Polypyrrole-containing Composite Particles: Preparation, Characterization and Application

DISSEETATION

Zur Erlangung des akademischen Grades

Doktor rerum naturalium
(Dr. rer. nat.)

vorgelegt

der Fakultät Mathematik und Naturwissenschaften
der Technischen Universität Dresden

von

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Geboren am 2 September 1976 in Wuxi, V. R. China

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Eingereicht am: Nov. 30th, 2004
Tag der Verteidigung: Feb. 2nd, 2005
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<th>Description</th>
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</thead>
<tbody>
<tr>
<td>AAEM</td>
<td>acetoacetoxyethyl methacrylate</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscope</td>
</tr>
<tr>
<td>AMPA</td>
<td>2,2'-azobis(2-methylpropioamidine), dihydrochloride</td>
</tr>
<tr>
<td>AIBN</td>
<td>azobisisobutyronitrile</td>
</tr>
<tr>
<td>CP</td>
<td>conducting polymer</td>
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<tr>
<td>CRS</td>
<td>cold-rolled steel</td>
</tr>
<tr>
<td>DLS</td>
<td>Dynamic light scattering</td>
</tr>
<tr>
<td>DVS</td>
<td>divinylsulfone</td>
</tr>
<tr>
<td>ER</td>
<td>electrorheology</td>
</tr>
<tr>
<td>FeCl₃</td>
<td>ferric chloride</td>
</tr>
<tr>
<td>FFF</td>
<td>Field-flow fractionation</td>
</tr>
<tr>
<td>HDG</td>
<td>hot dip galvanzing</td>
</tr>
<tr>
<td>H₃PMo₁₂O₴₀</td>
<td>phosphomolybdic acid</td>
</tr>
<tr>
<td>HPC</td>
<td>hydroxypropyl cellulose</td>
</tr>
<tr>
<td>LCST</td>
<td>Lower critical solution temperature</td>
</tr>
<tr>
<td>MBA</td>
<td>N, N'-methylenbisacrylamide</td>
</tr>
<tr>
<td>PANi</td>
<td>polyaniline</td>
</tr>
<tr>
<td>PEDOT</td>
<td>poly(3,4-ethylenedioxythiophene)</td>
</tr>
<tr>
<td>PEGMA</td>
<td>ω-hydroxy poly(ethylene glycol) methacrylate</td>
</tr>
<tr>
<td>Poly(ST-co-BuA)</td>
<td>poly(styrene-co-butylacrylate)</td>
</tr>
<tr>
<td>PP</td>
<td>polypropylene</td>
</tr>
<tr>
<td>PPy</td>
<td>polypyrrole</td>
</tr>
<tr>
<td>PS</td>
<td>polystyrene</td>
</tr>
<tr>
<td>PSS</td>
<td>poly(styrenesulfonate)</td>
</tr>
<tr>
<td>PVA</td>
<td>poly(vinyl alcohol)</td>
</tr>
<tr>
<td>PVAC</td>
<td>poly(vinyl acetate)</td>
</tr>
<tr>
<td>PVME</td>
<td>poly(vinyl methyl ether)</td>
</tr>
<tr>
<td>PVP</td>
<td>poly(vinyl-pyrrolidone)</td>
</tr>
<tr>
<td>Py</td>
<td>pyrrole</td>
</tr>
<tr>
<td>RVC</td>
<td>reticulated vitreous carbon</td>
</tr>
<tr>
<td>SDBS</td>
<td>sodium dodecylbenzensulfonate</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>SLS</td>
<td>Static light scattering</td>
</tr>
<tr>
<td>SPDS</td>
<td>sodium peroxydisulfate</td>
</tr>
<tr>
<td>ST</td>
<td>styrene</td>
</tr>
<tr>
<td>VCL</td>
<td>N-vinylcaprolactam</td>
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1. Introduction

Polymers with conjugated double bonds, distinguished from other types of polymers by their electronic conductivity, are called as conducting polymer. Conducting polymers show significantly different physical behavior because they can be switched between two or more redox states. These electronic properties are the basis for a growing world-wide interest in the use of conjugated polymers as advanced functional materials. The Nobel Prize for Chemistry in 2000 was awarded to Heeger, MacDiarmid and Shirakawa for the discovery and development of conducting iodine-doped polyacetylene films in 1977[1].

Polypyrrole (PPy) is one of the most studied conducting polymers because it offers a lot of attractiveness from several factors. Firstly, the most important advantage was undoubtedly the chemical and thermal stability of this polymer compared to other conducting polymers. Secondly, its ready ability to prepare derivatives, which had a range of conductivities, was distinguished. Thirdly, its ease of preparation was also appealing. All of these attributes encouraged us to believe that further effort to understand these somewhat intractable polymers would be worthwhile. Unfortunately, PPy is invariably obtained as a black precipitate. It is recognized that several limitations are imposed on the processing by lack of solubility and fusibility of these materials. The general intractability of PPy conducting polymers has already prevented it from further development. Therefore, new methods must be sought to improve the processability of this kind of polymer. The preparation of PPy particles in various colloidal forms was one of the most important and promising routes[2].

The research of our group in the frame work of “SFB Reactive Polymers” is focused on the synthesis, characterization and application of reactive dispersions. During our studies, it is clear that conducting PPy colloids are excellent “model” dispersions, which possess both academic and commercial potentials. A unique combination of physical properties are recognized for this kind of polypyrrole composite particles, such as remarkably high solid-state electrical conductivity, high intrinsic pigmentation, high density, bio-compatibility, easily variable particle size and relatively narrow particle size distribution. Numerous applications of polypyrrole derivatives have been proposed. A particular emphasis is placed on applications such as electrochromic displays, microwave welding, conductive paints, anticorrosion and antistatic coatings, electrochromatography, and immunodiagnostic assays. In summary, the preparation
of PPy dispersions with properties of “added-value” is an interesting subject and our understanding of this feature is still far from complete. Therefore, a novel approach is developed in this work to prepare and characterize polypyrrole dispersions with controlled morphology and applications.
2. Aim of the work

The technological success of polypyrrole composites depends critically on whether they offer additional “value-added” properties, such as well-defined colloidal dimensions or morphologies, biocompatibility, high surface area, potential surface functionalization and film-formation properties.

This research work is focused on preparation of polypyrrole conducting polymeric particles by using so-called template oxidative polymerization method. The use of different kinds of templates to prepare polypyrrole dispersions is an effective way to get polypyrrole dispersions with controlled morphology and properties. Several self-designed templates will be applied, such as water-soluble polymers, polymer latex particles, polymeric microgels or bulk gels (see in Fig.2.1). In all cases, two-step preparation procedure will be used to synthesize composite conducting particles, which consists of a) preparation of the template, and b) polymerization of pyrrole in the presence of template.

![Fig.2.1: Scheme of the different routes being used to prepare polypyrrole particles.](image)

Firstly, water-soluble polymer, poly (vinyl methyl ether) (PVME), has been chosen as the stabilizer to prepare polypyrrole dispersion with core-type morphology. Being
interested in controlling the polymerization process, we will investigate the influence of the oxidant, reaction medium, temperature and the addition of the dopants on the properties of final products. Different kind of anionic salts, such as sodium benzoate, potassium hydrogen phthalate and sodium hydrogen succinate, will be tried to use as dopant. Also different kinds of methods, such as SEM, elementary analysis, FT-IR spectroscopy have to be used to study the morphology and conductivity of the polypyrrole particles.

Next, polymeric microgels, such as crosslinked PVME microgels, were considered to be applied as templates for deposition of polypyrrole. For comparison, another kind of temperature-sensitive microgels, which were prepared by radical co-polymerization of N-vinylcaprolactam (VCL) and acetoacetoxyethyl methacrylate (AAEM), will be also tried to be used as the template. The influence of the reaction medium, temperature, oxidant addition mode and microgel structure on the kinetics of polymerization and properties of final particles should be investigated in detail.

Furthermore, specially designed sterically stabilized polystyrene (PS) particles with grafted poly(ethylene glycol) methacrylate (PEGMA) brush-like layer have been used as templates for polypyrrole deposition. It is expected to obtain PPy composite particles with core-shell morphology. Both the core size and PPy shell thickness are possible to be varied by changing the reaction condition. It is necessary to investigate the influence of the oxidants, deposited polypyrrole amount on the morphology and optical properties of obtained composite particles.

Finally, polymeric hydrogels containing PS/PEGMA particles prepared by chemical crosslinking of poly (vinyl alcohol) (PVA) or hydroxypropyl cellulose (HPC) were used for the chemical or electrochemical deposition of PPy. Obtained composite hydrogels will be characterized in terms of morphology, swelling degree, PPy load, conductivity etc. In addition, effects of the template parameters such as particle concentration, crosslinking degree on the final properties of composite hydrogels have to be investigated.

Overall, the proper design of the template should give a possibility to control effectively the morphology and properties of the composite particles. Different morphologies, such as spherical, core-shell, raspberry and needle-like, with different particle size are expected. The stable water-based PPy dispersions will be used in different applications, such as additives for anti-corrosion coatings, amino acid absorption and so on.
3. Theoretical background

3.1 Polymerization mechanism

A better idea of the place of conducting polymers among the three broad conductivity classification of materials, i.e. insulators, semiconductors and metals, can be generated from comparison of conductivities, as shown in Fig.3.1. In this figure, the conductivities are represented in Siemens/cm. The conductivity (generally denoted $\sigma$) is the reciprocal of the resistivity (generally denoted $\rho$, unit of $\Omega\text{cm}$), which can generally be defined as the potential drop across a given distance in a cross section of the material in question of given area, when a given current passes through this cross section, i.e. $\rho = (\Delta E/\text{distance})/(I/\text{Area})$, keeping in Ohm’s law, $E = IR$.

![Fig.3.1: Comparison of conductivities of various materials.](image)

The most interesting, and maybe important conducting polymers are polyaniline, polypyrrole, polyacetylene and polythiophene (Fig.3.2) \textsuperscript{[3]}. As we know, in the beginning polyacetylene was the prototype for scientific investigations, however polypyrrole (PPy) has also been deeply studied and became one of the most promising conducting polymers.
Conducting polymer syntheses fall broadly into the two categories one recollects from elementary polymer chemistry or organic chemistry courses, viz.

- Chemical
- Electrochemical

Synthesis of polypyrrole in electrochemical polymerizations involves use of an initial electrochemical step, generally oxidation via an applied potential, to generate the radical ion, which then initiates the polymerization. The chemical oxidation of pyrrole is less understood, but the principles leading to the formation of polymers are similar to its electrochemical polymerization, which involves use of a chemical oxidant to generate a radical cation from the monomer, which initiates the polymerization \[^{[4]}\].

To illustrate mechanisms of pyrrole polymerization in both the chemical and the electrochemical cases, the initial step is the generation of the radical cation, as shown in Scheme.3.1 below.
It is the next step then that the chemical and electrochemical polymerizations differ, according to most studies \cite{5}. In the chemical case, the radical cation then attacks another monomer molecule, which are in abundance in the reaction sphere, generating a dimmer radical cation. The polymer chain propagates in this fashion until termination (Scheme.3.2) In the electrochemical case the concentration of radical cations is much larger than that of neutral monomers in the vicinity of the electrode where reaction are occurring, and radical-radical coupling leads to radical dication. This then loses two protons, generating a neutral dimer, which is then oxidized to a radical cation, the polymerization thus progressing in this fashion to completion (Scheme.3.3). The mechanism in Scheme.3.3, especially its features of radical-radical coupling and proton elimination, has been established from studies on varied conducting polymers, and is widely accepted as applicable to most electrochemical polymerizations generally.

In an undoped (pristine), i.e. non-conducting state polypyrrole (PPy) is generally considered to have the so called benzoid structure, and is usually called the neutral
state of PPy. This benzoid structure of PPy in the neutral state, as well as its corresponding schematic band structure is shown in Fig.3.3.

![Fig.3.3: Two senses of bond alternation for polypyrrole: (a) aromatic and (b) quinoid structure.](image)

**Fig.3.4:** PPy at different oxidant levels (p-Type doping of PPy introducing a polaron and a bipolaron on the p-conjugated backbone).
In the reaction the monomer is polymerized and charge carriers are generated via doping. As doping of the neutral polymer proceeds, the formation of structure and electronic defects will take place. At low concentrations the first predominant kind of defect will be polarons, which give rise to the formation of two localized states within the bandgap. Further charge transfer from the polymer chain, i.e. higher doping levels, which one hole-polaron, may then proceed either by the formation of another polaron, or by removing the single electron in the lower polaron level. The removal of electrons (oxidation) can be achieved electrochemically by the application of sufficiently positive potential. This introduction of positive charge carriers makes the material electrically conducting; conjugated polymers are consequently also known as intrinsically conducting polymers or synthetic metals.

3.2 Preparation of polypyrrole dispersion

As we know that the general intractability of conducting polymers presents a serious problem, the preparation of various colloidal forms has been soon sought to improve the processibility. Three main approaches have been reported as methods for making conducting polymers processable: (1) synthesizing a soluble derivative, e.g. poly(3-octyl pyrrole); (2) polymerization in the matrix of a soluble polymer leading to a composite; (3) making dispersions of the insoluble conducting polymers. Among these different methods, the research of PPy microparticles has been promoted in the last decade. The preparation of the colloidal forms can be regarded as (1) the goal aimed at preparation of processible “soluble” forms of conducting polymers; (2) a way to prepare colored and/or conducting polymer microparticles for specific uses; and (3) a tool that enables to study conducting polymers during their formation and to investigate their structure after preparation. While in the first case conductivity and physical properties of the resulting bulk material are of the primary interest, the physico-chemical properties of the colloidal microparticles in relation to their size and morphology dominate the second field. The prevention of macroscopic precipitation of conducting polymers during their preparation is the common denominator for all three cases.

The dispersion polymerization producing particles of submicrometer size has been used as the preparation technique for polymerization of PPy. Dispersion polymerization has several typical features: (1) the monomer is miscible with the
reaction medium (in contrast to emulsion or suspension polymerization); (2) the polymer produced during polymerization is insoluble under the same conditions (like in the precipitation polymerization); and (3) the macroscopic precipitation of the polymer is prevented by the presence of a suitable stabilizer.

The formation of dispersions can be illustrated by an example of PPy particles. At the beginning, a particular stabilizer (soluble polymeric stabilizer) is present in the reaction mixture as the only colloidal component (Fig.3.5.a). By adding monomer into the system, pyrrole monomer droplets were swollen in the reaction medium and attach to stabilizer (Fig.3.5.b) by physical adsorption. After oxidant addition pyrrole polymerization proceeds and finally PPy particles are partly or completely coated with stabilizer and “glued” into larger dispersion particles (Fig.3.5.c). A part of soluble polymeric stabilizer may still be free and not attached to dispersion particles.

The vast majority of polypyrrole colloid syntheses have been carried out using FeCl₃ as an oxidant for pyrrole polymerization. This oxidant is known to polymerize pyrrole smoothly to high yield under a wide range of conditions at room temperature [6,7]. Persulfates (Na₂S₂O₈, (NH₄)₂S₂O₈), which are relatively strong oxidants, are also a kind of common oxidants used for pyrrole polymerization [8,9]. Yamamoto’s group reported the use of the milder H₂O₂/Fe³⁺/HBr oxidant system [10].
3.3 Stabilizers

As it was mentioned before, during the dispersion polymerization, a steric stabilizer becomes attached to the precipitating polymer. After the formation of dispersion, the stabilizer produces a shell of soluble chains over the particle surface, which sterically prevents the particles from aggregation. Clearly the stabilizer is the key component in such synthesis. And it has been found that the chemical structure of the stabilizer is the most important fact in determining the size of PPy particles prepared in aqueous media.

To fulfill its role, the stabilizer is expected to be bonded to the polymer being formed. The attachment of the stabilizer can be improved by the introduction of (1) reactive groups that provide chemical grafting to the conducting polymers, (2) anionic groups participating in the protonation of PPy polycations by the ionic bonding, (3) functional groups which are able to interact with nitrogen in conducting polymers, e.g., by the hydrogen bonding, and (4) of the structural segments that physically adsorb on the produced polymer.

3.3.1 Water-soluble polymers

Usually the sterically stabilized colloidal dispersions of polypyrrole have been prepared in aqueous media using commercially available water-soluble polymers, such as poly (vinyl alcohol-co-vinyl acetate), poly (ethylene oxide), poly (N-vinylpyrrolidone) or methyl cellulose as steric stabilizers. For example, Tarun K. Mandal used ethylhydroxyethylcellulose (EHEC) as a stabilizer. Pyrrole was added to a solution of FeCl₃ and EHEC in 50% aqueous ethanol. The reaction mixture was stirred magnetically for 6 h at 2 °C under N₂ atmosphere. Polypyrrole was obtained as a fine dispersion. Steven P. Armes reported that conducting polypyrrole particles in the size range 50-250 nm diameter have been prepared by a dispersion polymerization route in aqueous media using FeCl₃ as the initiator-dopant and poly (vinyl-pyrrolidone) (PVP, M≥40000) or poly (vinyl alcohol-co-acetate) (PVA, 88 or 96% alcohol, M≥95000) as the steric stabilizer. Nicolas Cawdery also reported that using poly (ethylene oxide) (PEO) samples of higher molecular weight (M>105 000), stable polypyrrole dispersions may be prepared using the route describes above.
**Tab.3.1:** The water-soluble stabilizers and oxidants reported for preparation of polypyrrole colloids.

