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Dispersion polymerization of pyrrole in the presence of poly(vinyl methyl ether) microgels

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Abstract

Oxidative polymerization of pyrrole (Py) has been studied in the presence of poly(vinyl methyl ether) (PVME) and crosslinked PVME microgels using $FeCl_3$ as oxidant and water or aqueous ethanol as a dispersion medium. The influences of the reaction medium and oxidant addition mode on the morphology as well as properties of final particles are discussed. SEM images of dispersions prepared in the presence of uncrosslinked PVME in water or water/ethanol mixtures indicate small spherical particles (40–100 nm). Large needle-like polypyrrole particles (approximately 400 nm long; aspect ratio 8:1) are formed in aqueous ethanol in the presence of crosslinked PVME microgels at Py/PVME ratio higher than 2:1.

Keywords: Polypyrrole; Poly(vinyl methyl ether); Microgel

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1. Introduction

During the last decade conductive polymers have received increased interest both for academic purposes and for potential applications. One of the important areas of research on conducting polymers concerns methods for making them processable. The main approaches can be divided into three main groups: (1) preparation of composites with other polymers, (2) synthesizing of soluble derivatives, and (3) synthesis of dispersions of insoluble conducting polymers.

Synthesis of polymeric dispersions requires the selection of an appropriate stabilizer to provide the effective stabilization of colloidal system and to control the morphology and size of polymer particles. Recently, there have been reports on the successful production of polypyrrole (PPy) latex particles by chemically oxidizing pyrrole (Py) in either water or other media in the presence of different stabilizers. The stabilizers used were poly(vinyl pyrrolidone) (PVP) and poly(vinyl alcohol-*co*-acetate) (PVA) [1,2], poly(ethyleneoxide) (PEO) [3], poly(2-vinyl pyridine-*co*-butyl methacrylate) (P2VP-BM) [4], poly(*N*,*N*′-dimethylaminoethyl methacrylate-*b*-*n*-butyl methacrylate) [5], poly(vinyl acetate) [6], poly(vinyl methyl ether) (PVME) [7], ethylhydroxycellulose (EHEC) [8,9], poly(2-(dimethylamino)ethylmethacrylate-*stat*-3-vinylthiophene) [10], poly(styrenesulfonate) (PSS) [11], etc. In nearly all studies the particle size of formed PPy dispersions was in the range of 30–200 nm and the morphology of particles was close to spherical. In the case of PVA stabilizer, the rate of addition of the pyrrole monomer affected the particle size; slower feed-rate leads to the formation of larger particles [1]. It was reported that the addition of an aqueous solution of initiator to a stirred solution of pyrrole monomer plus stabilizer led to non-spherical particles and varying the water/ethanol ratio did not lead to any systematic trends in particle size variations. Pickup and Qi [11] reported that the presence of PSS in the reaction medium allows the size of chemically synthesized PPy/PSS particles to be controlled by varying the concentration of the Fe(III) oxidant (the higher the concentration, the smaller the resulting polymer particles). Mandal and Mandal [9] found that in aqueous ethanol solution small and large particles (about a factor of ten larger) are formed during oxidative polymerization of pyrrole in the presence of ethylhydroxycellulose when $FeCl_3$ was used. But only large particles were obtained, when persulfate (APS) was employed as oxidant. However, in pure water small particles were not found, irrespective of the oxidant used. Additionally the particle size was found to decrease with an increase in molecular weight of the EHEC for the same stabilizer concentration. Vincent and Waterson

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[12] reported that the use of poly(ethylene oxide)-based homopolymer, graft copolymer, and reactive graft copolymer stabilizers can alter the polyaniline particle morphology from needles to rice grains to polydisperse spheres. Similarly, DeArmitt and Armes [13] showed that changing the chemical oxidant can also profoundly affect the particle morphology. Using a reactive statistical copolymer based on poly(*N*-vinylpyrrolidone), they obtained a rice grain morphology using the KIO_3 oxidant but spherical particles with the $(NH_4)_2S_2O_8$.

