

Influence of aniline oxidative-polymerization conditions and the type of dopant on PANI particles morphology

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The oxidative polymerization of aniline was studied in order to determine a favourable combination of reaction conditions leading to polyaniline (PANI) nano-sized particles of high aspect ratio and narrow polydispersity. The dimensions and morphology of PANI particles were tuned by the following reaction conditions: oxidant type, reaction temperature, reaction time, way of stirring the reaction mixture, and dopant type. The desired rod-shaped PANI morphology was achieved in the case of aniline oxidative polymerization carried out at 50 °C for 24 h and at constant stirring with a magnetic unit, when using (NH₄)₂S₂O₈ as the oxidant. The best aspect ratio under the above-mentioned conditions was reached by using HCl, p-toluenesulphonic acid, and H₂SO₄; all being used as dopants.

Keywords: Polyaniline; Oxidative polymerization; Morphology

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Introduction

Among conductive polymers, polyaniline (PANI) is known for probably the best combination of stability, conductivity, and low price. Although this substance has been found more than 150 years ago [1], scientists are still attracted to its interesting properties: PANI can be easily synthesized chemically (in the powder form), or electrochemically (as a film), representing a material that is cheap and stable against heat and air [2,3], PANI is the only conductive polymer whose electric properties can be effectively regulated by doping (protonation) [4,5]. Regarding its reversible electrochemical response during the anodic oxidation and cathodic reduction, PANI can be utilized as a secondary electrode in charging batteries, in electro-chromic imaging devices, and in sensors [6–8]. Organic coatings containing the conductive PANI show a fair anti-corrosion protection thanks to its redox properties [9,10]. The application of conductive PANI in alkyl-based paints has been reported to provide marked mechanical and anticorrosion properties of the resulting coating materials [11].

PANI is produced by electrochemical or chemical (oxidative) polymerization of the monomeric aniline. Chemical polymerization is quite simple and can be carried out with different oxidation agents (oxidants); ammonium persulfate $(\text{NH}_4)_2\text{S}_2\text{O}_8$ [12–19] being the one most frequently used. A combination of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and FeCl_3 [13–15] or $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and $\text{K}_2\text{Cr}_2\text{O}_7$ [13,15] has also been reported.

PANI can occur in three different oxidation states: fully oxidized, partially oxidized (as emeraldine base, EB) and fully reduced, while the EB state can be doped into the conductive form called emeraldine salt (ES, Fig. 1).