<table>
<thead>
<tr>
<th>Stabilizer</th>
<th>Oxidant</th>
<th>Medium</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylhydroxyethylcellulose (EHEC)</td>
<td>FeCl₃</td>
<td>50% aqueous ethanol</td>
<td>12, 13</td>
</tr>
<tr>
<td>Poly(vinyl methyl ether) (PVME)</td>
<td>FeCl₃</td>
<td>ethanol or 50% aqueous ethanol</td>
<td>16</td>
</tr>
<tr>
<td>Poly (vinyl acetate) (PVAC)</td>
<td>FeCl₃</td>
<td>2-methoxyethanol</td>
<td>9</td>
</tr>
<tr>
<td>Poly (vinylpyrrolidone) (PVP)</td>
<td>FeCl₃</td>
<td>Water or aqueous ethanol</td>
<td>14, 15</td>
</tr>
</tbody>
</table>

### 3.3.2 Functional polymers

Besides these steric stabilizers, some tailor-made copolymers can also be used as a stabilizer for polypyrrole dispersions under certain conditions (see in Tab.3.2). For instance, S.P. Armes \[^{17}\] prepared the poly (2-vinyl pyridine-co-butyl methacrylate) (P2VP-BM) random copolymer stabilizer by free-radical copolymerization of 2-vinyl pyridine and butyl methacrylate in toluene at 73 °C using AIBN as an initiator. The preparation of colloidal polypyrrole was then processed by using FeCl₃ as the oxidant and P2VP-BM as the stabilizer at 25 °C for at least 24 h. P. M. Beadle \[^{18}\] described the preparation and characterization of sterically stabilized polypyrrole colloids in aqueous media using a tailor-made poly (N, N’-dimethylaminoethyl methacrylate-b-n-butyl methacrylate) block copolymer stabilizer of narrow molecular weight distribution and using FeCl₃ as the oxidant. The polypyrrole particles seem to have a spherical morphology, are slightly flocculated and have a relatively high stabilizer content (54% w/w).
**Tab. 3.2:** The tailor-made stabilizers and oxidants reported for preparation of polypyrrole colloids.

<table>
<thead>
<tr>
<th>Stabilizer</th>
<th>Oxidant</th>
<th>Medium</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly (N, N’-dimethylaminoethyl methacrylate-b-n-butyl methacrylate)</td>
<td>FeCl$_3$</td>
<td>Water</td>
<td>21</td>
</tr>
<tr>
<td><img src="image" alt="Poly (N, N’-dimethylaminoethyl methacrylate-b-n-butyl methacrylate)" /></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Poly (2-vinyl pyridine-co-butyl methyacrylate) (P2VP-BM)</td>
<td>FeCl$_3$</td>
<td>Water</td>
<td>19</td>
</tr>
<tr>
<td><img src="image" alt="Poly (2-vinyl pyridine-co-butyl methyacrylate) (P2VP-BM)" /></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Poly (2-(dimethylamino)ethyl methacrylate-stat-3-vinylthiophene)</td>
<td>FeCl$_3$</td>
<td>Water</td>
<td>20</td>
</tr>
<tr>
<td><img src="image" alt="Poly (2-(dimethylamino)ethyl methacrylate-stat-3-vinylthiophene)" /></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Poly (styrenesulfonate) (PSS)</td>
<td>Fe(NO$_3$)$_3$</td>
<td>Water</td>
<td>21</td>
</tr>
<tr>
<td><img src="image" alt="Poly (styrenesulfonate) (PSS)" /></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3.3.3 Inorganic colloids
Several groups have also reported on the use of inorganic oxide dispersion as substrates for the deposition of conducting polymers. For example, silica nanoparticles proceed to be effective stabilizers of polypyrrole colloids. Polypyrrole-silica particles have been investigated by Maeda and Armes\textsuperscript{[22,23]} followed by other authors\textsuperscript{[24]}. A detailed study of the effect of the reaction conditions on the particle size, composition and colloidal stability was performed by Lascelles et al.\textsuperscript{[25]}. The use of silica particles as steric stabilizers has been extended to silica-coated magnetic particles.

3.3.4 Polymer latex
The logical extension of the principle of using silica nanoparticles as the effective stabilizer led to another class of particulate stabilizers, polymer latexes. If we abstain for a moment from the discussion whether the latex particles become coated with a conducting polymer or vice versa, it is the fact that the polymerization of pyrrole in the presence of various polymer latexes resulted occasionally in colloidal stable systems. So an alternative route to form colloidal dispersions of conducting polymers involves coating sterically stabilized latex particles with an ultra thin overlayer of conducting polymer, thus forming a composite particle with a core-shell morphology. The advantage of this approach is that far less conducting polymer is required to obtain particles with useful electrical properties. The conducting polymer is now the minor component, typically only 5 to 20 \% by mass. Thus, in principle, utilizing a “soft” low T\textsubscript{g} latex substrate leads to composite particles with good film-forming properties. Moreover, the latex particles have a much wider size range compared to the rather limited size range of sterically stabilized conducting polymer colloids (30-300 nm) or PPy-silica nano-composites (100-500 nm).

Already in 1987, Yassar et al.\textsuperscript{[26]} included polystyrene latex particles of 130 nm diameter and functionalized with sulfonic or carboxylic groups in the polymerization of pyrrole. No secondary PPy particles was produced and the stability of conducting PPy-latex particles was found to be good. The conductivity of the layers cast from the modified latex was as high as 0,25 S/cm. Although the approach of Yassar et al. met some criticisms concerning the stability of the end particles, it is nevertheless paved the way towards the general method of thin conducting polymer coatings onto preformed latex particles, resulting in “core-shell” particles\textsuperscript{[27]}. D.B. Cairns\textsuperscript{[28]} focused on the preparation and characterization of the analogous,
submicrometer-sized PS-PPy composites. The investigation results show that PS-PPy composites did not possess the expected “core-shell” morphology previously observed for micrometer-sized PPy-coated PS particles. Instead, TEM studies indicated that the PPy component was present as discrete 20-30 nm nanoparticles, which are absorbed onto the PS latex. Omastova et al. [29] have prepared the highly conductive polypyrrole composites in the presence of the 100 nm poly (methyl methacrylate) latex.

In general, stable colloidal dispersions of polypyrrole are easily prepared in different media with a wide range of polymeric stabilizers. The stabilizers and oxidants for the preparation of polypyrrole colloids normally used are shown in the following table.

**Tab.3.3:** The stabilizers and oxidants reported for preparation of polypyrrole colloids.

<table>
<thead>
<tr>
<th>Surfactants</th>
<th>Stabilizer</th>
<th>Oxidant</th>
<th>Medium</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium dodecylbenzenesulfonate (SDBS)</td>
<td>(NH₄)₂S₂O₈</td>
<td>Water</td>
<td>30,31,32</td>
<td></td>
</tr>
<tr>
<td><strong>Particular stabilizers</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silica</td>
<td>H₂O₂, HBr, FeCl₃</td>
<td>Water</td>
<td>33</td>
<td></td>
</tr>
<tr>
<td>Silica</td>
<td>FeCl₃</td>
<td>Water</td>
<td>34</td>
<td></td>
</tr>
<tr>
<td><strong>Polymer latexes</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polystyrene</td>
<td>FeCl₃</td>
<td>Water</td>
<td>28,35</td>
<td></td>
</tr>
<tr>
<td>Poly(butyl methacrylate)</td>
<td>FeCl₃</td>
<td>Water</td>
<td>36</td>
<td></td>
</tr>
<tr>
<td>Poly(urethane)</td>
<td>FeCl₃</td>
<td>Water</td>
<td>27</td>
<td></td>
</tr>
<tr>
<td>Poly(methyl methacrylate)</td>
<td>FeCl₃</td>
<td>Water</td>
<td>29</td>
<td></td>
</tr>
</tbody>
</table>

### 3.4 Structure and properties of dispersions

The studies of dispersion reported in the literature concentrate mainly on their colloidal, electrical and optical properties. Other characteristics, like the rheology viscosity of PPy dispersions in dependence on the PPy content or particle density, have been mentioned only rarely [37]. Colloidal properties in general and colloidal stability in particular are of fundamental importance for the preparation and application of PPy dispersions.
3.4.1 Colloidal properties

3.4.1.1 Particle Size

The long-term stability of PPy dispersions is outstanding. The particle diameter determined by DLS in typical PPy dispersions does not change even after months and years \[^{38}\]. Partial sedimentation of particles was observed after several months in dispersions stabilized with water-soluble polymers because the particles have higher density than the aqueous medium \[^{25}\]. Aggregation of the particles after preparation was detected with some steric stabilizer, e.g., hydroxypropylecellulose. The aggregates are remarkably stable and the extent of aggregation does not change during storage. Their presence is indicated by the DLS, which yields particle sizes several times larger than the particle diameter observed by electron microscopy.

The particle size can be conveniently characterized by DLS and electron microscopy. Particle size obtained by scattering methods is usually somewhat higher compared with dimensions found by electron microscopy. This difference has two fundamental reasons: (1) the particles observed in the liquid medium are partly swollen and thus larger in comparison with dry objects, and (2) scattering methods provide a hydrodynamic diameter based on the z-average diffusion coefficient, while the electron microscopy yields the number-average dimension. Besides light scattering, the disc-centrifuge photosedimentometry has been often used for the determination of the particle size and size distribution \[^{39}\].

![Fig.3.6: Particle size distribution of polypyrrole dispersion measured by DLS.](image)

The average size of PPy dispersion particles decreased with increasing the stabilizer/monomer ratio. At the same time the stabilizer fraction in dispersion
particles grew. Also an efficient stirring was able to reduce the particle size and narrow the size distribution in PPy-silica colloids [33]. Polypyrrole dispersions often showed bimodal distribution of the sizes (see in Fig.3.6). Electron microscopy revealed the presence of small, 20 nm particles in addition to particles 100-200 nm in diameter. This supports the hypothesis that large PPy particles are composed of small primary elements [40]. A detailed study of the effect of reaction conditions on the size and composition of PPy-silica particles was presented by Lascelles et al. [25].

3.4.1.2 Particle structure

The core-shell morphology (Fig.3.7) is often assumed to interpret properties and stability of dispersion particles. With conducting polymers synthesized by steric stabilizer, the particle core is most likely composed of both the polymer and the incorporated steric stabilizer, i.e. it has a composite nature (Fig.3.7a). The shell formed by the steric stabilizer is located on the surface. It prevents the contact of cores and it is thus responsible for the colloidal stability. Polymerization takes place in the continuous phase and the microprecipitated polymer, together with the larger objects (Fig.3.5). Also in this case the steric stabilizer forms the shell of particle, the particle body is likely to have a composite structure, similar as the case when inorganic particular stabilizers are used (Fig.3.7b). The steric stabilizer can be incorporated inside dispersion particles, especially when polymerization takes place at a high stabilizer/monomer ratio. Besides these, the chemical polymerization of conducting polymer-coated polymer latex particles also gives core-shell type morphology, where the “core” is a nonconducting polymeric material (Fig.3.7c). Continuous PPy overlayer can be obtained even at very low PPy loadings.

**Fig.3.7:** Morphology of polypyrrole dispersion particles by using different kinds of stabilizers. (a) PPy core coated with a shell of a soluble polymeric stabilizer, (b) PPy core coated with an overly of a particulate colloidal stabilizer, and (c) polymeric latex core coated with the PPy shell.
Dispersion particles produced in the dispersion polymerization of classic monomers have a perfect spherical shape and typical size in the micrometer range\cite{14, 17}. The dispersion polymerization of pyrrole often yields normal spherical morphologies. The unique feature is therefore of fundamental interest. An irregular non-spherical morphology was described in the case when low-molecular-weight surfactant, sodium dodecylbenzenesulfonate, was used for stabilization of PPy colloids \cite{31}, obviously due to the limited efficiency of the surfactant in stabilization of particles.

Different from the morphology of polyaniline (PANI), it is very difficult to prepare PPy dispersions with the needle-like, coral-like or other cylindrical objects morphologies. 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 \cite{41}. As a matter of interest, the confined polymerization of conducting polymers, which is a very pertinent way to give them controlled shape and dimension, has drawn more attention in these years. Recently, the microtubule of PPy has been synthesized by a template-synthesis method. Martin et al.\cite{42, 43} has reported the use of commercially available particle track-etched membranes (PTM’s) as template for the preparation of nanofibrils of metals, semiconductor, and conducting polymers. PPy nanotubules can be produced by the oxidation of pyrrole in the pores of polycarbonate membrane followed by the dissolution of template. Recently, Jerome et al. \cite{44} also reported synthesis of PPy nanowires by two-step electrochemical process where the poly (ethyl acrylate) grafted onto carbon electrode served as a temple. Marinakos et al. \cite{45} made the polymerization of PPy around Au nanoparticles followed by dilute ferricyanide etching which leads to the formation of hollow PPy nanocapsules. This synthetic method may potentially lead to new materials with useful electronic or small-molecule delivery properties on the nanoscale.

Wan et al. \cite{46, 47} created a template-free method to synthesize the microtubule of PPy in the presence of β-naphthalene sulfonic acid (β-NSA) as the dopant. Compared with the methods mentioned previously, the template-free method is simple and inexpensive, omitting the template and valuable apparatus.

Lopez-Cabarcos et al. \cite{48} reported the use of thermosensitive cross-linked poly (N-isopropylacrylamide) (poly (NIPAM)) microgels as a matrix to immobilized PPy.
PPy was entrapped within the microgels by polymerization of pyrrole in the colloidal dispersion of the microgel particles at different temperatures. It seems that polymerization of pyrrole, when the microgel particles are in the swollen state (20 °C), results in a uniform distribution of PPy within the particles. However, when the polymerization is carried out at the beginning of the volume phase transition temperature (32.5 °C) an outer shell of PPy could be formed. Finally, polymerization of pyrrole at 37 °C produced non-stable colloidal particles.

### 3.4.2 Electrical properties

#### 3.4.2.1 Electrical conductivity

Electrical conductivities are usually reported for compressed pellets made from the dried colloidal particles using the four-point probe technique. The observed conductivity is invariably at least an order of magnitude lower than the conductivity of the corresponding polymer bulk powder. This is not really surprising considering the presence of electrically insulating polymeric stabilizer and the increased number of resistive interparticle contacts at the submicrometer level. PPy composites may have the electrical conductivity from $10^{-6}$- $10^0$ S/cm depending on the reaction conditions and composition. And conductivities of up to 10 S/cm can be achieved with the addition of co-dopants. It is quite plausible that the spatial distribution of the stabilizer layer on the PPy particles may affect the solid-state conductivity values. Thus lower conductivities might be expected for a continuous stabilizer layer, whereas a “patchy” layer would allow direct electrical contacts between adjacent PPy particles in the solid-state. On the contrary, if the polymer latex were coated with PPy, the continuous conducting network would be produced in the solid composite. If the conducting polymer layer is continuous, relatively high conductivities can be obtained even at very low conducting polymer loadings. The percolation limit would be dramatically reduced, as observed for the coated polymer micro-spheres \(^{35}\).

#### 3.4.2.2 Electrochemical behavior

It is notable that the redox behavior of the colloidal PPy is very different from the PPy synthesized electrochemically \(^{49}\), which is apparently related to the process of preparation. S. Dong et al. \(^{50}\) have investigated the electrochemical behavior and charge transport of colloidal PPy particles (without stabilizer) modified electrode. The voltammetric results show that the electrochemical behavior of colloidal PPy is
different from that of PPy synthesized electrochemically. The broad redox curve cannot be found in the oxidized state of colloidal PPy. Both redox reactions of the PPy colloids and the electrochemically prepared PPy are quasireversible. The charge transport of the colloid-modified electrode is controlled by diffusion of counter ions. Odegard et al. [51] have found that PPy/PEO latex films prepared with FeCl₃ or K₂S₂O₈ as oxidants can be switched electrochemically between their oxidized and reduced states. Furthermore, the K₂S₂O₈ type of latex film is more easily switched than the corresponding FeCl₃ type of film. J. Joo [52] compared the charge transport and structural properties of electrochemically and chemically synthesized PPy materials. They observed the existence of one dopant per three pyrrole rings in both electrochemically synthesized and chemically synthesized PPy systems. The electrochemically synthesized PPy materials have a higher concentration of interchain links or side chains, and are in the critical or the metallic regime.

### 3.4.2.3 Electrorheological Fluids

Electrorheological (ER) response is defined as the dramatic change in rheological properties of a suspension of small particles owing to the application of a large electric field transverse to the direction of flow. Electrorheological fluids are composed of non-conducting or semi-conducting particles dispersed in a non-conducting medium, such as mineral oil or silicone oil. When particles become polarized in external electric field, the suspension increased its viscosity due to the interaction of induced dipoles and subsequent organization of particles into strands as shown in Fig.3.8.

![ER liquid with conducting particles](Fig3.8: Simplified model of the electrorheological effect.)
Recently, anhydrous ER suspensions using semiconducting polymer particles were reported\textsuperscript{[53,54]}. The ER suspensions of semiconducting polymer particles showed good ER responses. Y. D. Kim et al.\textsuperscript{[55]} investigated the ER response and dielectric properties of the suspensions of PPy-coated polyethylene (PE) particles. PPy was coated on PE particles to enhance the particle polarization by increasing the particle surface conductivity, which would lead to an enhanced ER response. The ER response of the PPy-coated PE suspensions is greatly enhanced compared to that of PE suspension. Furthermore the ER response is greatly enhanced by the poly (vinyl alcohol) coating on the PPy-coated PE particles, suggesting that the effective ER suspensions can be prepared by both enhancing the particle surface conductivity and restricting the increased conduction. The ER response of PPy-coated poly (ethyl methacrylate) (PEMA) suspensions in mineral oil was also investigated by the same group\textsuperscript{[56]}. It is found that the ER response initially increased with oxidant amount, passed through a maximum, and then decreased with further increase of oxidant.