Nowadays, the synthesis of molecular conductors is a field of intensive research, the purpose being to produce objects on the nanometer scale. Therefore, the control of the morphology of conducting polymers is a very stimulating challenge, with the production of molecular wires and tubules being particular targets. The confined polymerization of conducting polymers is a very pertinent way to give them controlled shape and dimension, which addresses the question of the availability of appropriate templates. The use of microtubules of PPy rather than films is much more efficient for the immobilization of biologically active species such as glucose oxidase and, in this case, for the direct electron transfer between the enzyme and the conducting polymer, so improving the electrochemical detection [14]. Martin et al. [15–18] used commercially available particle track-etched membranes (PTMs) as templates for the preparation of nanofibrils of metals, semiconductors, and conducting polymers. They focused on the synthesis of three conducting polymers, namely polypyrrole, poly(3-methylthiophene), and polyaniline, within the pores of a polycarbonate (PC) nucleopore membrane. Recently, Demoustier-Champagne et al. [19–22] reported on the use of these nanoporous PTMs as templates for the chemical and electrochemical synthesis of nanoshaped conducting polypyrrole nanostructures. Jerome et al. [23] reported the synthesis of PPy nanowires by two-step electrochemical process where the poly(ethyl acrylate) grafted onto carbon electrode served as a template. These authors found that the solvent used for pyrrole polymerization had a strong influence on the polymer morphology.

PPy wires were formed in dipolar aprotic solvents (DMF or DMSO), whereas the more traditional cauliflower-like morphology was observed in less polar solvents (acetonitrile, ACN) [24]. Wan and Liu [25] created a template-free method to synthesize microtubules of polyaniline (PANI) [26] and PPy [27] in the presence of β-naphthalene sulfonic acid (β-NSA) micelles. Compared with the methods mentioned previously, the template-free method is not so costly and rather more simple.

In the present paper, we describe the synthesis of composite polypyrrole particles in the presence of thermo-sensitive PVME microgels that, as expected, should play the roles of both template and stabilizer. Thermo-sensitive microgels were synthesized by irradiation of an aqueous solution of PVME with electron beam or γ-rays above the low critical solution temperature (LCST) [28]. The reason for the crosslinking process is the formation of radicals from water molecules, which attack the PVME chains. The microgels were found to be thermo-sensitive: they swell at temperatures below LCST and shrink above this temperature. Field emission scanning electron microscopy (FESEM) proved that microgels have a sponge-like structure and every particle can be considered as a fine porous micronetwork. In this paper, we describe the morphology of obtained particles prepared by oxidative polymerization of pyrrole in the presence of PVME microgels; more detailed results of particle characterization will be published elsewhere.

2. Experimental

2.1. Materials

Pyrrole was purchased from Aldrich Chemical Corp., distilled under vacuum, and stored in a refrigerator before use. Ferric chloride and ethanol were obtained from Aldrich Chemical Corp. and used as received. PVME was obtained as a 50 wt% aqueous solution (BASF, Lutonal® M40) and was used as supplied. The weight-average molecular weight, M_w, was determined by static light scattering in butanone to be 57,000 g/mol. The synthesis of PVME microgels is described elsewhere [29]. In the present study, we used samples crosslinked at 50 °C at a polymer concentration of 1 g/l with a radiation dose of 60 kGy (electron beam).

2.2. Polymerization of pyrrole

In case when non-crosslinked PVME was used as stabilizer, the polymerization runs were performed as follows. PVME was dissolved in appropriate amount of water (or water–ethanol) at 25 °C in a reactor equipped with stirrer. Then the pyrrole was added to the stirred solution and reactor was purged with nitrogen for 15 min. Oxidant was dissolved in water in separate flask and added to the reaction mixture to start the polymerization. Crosslinked PVME microgel particles stabilized in water dispersions were directly added to the reactor and then addition of other ingredients was similar as mentioned above. Polymerizations were allowed to proceed for 24 h.

Stable dispersions were cleaned by dialysis (Millipore membrane 100 000 MWCO), precipitate was washed several times with hot (80 °C) 0.1 mol/l HCl and twice more with hot water to remove oxidant and by-products. Dry samples were obtained by drying in vacuum for more than 12 h.