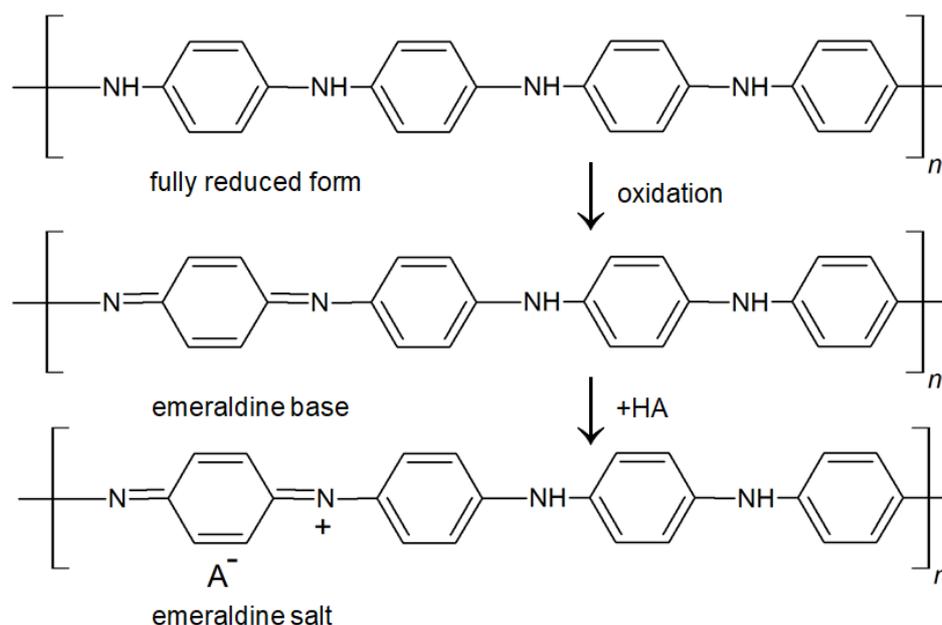


Fig. 1 PANI in the three existing forms

The EB doping process is performed using a strong acid (so-called acidic dopant) most often by dodecylbenzenesulphonic acid (DBSA) [2,16–18,20,21] or by hydrochloric acid [15,20,22]. Other acids can also be used, namely: camphorsulphonic acid (CSA) [23,24], *o*-phosphoric acid [25], *p*-toluenesulphonic acid (pTSA) [26,27], dodecylbenzenesulphonic acid in the form of sodium salt (SDS) [20], or di(2-ethylhexyl) sulphosuccinic acid (DESA) [20].

The conductive form of PANI has two limitations: adverse mechanical properties and insolubility in common organic solvents, which means that PANI cannot be processed by conventional methods. The properties depend on the chemical nature of PANI, on the dopant anion type and on the supramolecular aggregation incited by the presence of a dopant. Development of the PANI production with the required properties, especially with improved solubility of its conductive form, was addressed by several research works [20,28–30], which revealed that HCl-doped PANI is insoluble in almost all solvents while the DBSA, SDS or DESA doped PANI is partially soluble; e.g., in toluene, xylene, chloroform or acetone.

The above-indicated drawbacks limiting the use of the conductive PANI have been overcome by the preparation of conductive PANI mixtures and composites [2,17,21,31–33] which partially retain mechanical properties of an insulating host matrix while having electric properties comparable to the conductive polyaniline filler. To prepare the conductive PANI composites, we have to take in consideration the chemical reactivity and mixability of the individual components and also the value of the electric percolation threshold [34], which is the critical volume of the filler particles when the given material starts to behave as a conductor. After reaching this threshold, the particles of the filler can create conductive paths throughout the whole volume of the composite material. Because the percolation threshold may be largely affected by the filler particles morphology, attention has been recently paid to the ways of tuning the structure of the formed conductive PANI particles. In a view of the percolation threshold reduction, the most suitable constellation appeared to be the rod-shaped morphology PANI particles with a high aspect ratio [35,36].

This work tested the oxidative polymerization conditions and PANI doping, when focusing on the development of the rod-shaped PANI particles with high aspect ratio. Such particles, in combination with a suitable matrix, can be presumed to exhibit high conductivity and low electric percolation threshold. We monitored the influence of aniline polymerization conditions namely the oxidant type, temperature, polymerization time, way of stirring, and the dopant type on the formed PANI particles size and morphology. The main goal was to determine the combination of preparation conditions for the ES form of PANI which could generate rod-shaped particles of a high aspect ratio, uniform morphology and size.

Materials and methods

Materials and reagents

Aniline of ≥ 99.0 % purity was purchased from Merck (Prague, Czech Republic). Ammonium persulfate, $(\text{NH}_4)_2\text{S}_2\text{O}_8$, from Sigma-Aldrich (ACS reagent, ≥ 98 %, Prague, Czech Republic) and ferric chloride (FeCl_3) from Chemapol (Prague, Czech Republic) were used as oxidation agents. The PANI doping was performed by hydrochloric acid (HCl , 35 %, p.a.) and sulphuric acid (H_2SO_4 , 96 %, p.a.) from Penta (Chrudim, Czech Republic), *p*-toluenesulphonic acid (pTSA, ACS reagent, ≥ 98.5 %), dodecyl-benzenesulphonic acid (DBSA, ≥ 95 %), and camphorsulphonic acid (CSA, 98 %) purchased from Sigma-Aldrich (Prague, Czech Republic). Sigma-Aldrich also supplied a reference sample of PANI doped by an unspecified organic sulphonic acid.