### 3.4.2.4 Electrophoresis

The capability of polypyrrole to reversibly transform between its oxidized (or charged) and neutral state has made it possible for polypyrrole to be used as a functional material in the manufacture of ion-selective membranes, in the fabrication of pH sensors and biosensors, and so forth. For all these engineering applications mentioned above, the surface electric properties of polypyrrole in an aqueous solution play an important role. The surface electric properties of a solid in an aqueous solution can be characterized by its $\zeta$ potentials and surface charges, both of which are also dependent on the pH value and the ionic strength of the solution. It has been suggested that the different mechanisms of surface charge formation may be recognized by $\zeta$ potential versus pH plots at a constant ionic concentration, and $\zeta$ potential study may provide information on the surface complex formation at the solid/liquid interface. The capillary electrophoresis was found to be a tool for analytical separation of various types of particles. The electrophoretic mobility was controlled not only by the conducting polymer but also by the nature of the stabilizer shell. X. Zhang et al.\textsuperscript{[57,58]} found that the surface electric properties of polypyrrole in aqueous solutions greatly depend on the solution pH values. And in strong basic solution conditions, polypyrrole can possibly undergo molecular structure changes or
rearrangements at the polypyrrole/water interface, which consequently affects the electric properties of polypyrrole in aqueous solutions. The effect of solution pH on the electric properties of polypyrrole in aqueous solutions also largely influences the performance of polypyrrole as a potential adsorbent for the removal of macromolecules, such as humic acid, that carry negative charges.

### 3.4.3 Optical properties

The pronounced coloration belongs to the intrinsic properties of conducting polymers. A system of conjugated double bonds in their chemical structure leads to the absorption of light in visible region. The brown to black appearance is typical of PPy. Normally, changes in the optical properties occur with the excitation above the band gap (so called non-linear) or doping due to the formation of new absorption features in the energy gap that are associated with the polaron or bipolar excitations.

It is well known that the optical spectra of doped PPy in the visible range are dominated by the two characteristic bipolaronic absorption bands located at around 1 and 2.6 eV \(^{59,60}\). A variation in the energetic location of these bands can be due to various doping levels. R. Turcu et al. \(^{61}\) reported that polymer-solvent interactions result in different chain conformations that are responsible for the changes in the absorption spectra of dodecylbenzenesulphonate (DBS) doped PPy. S. Maeda et al.\(^{23}\) have compared the color intensity of the commercial blue latex with that of their black carboxylic acid-functionalized PPy-silica microparticles at the same solids concentration using visible absorption spectrophotometry. It is clear that the conducting polymer-based dispersion outperforms the commercial latex at all wavelengths in the visible spectrum. And they conclude that these PPy-silica particles have considerable potential for the development of diagnostic assays of increased sensitivity for the analyte of interest.

### 3.5 Application of conducting colloids

We should realize that the electrical conductivities of PPy composites are only comparable to much cheaper materials such as carbon black. Conductivity alone is not likely to justify the future commercial exploitation of conducting polymer colloids \(^{62}\). Instead, their future technological success will depend critically on whether they offer additional “value-added” properties. Such properties may well include well-defined
colloidal dimensions or morphologies, intense coloration, biocompatibility, high surface area, efficient radiation absorption, potential surface functionalization, good film-formation properties, etc.

3.5.1 Conducting coatings

Conducting polymers have been discussed in recent years as corrosion protection materials or, more specifically, as anti-corrosive pigments, because of their intrinsic insolubility in water and organic solvents [63]. The scientific discussion on how doped conductive polymers effect corrosion protection appears quite confusing and stimulated by misleading information from commercial distributors of conducting polymers. Basically, electrochemical corrosion protection of such kind means passivation of the corroding metal surfaces, i.e., anodic stimulation of metal dissolution until the crucial corrosion rates of the metals are exceeded, accompanied by the formation of a very thin (10 nm for steels) protective metal oxide layer [64]. In this model, oxygen reduction on the polymer film replenishes the polymer charge consumed by metal dissolution, thereby stabilizing the potential of the exposed metal in the passive regime and minimizing the rate of metal dissolution. Scheme.3.4 and Scheme.3.5 depict conducting reduction/ metal oxidation and conducting polymer oxidation by molecular oxygen, respectively:

\[
\frac{1}{n}M + \frac{1}{m}CP^{m^+} + \frac{y}{n}H_2O \rightarrow \left(\frac{1}{n}\right)M(OH)^{(n-y)^+} + \left(\frac{1}{m}\right)CP^0 + \left(\frac{y}{n}\right)H^+ \\
\text{Scheme.3.4}
\]

\[
\frac{m}{4}O_2 + \frac{m}{2}H_2O + CP^0 \rightarrow CP^{m^+} + mOH^- \\
\text{Scheme.3.5}
\]

where, M and CP are metal and conducting polymer, respectively.

Conducting polymer coatings are obtained after evaporation of PPy dispersions. Low–molecular-weight components have to be removed by dialysis if they are detrimental to the quality of films. Conductivity and mechanical properties are tuned by varying the composition of film and the type of stabilizer. Another interesting
approach to the preparation of coatings uses mixtures of PPy dispersion with conventional film-forming latex.

Recently the electropolymerization of pyrrole on iron electrodes has been investigated with the aim of producing uniform and strongly adherent coatings. Wencheng Su et al.\cite{65} systematically investigated the electro-deposition mechanism, adhesion and corrosion performance of the polypyrrole and poly (N-methylpyrrole) coatings on steel substrates. The results show that electrochemical process parameters had significant effects on the adhesion and corrosion performance of the electrodeposited polypyrrole and poly (N-methylpyrrole) coatings. Polypyrrole coatings exhibited better adhesion and corrosion performance than poly (N-methylpyrrole) coatings.

Conductive polymer film of polypyrrole doped by polymolybdate (PMo) anions was prepared on mild steels by anodic polymerization for corrosion prevention of the steels \cite{66}. The prepared PPy-PMo conductive film exhibits good adherence to the steel substrate. Corrosion of the steels is suppressed by the films: the corrosion rate in the neutral solution decreases by 1/3 compared with that of the bare steel and the rate in the acid solution by 1/4.

### 3.5.2 Conducting composites

Polypyrrole dispersions were used for the preparation of conducting composites. The material composed of dispersion particles is obtained as sediment after centrifugation of dispersions and drying. Both low-molecular-weight components (residual monomer and/or oxidant, potential oligomers, inorganic salts obtained from reduction of the oxidant and acids) and polymeric components (free steric stabilizer) remain in the supernatant liquid. If the dispersions are directly precipitated into the excess of non-solvent or evaporated after dialysis, free steric stabilizer is included in the material. Conductivity ranging from that of steric stabilizer, $10^{-10} - 10^{-8}$ S cm$^{-1}$, to conducting polymer, $10^{-1} - 10^1$ S cm$^{-1}$, depending on the content of conducting component have been reported \cite{67}.

Omastova et al. \cite{68} have tried to prepare polypropylene/polypyrrole (PP/PPy) composites by coating PP spheres (diameter 35 µm) with PPy in a chemical modification reaction. The content of PPy varied from 0.8 to 7.6 wt.-%. PP/PPy composite films approximate 0.2 mm thick were prepared by hot pressing modified powder samples. The electro-conductivity of the pressed samples reaches values from
4*10^{-10} to 5*10^{-3} \text{ S/cm}, depending on the concentration of PPy. Bhat et al \cite{69} have prepared composites of PPy with poly (vinylidene fluoride) (PVDF, Solef 108), and cellulose (cellophane film) by chemical polymerization of pyrrole in the presence of host polymers. Homogeneous composites were obtained, and the crystallinity of the host polymer decreased, whereas some crystallization of PPy was noticed. SAXS studies revealed that the diffusion of PPy takes place into amorphous regions of the matrix. The electro-conductivity of the composites was 10^{-8} to 10^{-4} \text{ S/cm}. The composites were evaluated for use in gas sensors for detection of chlorine and ammonia. Upon exposure to ammonia, the current response showed a decrease due to adsorption, chemisorption and diffusion into PPy. Exposure to electrophilic Cl gas led to increased conductivity of the composite due to electron withdrawing effects that generated hole carriers.

3.5.3 Diagnostics

Latex particles are suitable carriers for the immobilization of proteins in various diagnostic systems. In this regard, the basic requirements, which the prospective latexes must fulfill for diagnostic assay applications is the ability to adsorb or covalently immobilize proteins \cite{70,71,72}. The mechanism of this adsorption is similar to the interaction of components with the stationary phase of a Gas Chromatography column (as shown in Fig.3.9) \cite{73}. Once adsorbed, the volatile components modulate the conduction mechanism of the polymer giving rise to changes in resistance. Unlike Gas Chromatography there is no separation of components since all of the volatiles interact simultaneously. The polymers display reversible changes in electrical resistance when polar volatiles adsorb and desorb.

![Fig.3.9: Mechanism of PPy used as the diagnostics: polymer partitioning occurs in the top layer.](image)
B. Miksa and S. Slomkowski [74] used polypyrrole latex as seed for the radical polymerization of acrolein. The resulting polypyrrole core/polyacrolein shell latex was suitable for immobilization of up to 11 mg of human serum albumin and/or 33 mg of human gamma globulin per 1 g of latex particles.

The potential requirements for the marker particles in visual diagnostic assays were summarized by Armes and Maeda [75]:

(1) intense coloration (preferably intrinsic one),
(2) facile synthesis,
(3) compatibility with biological ligands,
(4) small particle size (< 200 nm),
(5) high degree of dispersion (no aggregates),
(6) good colloidal stability at physiological pH,
(7) surface functionalization (e. g., with carboxyl or amino groups).

### 3.5.4 Biomedical devices

Conjugated polymers, particularly PPy, are unique among the artificial muscles because of their applications as biomaterials. Biomedical applications are the most promising for initial commercialization of conjugated polymer actuators. They:

*♦* are biocompatible, both in vitro and in vivo [76],
*♦* are tissue-compatible and implantable for long periods [77],
*♦* improve regeneration of tissues [78],
*♦* can serve as suitable substrates for the growth of cell cultures [79],
*♦* can be produced in biodegradable/bio-erodible forms,
*♦* can be doped with and release biomolecules [80,81],
*♦* are widely studied as biosensors [82].

The background for conjugated polymer actuators is that a number of things change when the oxidation level of the polymer is altered, including the length of the carbon-carbon bonds on the polymer backbone [83], the angles between adjacent monomer units [84], cis-trans isomerization, changes in the interactions between polymer chains and solvent [85], backbone folding, and interchain interactions [86]. However, the primary mechanism for volume change is mass transport. When ions and/or solvent enter the polymer, it expands, and when they exit, it contracts [87, 88].
Ions can enter the polymer in either the oxidized (Scheme 3.6) or the reduced (Scheme 3.7) states:

\[
P^+ (A^-) + e^- \leftrightarrow P^0 + A^- \tag{Scheme 3.6}
\]

\[
P^+ (A^-) + C^+ + e^- \leftrightarrow P^0 (AC) \tag{Scheme 3.7}
\]

where \(P^+\) represents the doped (oxidized) state of the polymer and \(P^0\) the undoped (reduced, neutral) state. \(P^+(A^-)\) indicates that the anion \(A^-\), called the counter-ion, is incorporated in the polymer as a dopant, and \(P^0 (AC)\) indicates that a cation (co-ion) is inserted during reduction.

**Fig. 3.10:** Dominant mechanism for volume change in conjugated polymers. (a) Oxidized, doped state of the polymer: positive electronic charges on the polymer backbone are compensated by possibly solvated anions. Additional solvent may be present due to osmotic pressure. (b) Reduced, uncharged state if the anions are small: anions and solvent are expelled, causing contraction. (c) Reduced state if the anions are large and immobile: solvated cations are incorporated to maintain charge neutrality, causing expansion.

The polymer incorporates anions when it is oxidized and either expels the anions (Scheme 3.6) or incorporates cations (Scheme 3.7) when it is reduced to the neutral state (Fig. 3.10). In polymers prepared with a small, mobile anion, the process in Scheme 3.6 dominates, and the polymer expands in the oxidized state. However, in
polymers prepared with a large, immobile anion that cannot be expelled upon reduction, charge compensation instead occurs primarily through the incorporation of cations, and the polymer expands in the reduced state. In order to translate the molecular movements into macroscopic movements, Baughman [89], Otero [90] and co-workers have initially described the actuator concepts on PPy. Conducting polymer actuators can be operated in liquids, as well as in air. In principle, by separating two conjugated polymer films by a polymer electrolyte, it leads to either bending, rocking-chair-type actuators or linear, extensional actuators (see in Fig.3.11).

![Diagram of actuator concepts](image)

**Fig.3.11:** a) “Rocking chair” bending bimorph configuration. b) extensional “electrolyte storage” configuration using one cation exchanging polymer A and one anion exchanger B.

In a rocking-chair actuator, also called an electrode-storage arrangement, ions are shuttled between the two conjugated polymer films during electrochemical switching. When one polymer is oxidized, the second is reduced, and ions are transferred from one film to the other in the switching process, the electrolyte composition does not change [87] (Fig.3.11.a). A PPy polymer linear contracting actuator with an acrylamide hydrogel using this principle was reported by Lewis et al. [91]. Linear actuation is inherently stronger than bending, and bimorphs can also accomplish this. If one film is a cation-exchanger and the other an anion-exchanger, then the result is an extensional, or electrolyte-storage, actuator (Fig.3.11.b). Reducing the cation exchanger while oxidizing the anion exchanger causes both films to expend by pulling (oppositely charged) ions from the electrolyte (Scheme.3.6 and Scheme.3.7), and switching the voltage causes them both to expel the ions and contract. The electrolyte stores the ions in that second half of the cycle. L. Bay et al. [92,93] reported the highest
linear expansion (12 % at a load of 0.5 MPa) that has been published for a centimeter-scale conducting polymer actuator. The actuator operates in aqueous media, and the large expansion was obtained by combining choice of materials with optimized conditions of synthesis, and by forming the polymer actuator on a compliant, micro-structured gold electrode.

Polypyrrole dispersions and microparticles are interesting objects suited for interdisciplinary studies. In order to achieve improved performance for the applications, a better understanding is needed of how the synthesis conditions determine the material properties.
4. Analytical methods

4.1 Light scattering methods

There are many kinds of light scattering. If we limit ourselves just to the methods intended for solutions, there are two broad categories: dynamic light scattering (DLS) and static light scattering (SLS). Light scattering intensity is monitored either in the microsecond or in the second time range domain. This is the basic difference between DLS and SLS, respectively. Fluctuations in the intensity of light scattered by a small volume of a solution in the microsecond time range are directly related to the Brownian motion of the solute. Averaging the intensity over the second time range interval will cause a loss of the solute dynamic properties information; that is why light scattering is named either static or dynamic. In general, the differences between SLS and DLS are shown as the following:

1. Dynamic light scattering (DLS)
   - Alias: quasielastic light scattering, photon correlation spectroscopy, Brillouin scattering (a special variant).
   - Relies on rapid fluctuations in the scattered signal.
   - Can measure a transport property, the mutual diffusion coefficient, absolutely.
   - This size is easily converted to a hydrodynamic radius, \( R_h \).
   - The size range is very wide: < 1 nm to >500 nm.

2. Static light scattering (SLS)
   - Alias: total intensity light scattering.
   - Relies on the intensity of scattered light and its variation with concentration of polymer and/or scattering angle.
   - Can produce thermodynamic data: molecular weight and virial coefficient.
   - Can produce size (for sizes > about 10 nm).
   - The size returned is the so-called “radius of gyration”, \( R_g \).

The outlines of the theory related to light scattering techniques is described in biophysics (e.g., Brunner and Dransfeld, 1983; Marshall, 1978), chemistry (e.g., Oster, 1972), and polymer science textbooks (e.g., Munk, 1989). Introductory textbooks and review articles on light scattering applications in biochemistry are also available (e.g., Harding et al., 1992, Bloomfield, 1981). Some basic aspects will be briefly described...
Dynamic light scattering is one of the most popular methods used to determine the size of particles. Shining a monochromatic light beam, such as a laser, onto a solution with spherical particles in Brownian motion causes a Doppler Shift when the light hits the moving particle, changing the wavelength of the incoming light (See in Fig.4.1). This change is related to the size of the particle. It is possible to compute the sphere size distribution and give a description of the particle’s motion in the medium, measuring the diffusion coefficient of the particle and using the autocorrelation function.

![Schematic representation of experimental set up for DLS.](image)

**Fig.4.1:** Schematic representation of experimental set up for DLS.

In Dynamic Light Scattering, light is scattered by the interaction of the electrons with the incident radiation (only the electric component will be considered here). The oscillating electric field causes a vibration on the electrons turning them into oscillating dipoles. These dipoles reemit radiation. As the electrons are moving sources (due to the Brownian motion) of radiation, the frequency of the radiation is shifted to higher or lower frequencies depending on its velocity and direction relative to the detector (Doppler effect). Molecules in solution move in all directions with equal probability and have a continuous speed distribution, thus a continuous
broadening of the spectrum, relative to the incident frequency line ($\nu_0$) is observed.
The scattering of light is not exactly elastic, but quasi-elastic instead. This is why DLS is also named quasi-elastic light scattering (QELS). Because in SLS we are only concerned with the total intensity of the scattered light, ignoring the spectral distribution, SLS is also named intensity light scattering (ILS).

