around 1600 and 1500 cm^{-1} for 2SULFOPANI are attributed to stretching of $\text{N}=\text{Q}=\text{N}$ and $\text{N}-\text{B}-\text{N}$ (quinoid and benzenoid) units, respectively.¹⁰ The bands at 1310 and 1160 cm^{-1} and the high intensity band at 1175 cm^{-1} are attributed to $\text{C}=\text{N}$ stretching.¹⁰ The bands at 1245 cm^{-1} originate from $\text{C}-\text{N}$ stretching in the benzenoid rings. The peaks at 1030 cm^{-1} are related to stretching of the $\text{S}=\text{O}$ bond, whereas the peak at around 1010 cm^{-1} could arise from 1,4 substitution of the benzene ring. The bands at around 700 cm^{-1} are associated with special stretching of $\text{S}-\text{O}$ and $\text{C}-\text{S}$ bonds.²⁹ The FTIR spectroscopy for all samples (MW and CS) suggests the presence of copolymers and substituted PANI backbone structures.

SEM Results. The morphology of the fPANI samples obtained from MW (parts a–c of Figure 3, 2ABAPANI sample; parts a–c of Figure 4, 2SULFOPANI sample) and from CS synthesis (parts d–f of Figure 3, sample 2ABAPANI; and parts d–f of Figure 4, sample 2SULFOPANI) was determined by SEM. After 20 min from the beginning of the MW synthesis 2ABAPANI exhibits a nanofibrillar structure for the samples 2:1 and 1:1 (a, b). The sample 1:2 exhibits more featureless morphology characterized by more compact grainlike structures

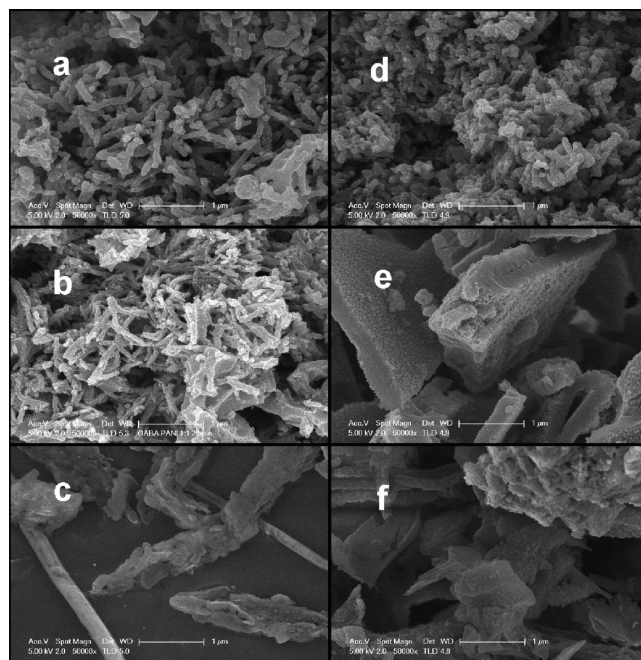


Figure 3. SEM micrographs of 2ABAPANI after 20 min under MW a) 2:1, b) 1:1, c) 1:2; and CS d) 2:1, e) 1:1, and f) 1:2 mol ratios.

(c), probably due to an excess of 2ABA content in the feed that is less *para*-coupling. The CS samples do not show clear nanofibrillar characteristics (although the 2:1 sample shows nanostructured grainlike morphology) and this is especially evident for the samples with 1:1 and 1:2 feed where lamellar structures prevail. The whole situation is similar for the 2SULFOPANI samples obtained after 10 min, although the

