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Thermo-sensitive poly(*N*-vinylcaprolactam-*co*-acetoacetoxyethyl methacrylate) microgels. 3. Incorporation of polypyrrole by selective microgel swelling in ethanol–water mixtures

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Abstract

Behaviour of temperature-sensitive core–shell VCL/AAEM microgels has been studied in binary alcohol/water mixtures. Amount of alcohol in binary mixture influences strongly the swelling and thermo-sensitive properties of microgels. Alcohol induces swelling of VCL-rich microgel shell leading to larger dimensions of microgel particles and larger surface area. Under these conditions pyrrole polymerization was carried out, and the influence of pyrrole concentration, oxidant nature and temperature on morphology and properties of composite particles was investigated. Contrary to the polymerization in water medium, this selective swelling method gives possibility to increase three times loaded polypyrrole amount and maintain the stability of the colloidal system. It was found that in case when persulfate was applied as oxidant it is possible to vary effectively the particle size of composite microgels by changing the ethanol concentration in water. Contrary, when $FeCl_3$ was used as oxidant formation of secondary particles was detected leading to dispersions with bimodal particle size distribution. The conductivity of the composite particles was much higher if polypyrrole synthesis was carried out in pure water.

Keywords: Microgel; Polypyrrole; Swelling

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1. Introduction

Conjugated polymers, also known as conducting polymers, belong to a broad class of electrically actuated polymeric materials known as electro active polymers. Conducting polymers have been studied recently and numerous useful applications were reported in the literature. Increasing effort is being devoted to the development of soft and wet devices, inspired by natural muscles that are capable of transforming electric and/or chemical energy into mechanical energy [1–5]. The microfabrication of actuators containing a film of conducting polymers allows the construction of devices capable of manipulating an individual cell [1–3]. Conjugated polymers are particularly well suited to bio-medical applications since they can operate well in blood, urine, and other bio-fluids [2], they are tissue-compatible and implantable for long periods [6–9], and can serve as suitable substrates for the growth of cell cultures [6–7,10]. Actuation strains of conducting polymers are large, from a few percent to over 30% [11–13] so the strain can be exploited in either bending geometries, which work well at the micro-scale, or directly through linear expansion/contraction, which is important on the macro-scale, at which greater forces are typically required.

Small size is desirable for many biomedical applications, so it is of interest to consider microfabricatability of conducting polymers. Our strategy is to prepare smart multi-stimuli responsive composite materials containing conducting polymers on sub-micro scale with desired properties and morphology. In a preliminary communication [14] we have reported oxidative polymerization of pyrrole (Py) has been studied in 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. Large needle-like polypyrrole (PPy) particles (appr. 400 nm) are

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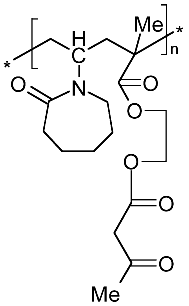


Scheme 1. Chemical structure of VCL/AAEM copolymer.

formed in aqueous ethanol in presence of crosslinked PVME microgels at Py:PVME ratio higher than 2:1. Pich et al. [15] reported selective polypyrrole deposition into the highly swollen hydrodynamic shell of monodisperse polymeric colloids leading to the well-organized conducting composite material.

In our previous papers [16,17] novel polymeric temperature-sensitive microgels have been prepared by surfactant-free emulsion co-polymerization of *N*-vinylcaprolactam (VCL) and acetoacetoxyethyl methacrylate (AAEM). Polypyrrole was successfully incorporated into microgel structure and obtained stable composite particles show fully reversible temperature-dependent collapse–swelling properties. The aim of present paper is to show how microgel morphology influences the properties of composite particles. The idea is to swell selectively the VCL-rich shell of the microgel by addition of alcohol into water medium. This should increase the effective surface area of the microgel template and the incorporation of PPy should be more effective. Additionally, one can expect that larger particles will be formed because more PPy can be stabilized by one microgel particle.

2. Experimental

2.1. Materials

Table 1
Synthesis parameters for reactions performed with $Na_2S_2O_8$ as oxidant

N	Microgel (g)	Py (g)	$Na_2S_2O_8$ (g)	Ethanol (g)	Water (g)	Ethanol (mol%)	*T* (°C)
1	20	0.05	0.25	22.5	2.5	28.1	20
2	20	0.08	0.4	22.5	2.5	28.1	20
3	20	0.1	0.5	22.5	2.5	28.1	20
4	20	0.12	0.6	22.5	2.5	28.1	20
5	20	0.15	0.75	22.5	2.5	28.1	20
6	20	0.20	1	22.5	2.5	28.1	20
7	20	0.1	0.5	13.5	11.5	14.4	20
8	20	0.1	0.5	4.5	20.5	4.2	20
9	20	0.1	0.5	–	25	–	20
10	20	0.20	1	22.5	2.5	28.1	0

Table 2
Synthesis parameters for reactions performed with $FeCl_3$ as oxidant

N	Microgel (g)	Py (g)	$FeCl_3{\cdot}6H_2O$ (g)	Ethanol (g)	Water (g)	Ethanol (mol%)	*T* (°C)
12	20	0.1	0.5	22.5	2.5	28.1	20
13	20	0.15	0.75	22.5	2.5	28.1	20
14	20	0.1	0.5	–	25	–	20
15	20	0.1	0.5	4.5	20.5	4.2	20
16	20	0.1	0.5	9	16	8.4	20
17	20	0.05	0.25	22.5	2.5	28.1	20
18	20	0.2	1	22.5	2.5	28.1	20
19	20	0.20	1	22.5	2.5	28.1	0

Acetoacetoxyethyl methacrylate was obtained from Aldrich and purified by conventional methods and then vacuum distilled under nitrogen *N*-vinylcaprolactam was obtained from Aldrich and purified by distillation. Initiator, 2,2′-azobis(2-methylpropioamidine) dihydrochloride (AMPA) was obtained from Aldrich and used as received. Deionized water was employed as polymerization medium. Cross-linker *N*,*N*′-methylenebisacrylamide (MBA) from Aldrich was used without further purification. Pyrrole (Py) was purchased from Aldrich, distilled under vacuum, and stored in a refrigerator before use. Sodium peroxydisulfate (SPDS) was obtained from Aldrich and used as received. Deionized water was employed as polymerization medium. Ethanol (96%) was obtained from Fluka.