2.3. Measurement

The nitrogen content of PPy was determined by semimicro technique [30]. The Cl content was estimated

Table 1
The recipe of the polymerization of pyrrole in water at 25 °C

Sample	Pyrrole (g)	PVME (g)	$FeCl_3 \cdot 6H_2O$ (g)	H_2O (g)	Yield (%)	Cl/N	*D* (nm)	Stability
WP1	0.1	0.1	0.548	75	95	0.30	53 ± 13	Stable
WP2	0.1	0.033	0.548	65	92	0.31	71 ± 18	Stable
WP3	0.1	0.02	0.548	65	93	0.30	85 ± 17	Unstable
WP9[a]	0.1	0.033	0.548	65	86	0.29	74 ± 16	Stable

[a] Oxidant was dropped at 0.05 ml/min).

by burning the samples in oxygen flask followed by adsorption of gases and titration according to standard procedure [31]. SEM micrographs were taken using a Zeiss DSM 982 Gemini microscope. Samples were prepared on Al supports, dried at room temperature and coated with gold prior to measurement. Images were taken at 4 kV. Approximately 100 particles were measured for each sample and results were used for the calculation of average particle size. FESEM measurements were performed with S-5000, Hitachi Ltd, Japan. Detailed sample preparation is described elsewhere [29].

3. Results and discussion

PVME in aqueous solution has a LCST of about 37 °C. At elevated temperatures, the enhanced motions of polymer chains destroy the hydrogen bonds and dehydrated PVME molecules start to aggregate. Dynamic light scattering measurements of aqueous PVME solution indicate that the hydrodynamic radius of aggregates at 25 °C is about 200 nm and shrinks down to 40 nm as the solution temperature approaches the LCST [29]. In aqueous ethanol solutions, the cloud point temperature is shifted to higher values [7]. This indicates that PVME chains in aqueous ethanol will not be so strongly aggregated in solution compared to pure water.

Uncrosslinked PVME was used as stabilizer in the oxidative polymerization of pyrrole in the presence of Fe(III). The reaction medium selected was water or water/ethanol mixtures. The PVME/Py ratio was varied from 1:1 to 1:5. Tables 1 and 2 give the details of Py dispersion polymerization at 25 °C.

When water/ethanol (50:50) mixture was used as the reaction medium all prepared dispersions were stable and showed no precipitation with time. In pure water, dispersions were unstable when PVME/Py ratio was as high as 1:5. All prepared dispersions were cleaned by dialysis to remove initiator residue and by-products. The Cl/N ratios mentioned in Tables 1 and 2 indicate that one of approximately every three pyrrole units in PPy is doped (oxidized). Both in water and water–ethanol mixtures, the average particle diameters determined by SEM measurements increase when the PVME content decreases. Fig. 1 shows SEM pictures of PPy particles prepared in pure water.

SEM pictures indicate that, at lower Py/PVME ratios, particles form a composite film after drying, but particle contours are still recognizable. At higher Py/PVME ratios, larger particles are formed, which are well separated and non-agglomerated. When water/ethanol (50:50) solution is used as the reaction medium (Fig. 2) much larger PPy particles are formed under similar reaction conditions (see samples WP2 and VP3).

Additionally, samples prepared in aqueous ethanol show enhanced film formation properties. At a 1:1 Py/PVME ratio, the PPy particles are embedded into the PVME matrix. Larger particle sizes obtained in water/ethanol mixtures can be explained by the increased hydrodynamic volume of PVME chains in solution and, probably by the slower rate of oxidation. This latter effect is attributable to $FeCl_3$ complexation with ethanol [32] and reduction of its oxidation power.

When the oxidant was dropped slowly into the reaction mixture larger particles were obtained both in water and aqueous ethanol. This effect is due to much lower polymerization rate if compared with runs where oxidant was added batch wise and lower rates of particle nucleation.