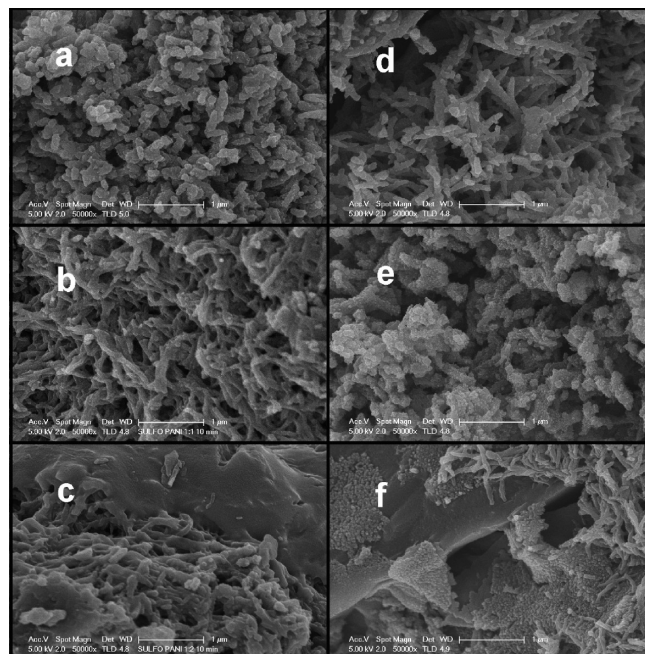


Figure 4. SEM micrographs of 2SULFOPANI after 10 min under MW a) 2:1, b) 1:1, c) 1:2; and CS d) 2:1, e) 1:1, and f) 1:2 mol ratios.

samples overall exhibit more nanofibrillar structures. At the same time, the samples obtained in MW and CS at the ratio 1:2 show the presence of flat, compact structures along with nanofibrillar morphologies. Obviously greater presence of functionalized aniline in the feed prevents 1–4 coupling which is essential for the formation of linear 1D structures, that is the functionalized anilines favor cross-linking and the formation of platelike structures. Sulfonic and carboxylic groups with strong electron-withdrawing and steric effects increase the oxidation potential of the monomer. In this way, it is difficult to form a free radical cation to initiate polymerization. If aniline is in excess, the polymerization is easier and the resulting copolymer polymer will exhibit more PANI-like characteristics. However, if the functionalized aniline monomer is in excess in the initial comonomer reaction mixture there are fewer aniline molecules that will form radical cations, which will be eventually transferred to 2SULFO monomer and the polymerization of aniline will be hindered. As a consequence, the reaction yield will be low. Because the ring-substituted groups decrease the electron spin density of N and C4 atoms the head-to-tail coupling will be partially obstructed.²⁹

To further probe the possible structural differences involved in the formation of the various assemblies, UV–vis spectroscopy was carried out.

UV–vis Spectroscopy. The emeraldine base form of PANI (EB PANI) typically absorbs strongly in two areas, with maxima at about 330 and 650 nm. The former band is assigned to π – π^* excitation of the *para*-substituted benzenoid segment (–B–NH–B–NH), whereas the latter is associated with the excitation of the quinoid segment (–N=Q=N–).²⁵

UV–vis spectra of the fPANI samples obtained from CS and MW are shown in Figure 5. The UV–vis spectra of 2ABAPANI (parts a and b of Figure 5) have π – π^* peaks at around 320–330 nm. The bands appear at shorter wavelengths compared with PANI because copolymers are less conjugated, which causes an increase in the transition energy.^{13,30} The peaks in the region 540–630 nm can be assigned to the transition (n – π^*) between the HOMO of the benzenoid ring (nonbonding nitrogen isolated pair) and the LUMO (π^*) of the quinoid ring.³ As the amount

of the 2ABA content increases in the feed, the 600 nm band undergoes a hypsochromic shift. This is because the carboxylic group disrupts the coplanarity of the π^* system (increase of the torsion angle between the close phenyl rings) and obstructs charge delocalization, resulting eventually in decrease in the conductivity. On the other hand the extended conjugation is disrupted by the electron withdrawing effects of –COOH group.^{3,30} Similarly, in the UV–vis spectra shown in parts c and d of Figure 5 for the 2SULFOPANI samples obtained in CS and MW synthesis, steric and electron withdrawing effects of the –SO₃H group also cause a hypsochromic shift due to restrictions to the conjugation.^{14,30} The behavior of all samples (CS and MW) revealed by UV–vis data is consistent with FTIR spectra and suggests that the structure has not been significantly changed when the samples are exposed to microwave irradiation.