Synthesis of PANI

PANI was prepared by a standard procedure (for details, see [11]). For the synthesis, 2 g of aniline was weighed to a 500 mL flask, then 200 mL solution of the appropriate acid (dopant) was added. This mixture was tempered to the required reaction temperature. Afterwards, at a constant stirring with solution, a portion of 4.8 g $(\text{NH}_4)_2\text{S}_2\text{O}_8$ was dissolved in 50 mL water and added dropwise (approx. 1 drop per second) to the reaction mixture. To prepare 1-B sample (Table 1), 3.75 g FeCl_3 in 50 mL water was used as oxidant for the aniline polymerization. For 1-C sample, the combination of $(\text{NH}_4)_2\text{S}_2\text{O}_8 + \text{FeCl}_3$ was used as oxidation agents, where the solution of 4.8 g $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in 50 mL water was gradually added dropwise, and consequently, the solution of 3.75 g FeCl_3 in 50 mL water also added into the reaction mixture in the same way [13].

Each sample was prepared according to a specific combination of reaction conditions — namely: the reaction temperature, way of stirring and the dopant used (again, see Table 1) — under which the polymerization reaction could be carried out. When completing the polymerization process, the mixture was vacuum-filtered and the product dried in a chamber filled with silica gel at a temperature of 50 °C for 24 h.

Used methods

The individual samples of the doped PANI prepared under the above-surveyed conditions were analysed by a scanning electron microscope (SEM; model LYRA 3 Appliance; Tescan, Brno, Czech Republic) in cooperation with the Center for Materials and Nanotechnologies (see affiliation).

Table 1 Overview of the reaction conditions used for the preparation of the individual PANI samples

Sample	Dopant	Oxidant	Temperature [°C]	Reaction time [h]	Stirring speed [rpm]
1-A	HCl	(NH ₄) ₂ S ₂ O ₈	50	2	300
1-B	HCl	FeCl ₃	50	2	300
1-C	HCl	(NH ₄) ₂ S ₂ O ₈ +FeCl ₃	50	2	300
1-D	HCl	(NH ₄) ₂ S ₂ O ₈	0	24	300
1-E	HCl	(NH ₄) ₂ S ₂ O ₈	50	24	300
2-A	pTSA	(NH ₄) ₂ S ₂ O ₈	0	24	300
2-B	pTSA	(NH ₄) ₂ S ₂ O ₈	50	24	300
2-C	pTSA	(NH ₄) ₂ S ₂ O ₈	50	24	–
2-D	pTSA	(NH ₄) ₂ S ₂ O ₈	50	24	ultrasound
3-A	CSA	(NH ₄) ₂ S ₂ O ₈	0	24	300
3-B	CSA	(NH ₄) ₂ S ₂ O ₈	50	24	300
4-A	DBSA	(NH ₄) ₂ S ₂ O ₈	0	24	300
4-B	DBSA	(NH ₄) ₂ S ₂ O ₈	50	24	300
5-A	H ₂ SO ₄	(NH ₄) ₂ S ₂ O ₈	0	24	300
5-B	H ₂ SO ₄	(NH ₄) ₂ S ₂ O ₈	50	24	300

The SEM photo-images were obtained at accelerating voltage of 10 kV on the sample area of $2 \times 2 \mu\text{m}^2$, with the magnification ratio of 173,000. The samples were sufficiently conductive and no special treatment was required.