Table 2
The recipe of the polymerization of pyrrole in water/ethanol (50:50, w/w) at 25 °C

Sample	Pyrrole (g)	PVME (g)	$FeCl_3 \cdot 6H_2O$ (g)	Et/H_2O (g)	Yield (%)	Cl/N	*D* (nm)	Stability
VP1	0.1	0.1	0.548	75	96	0.30	65 ± 12	Stable
VP2	0.1	0.05	0.548	70	95	0.31	73 ± 16	Stable
VP3	0.1	0.033	0.548	65	99	0.30	90 ± 13	Stable
VP4	0.1	0.02	0.548	65	98	0.31	115 ± 16	Stable
VP8[a]	0.1	0.033	0.548	65	98	0.31	105 ± 13	Stable

[a] Oxidant was dropped at 0.05 ml/min).

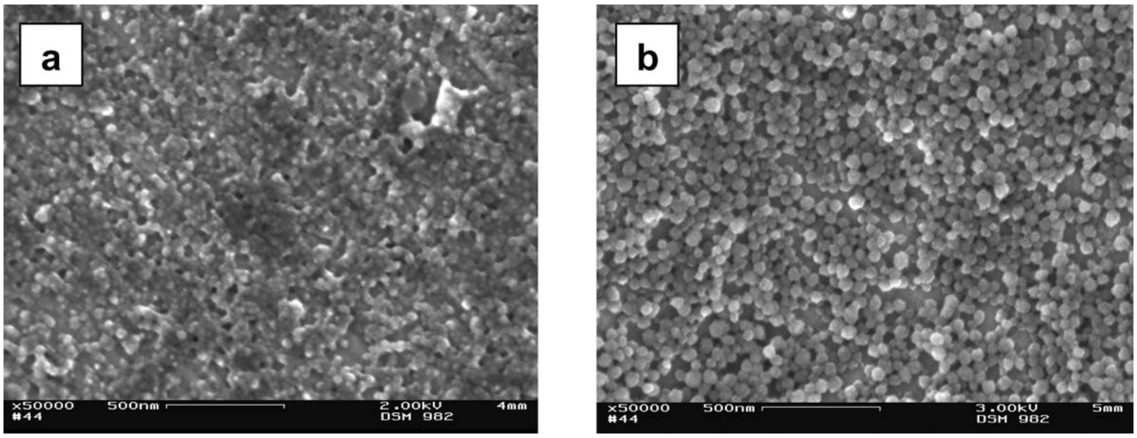

Fig. 1. SEM images: (a) sample WP1 (Py/PVME = 1:1); (b) sample WP2 (Py/PVME = 3:1).

A crosslinked PVME microgel with an average hydrodynamic radius 200 nm was used as stabilizer in the oxidative polymerization of pyrrole in the presence of Fe(III) using either water or water/ethanol mixture as the reaction medium. The PVME/Py ratio was varied from 1:1 to 1:5. Table 3 gives the details of Py dispersion polymerization at 25 °C.

SEM investigations indicate that the morphology of obtained particles is quite different from the morphology of the particles prepared with uncrosslinked PVME. Fig. 3(a) shows a micrograph of the PPy particles prepared without PVME.

In this case, the particles exhibit a 'cauliflower' morphology which was reported in other reviews [11,29] and the dispersion is unstable. A similar morphology is obtained when Py is polymerized in water without any stabilizer.

When crosslinked PVME microgels are present in the reaction mixture quite stable dispersions are obtained and microscopy investigations indicate that the morphology of the Py particles changes from spherical to needle-like. At low Py content mostly spherical particles are present (Fig. 3(b)). When the Py amount is increased, the needle-like morphology is dominant and the particles around 400 nm are formed (Fig. 3(c) and (d), see also Table 3).

However, when the ethanol content in the reaction mixture was decreased (water/ethanol = 90:10) the PPy particle morphology becomes spherical (Fig. 4(a)). It seems that small PPy particles were embedded into PVME microgels and after solvent evaporation formed a kind of porous membrane.