Antioxidant Properties. When the DPPH radical is scavenged by an antioxidant it transforms to DPPHH, which can be detected by decay in the absorbance at 516 nm.^{16,17}

The results show that with more FA in the copolymer the fPANI is a more effective radical scavenger. DPPH radical scavenged by copolymer increases with increase in the amount of the functionalized aniline present in the copolymer, from 5.27 to 8.99 μmol for 2ABAPANI or 5.90 to 9.99 μmol for 2SULFOPANI. Compared with the previously obtained results for CS synthesized 2ABAPANI and 2SULFOPANI 1:1 (3.1 μmol),^{14,30} MW nanostructured samples showed 2.1 for 2ABAPANI and 2.4 for 2SULFOPANI times better radical scavenging efficacy. Further work is in progress in our laboratory to identify the key factors that determine the free radical scavenging efficacy of these and other conductive polymers, with the aim of gaining an insight into the mechanism of the interaction of conductive polymers with DPPH. 0.3 mg of 2ABAPANI and 2SULFOPANI 1:2 completely eliminated 610 $\mu\text{mol L}^{-1}$ DPPH radicals within 30 min with comparable efficacy to that of PANI nanofibers (27 μg of which eliminate 50 $\mu\text{mol L}^{-1}$ DPPH radicals).²²

Formation of Functionalized Polyaniline Nanofibers in Microwave: A Tentative Explanation. The conditions for the formation of polyaniline nanofibers have been studied widely.^{24,31–35} However, until recently morphology of polyaniline nanostructures had not been investigated from the viewpoint of nucleation.²⁴ It was suggested in the cornerstone work of Li and Kaner that heterogeneous nucleation favors agglomerated structures, whereas homogeneous nucleation promotes more nanofibrillar morphologies. This was checked by using mechanical agitation which triggered heterogeneous nucleation and the aggregation of nanoparticles. It was found recently that introducing a small amount of initiator (*p*-aminodiphenylamine or *p*-phenylenediamine) into the aniline polymerization reaction results in very long nanofibers.³⁶ This phenomenon was attributed to a significantly increased rate of the reaction under these conditions: the additives have a lower oxidation potential than aniline and thus can rapidly form growth centers for polymerization.³⁶ Nucleation is initiated simultaneously throughout the solution (homogeneous nucleation). In this way, the addition of promoters such as aniline dimer suppresses secondary growth because the diffusion of nuclei to heterogeneous nuclei sites is limited. This factor appears to be very important in the remarkably accelerated MW polymerization. According to classical nucleation theory,³⁷ homogeneous nucleation in solutions is favored at sufficiently high level of supersaturation, as this level increases the activation energy and the critical nucleus size decreases. When the supersaturation level further increases the activation energy becomes low and rapid and spontaneous nucleation occurs.