2.2. VCL/AAEM microgel

The synthesis of VCL/AAEM microgels was described in details in our previous article [16] Appropriate amounts of AAEM, VCL and 0.06 g of cross-linker (3 mol%) were added in 145 ml deionized water. Double-wall glass reactor equipped with stirrer and reflux condenser was purged with nitrogen. Solution of the monomers was placed into reactor and stirred for 1 h at 70 °C with purging with nitrogen. After that the 5 ml water solution of initiator (5 g/l) was added under continuous stirring. Reaction was carried out for 8 h. The polymerization yield, determined gravimetrically, was around 80%. In present study, the VCL/AAEM microgel with 6.7 mol% AAEM has been used as a template for pyrrole polymerization. Some important characteristics of microgel sample: solid content 1.2%, pH = 7.2, hydrodynamic radius in water $R_h^{20}\,°C = 250$ nm. The chemical structure of VCL/AAEM copolymer is presented in Scheme 1.

PAAEM microgel was synthesised by batch emulsion polymerization of acetoacetoxyethyl methacrylate (AAEM). Appropriate amount of AAEM (4 g) was added to 196 ml deionizer water. Double-wall glass reactor equipped with stirrer and reflux condenser was purged with nitrogen. Pre-emulsion was placed into reactor and stirred for 1 h at 70 °C with purging with nitrogen. After that the 0.3 g SPDS was added under continuous stirring. Reaction was carried out for 8 h. The particle size in water determined by DLS—$R_h^{20}\,°C = 150$ nm.

Table 3
Properties of composite particles prepared with $Na_2S_2O_8$ as oxidant

N	Ethanol (mol%)	PPy^T (%)	PPy^P (%)	S (%)	Stability
1	28.1	17.24	6.72	39	+
2	28.1	25	12.3	49.2	+
3	28.1	29.41	16.35	55.59	+
4	28.1	33.3	27.22	81.74	+
5	28.1	38.46	35.13	91.34	+
6	28.1	45.45	41.12	90.47	+
7	14.4	29.41	29.40	99.90	−
8	4.2	29.41	27.97	95.1	+
9	–	29.41	26.18	89.0	+
10	28.1	45.45	43.09	94.81	+

T—theoretically predicted; P—determined by elementary analysis; S—PPy incorporation efficiency.

2.3. Polymerization of pyrrole

VCL/AAEM microgel was diluted with appropriate amount of ethanol/water mixture at 25 °C in 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. Polymerization was allowed to proceed for 10 h. The polypyrrole content in composite microgels was determined by elementary analysis. Detailed reaction recipes are shown in Tables 1 and 2. Tables 3 and 4 contain theoretically predicted and experimentally determined PPy amounts in composite particles as well as some other important characteristics such as polypyrrole incorporation efficiency, stability of dispersions, etc.

2.4. Cleaning procedure

Polymer dispersions were freed from monomer by dialysis Latexes were dialysed against water using Millipore Amicon Miniplate membrane (MWCO—10,000).

2.5. Particle size analysis

The dynamic light scattering (DLS) measurements were performed with commercial laser light scattering (LLS) spectrometer (ALV/DLS/SLS-5000) equipped with an ALV-5000/EPP multiple digital time correlator and laser goniometer system ALV/CGS-8F S/N 025 was used with a helium–neon laser (Uniphase 1145P, output power of 22 mW and wavelength of 632.8 nm) as the light source. In dynamic LLS, the intensity–intensity–time correlation function $g_2(q,t)$ in the self-beating mode was measured and can be expressed by the Siegert relation:

$$g_2(q,t) = A(1 + \beta|g_1(q,t)|^2) \tag{1}$$

where t is the decay time, A is a measured baseline, β is the coherence factor, and $g_1(q,t)$ is the normalized first-order electric field time correlation function and $g_1(q,t)$ is related to the measured relaxation rate Γ:

$$g_1(q,t) = \exp(-\Gamma t) = \int G(\Gamma)\exp(-\Gamma t)\mathrm{d}\Gamma \tag{2}$$

A line-width distribution $G(\Gamma)$ can be obtained from the Laplace inversion of $g_1(t)$ (CONTIN procedure). For a pure diffusive relaxation, Γ is related to the translational diffusion coefficient D at $q \to 0$ and $c \to 0$ by:

$$D = \Gamma/q^2 \tag{3}$$

or a hydrodynamic radius R_h given by:

$$R_h = k_B T/(6\pi\eta D) \tag{4}$$

with q, k_B, T and η being scattering vector, the Boltzmann constant, absolute temperature, and solvent viscosity, respectively. All DLS experiments were carried out at angles $\theta = 30–140°$. The concentration of the microgel in water was about 1.5×10^{-5} g/ml. Microgel solutions were filtrated using 5 μm nylon filters. Typically, the sample in a 10 mm test tube was immersed in a toluene bath and thermostated within an error of ±0.1 °C. Refractive index and viscosities of alcohol–water mixtures are reported in Refs. [18,19].