Particles prepared in pure water in the presence of PVME microgel (Fig. 4(b)) exhibit a cauliflower morphology. It should be noted that samples MP14 and MP16 were unstable and the morphology observed in SEM pictures is formed by aggregation of particles. It is supposed that this special particle morphology is formed because crosslinked PVME microgels play the role of a template in this particular system.

Fig. 5(a) shows an idealized representation of the particles formed in the presence of PVME microgels. FESEM studies (Fig. 5(b).) indicate that, in the swollen state, microgel particles have a sponge-like structure with a mean diameter of approximately 350 nm. Detailed microscopy investigations indicate that the outer membrane of these particles has small holes with a diameter of

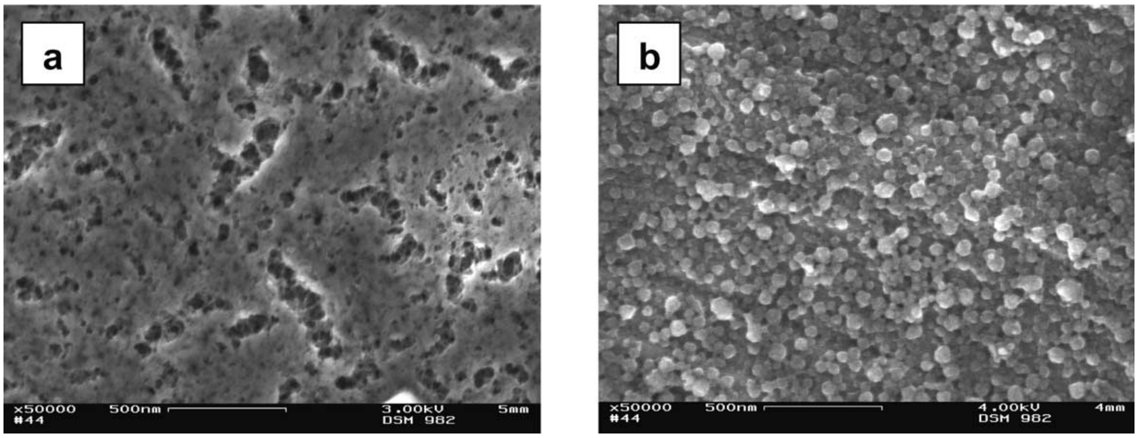

Fig. 2. SEM images: (a) sample VP1 (Py/PVME = 1:1); (b) sample VP3 (Py/PVME = 3:1).

Table 3
The recipe for pyrrole polymerization in different medium

Sample	PVME (g)	Pyrrole (g)	$FeCl_3\cdot 6H_2O$ (g)	Et/H_2O (g)	Yield (%)	Cl/N	*D* (nm)	Stability
MP8[a]	0.008	0.008	0.0435	20	98	0.30	70 ± 12	Stable
MP10[a]	0.008	0.016	0.087	20	95	0.30	300 ± 50	Stable
MP12[a]	0.008	0.024	0.131	20	92	0.29	514 ± 45	Stable
MP13[a]	–	0.025	0.137	20	86	0.30	–	Aggregation
MP15[b]	0.013	0.013	0.0738	20	95	0.31	115 ± 16	Stable
MP16[c]	0.013	0.013	0.0738	20	94	0.30	84 ± 10	Unstable
MP14[d]	0.013	0.013	0.0738	20	95	0.31	70 ± 15	Unstable

[a] Water/ethanol = 50:50.
[b] Water/ethanol = 70:30.
[c] Water/ethanol = 90:10.
[d] Water.

5–10 nm, which provide a corresponding membrane permeability. Since Py monomer is hardly soluble in water (1–2%) we believe that it can penetrate into the microgel particle interior. Addition of oxidant causes rapid polymerization (oxidant was added batch wise) and PPy particles with granular morphology are formed, which are probably embedded into the PVME microgel network (Fig. 5(a)). A similar effect was observed by Liu and Wan [25] when β-naphthalene sulfonic acid (β-NSA) micelles were used as templates for pyrrole polymerization. In their case, rapid addition of the oxidant gave granular PPy–NSA. On the other hand, tubular PPy–NSA was obtained at slow oxidant addition.