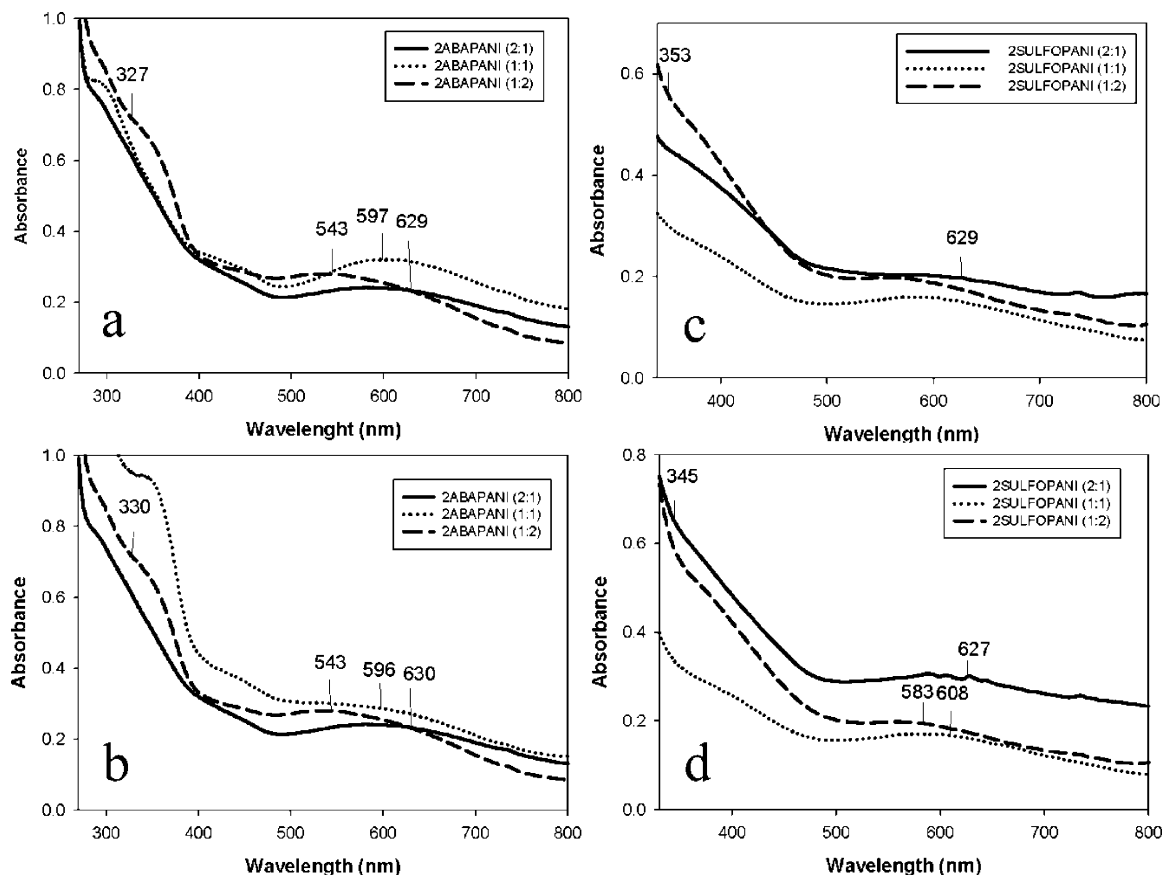


Figure 5. UV-vis spectra of 2ABAPANI and 2SULFOPANI samples synthesized by CS (a and c), and MW (b and d), respectively.

Here, we can apply the same hypothesis of classical nucleation theory and explain the rather fast formation of (functionalized) polyaniline nanofibers using MW as an activation source. In general, the increasing rate of reactions by MW irradiation results from *material-waves* interactions between polar molecules and the electromagnetic field.³⁸ There are two outcomes of this interaction: thermal and specific (nonpurely thermal) effects.³⁸ Usually, both of these effects can affect a reaction. However, in our case the thermal effect was largely marginalized since we maintained ambient temperature in the reaction vessel. According to the Arrhenius law the following specific factors can influence MW activation and accelerate aniline polymerization:³⁸

- 1) Decrease in activation energy.
- 2) Increased probability of molecular impacts.

Thus, a change of the rate of a reaction due to these factors could affect the nucleation mechanism for the formation of polyaniline nanofibers in similar way to the case of physically introduced additives³⁶ or mechanical agitation.³⁹ At some point when the activation energy reaches its lowest value spontaneous and rapid nucleation can occur and this results in nanofibrillar morphologies. However the morphology of long and disentangled nanofibers as in case of polymerization with additives,³⁶ is not achieved. This could be because the other counteracting effect for example the increasing probability of molecular impacts and faster diffusion rates, can raise the probability of heterogeneous nucleation. This could be compared to the experiment where mechanical agitation was used.³⁹ Therefore, the final sample looks more like a nanofibrillar mat.

Besides these specific (nonpurely thermal) effects, there could be also a thermal influence even under conditions of constant temperature during the polymerization. We can assume that

ambient temperature was maintained at macro level during the reaction. However, hot spots formed at the *molecular level*³⁸ and homogeneously distributed throughout the solution can create high level supersaturation sites which can be additional promoters for homogeneous nucleation.

The complex interplay between these factors seems to be a key factor for the fast formation of polyaniline nanofibers and their functionalized counterparts. We believe that this concept explains why polyaniline nanostructures are formed rapidly and why they have predominant fibrillar morphology (part b of Figure 3 and Figure 4).²³ However, these are not the only factors that can influence the aniline polymerization. The reaction could be also affected by reagent concentration, type of a dopant acid, type of an oxidant, and so forth.³⁶ Further work regarding the formation mechanism under microwave conditions is underway in our laboratory.