Results and discussion

Influence of the oxidant type

The most often used oxidant for the oxidative polymerization of aniline is (NH₄)₂S₂O₈ which was the first-choice oxidant in the research reported herein. Certain resources [13–15] quote that the presence of ferric ions, Fe³⁺, in the reaction mixture supports the development of rod-shaped structures; therefore, FeCl₃ has also been tested as an oxidant. The influence of this compound on the structure and conductivity of PANI was also tested in the mixture with (NH₄)₂S₂O₈ (Fig. 2). The indicated positive effect was not noticed for any of the two variants. On the contrary, when compared with oxidative polymerization made with the use of (NH₄)₂S₂O₈ only, the PANI particles were too large, polydisperse, and non-uniform in terms of morphology. Yet another drawback of

the FeCl_3 -based procedures is the need of its removal from the resultant product. Due to these reasons, $(\text{NH}_4)_2\text{S}_2\text{O}_8$ alone was used exclusively as the oxidant in all further experiments.

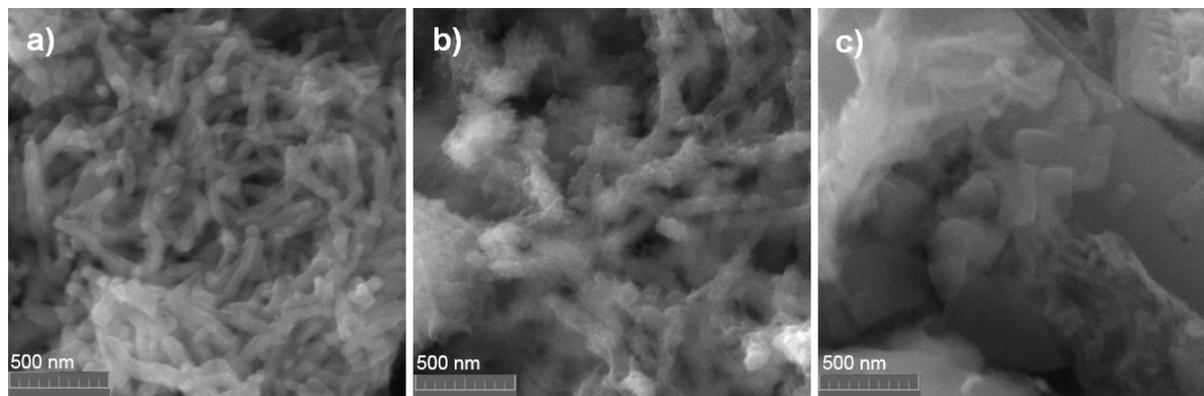


Fig. 2 SEM images showing the influence of oxidant in the oxidative polymerization of aniline on the structure of the formed PANI particles: a) $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (sample 1-A), b) $(\text{NH}_4)_2\text{S}_2\text{O}_8 + \text{FeCl}_3$ (sample 1-B), c) FeCl_3 (sample 1-C)

Influence of the reaction temperature

Another parameter studied during preparation was the reaction temperature at polymerization. According to the relevant literature search, a lower polymerization temperature results in a better yield of PANI, but its particles formed are larger, while a higher polymerization temperature results in smaller and more rod-shaped PANI particles [13]. Two reaction temperatures have been tested for aniline polymerization: 0 °C (cooled in an ice bath) and 50 °C (heated in oil bath; Fig. 3).

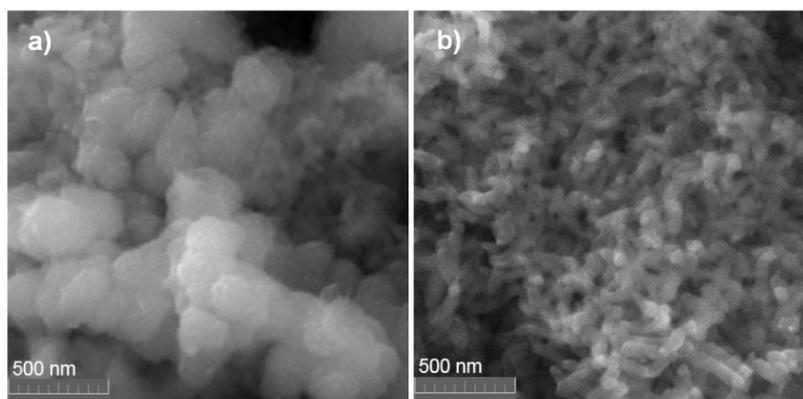


Fig. 3 SEM images showing the influence of the reaction temperature during oxidative polymerization of aniline on the structure of the formed PANI particles: a) 0 °C (sample 2-A), b) 50 °C (sample 2-B)