When microgel particles are in water/ethanol mixtures (Fig. 5(a)), the network expands and the pores are probably larger. Additionally, as mentioned before, the polymerization rate in aqueous ethanol is much slower compared with that in pure water, even if the same oxidant concentration is

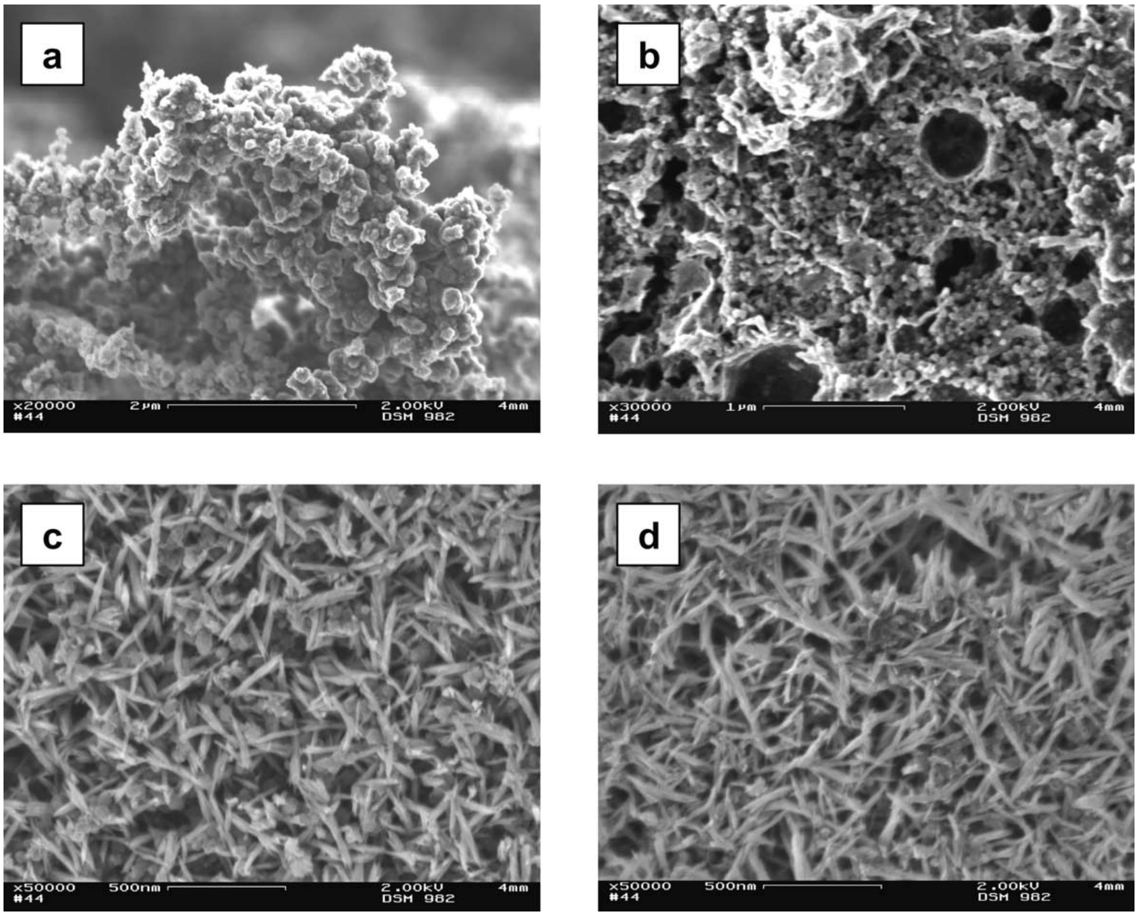

Fig. 3. SEM images: (a) sample MP13 (no PVME); (b) sample MP8 (Py/PVME = 1:1); (c) sample MP10 (Py/PVME = 2:1); (d) sample MP12 (Py/PVME = 3:1) (medium: water/ethanol = 50:50).