Table 4
Properties of composite particles prepared with $FeCl_3$ as oxidant

N	Ethanol (mol%)	PPy^T (%)	PPy^P (%)	S (%)	Stability
12	28.1	29.41	10	34	+
13	28.1	38.46	25.41	66.07	+
14	–	29.41	16.64	56.58	+
15	4.2	29.41	8.41	28.6	+
16	8.4	29.41	23.55	80.7	−
17	28.1	17.24	2.25	13.0	+
18	28.1	45.45	26.64	58.61	+
19	28.1	45.45	24.6	54.13	+

T—theoretically predicted; P—determined by elementary analysis; S—PPy incorporation efficiency.

2.6. Scanning electron microscopy

SEM images were taken with Gemini microscope (Zeiss, Germany). Samples were prepared in the following manner. Dispersions were diluted with distilled water, dropped onto aluminium support and dried at room temperature. Prior to SEM measurements samples were coated with thin Pd layer to enhance the contrast. Pictures were taken at voltage of 4 kV.

2.7. Conductivity measurements

The conductivity measurements were carried out by measuring the conductivity of the film of the polypyrrole composites dispersion using the conventional two-probe technique with a source-measure-unit (SMU 236) from Keithley Instruments, Inc., Cleveland, USA. The conducting film was prepared by dropping the polypyrrole

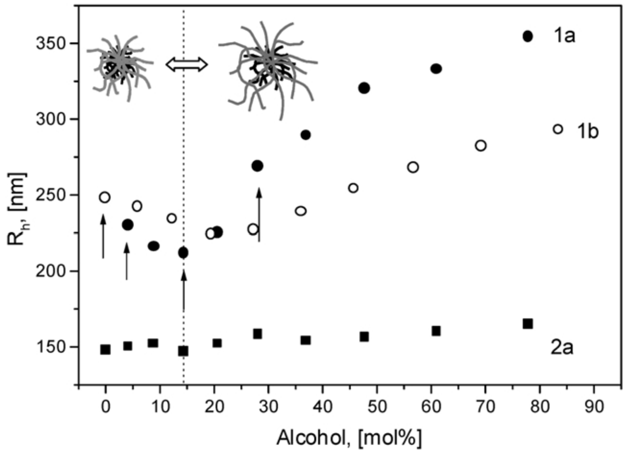


Fig. 1. Hydrodynamic radius of microgel as a function of binary solvent composition: 1, VCL/AAEM microgel; 2, PAAEM microgel (a, ethanol; b, methanol; $T = 20$ °C).

dispersion on the electrode quantitatively and dried under vacuum for 24 h. The dimensions of the film were measured using a travelling microscope (L.C. = 0.001 cm). The conductivity (σ) of the sample was calculated using the relation:

$$\sigma = d/(RA) \tag{5}$$

where R is the measured resistance, d the thickness of the sample film (about 5×10^{-6} m) and A the area of conducting film in contact with the electrode.

3. Results and discussion

3.1. Behaviour of VCL/AAEM microgels in ethanol/water mixtures

It has been shown in our previous study [16] that VCL/AAEM microgels possess large structural heterogeneities due to the different reactivity of monomers used. Obtained particles possess more compact AAEM-rich core, highly swollen thermo-sensitive VCL-rich shell which can undergo reversible swelling–deswelling transition by changing the temperature of surrounding medium (water). To investigate the influence of the alcohol on the microgel dimensions VCL/AAEM particles were diluted by different ethanol/water mixtures and the particle size was measured by DLS. Fig. 1 shows the hydrodynamic radii of the microgel sample measured in solutions which contain different amounts of methanol or ethanol (measurements were made at 20 °C).

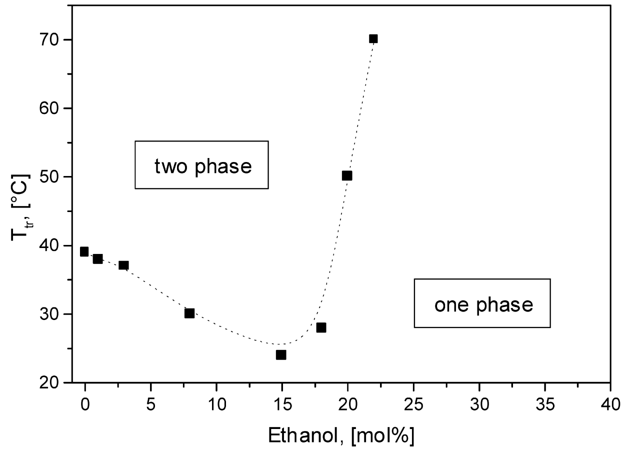


Fig. 2. Transition temperature of linear PVCL as a function of binary solvent composition (data used from Ref. [20]).

Fig. 1 indicates that PAAEM particles are not sensitive to the addition of alcohol and R_h value is nearly constant in broad alcohol concentration range. This indicates that AAEM-rich microgel core must be nearly not influenced by presence of alcohol molecules. For VCL/AAEM particles both for methanol and ethanol systems opposite effect was observed: decrease of R_h up to 15 mol% of ethanol and ~20 mol% of methanol in solution (partial collapse of VCL-rich shell) and then increase of the R_h with further increase of alcohol in solution (swelling of VCL-rich shell). These results may be explained taking to account a dehydration of polymer chains caused by the presence of solvent molecules with hydrophobic groups. When a small amount of low polarity organic solvent is added to water, cages of water molecules surround these solute molecules, this phenomenon is well known as hydrophobic hydration. Interaction between water and alcohol in this case is stronger than their interaction with polymer. This effect is limited by the capacity of water to hydrate certain amounts of solute and more hydrophobic solute demands a larger number of water molecules to hydrate it. The minimum in $R_h - c_{\text{ethanol}}$ function in Fig. 1 correlates with minimum in phase diagram of linear PVCL in water/ethanol mixture reported by Kirsh et al. [20]. Fig. 2 indicates that the transition temperature of PVCL is strongly influenced by alcohol molecules present in water solution. Up to 15 mol% ethanol in binary mixture the phase transition temperature decreases (solvent quality decreases). When alcohol amount is larger than 15 mol% phase transition temperature increases rapidly and for solutions containing >25 mol% ethanol T_{tr} disappears.