It was demonstrated that the reactions carried out at 50 °C had given rise to rod-shaped particles while the particles formed at a lower polymerization temperature were larger and sphere-shaped. Aniline polymerization at the reaction temperature above 50 °C was not examined due to the heat sensitivity of PANI [2,13].

Influence of the reaction time

A universal reaction time for the polymerization is not clearly indicated, the process of polymerization is usually carried out in the range between 2 to 24 hours, therefore the same threshold values could be selected to compare the influence of the reaction time on the morphology of PANI particles. The oxidant was added to the reaction mixture dropwise (approx. 1 drop per second). The reaction started to occur in a few minutes, which could be seen via the colour change of the reaction mixture – from colourless (transparent) to a dark green of the PANI formed. The SEM images (Fig. 4) showed that the 24-hour polymerization had led to larger and more developed particles, which was more or less expected. In both cases, rod-shaped uniform particles were formed, indicating that the reaction time did not essentially affect the morphology of the PANI product.

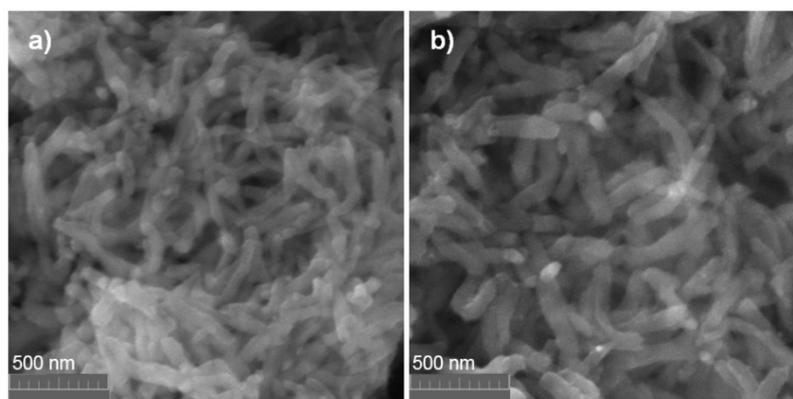


Fig. 4 Images from the electron microscope showing the influence of the oxidative polymerization reaction time on the resultant structure of the PANI particles: a) 2 h (sample 1-A), b) 24 h (sample 1-E)

Influence of stirring

Unlike the reaction time, it has been demonstrated that the stirring has a key influence on the nature of the resulting product in terms of its morphology, uniformity, and particles size. Stirring also ensures the properly distribution of oxidant in the whole volume of the reaction mixture. Nevertheless, the authors

Jang, Bae, and Lee [13] also succeeded in the preparation of PANI particles of high aspect ratio without stirring of any kind. Therefore, we carried out three sets of experiments: (a) the reaction mixture was not stirred, (b) stirring by ultrasound, and (c) stirring with a standard magnetic device at the rate of 300 rpm (Fig. 5). Stirring-free polymerization rendered non-uniform PANI particles in terms of its morphology and size, when the resulting particles were not rod-shaped. This observation can be justified by an uneven course of the reaction and as a result of the existence of the concentration gradient of the oxidant across the reaction mixture. A similar phenomenon was noticed after ultrasound-assisted stirring: rod-shaped particles were formed; however, we also observed lamellar-structure particles, as well as their small fragments. The best result had therefore been reached with the use of magnetic stirring which resulted in rod-shaped particles manifesting the highest uniformity in terms of morphology and the size of the PANI particles.