The power spectrum broadening is related to the Brownian motion of the particles in solution and hence to their diffusion coefficient, $D$, which in turn is related to the size and shape. However, the motion of large molecules is so slow that the broadening in the power spectrum is too small to be studied by interferometry. Therefore, instead of working in the frequency domain, we will work in the time domain (Fourier transform of the power spectrum). And the attention will be focused on how to obtain the time domain function to obtain the characteristic decay time of this function.

Light scattering intensity fluctuations detected in a small volume and in the microsecond time range are related to the Brownian motion of the particles due to density fluctuations, caused by incidental agglomeration of molecules and variation in the number of molecules in the scattering volume. The diffusion coefficient of the solute can be measured by means of an autocorrelation function ($g_2(t)$). Consider $I_t$, the number of photons arriving at the detector at the time interval $t'$. The correlation function is built multiplying the number of photons from two successive time intervals and storing the result in the first instrumental channel. This calculation is repeated hundreds of thousands of times, averaged and stored in channel 1. In the successive channels the average products of $I_t I_{t+t}$ are stored where $t$ is the delay time:

$$g_2(t) = \langle I_t \bullet I_{t+t} \rangle$$

Eq.4.1

$$\lim_{t \to 0} g_2(t) = \langle I_t^2 \rangle$$

Eq.4.2

$$\lim_{t \to \infty} g_2(t) = \langle I_t \rangle^2$$

Eq.4.3

because correlation is maximal for close instants (most molecules have not collided, yet) and does not exist for very distant instants. For small monodispersed particles and
homogeneous spheres of any size the normalized scattered electric field autocorrelation function \( g_1(t) \) is:

\[
g_1(t) = e^{-\Gamma t}
\]

\textbf{Eq.4.4}

which is related to the intensity correlation function (Eq.4.1) by the Siegert relation (Eq.4.5); the quadratic dependence comes from the relation between the amplitude of the electric wave and the intensity, i.e., the rate of flow of radiation through unit area.

\[
g_2(t) = \left\langle I_i^2 \right\rangle \cdot b \cdot g_1^2(t) + \left\langle I_i \right\rangle^2
\]

\textbf{Eq.4.5}

where \( b \) is an instrumental constant that reflects the deviations from ideal correlation (ideally \( b = 1 \)) and

\[
\Gamma = \frac{D}{q^2}
\]

\textbf{Eq.4.6}

\[
q = \frac{4n_o\pi}{\lambda} \sin\left(\frac{\theta}{2}\right)
\]

\textbf{Eq.4.7}

where \( D \) is the diffusion coefficient, and is the reciprocal of the characteristic decay time (\( \tau = 1/\Gamma \)).

\[
g_1(t) = \int_0^\infty G(\Gamma) e^{-\Gamma t} d\Gamma
\]

\textbf{Eq.4.8}

\( G(\Gamma) \) is the \( \Gamma \) distribution function and can be evaluated by inverse Laplace transform techniques, as \( g_1(t) \) is the Laplace transform of \( G(\Gamma) \). The most common routine used to perform the inverse Laplace Transform (ILT) is CONTIN (Provencher, 1982). CONTIN is a numerical method that starts from a preliminary unsmoothed solution in a frame of equally spaced \( \log(\Gamma) \). After that, a regularization process it used according to statistical criteria. In the end, a "chosen solution" is selected. Such a chosen solution might be misleading; and very high signal-to-noise ratio data are required so that a unique solution can be admitted as the chosen solution. Anyone using CONTIN or related methods should be aware of its limitations and artifacts that might be generated by this routine, including spurious peaks. These artifacts are related to integration processes (e.g., oversmooth and undersmooth), baseline definition (e.g., spurious peaks in skewed distributions), and edge effects (e.g., ripples in the
distribution). All these aspects were very clearly discussed by Johnsen and Brown (1992).

If other variables related to $\Gamma$ are used instead of $\Gamma$, a transformation of Eq.4.7 has to be considered (see Appendix II). The measured $D$ value changes according to angle and concentration:

$$D = D_0 \left(1 + k'_D R_k^2 q \right) \left(1 + k_D c \right)$$

Eq.4.9

where $k'_D$ and $k_D$ are constants and $D_0 = \lim_{q,c,\rightarrow 0} D$. $D_0$ is related to the hydrodynamic radius ($R_h$) by the Stokes-Einstein relationship:

$$D_0 = \frac{kT}{6\pi \eta R_h}$$

Eq.4.10

where: $k$ is the Boltzman constant, and
\[\eta\] is the solvent viscosity.

For broad distributions and even for narrow distributions (i.e., quasi-monodispersed) the reference $D$ value, commonly named effective diffusion coefficient ($D_{eff}$) used for calculation is:

$$D_{eff} = \frac{\langle \Gamma \rangle}{q^2}$$

Eq.4.11

The ratio: where $\langle \Gamma \rangle$ is the average value of $\Gamma$ in a peak. $D_{eff}$ is the so-called $z$-average diffusion coefficient ($D_z$) (Eq. 20).

$$D_{eff} = \langle D \rangle = \sum_i w_i M_i D_i / \sum_i w_i M_i = D_z$$

Eq.4.12

($D_i$ is averaged by the scattered intensities since in Rayleigh scattering $I_i \propto n_i V_i^2 \propto w_i M_i$, where $V_i$ is the volume of the particle $i$ and $n_i$ is the number of particles $i$ in solution, per unit volume). Multimodal are usually described by several $\langle \Gamma \rangle$, one for each peak of the distribution. If peaks are overlapped, it is impossible in practical terms to evaluate $\langle \Gamma \rangle$. In this situation it is a common procedure to consider the $\Gamma$ value where the maximal value of peak occurs ($\Gamma_{\text{max}}$) instead. If the peaks are symmetrical, this approximation is always valid.

It should be stressed that some methods of data treatment lead to information on average diffusion coefficients over all the distribution function. This is the case, for
instance, for the method proposed by Koppel (1972) (CUMULANTS) which results from the application of the statistical cumulants generating function. (The cumulants generating function of $G_s(t)$ is simply defined as $G_s(t) = \ln G_s(t)$.) If the constant baseline has already been subtracted from $g_2(t)$ the plot of $\ln(g_2(t))$ versus $t$ should be strictly linear for a monodispersed system. Any deviation from the linear dependence is indicative of polydispersity. A series expansion yields:

$$\ln(g_1(t)) = K_0 - K_1t + \frac{K_2t^2}{2!} - \frac{K_3t^3}{3!} + \ldots$$

Eq.4.13

where: $K_0$ is just an amplitude factor and

$$K_1 = \langle \Gamma \rangle$$

Eq.4.14

$$K_2 = \langle (\Gamma - \langle \Gamma \rangle)^2 \rangle$$

Eq.4.15

$$K_3 = \langle (\Gamma - \langle \Gamma \rangle)^3 \rangle$$

Eq.4.16

$$K_4 = \langle (\Gamma - \langle \Gamma \rangle)^4 \rangle - 3K_2^2$$

Eq.4.17

$$K_n = \left[ (-1)^n \frac{d^n}{dt^n} \ln(g_1(t)) \right]_{t=0}$$

Eq.4.18

where: $K_n$ is the $n$th cumulant of $g_1(t)$,

$K_1$ is the mean of $\Gamma$ (ensemble average),

and $K_2$ is the variance of the distribution.

The ratio:

$$P = \frac{K_2}{K_1^2}$$

Eq.4.19

is the square of the relative SD (also known as the square of the coefficient of variation) and is called the polydispersity index. The bigger $P$ is, the wider the distribution.
4.1.2 Static Light Scattering (SLS)\textsuperscript{[99,100,101]}

Light scattering intensity integrated over a period of time of seconds or more varies with the measurement angle and concentration according to (Zimm, 1948):

\[
\frac{K \cdot c}{R_\theta} = \frac{1}{M P_\theta} + 2 A_2 c
\]
\text{Eq.4.20}

\[
K = \frac{4\pi^2 n_0^2 (dn / dc)^2}{N_A \lambda^4}
\]
\text{Eq.4.21}

\[
R_\theta = \frac{d^2}{\sin^2 \theta} \frac{I_s}{I_0}
\]
\text{Eq.4.22}

where: \(c\) represents concentration,

- \(I_o\) is the intensity of the incident light (vertical polarization),
- \(I_s\) is the scattered light intensity,
- \(z\) is the measurement angle relative to the vertical axis,
- \(d\) is the sample - detector distance,
- \(n_0\) is the refractive index of the solvent,
- \(n\) is the refractive index of the solution,
- \(A_2\) is the second virial coefficient (which accounts for interparticle interaction),
- \(M\) is the molecular weight,

and,

\[
P_\theta = \frac{I_{s,\theta}}{I_{s,\theta=0}}
\]
\text{Eq.4.23}

is the intra-particle structure factor, which accounts for the interference of light scattered from different points in the same molecule or molecular assembly. \(P_\theta\) can be evaluated by (e.g., Oster, 1972):

\[
P_\theta \approx 1 - \frac{16\pi^2 n_0^2 R_g^2}{3\lambda^2} \sin^2 \left( \frac{\theta}{2} \right)
\]
\text{Eq.4.24}

where: \(R_g\) is the radius of gyration.
**Fig. 4.2:** Schematic representation of a light scattering apparatus. Light scattering intensities are recorded according to sample concentration and angle (by means of a goniometer). The detector might rotate, as depicted, or be fixed and connected to an optical fiber supported by the rotating arm. In any case, the detection device and the laser source must be aligned toward the geometrical center of the sample cell. The measurement angle ($\theta$) origin is the way of the transmitted laser beam.

**Fig. 4.3:** A geometrical effect has to be considered when light scattering intensities are recorded according to angle. As the detection angle deviates from 90°, the probed volume increases, including particles that are not detected at right angle (open circles). This geometric effect is corrected by a sinus function.

If the samples are polydisperse, then the values of $M$, $R_g$, and $A_2$ obtained by means of Eq. 4.20 are averaged. Textbooks and scientific papers often mention the averaged $M(<M>)$ as the weight average molecular weight ($M_w$), but a demonstration is hard to find. Moreover, what kind of average is obtained for $R_g$, and $A_2$ is usually overlooked. In Appendix I it is demonstrated that:

$$\langle M \rangle = \frac{\sum_i w_i M_i}{\sum_i w_i} = M_w$$

Eq. 4.25
\[
\langle R_g^2 \rangle^{1/2} = \sqrt{\sum_i w_i R_{g,i}^2 / \sum_i w_i}
\]

Eq. 4.26

\[
\langle A_2 \rangle = \sum_i w_i^2 M_i A_{2,i} / \left( \sum_i w_i \sum_i w_i M_i \right)
\]

Eq. 4.27

where \(w_i\), \(M_i\), \(R_{g,i}\), and \(A_{2,i}\) represent the total mass, molecular weight, radius of gyration, and second virial coefficient, respectively, of kind \(i\) particles, in a polydisperse sample. The parameters between angle brackets represent the average value.

The comparison of \(R_h\) with the radius of the gyration \(R_g\) which can be determined from static light scattering measurements was defined as parameter \(\rho\) (Burchard, 1979):

\[
\rho = \frac{R_g}{R_h}
\]

Eq. 4.28

For polydisperse coil \(\rho = 1.73\); for spheres \(\rho = 0.775\).

4.2 Field-flow fractionation (FFF)\textsuperscript{102,103,104,105}

Field-flow fractionation is a chromatographic method. Separation is achieved by the influence of diffusion on elution time. Elution occurs by means of a laminar flow through the channel, exhibiting a parabolic flow profile. The principle is illustrated in Fig. 4.4. When the probe reaches the inner of the channel the channel flow is bypassed. This allows the sample to get an equilibrium position by the influence of a force field, which is perpendicular to the channel flow. The force field “pushes” particles to the bottom of the channel. Due to the Brownian motion smaller particles may diffuse faster and therefore move more towards the middle of the channel. After this “relaxation step” the channel flow again is directed through the channel and the separation process starts. Smaller particle which where more in the middle of the channel are in layers of the parabolic velocity profile which elutes faster. In consequence smaller particle elute earlier then larger particles.

Different types of force fields are commonly used (hydrodynamic, centrifugal, thermal and electrical field). According to the type of force field the separation occurs in dependence of different physical properties. In case of Flow-FFF (F-FFF) the field
is obtained by a crossflow of the carrier liquid using porous walls. So in Flow-FFF the retention time depends on one property, the diffusion coefficient. The field should interact with the sample components so that they are driven down to the bottom wall, termed the accumulation wall. Depending on the distance that a component obtains from the accumulation wall, it will be transported with a specific velocity down the channel. This velocity is that which is present in the parabolic velocity profile at the specific elevation from the accumulation wall.

![Diagram of F-FFF channel](image)

**Fig.4.4:** The principle for separation in F-FFF channel.

A few fundamental relationships can be used to express the retention of components during their elution through the channel. For the concentration profile of a sample which has been driven towards the accumulation wall by the physical field, the general transport theory yields for the flux density $J_x$ of the solute:

$$J_x = -D \frac{dc(x)}{dx} + U_c(x)$$

**Eq.4.29**

where: $D$ is the translational diffusion coefficient,
$x$ is the distance from the accumulation wall,
$U_c$ is the velocity of the cross-flow caused by the external field,
\( c(x) \) is concentration gradient of the component in \( x \)-direction.

As indicated in Eq.4.29, there are two contributions to the \( J_x \) density of the solute: (a) the flux caused by the solute drift due to the external field and (b) the back diffusion away from the accumulation wall according to Fick’s law due to the established solute concentration gradient. After some time the mass transport of a component becomes the same in both directions and then a steady-state is reached which is characterized by an exponential concentration distribution:

\[
 c(x) = c_0 \ e^{-\frac{x}{l}}
\]

Eq.4.30

with

\[
 l = \frac{D}{U}
\]

Eq.4.31

where: \( c_0 \) is the concentration of the component at accumulation wall,

\( l \) is the average layer thickness.

The diffusion coefficient is according to the Stokes-Einstein equation:

\[
 D_0 = \frac{kT}{6\pi\eta R_h}
\]

Eq.4.10

When the components are driven to the accumulation wall by the field they are subject to a certain magnitude of force \( F \) which accelerates them. Because this forces them to permeate between the surrounding solvent molecules they are subject to the frictional force. Therefore, a drift velocity is defined as \( U = F / f \). Incorporated this equation with Eq.4.31 one can get:

\[
 l = \frac{kT}{F}
\]

Eq.4.32

It is advantageous to express the distance from the wall not by the absolute distance, \( l \), but by a reduced distance, \( \lambda \), which is scaled to the thickness of the channel:

\[
 \lambda = l = \frac{kT}{wF}
\]

Eq.4.33

where: \( w \) is the channel thickness.
This equation can be transformed to:

\[ \lambda = \frac{k T A}{6 \pi R_h V_s w} \]

Eq.4.34

Eq.4.34 shows that particles will be transported in x-direction according to their \( R_h \). The parabolic laminar flow in the channel will transport the components of the sample with different velocities. Therefore, the fractionation of the particles according to their size takes place. In case of F-FFF smaller particles will eluate from the channel faster than bigger particles. Conclusively, in F-FFF one separates strictly according to hydrodynamic radius and because a crossflow will interact with every component, this method is almost an universal size separating tool. It applies to a very large range of molecular and particle sizes ranging from 1 nm diameter through the colloidal size region to micrometer particles.

![Schematic representation of experimental set up](image)

Fig.4.5: Schematic representation of experimental set up (MALLS – Multi –Angle-Laser-Light-Scattering).

The experimental set-up is presented in Fig.4.5. After separation in the channel the sample firstly is moving through the UV-detector and later through MALLS detector. The UV-detector gives the distribution function of the average hydrodynamic diameter. For the calculation of the experimental light scattering data from MALLS the ASTRA software was used.

### 4.3 Zeta potential

The electrostatic potential near the particle surface is shown in Fig.4.6. It changes very quickly (and linearly) from its value at the surface through the first layer of counter ions and then changes more or less exponentially through the diffuse layer. The junction between the bound charges and the diffuse layer is again marked by the broken line. That surface, which separates the bound charge from the diffuse charge around the particle, marks where the solution and the particle move in opposite
directions when an external field is applied. It is called the shear surface. The electric potential at the shear plane is called zeta potential and it is that potential which is measured, when one measures the velocity of the particles in a d.c. electric field. The velocity (in metre/second) for a unit field strength (1 Volt per metre) is called the electrophoretic mobility, and is given the symbol $\mu E$. It is related to the zeta potential ($\zeta$), and is usually assumed to measure the potential at the point marked by the broken line in Fig.4.6.

Smoluchowski equation is normally used to calculate the zeta potential from electrokinetic mobility:

$$\mu = \frac{\zeta \epsilon}{\eta}$$  \hspace{1cm} Eq.4.35

where: $\mu$ is the electrophoretic mobility,
$\epsilon$ is the electric permittivity of the liquid, and
$\eta$ is the viscosity.

In this simplified approach, the electrostatic driving force is opposed by the frictional force and the other effects are neglected. Only when the zeta potential is not too high, for large colloidal particles and high ionic strengths this equation gives good results. For the values of zeta potentials with a practical meaning ($\zeta < 120$ mV) the error is
negligible when Kappa*a > 100, where a is the particle radius and the Debye parameter kappa is defined as:

\[ \kappa^2 = \frac{F^2 \sum_i C_i Z_i^2}{\varepsilon R T} \]

Eq.4.36

where: 
- F is the Faraday constant,
- \( C_i \) is the concentration of the i-th ion (in mol/m³),
- Z is the valency of this ion,
- R is the gas constant, and
- T is the absolute temperature.