Facts described above lead to suggestion, that initial decrease of the hydrodynamic radius of microgel particles (see Fig. 1) is induced by partial collapse of PVCL-rich shell due to the shift of T_{tr} to lower temperatures (DLS measurements were performed at 20 °C!). Further addition of alcohol increases T_{tr} and the VCL-rich shell starts to swell rapidly. Investigated system remains stable at different alcohol concentrations and no aggregation effects were detected. It can be expected that the chemical composition of the microgels should also influence particle behaviour in mixed solvent. Higher VCL content in microgels should lead to more pronounced changes of hydrodynamic radii of particles with addition of alcohol, but it is expected that minima observed in Fig. 1 will remain in the same position

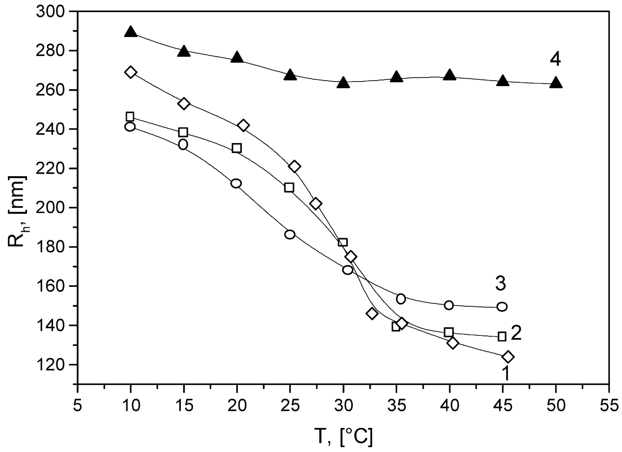


Fig. 3. Hydrodynamic radius of microgel in different ethanol/water mixtures as a function of temperature (1, water; 2, 4.2 mol%; 3, 14.4 mol%; 4, 28.1 mol%).

for certain alcohol type. Similarly, in our previous work [16, 17] the volume transition temperature of VCL-rich shell in microgels was not influenced by the VCL/AAEM ratio, but the particle shrinkage was more obvious at higher VCL contents.

From experimental data presented in Fig. 2 it is possible to conclude that VCL/AAEM microgels will lose their thermo-sensitivity in binary alcohol/water solutions when alcohol concentration is higher as indicated by minimum in Figs. 1 and 2. Experimental results confirm this idea. Fig. 3 presents the hydrodynamic radii of VCL/AAEM microgel as a function of the temperature measured in different ethanol/water solutions (see arrows in Fig. 1).

Fig. 3 indicates that VCL/AAEM microgels possess thermo-sensitive properties in water and alcohol/water mixtures up to the certain alcohol concentration. At higher alcohol contents the VCL rich shell of the microgels swells and this leads to the change of particle dimensions. With increasing of alcohol concentration phase transition becomes broader and disappears in the mixture, which is good solvent for whole temperature range. It should be noted that microgel never reaches fully collapsed state in the presence of alcohol even at elevated temperatures probably due to hydrophobic interaction between polymer and alcohol. This interaction is stronger than in the case of microgels, based on more hydrophilic *N*-isopropylacrylamide, which have size in collapsed state in mixture lower than in water [21,22]. In summary, addition of alcohol leads to the controlled collapse–swelling of the VCL-rich shell on the particle surface. This gives a possibility to change the surface area of the microgel particles at constant VCL/AAEM ratio and constant temperature. In other words, the dimensions of polymeric template can be varied before the pyrrole polymerization.