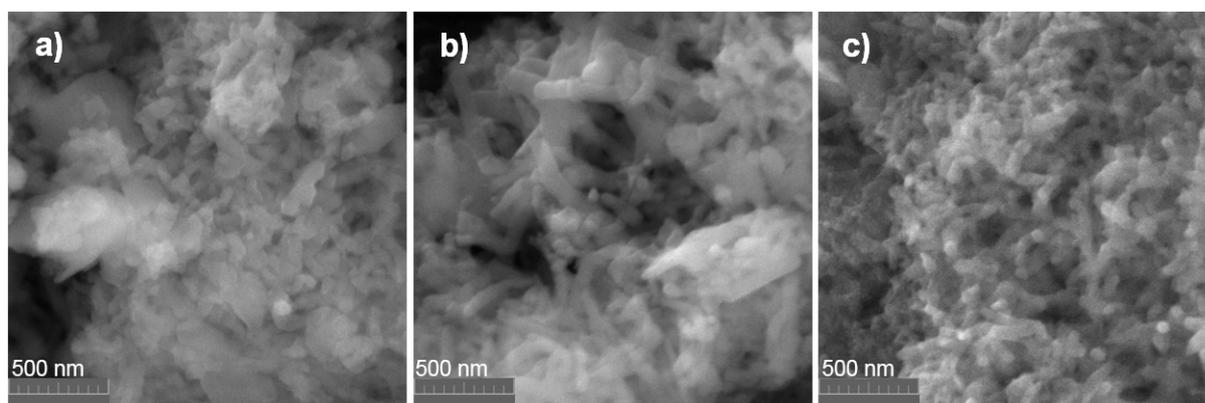


Fig. 5 SEM images showing the influence of the reaction mixture stirring method during aniline oxidative polymerization on the structure of the formed PANI particles a) stirring-free, (sample 2-C), b) ultrasound (sample 2-D), c) magnetic stirring (sample 2-B)

Influence of the dopant type

The last parameter examined was the dopant type and its effect upon the morphology and the size of the PANI particles. A relevant literature reports on several organic and inorganic acids by which the conductive form of PANI can be prepared (ES). This can be carried out by doping of the non-conductive PANI form (EB) or by polymerization of aniline directly in a suitable acid solution; the second option being used in this work. From the literature search, we chose a quintet of doping acids: HCl, H₂SO₄, pTSA, CSA, and DBSA (for full meaning of the abbreviation used, see *Experimental*). Polymerization in the given acidic medium was carried out in standard way, except DBSA causing a formation of a

very fine dispersion of the PANI particles that had to be isolated from the reaction mixture by precipitating with methanol. For comparison, a sample of PANI from Sigma-Aldrich was used doped by unspecified sulphonic acid.

As illustrated in Fig. 6 and regarding the morphology, uniformity, and polydispersity of the particles, the best result was obtained for polymerization in the HCl, pTSA or H₂SO₄ environment. Here, the PANI had formed the agglomerates from the primary nano-particles of rod-shaped morphology, while the use of HCl led to a more individual character, including a high aspect ratio.