The reciprocal kappa is often termed as the thickness of the electric double layer so Smoluchowski equation applies for thin double layers (as compared with the particle radius). In general, a zeta potential versus pH curve will be positive at low pH and lower or negative at high pH. There may be a point where the curve passes through zero zeta potential. This point is called the isoelectric point and is very important from a practical consideration. It is normally the point where the colloidal system is least stable.

4.4 Electron microscopy

4.4.1 Scanning electron microscope (SEM)

The SEM uses electrons instead of light to form an image. Unlike the light in an optical microscope, the electrons in a SEM never form a real image of the sample. Instead, the SEM constructs a virtual image from the signals emitted by the sample. Fig.4.7 shows the schematic representation of a scanning electron microscope with secondary electrons. A beam of electrons is generated in the electron gun by heating of a metallic filament, located at the top of the column, which is pictured to the left. The electron beam follows a vertical path through the column of the microscope. This beam is attracted through the anode, condensed by a condenser lens, and focused as a very fine point on the sample by the objective lens. The scan coils are energized (by varying the voltage produced by the scan generator) and create a magnetic field, which deflects the beam back and forth in a controlled pattern. The varying voltage is also applied to the coils around the neck of the Cathode-ray tube (CRT), which produces a pattern of light deflected back and forth on the surface of the CRT. The
pattern of deflection of the electron beam is the same as the pattern of deflection of the spot of light on the CRT.

**Fig.4.7:** Schematic representation of a scanning electron microscope with secondary electrons forming the image on the TV screen.

The electron beam hits the sample, producing secondary electrons from the sample. Once it hits the sample, other electrons (backscattered or secondary) are ejected from the sample. These electrons are collected by a secondary detector or a backscatter detector, converted to a voltage, and amplified. The amplified voltage is applied to the grid of the CRT and causes the intensity of the spot of light to change. The image
consists of thousands of spots of varying intensity on the face of a CRT that correspond to the topography of the sample. The intensity of the image (brightness) is determined by the number of secondary particles that hit the cathode-ray tube, which is dependent upon the angle the electrons bounce off the specimen. Thus, the image of the specimen depends on the topography of the specimen.

4.4.2 Atomic force microscope (AFM)

The atomic force microscope (AFM), or scanning force microscope (SFM) was invented in 1986 by BINNIG, QUATE and GEBER. AFM has been used successfully to study the surfaces of various materials at nanometer level, and at best even an atomic resolution can be achieved. The resolution is typically in x- and y-directions 0.1 - 3.0 nm and in z direction at best 0.01 nm. The AFM utilizes a sharp probe moving over the surface of a sample in a raster scan. In case of the AFM, the probe is a tip on the end of a cantilever which bends in response to the force between the tip and the sample (Fig. 4.8).

![Fig.4.8: A schematic drawing of the principle of the atomic force microscopy.](image)

Measurements can be carried out in air, other atmospheres, vacuum and liquids. Little or no sample preparation is needed. However, the sample surface has to be quite smooth with no excessive variations in the surface height. The basic principle of the AFM is the measurement of forces between the sample surface and a sharp tip. The sample is mounted on a piezoelectric tub scanner that provides sub-Ångström motion.
of the sample in x, y and z directions. The tip is secured to the end of a cantilever and, as the sample passes beneath the tip, changes in topography cause the tip and cantilever to deflect. This deflection is measured by reflecting a laser beam from the back of the cantilever to a position-sensitive detector (photodiode). The deflection signal can be used in two different ways to generate the topographic image. The measurement of the deflection of the cantilever can be used to measure the z information directly or, alternatively the cantilever deflection can be held constant by the feedback loop of the system that moves the piezoelectric stage the measured distance in the z direction. A raster scan of the sample provides a digital image of the surface topography.

The tapping mode atomic force microscope (TM-AFM) is a development of the contact mode AFM. In TM-AFM, the cantilever on which the tip is mounted, is oscillated at a frequency near its resonance (typically 200-400 kHz) while separated from the sample surface. The oscillation is driven by a constant driving force and the amplitude of its oscillation is monitored. The tip touches the surface at the bottom of each oscillation, and this reduces the oscillation amplitude of the cantilever. The feedback control loop of the system then maintains this new amplitude constant as the oscillating, or tapping, tip scans the surface. This is done by the z component of the scanner, changing the tip height to adjust exactly for the surface topographic variations as the tip scans the sample surface. One of the advantages of TM-AFM over the contact mode AFM is the elimination of lateral shear forces, which are often responsible for sample damage in soft or sticky samples. An extension in TM-AFM technique is the so-called phase mode, where the phase lag of the cantilever is used to collect information about variations in composition, adhesion, friction and viscoelasticity. In such a phase contrast image, lighter areas correspond to regions of higher stiffness.

AFM has been widely used in different research fields, such as:
- studies on the surface structure, especially the microfibrillar structure of fibres, pulps and papers;
- investigations on adsorbed surface contaminants and lignin (amount, distribution and structure);
- microroughness studies of coatings and papers;
- mapping of different components in coatings;
- studies on the cross-sectional structure of wood, fibres, papers and coatings.
4.5 Separation analyser (LUMiFuge114)

The LUMiFuge is an analytical centrifuge. The measuring scheme is depicted in Fig. 4.9. The principle of functionality is based on a continuous definition of the light transmission of the specimen over the total length of the vessel. The resulting transmission profile shows the intensity of the light transmitted as a function of the radial co-ordinates. The radius specifies the distance from the centre of the rotor. Therefore the largest radius corresponds with the bottom of the vessel. The separation process can be depicted as a time course of the relative position of the boundary between supernatant and sediment (resolution better than 100 µm) or of the transmission averaged over the entire or a chosen part of the sample length. Through the quantitative data provided by integration of the transmission profiles displayed against the measuring time, the stability and separation behavior of the dispersions can be investigated rapidly and reliably. And it provides an objective direct assessment and a quantified analysis of stability and destabilization phenomena in disperse systems for product control.

Fig.4.9: Measuring scheme of the separation analyser.
5. Results and discussions

5.1 Core-type PPy/PVME composite particles

5.1.1 Introduction

The colloidal polypyrrole particles can be synthesized by oxidation of pyrrole in the presence of a polymeric stabilizer, which is adsorbed onto the precipitating microscopic conducting polymer nuclei and prevents their aggregation via a steric stabilisation mechanism \[^{[108]}\]. The particle size and the stability of the resulting dispersions depended on the amounts and types of stabilizers and oxidizers used. Different polymers, such as poly(vinylpyrrolidone) (PVP) and poly(vinyl alcohol-co-acetate) (PVA) \[^{[14, 109]}\], polyethylene-oxide (PEO) \[^{[51]}\], poly(2-vinyl pyridine-co-butyl methacrylate) (P2VP-BM) \[^{[17]}\], poly(N,N'-dimethylaminoethyl methacrylate-b-n-butyl methacrylate) \[^{[18]}\], poly(vinyl acetate) \[^{[9]}\], poly(vinyl methyl ether) (PVME) \[^{[16]}\], ethylhydroxycellulose (EHEC) \[^{[12,13]}\], poly(styrenesulfonate) (PSS) \[^{[21]}\] and oxidizers, including FeCl\(_3\), Na\(_2\)S\(_2\)O\(_8\), yielded polypyrrole particles of varying degrees of polydispersity, with modal diameters ranging between 50 and 400 nm.

In this chapter, we describe the morphology of obtained polypyrrole particles prepared by oxidative polymerization of pyrrole in the presence of thermo-sensitive polymer, PVME, as the stabilizer in water or aqueous ethanol. Furthermore, three different anionic salts – sodium benzoate, potassium hydrogen phthalate and sodium hydrogen succinate were used as dopants in the polymerization of pyrrole. The properties of the polypyrrole with respect to morphology, conductivity, stability, and processibility were affected by the addition of the salts \[^{[110,111]}\].

5.1.2 Effect of Py:PVME ratio and reaction medium

Poly(vinyl methyl ether) (PVME) in aqueous solution has a lower critical solution temperature (LCST) of about 37 °C \[^{[16]}\]. 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 gradually with increasing the temperature down to 40 nm when the solution is close to LCST\textsuperscript{[112]}. In aqueous ethanol solutions the cloud point temperature is shifted to higher values\textsuperscript{[16]}. This indicates that PVME polymer chains in aqueous ethanol will be not so strongly aggregated in solution if to compare with pure water.

Uncrosslinked PVME polymer was used as stabilizer in oxidative polymerization of pyrrole in presence of Fe(III). As reaction medium we selected water or water:ethanol mixtures. The PVME:Py ratio was changed from 1:1 to 1:5. Tables 5.1.1 and 5.1.2 give the details of Py dispersion polymerization at 25 °C.

\textbf{Tab.5.1.1:} The recipe of the polymerization of pyrrole in water at 25°C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pyrrole, [g]</th>
<th>PVME, [g]</th>
<th>FeCl\textsubscript{3},6H\textsubscript{2}O, [g]</th>
<th>H\textsubscript{2}O, [g]</th>
<th>Cl/N</th>
<th>D\textsubscript{r} (nm)</th>
<th>Stability</th>
</tr>
</thead>
<tbody>
<tr>
<td>WP1</td>
<td>0,1</td>
<td>0,1</td>
<td>0,548</td>
<td>75</td>
<td>0,30</td>
<td>53±13</td>
<td>Stable</td>
</tr>
<tr>
<td>WP2</td>
<td>0,1</td>
<td>0,033</td>
<td>0,548</td>
<td>65</td>
<td>0,31</td>
<td>71±18</td>
<td>Stable</td>
</tr>
<tr>
<td>WP3</td>
<td>0,1</td>
<td>0,02</td>
<td>0,548</td>
<td>65</td>
<td>0,30</td>
<td>85±17</td>
<td>Unstable</td>
</tr>
<tr>
<td>WP9*</td>
<td>0,1</td>
<td>0,033</td>
<td>0,548</td>
<td>65</td>
<td>0,29</td>
<td>74±16</td>
<td>Stable</td>
</tr>
</tbody>
</table>

* - oxidant was dropped at 0,05 ml/min

\textbf{Tab.5.1.2:} The recipe of the polymerization of pyrrole in water:ethanol (50:50 wt./wt.) at 25°C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pyrrole, [g]</th>
<th>PVME, [g]</th>
<th>FeCl\textsubscript{3},6H\textsubscript{2}O, [g]</th>
<th>Et/H\textsubscript{2}O, [g]</th>
<th>Cl/N</th>
<th>D\textsubscript{r} (nm)</th>
<th>Stability</th>
</tr>
</thead>
<tbody>
<tr>
<td>VP1</td>
<td>0,1</td>
<td>0,1</td>
<td>0,548</td>
<td>75</td>
<td>0,30</td>
<td>65±12</td>
<td>Stable</td>
</tr>
<tr>
<td>VP2</td>
<td>0,1</td>
<td>0,05</td>
<td>0,548</td>
<td>70</td>
<td>0,31</td>
<td>73±16</td>
<td>Stable</td>
</tr>
<tr>
<td>VP3</td>
<td>0,1</td>
<td>0,033</td>
<td>0,548</td>
<td>65</td>
<td>0,30</td>
<td>90±13</td>
<td>Stable</td>
</tr>
<tr>
<td>VP4</td>
<td>0,1</td>
<td>0,02</td>
<td>0,548</td>
<td>65</td>
<td>0,31</td>
<td>115±16</td>
<td>Stable</td>
</tr>
<tr>
<td>VP8*</td>
<td>0,1</td>
<td>0,033</td>
<td>0,548</td>
<td>65</td>
<td>0,31</td>
<td>105±13</td>
<td>Stable</td>
</tr>
</tbody>
</table>

* - oxidant was dropped at 0,05 ml/min

When water:ethanol (50:50) mixture was used as reaction medium all prepared dispersions were stable and show no precipitation with time. In pure water dispersions were unstable when PVME:Py ratio was high as 1:5. All prepared dispersions were cleaned by dialysis to remove initiator residue and by-products. Fig.5.1.1 shows SEM images 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 good separated and don’t stick together. When water:ethanol (50:50) solution is used as reaction medium (Fig.5.1.2) much larger PPy particles are formed at the similar reaction conditions (see samples WP2 and VP3).

Additionally, samples prepared in aqueous ethanol show better enhanced film formation properties. At ratio Py:PVME=1:1 the PPy particles are embedded into PVME matrix. Larger particle sizes obtained in water:ethanol mixtures can be explained by increased hydrodynamic volume of PVME chains in solution and, probably by slower oxidizing rate. This later effect is attributable to FeCl₃ complexation with ethanol [113] and reduction of its oxidation power.
The IR spectra of all the PPy/PVME composites (Fig.5.1.3) represent a superposition spectrum of pure components. The peak of 1546 cm$^{-1}$ (a) is from $\nu$ ring vibration of the pyrrole. The peak of 1036 cm$^{-1}$ results from $\delta$ vibration of C-H and N-H of pyrrole. The peaks at 901 cm$^{-1}$ and 781 cm$^{-1}$ present the vibration of $\delta$(C-H) and $\nu$(C-H) of pyrrole, respectively. The increased intensity of this PPy band corresponds to the increasing amount of PPy in the composites. Moreover, the peak at 1183 cm$^{-1}$ (b), which results from the $\nu$ vibration of C-O-C band, indicates the presence of PVME in the PPy composite particles.

The particle sizes of PPy dispersions prepared in aqueous ethanol measured by DLS and SLS are presented in Fig.5.1.4.

Fig.5.1.3: Infrared spectra of PPy/PVME composites.

Fig.5.1.4: Hydrodynamic Radius (DLS) and radius of gyration (SLS) as a function of Py:PVME ratio in reaction mixture (medium: water:ethanol=50:50).
Light scattering experiments indicate that particles possess highly swollen hydrodynamic PVME shell on the surface therefore measured particle dimensions are larger than the data observed by SEM. Additionally particle size decreases strongly up to Py:PVME ratio 3:1 and then remains constant. This result is a contradiction to our SEM observations. On microscopy images particles are with relatively narrow distribution and DLS data indicates broad PSD. This leads to conclusion that at lower Py:PVME ratios non-adsorbed PVME chains induce partial bridging flocculation in the system and particles build up flocks in solution (see in Fig. 5.1.5). Particle diameters of the samples prepared at higher Py contents are in reasonable agreement with microscopy measurements if to take into account the mobile shell of protecting colloid.

![Fig.5.1.5: Particle morphology (a) at low stabilizer concentration (b) at high stabilizer concentration.](image)

When the oxidant was dropped slowly into the reaction mixture smaller particles were obtained both in water or aqueous ethanol (Fig. 5.1.6).

![Fig.5.1.6: SEM images: a) sample WP9 ; b) sample VP8 (Py:PVME=3:1, oxidant dropping rate 0,05 ml/min).](image)
This effect is due to much lower polymerization rate if to compare with runs where oxidant was added batch wise. With lower nucleation speed in the system the aggregation of nuclei is suppressed and stabilization is more effective.

### 5.1.3. Effect of the reaction temperature

As it was mentioned in the beginning, PVME is known as a kind of thermo-sensitive polymer and in aqueous solution it has a lower critical solution temperature (LCST) of about 37 °C. The solvent power of water as well as of aqueous ethanol towards PVME increases with decreasing temperature \[16\]. The influence of the reaction temperature on the polymerization behavior of PPy is quite interesting and has also been investigated. Tab.5.1.3 and Tab.5.1.4 give the details of the polymerization at different temperatures using water and 50 % aqueous ethanol as the polymerization medium, respectively. From Table 5.1.3 it is shown that dispersion polymerization is not supported in water when the reaction temperature is higher than 45 °C but only can be carried out in water at lower temperature.

#### Tab.5.1.3: The recipe of the polymerization of polypyrrole in water.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Reaction temperature [°C]</th>
<th>Pyrrole, [g]</th>
<th>PVME, [g]</th>
<th>FeCl₃·6H₂O, [g]</th>
<th>H₂O, [g]</th>
<th>Cl/N</th>
<th>Stability</th>
</tr>
</thead>
<tbody>
<tr>
<td>WP8</td>
<td>0</td>
<td>0,1</td>
<td>0,033</td>
<td>0,548</td>
<td>65</td>
<td>0,31</td>
<td>Stable</td>
</tr>
<tr>
<td>WP2</td>
<td>20</td>
<td>0,1</td>
<td>0,033</td>
<td>0,548</td>
<td>65</td>
<td>0,3</td>
<td>Stable</td>
</tr>
<tr>
<td>WP6</td>
<td>45</td>
<td>0,1</td>
<td>0,1</td>
<td>0,548</td>
<td>75</td>
<td>0,3</td>
<td>Unstable</td>
</tr>
<tr>
<td>WP7</td>
<td>45</td>
<td>0,1</td>
<td>0,033</td>
<td>0,548</td>
<td>65</td>
<td>0,3</td>
<td>Unstable</td>
</tr>
</tbody>
</table>

#### Tab.5.1.4: The recipe of the polymerization of polypyrrole in ethanol : water = 50:50(wt:wt).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Reaction temperature [°C]</th>
<th>Pyrrole, [g]</th>
<th>PVME, [g]</th>
<th>FeCl₃·6H₂O, [g]</th>
<th>H₂O, [g]</th>
<th>Cl/N</th>
<th>Stability</th>
</tr>
</thead>
<tbody>
<tr>
<td>VP7</td>
<td>0</td>
<td>0,1</td>
<td>0,033</td>
<td>0,548</td>
<td>65</td>
<td>0,3</td>
<td>Stable</td>
</tr>
<tr>
<td>VP3</td>
<td>20</td>
<td>0,1</td>
<td>0,033</td>
<td>0,548</td>
<td>65</td>
<td>0,31</td>
<td>Stable</td>
</tr>
</tbody>
</table>
Fig. 5.1.7 shows the SEM images for sample WP8 and VP7 respectively. Compared with the SEM images for sample WP2 and VP3, it can be seen clearly that the particle size of VP7 is much bigger than that of VP3. It is known that the final morphology of particles is the co-effect of both the conformation of the stabilizer and the rate of polymerization. The conformation of the stabilizer PVME strongly depends on the temperature, especially in the medium of ethanol/water = 50/50(wt:wt). At 0°C the structure of PVME in ethanol/water=50/50 is much more stretched than it was at room temperature and this made it difficult to surround the monomer to form stable micelles. So in this case the initiation rate is slower with fewer nucleated particles and this induced to the bigger particles in the end. Moreover, no matter at lower temperature or at higher temperature, PPy colloidal particles prepared in water are spherical and much smaller than that was prepared in 50 wt.-% aqueous ethanol. This may due to the reason that if water is reaction medium pyrrole is initiated and polymerized in a higher rate and induced production with smaller but more particles.