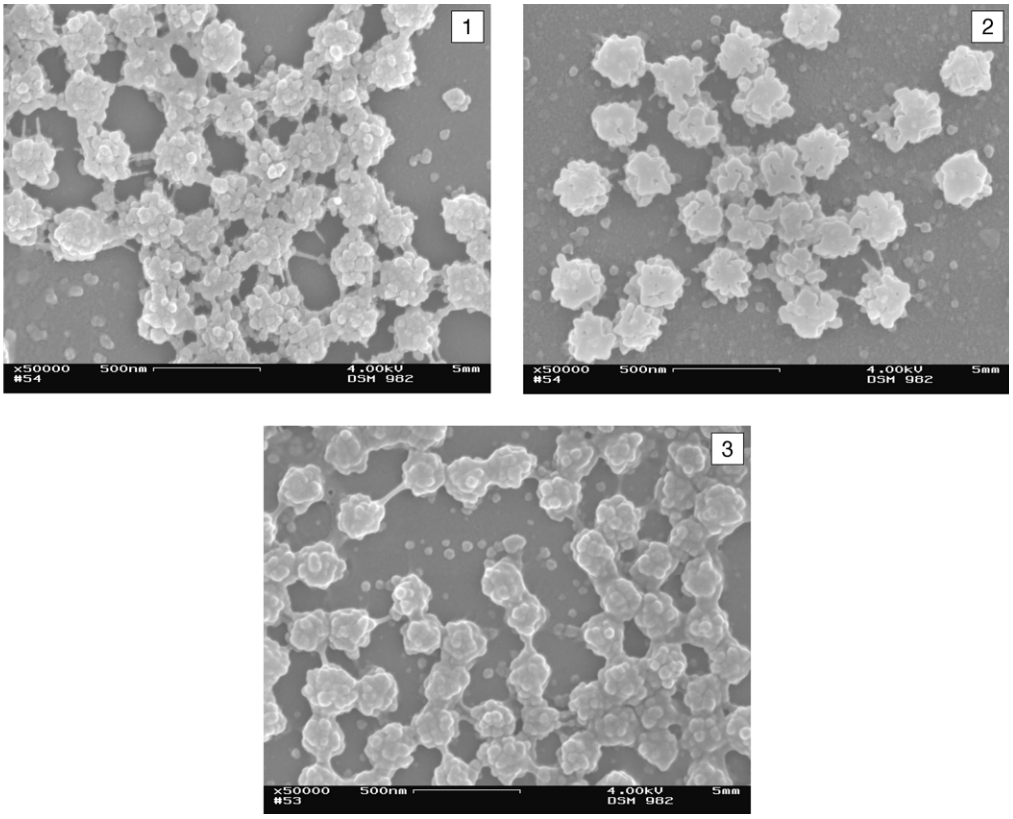


Fig. 4. SEM images of composite microgels prepared in: (1) water (PPy load, 26.18%), (2) 4.2 mol% ethanol (PPy load, 27.97%), (3) 14.4 mol% ethanol (PPy load, 29.4%).

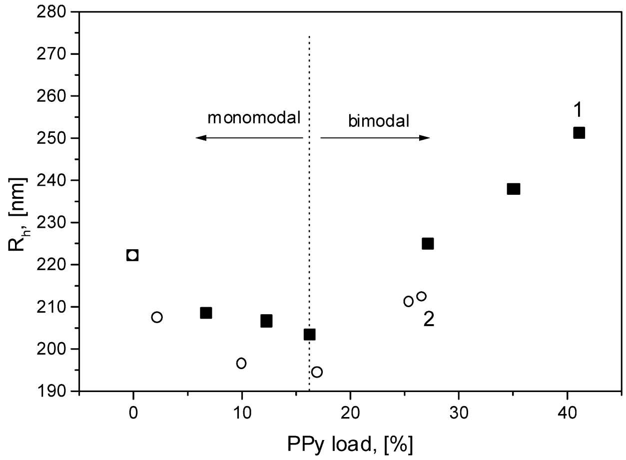


Fig. 5. Hydrodynamic radius of composite microgels prepared with different Py contents ($T = 20$ °C; 1, SPDS; 2, $FeCl_3$).

3.2. Polymerization of pyrrole

3.2.1. Influence of reaction medium

In this reaction set, pyrrole polymerization was carried out in different reaction mediums ethanol concentration was increased gradually and initial pyrrole concentration as well as the oxidant concentration (persulfate) was kept constant. Fig. 4 presents the morphology of obtained particles. It is evident that increase of the ethanol content in the reaction medium leads to smoother surface of composite particles. SEM images indicate also that the size of PPy inclusions decreases at higher alcohol contents. This effect was observed in our previous study [14] and is probably due to the lower surface tensions of alcohol/water solution which leads to formation of smaller PPy particles. On the other hand, the polymerization kinetics of Py can be also influenced by presence of ethanol molecules resulting in reduced polymerization rates [23]. More detailed kinetic investigations can help also to explain the formation process of composite microgels.

Fig. 4 indicates that pyrrole was polymerized mostly in microgel network, and the morphology of the particles is spherical in all cases. A small fraction of secondary particles is clearly observed in all micrographs presented in Fig. 4. Since no bimodal particle size distribution was detected by DLS experiments in this case, formation of secondary particles can take place during drying. Water removal from VCL/AAEM microgels induces shrinkage of the network and some PPy inclusions can be pushed out of the microgel. It is evident that the size of composite particles decreases with increased amount of ethanol in reaction system and this result correlated with DLS measurements presented in Fig. 1. In this case addition of ethanol induces collapse of microgel, and therefore the final size of composite particles decreases. Table 3 indicates that up to 14.4 mol% ethanol in the solution the final PPy incorporation efficiency is quite high. Only when 28.1 mol% ethanol–water mixture was used the amount of incorporated PPy is only 55% of theoretically expected value. It should be noted that dispersion prepared in 14.4 mol% ethanol–water mixture was not quite stable. At this ethanol content the minimal particle size of microgel was detected by DLS indicating that protecting hydrodynamic shell of the microgel is partially collapsed. The additional incorporation of PPy leads in this case to destabilization of the colloidal system.

3.2.2. Influence of oxidant nature and pyrrole concentration

In this set of experiments composite particles were prepared at 20 °C in ethanol/water mixture containing 28.1 mol% ethanol. The amount of pyrrole added initially was varied and two oxidants were selected (SPDS and $FeCl_3$) to initiate the pyrrole polymerization.

The particle size of obtained composite particles was analysed by DLS. Experimental results are presented in Fig. 5. It is clear that the behaviour of the particle size is very similar to that of measured in water [17]: initial decrease due to the interaction of PPy inclusions with microgel network and then expansion of the composite particles due to increase of PPy amount. It should be noted that contrary to our previous work [17] when Py was polymerized in water, composite particles are stable even when the PPy