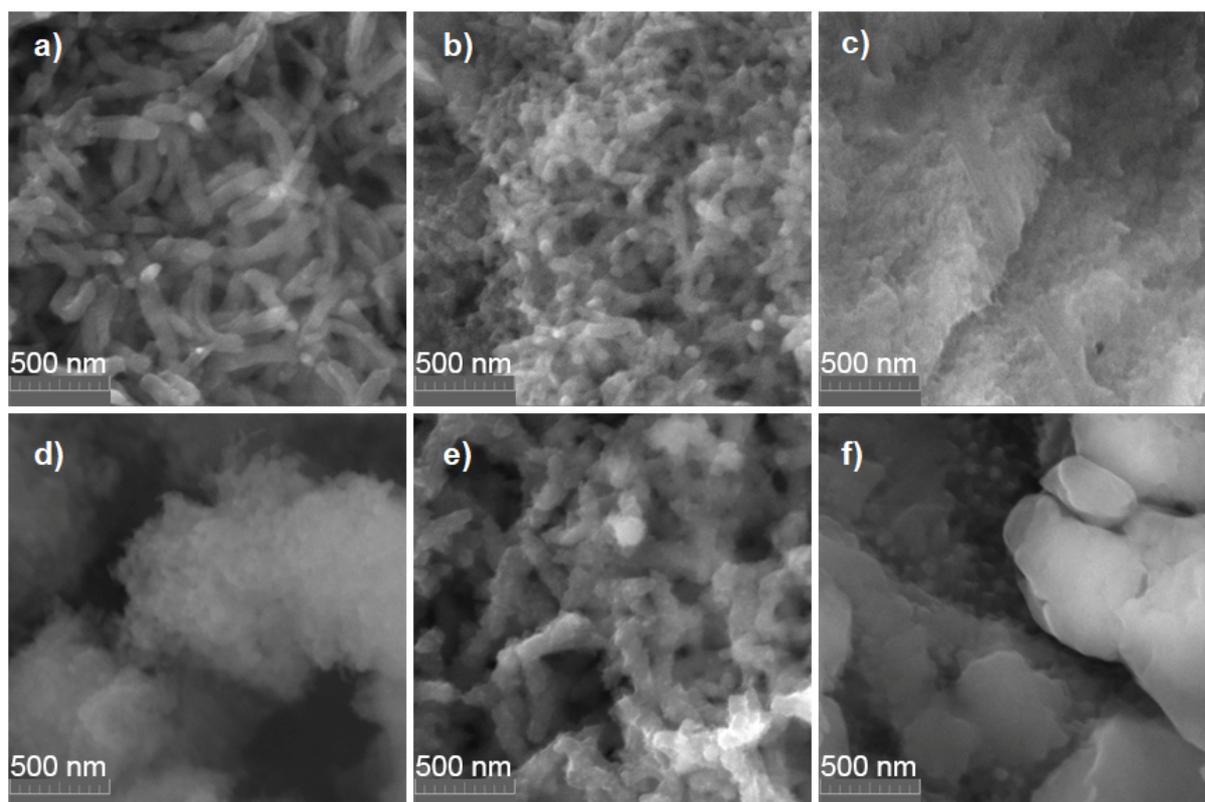


Fig. 6 Comparison of PANI morphology prepared using different dopants: a) HCl (sample 1-E), b) pTSA (sample 2-B), c) DBSA (sample 4-B), d) CSA (sample 3-B), e) H₂SO₄ (sample 5-B), f) unspecified organic sulphonic acid (reference commercial PANI)

Nevertheless, we can assume that the PANI prepared with one of the three above-specified dopants could be a suitable filler if the proper dispergation method is used to disintegrate the agglomerates back into the primary particles. On the contrary, both DBSA and CSA used as dopants have resulted in the aggregates of PANI with a badly distinguishable structure of the primary particles, suggesting us their difficult or even impossible dispergation. In the case of DBSA doping, the reason for PANI-aggregates formation could be due to a more complex preparation involving the additional precipitation by methanol.

Conclusions

It was proved that the morphology, size and the aspect ratio of the PANI particles were affected by several reaction parameters, namely: the reaction temperature, oxidant type, stirring during the polymerization and by the type of doping acid. On the contrary, the time of polymerization was shown to have no significant influence on the resulting product. In perspective of potential use of PANI as a conductive filler for composite polymeric materials, the best result in terms of the particles morphology was reached in the oxidative polymerization carried out at 50°C for 24 h, when using constant stirring by a magnetic bar and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ as the oxidant. The best aspect ratio under the above-stated conditions was attained by using HCl, pTSA, and H_2SO_4 as acid dopants.

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