5.1.4 Influence of the dopants

It was also reported that the use of dopants such as benzenesulfonic, toluenesulfonic, and styrenesulfonic acids enhanced the conductivity of polypyrrole particles. In our study, three different anionic salts – sodium benzoate, potassium hydrogen phthalate and sodium hydrogen succinate were used as dopants in the polymerization of pyrrole in the presence of PVME as the stabilizer (see in Fig. 5.1.8). However, instead of FeCl₃,
Na$_2$S$_2$O$_8$ was used as the oxidant since in this case polypyrrole became doped with FeCl$_4^-$ ions formed in the reaction. Tab.5.1.5 gives detail information of Py dispension polymerization at room temperature. And in all runs stable PPy colloids were formed in the presence of different salts.

![Chemical structures of benzoic acid, sodium salt (Benzoic acid, sodium salt) and KH- Phthalat (KH- Phthalat) and NaH- Succinate (NaH- Succinate)](Fig.5.1.8: The structure of the dopants.)

Tab.5.1.5: The recipe of the polymerization pyrrole in water at 25°C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dopant</th>
<th>Dopant amount [g]</th>
<th>Pyrrole [g]</th>
<th>PVME [g]</th>
<th>Na$_2$S$_2$O$_8$ [g]</th>
<th>Water [g]</th>
<th>Stability</th>
</tr>
</thead>
<tbody>
<tr>
<td>WP1-1</td>
<td>-</td>
<td>-</td>
<td>0,1</td>
<td>0,1</td>
<td>0,5</td>
<td>75</td>
<td>Stable</td>
</tr>
<tr>
<td>WP1-2</td>
<td>Na-benzoate</td>
<td>0,21</td>
<td>0,1</td>
<td>0,1</td>
<td>0,5</td>
<td>75</td>
<td>Stable</td>
</tr>
<tr>
<td>WP1-2a</td>
<td>Na-benzoate</td>
<td>0,043</td>
<td>0,1</td>
<td>0,1</td>
<td>0,5</td>
<td>75</td>
<td>Stable</td>
</tr>
<tr>
<td>WP1-2b</td>
<td>Na-benzoate</td>
<td>1,08</td>
<td>0,1</td>
<td>0,1</td>
<td>0,5</td>
<td>75</td>
<td>Stable</td>
</tr>
<tr>
<td>WP1-3</td>
<td>KH- phthalate</td>
<td>0,31</td>
<td>0,1</td>
<td>0,1</td>
<td>0,5</td>
<td>75</td>
<td>Stable</td>
</tr>
<tr>
<td>WP1-4</td>
<td>NaH-succinate</td>
<td>0,21</td>
<td>0,1</td>
<td>0,1</td>
<td>0,5</td>
<td>75</td>
<td>Stable</td>
</tr>
</tbody>
</table>

By following the polymerization process, the results indicate that the effect of the presence of benzoate, phthalate and succinate on the rate of PPy formation is marginal (Fig.5.1.9). Gill et al. [114] has reported that the oxidation of aniline proceeds slowly when sodium dodecylbenzenesulfonate (DBSNa) was added to reaction mixture. But, Kudoh [115] noted that Py polymerization was faster in the presence of anionic surfactant. Our results show that retardation of the polymerization has been observed in all runs with salts, possibly as a consequence of the limited miscibility of monomer and salt solutions. Furthermore, it is also easy to see that the retardation of pyrrole polymerization is henced with the increase of the dopant’s amount, which indicates a more active involvement of the anionic salt in the reaction course (Fig.5.1.9(b)).
**Fig.5.1.9:** Temperature profile of the exothermic oxidation of pyrrole in the presence of various salts (a) and various amount of salts (b).

**Tab.5.1.6:** Elemental composition (wt.-%) of PPy prepared in the presence of dopants.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dopant</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>WP1-1</td>
<td>None</td>
<td>56,46</td>
<td>4,98</td>
<td>12,90</td>
<td>0,59</td>
</tr>
<tr>
<td>WP1-2</td>
<td>Benzoate</td>
<td>49,80</td>
<td>5,64</td>
<td>7,69</td>
<td>3,11</td>
</tr>
<tr>
<td>WP1-3</td>
<td>Phthalate</td>
<td>56,09</td>
<td>5,24</td>
<td>11,12</td>
<td>1,48</td>
</tr>
<tr>
<td>WP1-4</td>
<td>Succinate</td>
<td>51,20</td>
<td>6,32</td>
<td>7,94</td>
<td>2,91</td>
</tr>
</tbody>
</table>

Tab.5.1.6 shows the elemental composition of final products. And the results of elemental analysis show the reduction of the nitrogen content in the final products, which demonstrates the incorporation of dopants into PPy after Py polymerization.
Fig. 5.1.10: Infrared spectra of polypyrrole prepared in the absence and in the presence of different dopants and the spectrum of neat dopants.
Tab.5.1.7: Infrared band position and assignments of polypyrrole prepared in the absence and in the presence of different dopants and the spectrum of neat dopants.

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavenumber [cm⁻¹]</td>
<td>Functional groups</td>
<td>Wavenumber [cm⁻¹]</td>
</tr>
<tr>
<td>1452</td>
<td>carboxylate</td>
<td>1381</td>
</tr>
<tr>
<td></td>
<td>stretching</td>
<td></td>
</tr>
<tr>
<td>926</td>
<td>δ(CH), pyrrole</td>
<td>931</td>
</tr>
<tr>
<td>791</td>
<td>γ(CH), pyrrole</td>
<td>787</td>
</tr>
</tbody>
</table>

Moreover, the presence of anionic salts in PPy as dopants is also confirmed by a comparison of the infrared spectra of PPy prepared in the presence and absence of the salt (Fig.5.1.10). The peak at about 1452 cm⁻¹ belonging to the carboxylate stretching of neat Na-benzoate is observed also in the spectra of polypyrrole polymer (WP1-2) prepared in presence of this salt. And the peaks at about 926 and 791 cm⁻¹ are responsible for the δ(CH) and γ(CH) vibration of pyrrole, respectively. Similar results have been also investigated in the infrared spectra of polypyrrole prepared in the presence of other anionic salts (see in Tab.5.1.7).

Fig.5.1.11: SEM images for sample (a) WP1-1, (b) WP1-2, (c) WP1-3, (d) WP1-4.

Electron microscopy images of polypyrrole colloids are shown in Fig.5.1.11. Compare the SEM image of polypyrrole particles (Fig.5.1.11a) with the particles
prepared at the same condition but use FeCl₃ as oxidant (Fig.5.1.1a), we can see that larger particles can be got by using persulfate as oxidant. This may due to the reason that persulfates are relatively strong oxidants \((E^0 = 2.1 \text{ V})\) compared to \(\text{Fe}^{3+} (E^0 = 0.77 \text{ V})\). So in the case of using persulfates as oxidant, it has much faster polymerization rate if to compare with runs when FeCl₃ was used as oxidant. The higher nucleation speed in the system increases the aggregation of nuclei and the stabilization is less effective, which results to larger particles in the final dispersion. Furthermore, SEM investigations (Fig.5.1.11) indicate that the morphology of obtained polypyrrole particles prepared in the presence of anionic salts are quite similar as the particles prepared in the absence of salt. In all cases, the spherical particles exhibit a “cauliflower” morphology, which was reported in other reviews \(^{21}\). Additionally, it can be observed that larger particle size (about 180 nm) is obtained by PPy samples prepared with salts and this observation can be explained by the slower rate of oxidation of Py polymerization in the presence of salt, which has been shown in Fig.5.1.9.

![Fig.5.1.12: Particle size distribution of polypyrrole dispersions prepared in the presence of dopants.](image)

Fig.5.1.12 shows the particle size distribution of polypyrrole dispersions prepared in the presence of dopants measured by DLS. Polypyrrole dispersion prepared without dopant presents bimodal distribution of the particle size with one peak at 150 nm and another at 980 nm. Compared the DLS results with SEM image (Fig.5.1.11a), it is clearly to see that sample WP1-1 shows nice monomodal spherical morphology with particle size around 150 nm, which indicates that the secondary peak at 980 nm got from DLS is from the aggregation of the polypyrrole particles in the dispersion.
Larger and monodispersed polymeric particles without aggregation were observed when pyrrole dispersions were prepared in the presence of dopants, which is coincident with the results of SEM images. Tab.5.1.8 shows the conductivity of PPy samples which was measured at room temperature. The lower conductivity value obtained by PPy samples prepared without any dopant may due to the reason that PPy particles were covered by insulator out layer of PVME stabilizer, which resulted in the difficulties to transport the charge carriers. In the case of PPy prepared in the presence of dopants, an improvement of the conductivity has been observed even at much lower PPy loads. While phthalate and succinate were used as dopant, the conductivity of the final products has increased by 1-2 orders of magnitude, and while benzoate is used, the conductivity has increased by 3-4 orders.

**Tab.5.1.8: Influence of presence of the dopants on conductivity of the PPy dispersions.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Py, [g]</th>
<th>PPy, [%]</th>
<th>( \sigma, [\text{Scm}^{-1}] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>WP1-1</td>
<td>0,1</td>
<td>61,73</td>
<td>( 8,5\times10^{-9} )</td>
</tr>
<tr>
<td>WP1-2</td>
<td>0,1</td>
<td>36,80</td>
<td>( 1,17\times10^{-5} )</td>
</tr>
<tr>
<td>WP1-3</td>
<td>0,1</td>
<td>53,21</td>
<td>( 4,55\times10^{-7} )</td>
</tr>
<tr>
<td>WP1-4</td>
<td>0,1</td>
<td>40,00</td>
<td>( 1,5\times10^{-7} )</td>
</tr>
</tbody>
</table>

**Conclusions**

- 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 when uncrosslinked PVME was used as stabilizer, small spherical particles in the range of 50-100 nm were formed in both aqueous ethanol and water.

- Results of the elementary analysis, IR spectroscopy confirmed that the anionic salts can be incorporated in the conducting polymers and play as the dopants. The presence of dopants in polypyrrole enhances the conductivity, especially in the case of sodium benzoate the conductivity of the final product has been improved by 3 orders.
5.2 IPN type polypyrrole composites

5.2.1 Introduction

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 \[^{[116]}\]. Martin et al.\[^{[117,118,119]}\] used commercially available particle track-etched membranes (PTM’s) 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, Jerome et al. \[^{[120]}\] reported 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) \[^{[121]}\]. Wan et al. \[^{[47]}\] created a template-free method to synthesize microtubules of polyaniline (PANI) \[^{[122]}\] and PPy \[^{[123]}\] in the presence of \(\beta\)-naphthalene sulfonic acid (\(\beta\)-NSA) micelles. Compared with the methods mentioned previously, the template-free method is not so costly and rather simple.

The idea behind this work was to prepare “smart” polymer sub-micron particles containing conjugated polymer. Polymeric microgels, such as crosslinked PVME microgels, were considered to be applied as templates for deposition of polypyrrole. For comparison, another kind of temperature-sensitive microgels, which were prepared by radical co-polymerization of N-vinylcaprolactam (VCL) and acetoacetoxyethyl methacrylate (AAEM), were also tried to be used as the template. The influence of the reaction medium, temperature, oxidant addition mode and microgel structure on the morphology and properties of final particles was investigated \[^{[124,125,126]}\].
5.2.2 Using crosslinked PVME microgel as the template

Crosslinked PVME microgel with average hydrodynamic radius 200 nm was used as stabilizer in oxidative polymerization of pyrrole in presence of Fe(III). Similarly to previous system we selected water or water:ethanol mixtures as reaction medium. The PVME:Py ratio was varied from 1:1 to 1:5. Tab.5.2.1 gives the details of Py dispersion polymerization at 25 °C.

**Tab.5.2.1:** The recipe for pyrrole polymerization in different medium.

<table>
<thead>
<tr>
<th>Sample</th>
<th>PVME, [g]</th>
<th>Pyrrole, [g]</th>
<th>FeCl₃·6H₂O, [g]</th>
<th>Et/H₂O, [g]</th>
<th>Et:H₂O, [wt:wt]</th>
<th>Stablility</th>
</tr>
</thead>
<tbody>
<tr>
<td>MP8</td>
<td>0.008</td>
<td>0.008</td>
<td>0.0435</td>
<td>20</td>
<td>50:50</td>
<td>Stable</td>
</tr>
<tr>
<td>MP10</td>
<td>0.008</td>
<td>0.016</td>
<td>0.087</td>
<td>20</td>
<td>50:50</td>
<td>Stable</td>
</tr>
<tr>
<td>MP12</td>
<td>0.008</td>
<td>0.024</td>
<td>0.131</td>
<td>20</td>
<td>50:50</td>
<td>Stable</td>
</tr>
<tr>
<td>MP13</td>
<td>-</td>
<td>0.025</td>
<td>0.137</td>
<td>20</td>
<td>50:50</td>
<td>Aggregation</td>
</tr>
<tr>
<td>MP15</td>
<td>0.013</td>
<td>0.013</td>
<td>0.0738</td>
<td>20</td>
<td>30:70</td>
<td>Stable</td>
</tr>
<tr>
<td>MP16</td>
<td>0.013</td>
<td>0.013</td>
<td>0.0738</td>
<td>20</td>
<td>10:90</td>
<td>Unstable</td>
</tr>
<tr>
<td>MP14</td>
<td>0.013</td>
<td>0.013</td>
<td>0.0738</td>
<td>20</td>
<td>0:100</td>
<td>Unstable</td>
</tr>
</tbody>
</table>

SEM investigations indicate that the morphology of obtained particles is quite different from the particles prepared with uncroslinked PVME. Fig.5.2.1(a) shows a micrograph of the PPy particles prepared without PVME.

In this case particles exhibit “cauliflower” morphology which was reported in other reviews [21,30] and dispersion is unstable. Similar morphology is obtained when Py is polymerized in water without any stabilizer.

When crosslinked PVME microgels are present in reaction mixture quite, stable dispersions are obtained and microscopy investigations indicate that morphology of the Py particles is changing from spherical to needle-like. At low Py content mostly spherical particles are present (Fig.5.2.1(b)). When the Py amount is increased needle-like morphology is dominant and particles are larger (Fig.5.2.1(c,d)). However when the ethanol content in reaction mixture was decreased (water:ethanol = 90:10) PPy particle morphology is switched again to spherical (see Fig.5.2.2(a)). It seems that small PPy particles were embedded into PVME microgels and after solvent evaporation formed a kind of porous membrane.
Fig. 5.2.1: 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. 5.2.2: SEM images of PPy particles prepared at Py:PVME ratio 1:1 in different medium: (a) water:ethanol =90:10 (MP16); (b) water (MP14).

Particles prepared in pure water in presence of PVME microgel (see in Fig. 5.2.2(b)) exhibit 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 a role of a template in this particular system.

Fig.5.2.3 shows the FESEM picture of PVME microgels in the swollen state [112]. It indicates that in swollen state microgel particles have sponge-like structure with a mean diameter of approximately 350 nm. Detailed microscopy investigations indicate that outer membrane of these particles has small holes with a diameter of 5-10 nm, which provide a corresponding membrane permeability. Since the solubility of Py monomer in water is very low we believe that it can penetrate into microgel particle interior. Addition of oxidant causes rapid polymerization process (oxidant was added batchwise) and PPy particles with granular morphology are formed which are probably embedded into PVME microgel network (see Fig.5.2.4). Similar effect was observed by Liu et. al [47] when a β-naphtalene sulfonic acid (β-NSA) micelles were used as a templates for pyrrole polymerization. In there case at quick addition of the oxidant granular PPy-NSA was obtained. On the other hand, the tubular PPy-NSA was obtained at slow oxidant addition.

Fig.5.2.3: FESEM image of PVME microgel particle in swollen state [112].

Fig.5.2.4 represents an idealized representation of formed particles in presence of PVME microgels. When microgel particles are in water:ethanol mixture the network expands and the pores are probably larger. Additionally, as it was mentioned before the polymerization rate in aqueous ethanol is much lower if to compare with that in pure water even if the same oxidant concentration is used. These both effects provide suitable conditions for PPy to self-assemble to form needles and increased Py content in
reaction mixture led to larger needles. If the ethanol content is less than 50 % again granular morphology appears.

![Scheme of PPy particle morphology in presence of PVME microgels.](image.png)

These considerations led to conclusion that the pore size of the microgel particles and Py polymerization rate has dramatic influence on the morphology of the final product. The pore size of 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 factor, which has to be considered is the presence of the solvent what is better solvent for PVME than water. The polymerization rate can be changed by varying the nature of the oxidant and its addition mode.