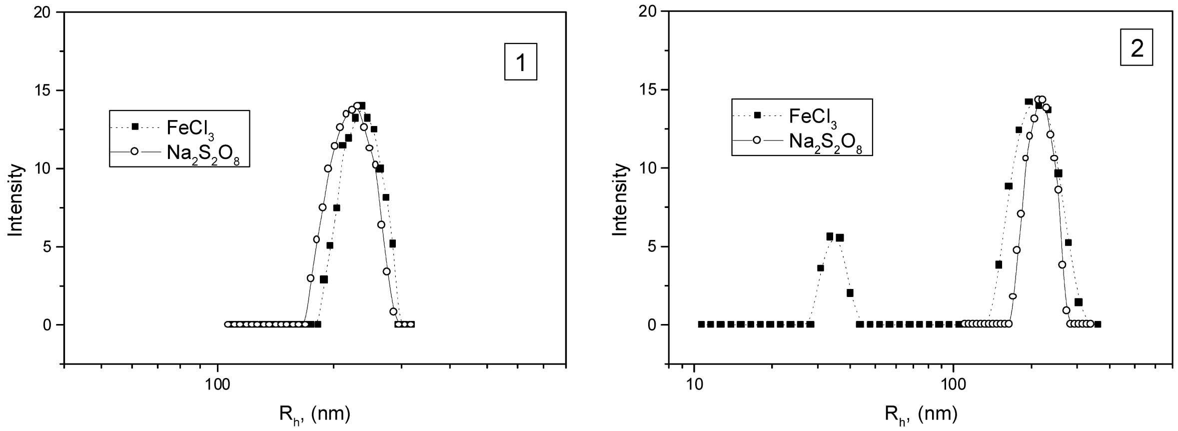


Fig. 6. Particle size distribution of composite microgels prepared with different PPy contents (PPy loads: 1) 2.25 and 6.72%; 2) 25.4 and 35.13% for $FeCl_3$ and SPDS respectively).

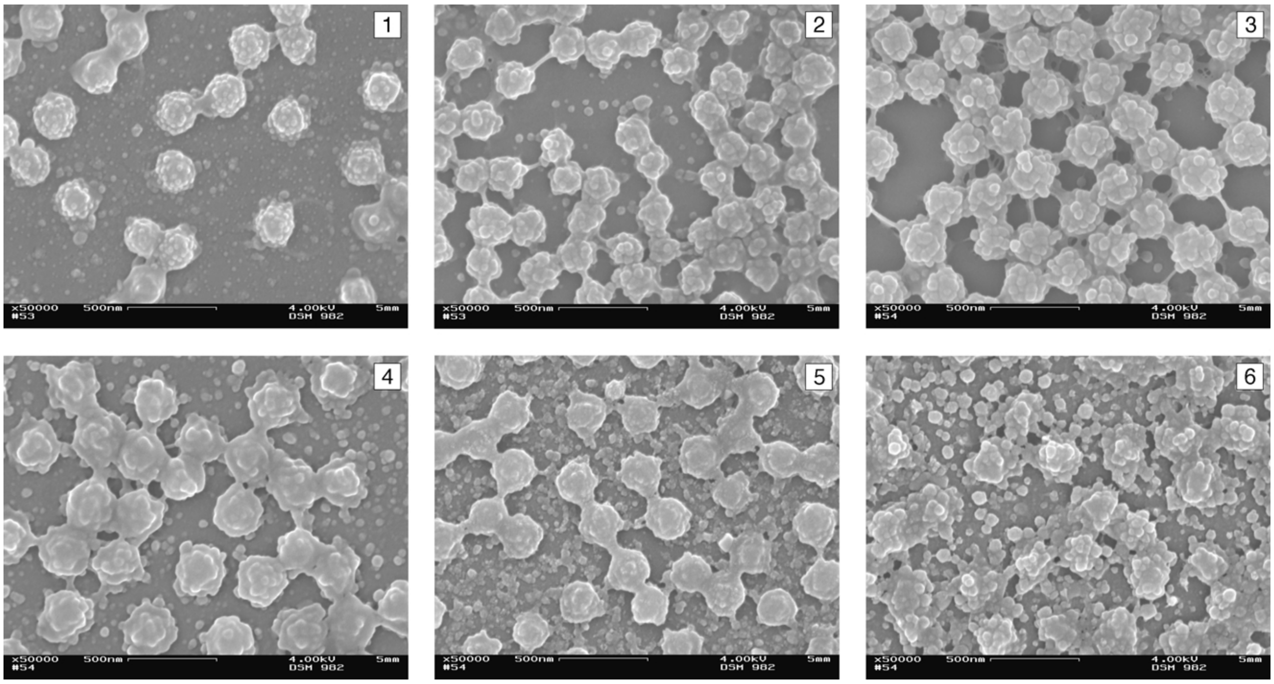


Fig. 7. SEM images of composite microgels prepared with SPDS: (1) 6.72% PPy, (2) 16.35% PPy, (3) 41.12% PPy and $FeCl_3$: (4) 2.25% PPy, (5) 10% PPy, (6) 26.64% PPy.

load is 40% probably due to enhanced stability of the microgel template in water/ethanol solution. Fig. 5 indicates that the hydrodynamic radii of particles prepared with SPDS are larger if to compare with particles prepared with $FeCl_3$. This effect can be explained by lower PPy load when $FeCl_3$ was used (Tables 3 and 4) due to the complex formation of the oxidant with alcohol molecules [23]. At higher PPy load dispersions prepared with $FeCl_3$ show bimodal particle size distribution. Fig. 6 shows particle size distribution of composite microgels prepared with different oxidants at low and high PPy load.

At low PPy load no secondary particle formation was detected for runs performed with persulfate and $FeCl_3$. Contrary bimodal particle size distribution shown in DLS spectrum in Fig. 6b indicates clearly that secondary PPy particles are formed in reaction system at high pyrrole concentrations when $FeCl_3$ is used as oxidant. Fig. 7 shows SEM images of composite particles prepared with different oxidants. Samples prepared with $FeCl_3$ at high PPy load exhibit a lot of small secondary PPy particles which are not integrated into microgel template. Contrary, microscopy images of samples prepared with persulfate as oxidizing agent indicate that mostly PPy has been incorporated into microgels.