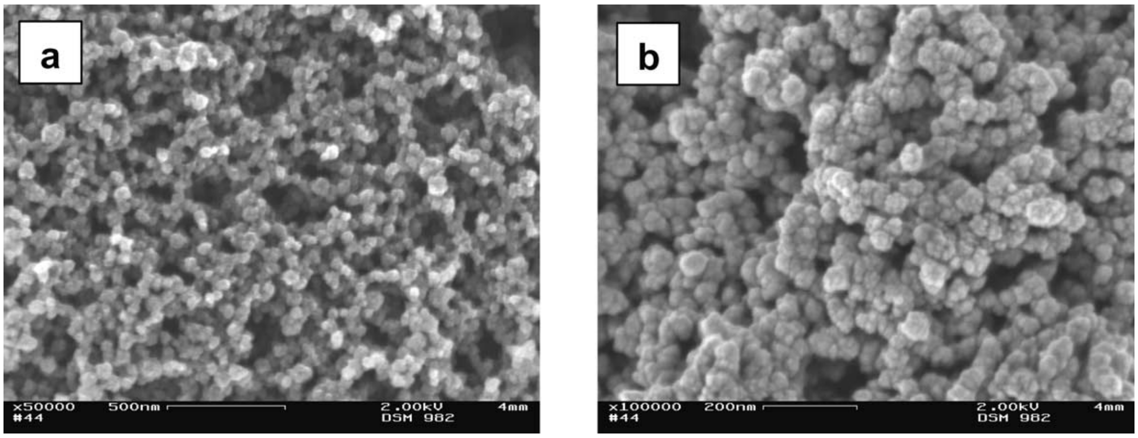

Fig. 4. SEM images of PPy particles prepared at Py/PVME ratio 1:1 in different medium: (a) water/ethanol = 90:10 (MP16); (b) water (MP14).

used. Both these effects provide suitable conditions for PPy to self-assemble to form needles and the increased Py content in the reaction mixture led to larger needles. If the ethanol content is less than 50% the granular morphology appears.

These considerations led to the conclusion that the pore size of the microgel particles and the Py polymerization rate has a dramatic influence on the morphology of the final product. The pore size of the microgel can be easily changed by the irradiation dose or crosslinking temperature. Additionally, if PVME microgels are temperature sensitive, the pore size is also influenced by the temperature of the medium. Another fact that has to be considered is the presence of solvents that are better solvents for PVME than water. The polymerization rate can be changed by varying the nature of the oxidant and its addition mode. These important points will be considered in our future work, which will focus on controlling the size and properties of the PPy particles by changing the above mentioned reaction parameters.

4. Conclusions

The experimental results presented in this paper clearly indicates that the architecture of the polymeric stabilizer in the reaction medium has a strong influence on the morphology of particles formed during oxidative polymerization of pyrrole. In the case where uncrosslinked PVME was used as stabilizer, small spherical particles in the range of 50–100 nm were formed in both aqueous ethanol and water. On the other hand, when crosslinked PVME microgels were used in the same reaction procedure large PPy fibrils were formed. Needle-like particles were formed due to the porous structure of microgels, which play a template role in the pyrrole polymerization process. We predict that the dimensions of the PPy fibrils can be controlled by changing the pore size of the microgel particles and adjusting the polymerization rate.

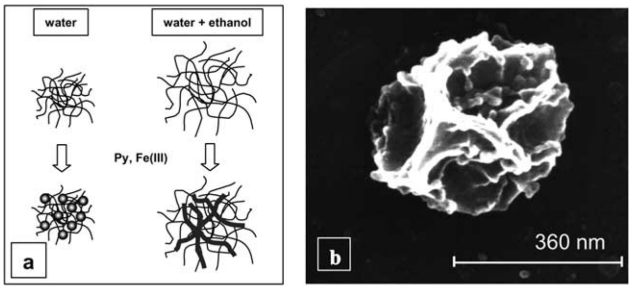

Fig. 5. Scheme of PPy particle morphology in the presence of PVME microgels (a); FESEM image of PVME microgel particle in swollen state (b).

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