5.2.3 Using VCL/AAEM microgel as the template

Thermosensitive microgels based on VCL and AAEM have also been used as templates for oxidative polymerization of pyrrole. VCL/AAEM microgel particles have been prepared in surfactant free conditions. Overall VCL:AAEM ratio determines size of microgels below LCST due to regulation of crosslinking and at low temperatures particles swell to different extent. It has been assumed that the microgels have core-shell structure due to fast consumption of more reactive methacrylic
monomer in the beginning of reaction. AAEM-rich particle core is more hydrophobic and is less temperature sensitive if to compare with VCL-rich shell. VCL/AAEM microgel particles exhibit completely reversible “soft - hard sphere“ transition induced by collapse of highly swollen VCL-rich shell during heating. The polymerization of pyrrole in presence of VCL/AAEM microgels can result in novel composite microgels filled with conducting polypyrrole inclusions and additionally possessing thermo-sensitive properties \[^{126}\]. Some important characteristics of microgels used in this study are summarized in Tab.5.2.2.

**Tab.5.2.2:** Composition and some properties of VCL/AAEM microgels.

<table>
<thead>
<tr>
<th>Run</th>
<th>VCL, [g]</th>
<th>AAEM, [g]</th>
<th>AAEM*, [mol-%]</th>
<th>Solids, [%]</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2,06</td>
<td>0,04</td>
<td>4,3</td>
<td>1,2</td>
<td>7,1</td>
</tr>
<tr>
<td>2</td>
<td>2,04</td>
<td>0,08</td>
<td>4,8</td>
<td>1,2</td>
<td>7,0</td>
</tr>
<tr>
<td>3</td>
<td>1,98</td>
<td>0,16</td>
<td>6,7</td>
<td>1,2</td>
<td>7,2</td>
</tr>
<tr>
<td>4</td>
<td>1,93</td>
<td>0,24</td>
<td>11,8</td>
<td>1,2</td>
<td>7,1</td>
</tr>
<tr>
<td>5</td>
<td>1,88</td>
<td>0,32</td>
<td>15,2</td>
<td>1,2</td>
<td>7,1</td>
</tr>
</tbody>
</table>

Fig.5.2.5 shows schematically the incorporation of polypyrrole into microgels.

**Fig.5.2.5:** Polymerization of pyrrole in presence of AAEM/VCL microgels.

In the first step (1) pyrrole was added to microgel dispersion. Since pyrrole has limited solubility in water, it can be assumed that some amount of monomer is solubilized in hydrophobic domains of microgel network. In the second step (2) the addition of oxidant (sodium peroxydiulphate, SPDS) starts oxidative polymerization
of pyrrole in the system. At this stage two possible scenario can be considered: a) incorporation of polypyrrole (PPy) particles into microgel structure and formation of composite particles without strong change in polydispersity of the system; and b) partial incorporation of PPy into microgels and formation of secondary PPy particles which are not deposited into microgel network. Naturally, scenario a) is preferable since such system is easily to handle and more suitable for future applications. Additionally, since VCL/AAEM microgels are thermo-sensitive and collapse when solution is warmed up (LCST around 28 °C) it is expected that composite microgels will also show thermo-sensitive properties to some extent combining this interesting feature with conductivity provided by PPy inclusions.

5.2.3.1 Influence of AAEM content

The amounts of reagents used for polymerization of pyrrole in presence of VCL/AAEM microgels are summarized in Tab.5.2.3.

<table>
<thead>
<tr>
<th>Run</th>
<th>AAEM, [mol-%]</th>
<th>Microgel solution, [g]</th>
<th>Py, [g]</th>
<th>Water, [g]</th>
<th>SPDS, [g]</th>
<th>T, [°C]</th>
<th>PPy¹, [%]</th>
<th>PPy*, [%]</th>
<th>Conversion [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>4,3</td>
<td>40</td>
<td>0,05</td>
<td>5</td>
<td>0,25</td>
<td>20</td>
<td>9,43</td>
<td>7,58</td>
<td>80,4</td>
</tr>
<tr>
<td>7</td>
<td>4,8</td>
<td>40</td>
<td>0,05</td>
<td>5</td>
<td>0,25</td>
<td>20</td>
<td>9,43</td>
<td>8,68</td>
<td>92,1</td>
</tr>
<tr>
<td>8</td>
<td>6,7</td>
<td>40</td>
<td>0,05</td>
<td>5</td>
<td>0,25</td>
<td>20</td>
<td>9,43</td>
<td>5,54</td>
<td>58,8</td>
</tr>
<tr>
<td>9</td>
<td>11,8</td>
<td>40</td>
<td>0,05</td>
<td>5</td>
<td>0,25</td>
<td>20</td>
<td>9,43</td>
<td>6,55</td>
<td>69,5</td>
</tr>
<tr>
<td>10</td>
<td>15,2</td>
<td>40</td>
<td>0,05</td>
<td>5</td>
<td>0,25</td>
<td>20</td>
<td>9,43</td>
<td>7,39</td>
<td>78,4</td>
</tr>
</tbody>
</table>

¹ – theoretical value, * - determined by elementary analysis

In this set of experiments equal pyrrole amounts were incorporated into microgel networks. The amount of PPy incorporated into microgels was determined by elementary analysis. Results presented in Tab.5.2.3 indicate that microgels contain around 6-7 % PPy (theoretical value was 9,4 %). It is evident, that polypyrrole contains certain amount of sulfate anions as dopant ions from oxidant. Fig.5.2.6 shows the average hydrodynamic radius ($R_h$) of VCL/AAEM microgels and their composite analogues.

It is clear from Fig.5.2.6 that incorporation of large amounts of AAEM into microgel structure reduces the particle size. This behaviour is not surprising since effective
steric stabilization at room temperature arises from VCL segments which probably form a hairy layer around particles. Increase of AAEM content leads to increased tendency of crosslinking reactions and more defined heterogeneity of the particles due to large difference in reactivity of VCL and AAEM. Furthermore, from Fig.5.2.6 it is also clear to see that composite microgels with integrated polypyrrole domains are considerably smaller than original particles. Incorporation of pyrrole causes the shrinkage of the microgel network probably due to the interaction between polypyrrole domains and polymer network. In this case it is possible to assume that the carbonyl functions of AAEM units will form hydrogen bonds with nitrogen atoms of pyrrole rings. Similar kind of interactions was observed by Armes et al. [17] for polypyrrole particles stabilized by poly(2-vinyl pyridine-co-butyl methacrylate) steric stabilizers. In all cases DLS spectra were monomodal and no broadening of particle size distribution was detected after pyrrole polymerization. This indicates that polypyrrole domains are located in microgel network and these microgels can be considered as effective templates.

![Graph](image)

**Fig. 5.2.6:** Average hydrodynamic radius of microgels as a function of AAEM content.

Additional proof for that is presented in Fig.5.2.7. In this case in run 9 the pyrrole polymerization process was followed by DLS measurements. Fig.5.2.7 indicates that hydrodynamic radius decreases continuously from the beginning of polymerization and finally reaches the plateau after 100 min. It is also evident that the particle size distribution remains without strong changes and no separate polypyrrole particles in water medium were detected. Therefore, microgel network can be considered as polymerization loci in present system.
Fig. 5.2.7: Average hydrodynamic radius (a) and particle size distribution of the composite particles (b) as a function of reaction time (run 9: microgel with 11.8 mol-% AAEM).

The particle size of obtained microgels was also measured at different temperatures. Fig.5.2.8(a) indicates that the size of VCL/AAEM microgels decreases with increasing temperature. This typical LCST behaviour was detected also from composite microgels(Fig.5.2.8(b)).

The deswelling process for both systems takes place in the same temperature region, but the shrinkage of pyrrole-containing particles represented as the ratio of average hydrodynamic radii at 10 and 45 °C ($R_h^{10}/R_h^{45}$) is smaller (see Tab.5.2.4). This indicates that PPy inclusions interact with microgel network and this leads to decrease of microgel size at temperatures below LCST. It can be assumed that PPy chains form hydrogen bonds with nitrogen atoms of VCL. For samples with highest AAEM content the ratio $R_h^{10}/R_h^{45}$ is nearly the same for both VCL/AAEM and
VCL/AAEM/PPy particles, which is probably due to higher crosslinking density of the microgel template.

**Fig.5.2.8:** Average hydrodynamic radius of AAEM/VCL microgels (a) (1 – run 1; 2 – run 3; 3 – run 5) and composite microgels (b) (1 – run 6; 2 – run 8; 3 – run 10) as a function of the temperature.

**Tab.5.2.4:** Thermal shrinkage of the VCL/AAEM (run 1-5) and VCL/AAEM/PPy (run 6-10) microgels.

<table>
<thead>
<tr>
<th>Run</th>
<th>(R_h^{10}), [nm]</th>
<th>(R_h^{45}), [nm]</th>
<th>(R_h^{10}/R_h^{45})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>308</td>
<td>137</td>
<td>2,25</td>
</tr>
<tr>
<td>3</td>
<td>269</td>
<td>124</td>
<td>2,17</td>
</tr>
<tr>
<td>5</td>
<td>219</td>
<td>130</td>
<td>1,68</td>
</tr>
<tr>
<td>6</td>
<td>253,5</td>
<td>119,7</td>
<td>2,12</td>
</tr>
<tr>
<td>8</td>
<td>233,5</td>
<td>127,8</td>
<td>1,83</td>
</tr>
<tr>
<td>10</td>
<td>206,8</td>
<td>123,3</td>
<td>1,67</td>
</tr>
</tbody>
</table>

Both VCL/AAEM and corresponding composite particles collapse to the same size and this indicates that the pyrrole amount incorporated in microgel structure is not sufficient to form the IPN-structure. So, polypyrrole inclusions not disturb the deswelling process. It is also surprising that charged polypyrrole particles don’t influence the collapse temperature of microgels.

**5.2.3.2 Influence of PPy content**

In this set of experiments microgel prepared at 4.8 mol-% AAEM content (run 2) was used and the pyrrole concentration was varied. Tab.5.2.5 presents the amounts of ingredients used in these reactions.
Tab.5.2.5: Reaction recipe for preparation of composite microgels with different PPy content.

<table>
<thead>
<tr>
<th>Run</th>
<th>Microgel solution**, [g]</th>
<th>Py, [g]</th>
<th>Water, [g]</th>
<th>SPDS, [g]</th>
<th>T°, [°C]</th>
<th>PPy°, [%]</th>
<th>PPy*, [%]</th>
<th>Conversion [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>40</td>
<td>0,025</td>
<td>5</td>
<td>0,125</td>
<td>20</td>
<td>4,95</td>
<td>3,04</td>
<td>61,4</td>
</tr>
<tr>
<td>12</td>
<td>40</td>
<td>0,04</td>
<td>5</td>
<td>0,20</td>
<td>20</td>
<td>7,69</td>
<td>4,07</td>
<td>52,9</td>
</tr>
<tr>
<td>13</td>
<td>40</td>
<td>0,05</td>
<td>5</td>
<td>0,25</td>
<td>20</td>
<td>9,43</td>
<td>8,68</td>
<td>92,1</td>
</tr>
<tr>
<td>14</td>
<td>40</td>
<td>0,065</td>
<td>5</td>
<td>0,325</td>
<td>20</td>
<td>11,93</td>
<td>9,77</td>
<td>81,9</td>
</tr>
<tr>
<td>15</td>
<td>40</td>
<td>0,1</td>
<td>5</td>
<td>0,40</td>
<td>20</td>
<td>14,29</td>
<td>14,23</td>
<td>99,6</td>
</tr>
<tr>
<td>16</td>
<td>40</td>
<td>0,1</td>
<td>5</td>
<td>0,50</td>
<td>20</td>
<td>16,67</td>
<td>16,33</td>
<td>97,9</td>
</tr>
</tbody>
</table>

* - determined by elementary analysis; ** - run 2: 4,8 mol% AAEM

The oxidation of pyrrole is exothermic so the temperature of the reaction mixture can be used to monitor the progress of reaction. Fig.5.2.9 shows a typical course of pyrrole polymerization. After an induction period, where the temperature stays virtually constant, the exothermic polymerization of pyrrole takes place and the temperature rises. The increase in temperature reflects the conversion of pyrrole to polypyrrole. After PPy has been produced and the reaction completed, the reaction mixture slowly cools. It was shown in Fig.5.2.9 that increasing the pyrrole amount in the system accelerated pyrrole polymerization process and also the induction period was reduced. Similar results have been reported for the polymerization of polyaniline by J. Stejskal [127].

![Fig.5.2.9: Temperature profile of the exothermic oxidation of pyrrole with various pyrrole amount.](image)

Experimental results of particle size measurements for obtained composite microgels are presented in Fig.5.2.10(a). When the oxidant was added to the VCL/AAEM microgel and Py was not present in reaction mixture the average hydrodynamic radius
of particles slightly decreases. It is well known, that hydrogels exhibit different equilibrium degrees of swelling in response to various kinds of salts as well as their concentrations. Donnan equilibrium has been successfully used to predict the swelling behaviour of charged gels in electrolyte solutions\cite{128,129,130}. In the case of nonionic gels, increased salt concentration in the bulk medium affects inter- and intramolecular hydrogen-bonding and polar interactions as well as hydrophobic interactions associated with water molecules. Thus, it can be anticipated that, even though nonionic gels demonstrate the salting-out (or salting-in) behaviour, they normally induce a far weaker salt-induced swelling change compared to the ionic gels.

According to an empirical equation of the salting-out, the solubility of any particular water-soluble polymer decreases gradually with increasing ionic strength. Kirsh et al.\cite{131} investigated influence of different salts on transition temperature of PVCL.

Fig. 5.2.10: Average hydrodynamic radius (a) and particle size distribution (b) of composite microgels as a function of PPy content.
Mostly linear decrease of LCST with increasing salt concentration was detected for different anions, and the coefficient of stabilization for sulfate was found to be minimal among tested salts. Park et al. [132] reported that different salts lower the LCST of nonionic poly(N-isopropylamide) gel with increasing concentration. VCL/AAEM microgel is not an example of charged system, however some charges from initiator molecules incorporated in to microgel network can’t be neglected. In this case it could be proposed that adding salt in nonionic microgels would affect Flory interaction parameter for the polymer chains with the solvent molecules, which consequently results in a decrease of LCST. Probably, oxidant molecules shift the LCST to lower temperatures and particles dimensions decrease at 20 °C as it is shown in Fig.5.2.10(a). The average hydrodynamic radius of microgels decreases much strongly when the PPy content increases and when the minimal value is reached particle size starts to increase. Fig.5.2.10(b) indicates that there was no strong changes in particle size distribution, so this effect can’t be caused by presence of small PPy particles beside large composites (arrows in Fig.5.2.10(a) indicate the samples measured by DLS presented in Fig.5.2.10(b)). When the PPy content was higher than 16 % system became unstable. Initial decrease of the particle size can be explained by some specific interaction of polypyrrole domains and polymer network. When the PPy amount is low filler particles are located with certain distance from each other and the VCL/AAEM polymer chains can interact effectively with polypyrrole particle surface. So, stepwise increase of the PPy particles content leads to the shrinkage of the microgel template. This situation is possible up to certain content of PPy particles in microgel structure. If PPy content reaches certain value, the distance between inclusions will be smaller. Therefore, the repulsion forces between charged polypyrrole filler particles will dominate and the size of composite microgel increases with further increase of PPy content. This situation is presented in Fig.5.2.11.

![Microgels with different PPy content.](image)

Fig.5.2.11: Microgels with different PPy content.
Fig.5.2.12 presents the $R_{h}^{10}/R_{h}^{45}$ ratio for composite microgels (runs 11 – 16) plotted against PPy contents in microgel structure. This dependency is quite similar to the behaviour of hydrodynamic radius in Fig.5.2.10(a). It was found that microgels prepared with different PPy contents collapse nearly to the same size, but swell to different extent at lower temperatures. Therefore, dependency in Fig.5.2.12 is determined actually by change of the size of microgels in swollen state.

From this it can be concluded, that if the template is in swollen state (low temperatures) the polypyrrole inclusions affect the microgel size by combination of attraction/repulsion forces. Contrary, at high temperatures, the dimensions of composite microgels are determined exclusively by the shrinkage of VCL/AAEM network.

It was already mentioned that at certain polypyrrole content microgel particles are loosing stability in water. This fact is not surprising, since according to the idea described before, at high concentration of PPy particles the surface of composite microgels will be totally covered by filler particles. This can cause compression of the hydrophilic hairy layer of microgels responsible for stabilization of the particles with next flock formation or total destabilization of colloidal system.

The modification of VCL/AAEM particles with polypyrrole was confirmed by IR spectroscopy. In Fig.5.2.13 the IR spectra of chemically prepared PPy, VCL/AAEM copolymer (11,8 % AAEM) and same VCL/AAEM modified with 16,33 % PPy are shown. Major changes can be observed in the region 1500 – 400 cm$^{-1}$. The spectrum
of VCL/AAEM/PPy composite represents a superposition spectrum of pure components. The \( \nu_{\text{ring}} \) vibration of PPy at 1558 cm\(^{-1} \) is overlapped by strong C=O signals of both VCL and AAEM and not shown in Fig.5.2.12. Other characteristic polypyrrole signals such as \( \delta (\text{C-H}) \) (m) at 1037 cm\(^{-1} \); \( \delta (\text{C-H}) \) out of plane (s) at 910 cm\(^{-1} \); and \( \gamma (\text{C-H}) \) (w) at 672 cm\(^{-1} \) are marked with the arrows.