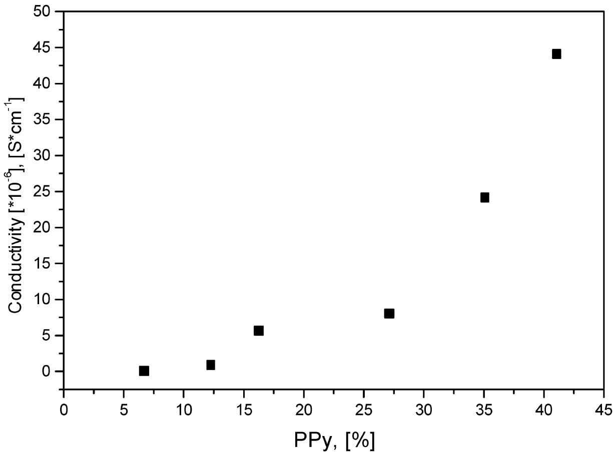


Fig. 8. Conductivity of composite microgels vs amount of loaded PPy (samples 1–6).

The strong complexation of $FeCl_3$ with alcohol molecules is probably the reason for appearance of secondary PPy particles. It can be assumed that in this case formed PPy nuclei are better stabilized in the surrounding medium and growing particles remain beside microgel template.

3.3. Conductivity of composite microgels

The conductivity of composite microgels prepared with

Table 5
Influence of the reaction temperature, oxidant nature and reaction medium on conductivity of the composite particles

N	Py (g)	PPy^P (%)	Ethanol (mol%)	Oxidant	T (°C)	σ, ($S\ cm^{-1}$)
3	0.1	16.35	28.1	SPDS	20	5.64×10^{-6}
9	0.1	26.18	–	SPDS	20	1.58×10^{-3}
12	0.1	10.00	28.1	$FeCl_3$	20	3.07×10^{-9}
14	0.1	16.64	–	$FeCl_3$	20	1.74×10^{-2}
6	0.2	41.12	28.1	SPDS	20	4.03×10^{-6}
10	0.2	43.09	28.1	SPDS	0	1.87×10^{-5}
19	0.2	24.6	28.1	$FeCl_3$	0	5.98×10^{-7}

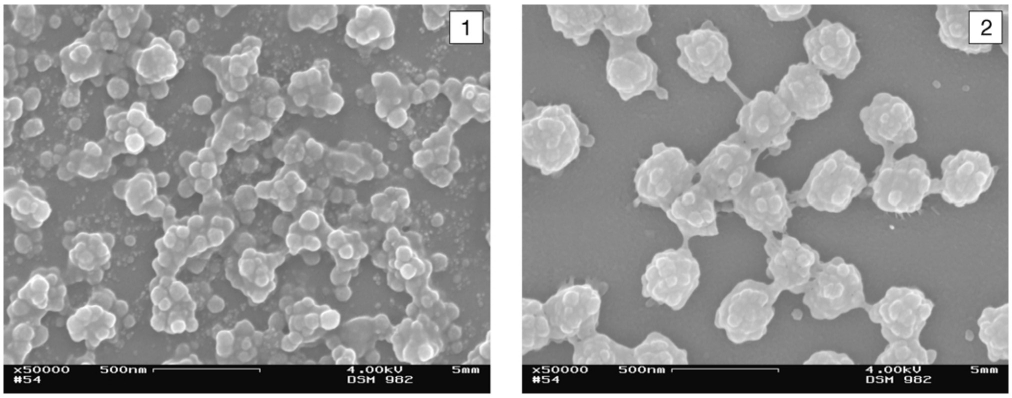


Fig. 9. SEM images of composite microgels prepared with: 1) $FeCl_3$ (24.6% PPy), (2) SPDS (43.09% PPy) (28.1 mol% ethanol; $T = 0$ °C).

different PPy contents was measured by 2-point method. Experimental results are presented in Fig. 8. It is evident that conductivity increases with increased PPy content. At low PPy contents the conductivity is very small probably due to the insulating behaviour of the microgel template. Increase of PPy content in composite particles provides better interparticle contacts of PPy domains and therefore conductivity of composite material increases rapidly.

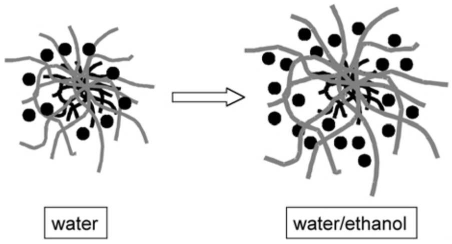
It has been found that reaction temperature, oxidant nature and reaction medium have strong influence on conductivity of the composite particles. Table 5 summarizes some selected results. First of all, for samples prepared in water measured conductivity was considerably higher if to compare with samples prepared in ethanol–water mixtures independently on oxidant nature. This effect may be attributed to the poor oxidative environment provided in ethanol/water mixtures. As it is shown in Table 3 the final PPy incorporation efficiency increases continuously with increasing pyrrole and oxidant concentration (the molar ratio pyrrole/oxidant was kept constant) in presence of 28.1 mol% ethanol in water. Similar results were obtained when $FeCl_3$ was used as oxidant. This supports the idea that the oxidation power of SPDS and $FeCl_3$ in water/ethanol mixtures is reduced. Similar observations were reported by Mandal et al. [23] when pyrrole was polymerized in water/ethanol mixtures or in pure ethanol with $FeCl_3$. The low level of conductivity was explained by complexation of $FeCl_3$ with ethanol. It has been also reported by Machida et al. that the oxidation potential of the Fe(II)/Fe(III) system in methanol increases with increase in $FeCl_3$ concentration [24].