Conclusions

Nanostructured 2ABAPANI and 2SULFOPANI were prepared by aniline oxidation with potassium iodate (KIO_3) by fast, MW-assisted synthesis. This method provides a convenient and environmentally friendly way to produce fPANI nanostructures. The polymerization was substantially completed after 5–10 min and nanofibers of 2ABAPANI and 2SULFOPANI copolymers were obtained with 2.5–3 times higher yield than the copolymers prepared by CS. As the amount of the 2ABA or 2SULFO content increases in the feed, UV-vis spectra showed hypsochromic shifts of the quinoid band. The behavior of all fPANI samples (MW and CS) revealed by UV-vis and FTIR data suggests that the structure was not significantly changed when the samples were exposed to microwave irradiation. MW

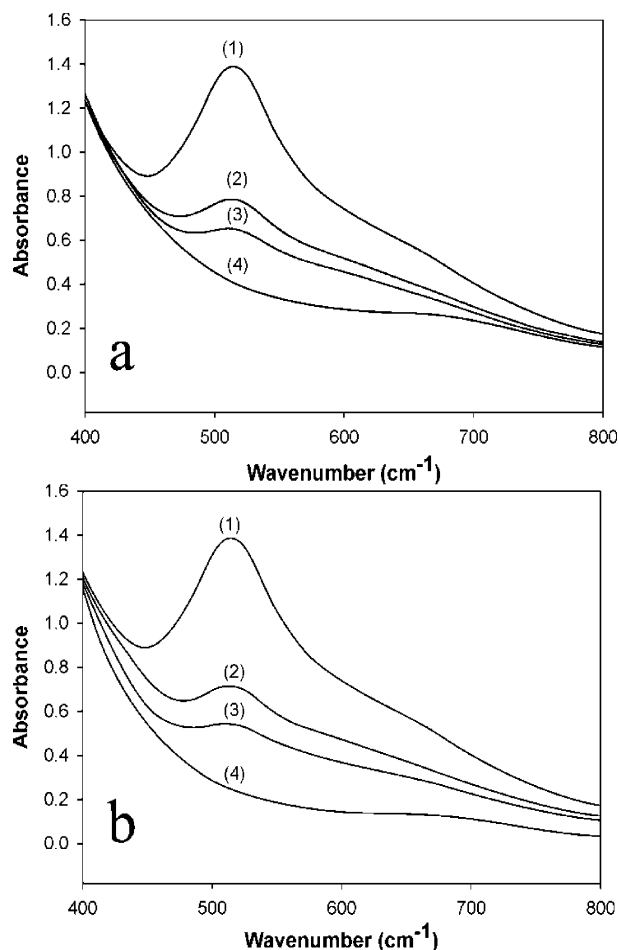


Figure 6. UV-vis absorption spectra of DPPH radical 30 min after the addition of 0.3 mg of a) 2ABAPANI (MW) and b) 2SULFOPANI (MW). UV-vis spectra labeled (1–4) correspond to (1) unreacted DPPH radicals, (2) 2:1, (3) 1:1, and (4) 1:2 aniline to FA mole ratios.

TABLE 3: Antioxidant Efficacy of 2ABAPANI and 2SULFOPANI Synthesized by MW

samples (MW)	A:FA mole ratio	DPPH scavenged by copolymer (μmol)
2ABAPANI	2:1	5.27
	1:1	6.45
	1:2	8.99
2SULFOPANI	2:1	5.90
	1:1	7.40
	1:2	9.99

synthesized nanostructured 2ABAPANI and 2SULFOPANI samples showed 2.1–2.4 times better radical scavenging efficacy, which suggests that these materials may act as promising radical scavengers. A formation mechanism of polyaniline nanofibers in MW is proposed by invoking thermal and nonpurely thermal effects. The proposed mechanism appears to be consistent with the previously used approaches of polyaniline polymerization using additives and mechanical agitation and their effects on nucleation modes.

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