Table 5 indicates also that composite particles prepared with $FeCl_3$ as oxidant exhibit much higher conductivity when synthesis was carried out in water, but particles prepared with persulfate show higher conductivity values when synthesis was performed in ethanol–water mixture. Lowering of the reaction temperature improves the conductivity, but this effect in our case is not significant. It has been reported in [18,19] that the conductivity of PPy particles has been improved by two orders of magnitude when the polymerization temperature was lowered from 20 to 5 °C. Fig. 9 indicates that the reaction temperature has strong influence on the morphology of composite particles.

Images in Fig. 9 (1) and (2) can be directly compared with electron micrographs presented previously in Fig. 7 (6) and (3), respectively. When SPDS has been used as oxidant particle morphology is not influenced by reaction temperature. Contrary, composite particles prepared with $FeCl_3$ at lower temperature show dramatic increase of polydispersity and paricles with non-uniform shapes have been obtained. Since at 28.1 mol% ethanol in water solution VCL/AAEM microgels are not temperature-sensitive, the influence of the template on final particle morphology during Py polymerization at low temperature can be excluded. Lowering the temperature should decrease the polymerization rate of pyrrole, and slower nucleation process will lead to formation of larger PPy domains which probably cannot penetrate into template and prefer to stay beside the microgel. The above mentioned ability of Fe to form complexes with ethanol molecules additionally supports PPy formation outside of the microgel template.

4. Conclusions

Thermo-sensitive VCL-rich shell of VCL/AAEM microgels can be selectively swollen by ethanol molecules leading to expansion of the polymer network and change of microgel dimensions. Relatively high polypyrrole amounts were successfully incorporated under these conditions into microgels and stable colloidal systems have been obtained. It has been shown that the dimensions and morphology of composite microgel particles can be influenced by ethanol concentration in water, amount of loaded PPy, and oxidant nature. It has been found that when $Na_2S_2O_8$ has been used as oxidant no secondary PPy particles were detected and dispersions with monomodal particle size distribution were obtained. Contrary, using $FeCl_3$ in similar reaction conditions leads to formation of non-organized systems where PPy particles remain beside microgel template. It has been demonstrated, that the selective swelling method gives possibility to increase three



Scheme 2. Polypyrrole functionalized VCL/AAEM microgels.

times loaded PPy amount (if to compare with the polymerization in water medium), and maintain the stability of the colloidal system.

As it is shown in Scheme 2 selective swelling of VCL-rich shell by addition of alcohol increases the surface area of domains for PPy deposition. Therefore larger polypyrrole amounts can be effectively stabilized by similar microgels in different medium. It is also suggested that PPy domains occupy mostly the rigid shell area of the VCL/AAEM microgels and penetration inside compact AAEM-rich core is sterically hindered. When the surface layer is saturated by PPy inclusions, new formed nuclei deposit directly onto the microgel surface leading to destabilization of colloidal system. Therefore, considering microgels as template or reservoir for deposition of PPy one should keep in mind that the effective stabilizing capacity depends on thickness of VCL-rich shell. As it was shown this thickness can be varied by changing the chemical composition of microgel [16,17] and addition of organic solvent. Increase of PPy content in composite particles increases conductivity of the composite material. The conductivity of composite particles prepared in water was much higher than that of prepared in water/ethanol mixtures.

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References

[1] Smela E, Inganäs O, Lundström I. Science 1995;268:1735.
[2] Jager EWH, Smela E, Inganäs O. Science 2000;290:1540.
[3] Jager EWH, Inganäs O, Lundström I. Science 2000;288:2335.
[4] Osada Y, Okuzaki H, Hori H. Nature 1992;355:242.
[5] Zhang QM, Bharti V, Zhao X. Science 1998;28:2101.
[6] Williams RL, Doherty J. J Mater Sci: Mater Med 1994;5:429.
[7] Schmidt CE, Shastri VR, Vacanti JP, Langer R. Proc Natl Acad Sci USA 1997;94:8948.
[8] Wong JY, Langer R, Ingber DE. Proc Natl Acad Sci USA 1994;91:3201.
[9] Kovacs GTA. In: Director SW, editor. Micromachined transducers sourcebook. Boston: WCB McGraw-Hill; 1998.
[10] Aoki T, Tanino M, Sanui K, Ogata N, Kumakura K. Biomaterials 1996;17:1971.
[11] Madden J, Cush R, Kanigan T, Brenan C, Hunter I. Synth Met 1999;105:61.
[12] Irvin DJ, Goods SH, Whinnery LL. Chem Mater 2001;13:1143.
[13] Marsella MJ, Reid RJ, McCormick MT. Synth Met 2001;118:171.
[14] Pich A, Lu Y, Adler HJP, Schmidt T, Arndt KF. Polymer 2002;43:5723.
[15] Lu Y, Pich A, Adler HJP. Synth Met 2003;135–136:37.
[16] Boyko V, Pich A, Lu Y, Richter S, Arndt KF, Adler HJP. Polymer 2003;44(25):7821.
[17] Pich A, Lu Y, Boyko V, Arndt KF, Adler HJP. Polymer 2003;44(25):7651.
[18] Dizechl M, Marschall E. J Chem Engng Data 1982;27:358.
[19] Mikhail SZ, Kimel WR. J Chem Engng Data 1961;6:533.
[20] Kirsh YuE, Soos TA, Karaputadze TM. Vysokomolekularnyje Sojedinenija A 1979;21:519.
[21] Crowther HM, Vincent B. Coll Polym Sci 1998;276:46.
[22] Zhu PW, Napper DH. J Colloid Interface Sci 1996;177:343.
[23] Digar ML, Bhattacharyya SN, Mandal BM. Polymer 1994;35:377.
[24] Machida S, Miyata S, Techagumpuch T. Synth Met 1989;31:311.