![IR spectra](image)

**Fig.5.2.13:** IR spectra of  (a) pure PPy, (b) VCL/AAEM copolymer (run 4), and (c) VCL/AAEM/PPy composite (run 16).

Incorporation of PPy into microgels induces visible changes in \( \xi \)-potential behaviour. Particle charge becomes negative when pH value is larger than 4,5 for composite particles with higher PPy load. Isoelectric point is clearly observed for both samples with loaded 8,68 % and 3,04 % PPy. Previous investigations in order to investigate \( \xi \)-potential of composite PPy particles stabilized by inorganic oxide nanoparticles\(^{[133]} \) or polyacrylate latices\(^{[134]} \) resulted in conclusion that both isoelectric points and \( \xi \)-potentials of such nanocomposite particles are governed by the nature of the charged groups at the stabilizer particle surface rather than by the conducting polymer component. Markham et. al\(^{[135]} \) reported that when PPy particles were prepared with PEO stabilizer it was possible to strip PEO chains from the PPy surface. In this case bare PPy particles prepared with FeCl\(_3\) or (NH\(_4\))\(_2\)S\(_2\)O\(_8\) exhibit isoelectric points (8,5 and 6 respectively), so this correlates to some extent with our result presented in Fig.5.2.14. The charging mechanism for PPy is probably a combination of the bulk charge on the polypyrrole chains, arising from oxidation of the pyrrole rings and surface charging possibly due to protonation/deprotonation of the secondary amino groups exposed to the aqueous environment\(^{[134]} \). \( \xi \)-potential values measured for composite microgels are probably influenced by the localization of PPy inclusions in
the microgel network. We believe that when composite microgel particle is in swollen state PPy domains are not really located on the surface, but embedded into VCL-rich shell. Therefore the effect which we measure is actually a result of the charge compensation of bare PPy particles and microgel network.

**Fig.5.2.14:** Variation of the $\xi$-potential of microgel (run 3) (1) and corresponding composite microgels filled with 3.04% (2), 8.68 % (3) and 14.23 % PPy (4).

Electron microscopy image and AFM images of composite microgels are shown in Fig.5.2.15 and Fig.5.2.16, respectively. Microgel particles in these images are in the dried state, so the diameter is nearly 2 times less than what was measured by DLS in water solution due to the shrinkage of the VCL/AAEM polymer network. The morphology of the composite particles is quite interesting: small polypyrrole domains are incorporated into microgel network, which acts as support for this complicated structure providing spherical shape for whole composite.

**Fig.5.2.15:** SEM image of composite microgels filled with 16.33 % PPy (run 16).
Fig. 5.2.16: AFM images for composite microgels filled with 16.33 % PPy (run 16) made in tapping mode: (a) height images and (b) phase images.

It can be also seen that if microgel is in deswollen state polypyrrole inclusions touch with each other. Probably, in water solution the situation is different and polypyrrole particles are separated by highly swollen polymer chains of the microgel template.

5.2.3.3 Influence of the reaction temperature

Selected pyrrole polymerizations were also performed at different temperatures. It is expected that at different reaction temperatures microgel template will be in different swelling state: lower temperature will induce swelling of the microgel and higher temperature will provide contraction of the network. In this way, the particle number
remains constant, but the effective surface area and the porosity of the microgel template can be changed. For this set of experiments microgels containing 4.8 mol% and 11.8 mol% AAEM (runs 2 and 4 respectively) were selected and the pyrrole concentration was constant (see Tab.5.2.6). Reactions were performed at 10, 20 and 30 °C.

Tab.5.2.6: Composite microgels prepared at different temperatures.

<table>
<thead>
<tr>
<th></th>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>17</td>
<td>11.8</td>
<td>0.05</td>
<td>30</td>
<td>9.43</td>
<td>9.04</td>
<td>95.9</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>11.8</td>
<td>0.05</td>
<td>20</td>
<td>9.43</td>
<td>6.55</td>
<td>69.5</td>
<td>+</td>
<td>212.7</td>
<td>122.0</td>
<td>1.74</td>
</tr>
<tr>
<td>18</td>
<td>11.8</td>
<td>0.05</td>
<td>10</td>
<td>9.43</td>
<td>5.64</td>
<td>59.8</td>
<td>+</td>
<td>215.9</td>
<td>125.6</td>
<td>1.72</td>
</tr>
<tr>
<td>19</td>
<td>4.8</td>
<td>0.1</td>
<td>30</td>
<td>16.67</td>
<td>16.60</td>
<td>99.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>16</td>
<td>4.8</td>
<td>0.1</td>
<td>20</td>
<td>16.67</td>
<td>16.33</td>
<td>97.9</td>
<td>+</td>
<td>260.5</td>
<td>142.7</td>
<td>2.02</td>
</tr>
<tr>
<td>20</td>
<td>4.8</td>
<td>0.1</td>
<td>10</td>
<td>16.67</td>
<td>15.87</td>
<td>95.2</td>
<td>+</td>
<td>261.8</td>
<td>144.5</td>
<td>1.81</td>
</tr>
</tbody>
</table>

* - determined by elementary analysis; + stable; - unstable

Tab.5.2.6 indicates that experiments performed at 30 °C failed independently on microgel composition and pyrrole amount used. Obtained dispersions were unstable and precipitated immediately when oxidant was added and pyrrole polymerization took place. Colloid stability depends upon the balance of van der Waals attraction, which causes aggregation, and steric or electrostatic forces that oppose aggregation. Below LCST VCL/AAEM microgels are swollen and polymer tails extend from the microgel structure to act as steric stabilizers enhancing colloidal stability. At elevated temperatures the water content of the microgels is reduced to give a higher density and thus a greater Hamaker constant than that at low temperature. Above LCST polymer tails on the microgel surface will be collapsed and thus not contribute to colloidal stability. The electrical charges which originate from the ionic free radical initiator can play more dominant role in stabilization of colloidal system. Addition of electrolyte induces the compression of double layer and coagulation of VCL/AAEM microgels takes place.

Results of particle size shrinkage for samples prepared at different temperatures presented in Tab.5.2.6 indicate no considerable difference. It seems, that the swelling degree of the VCL/AAEM template during pyrrole polymerization has no strong influence on particle size and temperature-induced contraction of composite particles.
The progress of oxidation is conveniently followed by the temperature changes. Fig.5.2.17 shows the temperature profile of the exothermic oxidation of pyrrole at different reaction temperature. It can be investigated from Fig.5.2.17 that the induction period of the polymerisation at 20 °C is shorter than that at 5 °C, which indicates that at higher temperature the pyrrole polymerization process is faster than that at low temperature. It is also logical as we know the mobility of the molecules is decreased with the decrease of the temperature, that’s why the reaction runs slowly at lower temperature \[^{[136]}\].

5.2.3.4 Influence of reaction medium

- Behaviour of VCL/AAEM microgels in ethanol:water mixtures

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.5.2.28 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.5.2.18 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.5.2.18 correlates with minimum in phase diagram of linear PVCL in water:ethanol mixture reported by Kirsh et al. \[137\]. Fig.5.2.19 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.5.2.18) 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.

From experimental data presented in Fig.5.2.19 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 Fig.5.2.18 and Fig.5.2.19. Experimental results confirm this idea. Fig.5.2.20 presents the hydrodynamic radii of VCL/AAEM microgel as a function of the temperature measured in different ethanol : water solutions (see arrows in Fig.5.2.18).
Fig. 5.2.20: 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-% ethanol).

Fig. 5.2.20 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 became broader and disappears in the mixture, which is good solvent for whole temperature range. It should be noted that microgel never riches 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 \[138,139]. 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.

- Polymerization of pyrrole

In this reaction set pyrrole polymerization was carried out in different reaction mediums c.a. ethanol concentration was increased gradually and initial pyrrole concentration as well as the oxidant concentration (persulfate) were kept constant. The
VCL/AEM microgel with 6.7 mol-% AEM and hydrodynamic radius $R_h^{20°C}=250$ nm (run 3) has been used as a template for pyrrole polymerization. Detailed reaction recipes are shown in Tab.5.2.7 and Tab.5.2.9. Tab.5.2.8 and 5.2.10 contain theoretically predicted and experimentally determined PPy amounts in composite particles as well as some other important characteristics such as conversion, stability of dispersions etc.

Tab.5.2.7: Synthesis parameters for reactions performed with Na$_2$S$_2$O$_8$ as oxidant.

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<th>Ethanol, [mol-%]</th>
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Tab.5.2.8: Properties of composite particles prepared with Na$_2$S$_2$O$_8$ as oxidant.

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T – theoretically predicted; P – determined by elementary analysis
Tab.5.2.9: Synthesis parameters for reactions performed with FeCl₃ as oxidant.

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Tab.5.2.10: Properties of composite particles prepared with FeCl₃ as oxidant.

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<td>54,13</td>
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T – theoretically predicted; P – determined by elementary analysis

Fig.5.2.21 presents the morphology of obtained particles. It is evident that increase of the ethanol content in the reaction medium leads to more smooth 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 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\textsuperscript{[14]}. 

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Fig.5.2.21: SEM images of composite microgels prepared in: (a) water (PPy load – 26.18%), (b) 4.2 mol-% ethanol (PPy load – 27.97%), (c) 14.4 mol-% ethanol (PPy load – 29.4%).

Fig.5.2.21 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.5.2.21. 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.5.2.18. In this case addition of ethanol induces collapse of microgel, and therefore the final size of composite particles decreases. Tab.5.2.8 indicates that up to 14.4 mol-% ethanol in the solution the final PPy conversion is quite high. Only when 28.1 mol-% ethanol-water mixture was used conversion decreases rapidly to 55%. 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.

![Temperature profile of the exothermic oxidation of pyrrole](image)

**Fig.5.2.22:** Temperature profile of the exothermic oxidation of pyrrole at different reaction medium (a) with and (b) without microgel with 4,8 mol-% AAEM.

The polymerization kinetics of Py can be also influenced by presence of ethanol molecules. Fig.5.2.22 shows the temperature profile of the exothermic oxidation of pyrrole at different reaction medium with and without microgel. After an induction period, polymerization commences and the temperature of the reaction mixture increases, it passes through a maximum after the reaction is finished, and the medium cools down. From Fig.5.2.22(a), it can be observed that when the reaction is made in 28,1 mol-% ethanol solution by using microgel as the template, the induction period is quite long and pyrrole polymerization starts in 50 minutes after adding the oxidant. And the formation of PPy is accelerated with decrease of the ethanol amount in the reaction medium. The reaction in water runs fastest in all cases. Similar results can be
also got for the oxidation of pyrrole without microgel (see in Fig.5.2.22(b)). B. M. Mandal et al. [16] has investigated the polymerization rate \( R_p \) of polypyrrole in different mediums by using PVME as the stabilizer. It is reported that the \( R_p \) is decreased greatly when the medium is changed from 50 % ethanol to absolute ethanol.

- 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.

![Fig.5.2.23: Hydrodynamic radius of composite microgels prepared with different Py contents (T=20°C; 1- SPDS; 2 - FeCl\(_3\)).](image)

The particle size of obtained composite particles was analysed by DLS. Experimental results are presented in Fig.5.2.23. It is clear that the behaviour of the particle size is very similar to that of measured in water: 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 when Py was polymerized in water, composite particles are stable even when the PPy load is 40 %. This effect can be explained by enhanced stability of the microgel template in water:ethanol solution. Fig.5.2.23 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.
(Tab.5.2.9 and Tab.5.2.10) due to the complexation of the oxidant with alcohol molecules. At higher PPy load dispersions prepared with FeCl₃ show bimodal particle size distribution. Fig.5.2.24 shows particle size distribution of composite microgels prepared with different oxidants at low and high PPy load.

![Particle size distribution of composite microgels prepared with different PPy contents (PPy loads: a) 2,25 % and 6,72 %; b) 25,4 % and 35,13 % for FeCl₃ and SPDS respectively).](image)

At low PPy load no secondary particle formation was detected for runs performed with persulfate and FeCl₃. Contrary bimodal particle size distribution shown in DLS spectrum on Fig.5.2.24(b) indicates clearly that secondary PPy particles are formed in reaction system at high pyrrole concentrations when FeCl₃ is used as oxidant.

Fig.5.2.25 shows SEM images of composite particles prepared with different oxidants. Samples prepared with FeCl₃ 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.
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.

**Fig.5.2.25:** SEM images of composite microgels prepared with SPDS: (a) 6,72 % PPy, (b) 16,35 % PPy, (c) 41,12 % PPy and FeCl$_3$: (d) 2,25 % PPy, (e) 10 % PPy, (f) 26,64 % PPy.

### 5.2.3.5 Conductivity of composite microgels

The conductivity of composite microgels prepared with different PPy contents was measured by 2-point method. Experimental results are presented in Fig.5.2.26. 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. Tab. 5.2.11 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 Tab.5.2.8 the final Py polymerization yield 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 FeCl₃ was used as oxidant. This supports the idea that the oxidation power of SPDS and FeCl₃ in water:ethanol mixtures is reduced. Similar observations were reported by Mandal et al. [12] when pyrrole was polymerized in water:ethanol mixtures or in pure ethanol with FeCl₃. The low level of conductivity was explained by complexation of FeCl₃ 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 FeCl₃ concentration [140].

Tab.5.2.11 indicates also that composite particles prepared with FeCl₃ 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 [141,142] 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.5.2.27 indicates that the reaction temperature has strong influence on the morphology of composite particles.

**Tab.5.2.11:** Influence of the reaction temperature, oxidant nature and reaction medium on conductivity of the composite particles.

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Fig.5.2.27: SEM images of composite microgels prepared with: (a) FeCl₃ (24,6 % PPy), (b) SPDS (43,09 % PPy) (28,1 mol-% ethanol; T=0°C)

Images in Fig.5.2.27(a) and (b) can be directly compared with electron micrographs presented previously in Fig.5.2.25 (f) and (c) respectively. When SPDS has been used as oxidant particle morphology is not influenced by reaction temperature. Contrary, composite particles prepared with FeCl₃ at lower temperature show dramatic increase of polydispersity and particles 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 can’t 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.

**Conclusions**

- When crosslinked PVME microgels were used in the oxidation polymerization of pyrrole, 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.

- When VCL/AAEM microgels were used as a template for oxidative polymerization of pyrrole, different PPy amounts can be incorporated into microgel structure. It was found that pyrrole polymerization takes place directly in microgel network leading to formation of composite particles. It seems, that PPy particles interact strongly with VCL/AAEM network and this leads to the change of microgel diameter if the filler content increases. Obtained stable composite microgels show similar thermal sensitivity as VCL/AAEM particles with fully reversible collapse-swelling properties.

- 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. 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.

- 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.
5.3 Core-shell type PPy composite particles

5.3.1 Introduction

Besides the preparation of sterically stabilized dispersions of PPy particles, the chemical synthesis of conducting polymer-coated polymer particles, where the “core” is a nonconducting polymeric material, has been reported by several groups \cite{10,29,143,144,145}. If the conducting polymer overlayer is continuous, relatively high conductivities can be obtained even at very low conducting polymer loadings. Furthermore, the latex particles have a much wider size range compared to the rather limited size range of sterically stabilized conducting polymer colloids (30-300 nm) \cite{146}. Yassar et al. have described the synthesis of polypyrrole-coated polystyrene latexes by the polymerization of pyrrole in the presence of PS particles having sulfonic or carboxylic groups at the surface \cite{26}. Although the approach of Yassar et al. met some criticisms concerning the stability of the end particles, it nevertheless paved the way towards the general method of thin conducting polymer coatings onto the preformed latex particles resulting in “core-shell” particles. The core-shell morphology of the coated polymers was evidenced from transmission electron microscopy (TEM) and also from both aqueous electrophoresis and dielectric measurements \cite{35,147}.

The scope of present study was to prepare composite particles with dielectric cores and conducting shells. Synthesis of composites was examined in two stages: 1) preparation of monodispersed polystyrene particles with appropriate surface and controlled size; and 2) deposition of polypyrrole by oxidative polymerization process. Praxis shows that most important step in this case is preparation of core particles or templates, because the morphology of the template and nature of the surface layer is quite important for successful incorporation of polypyrrole and also has strong influence on the properties of composite particles \cite{148,149}.

5.3.2 PS-PEGMA core

5.3.2.1 Preparation of PS-PEGMA core

The reaction recipe for emulsion polymerizations performed in this study is summarized in Tab.5.3.1. In all runs the final monomer conversion was around 95%.
The incorporation of the PEGMA into the latex particles was determined by IR analysis indicating nearly quantitative yield ($S$). Dispersions prepared with water soluble initiators were stable and no precipitation was observed during storage. When AIBN was used in the polymerization recipe, the compact coagulum was formed independently on PEGMA content.

**Tab.5.3.1:** Amounts of ingredients used in emulsion polymerization (reaction temperature – 70°C).

<table>
<thead>
<tr>
<th>N</th>
<th>ST, [g]</th>
<th>PEGMA, [g]</th>
<th>PEGMA, [wt-%]</th>
<th>Crosslinker, [g]</th>
<th>Initiator, [g]</th>
<th>Water, [g]</th>
<th>$S$, [%]</th>
<th>pH</th>
<th>$\sigma$, [mN/m]</th>
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<td>180</td>
<td>coagulum</td>
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<td></td>
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<tr>
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<td>2</td>
<td>10</td>
<td>-</td>
<td>0.3***</td>
<td>180</td>
<td>coagulum</td>
<td></td>
<td></td>
</tr>
<tr>
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<td>16.9</td>
<td>3.1</td>
<td>15.5</td>
<td>-</td>
<td>0.3***</td>
<td>180</td>
<td>coagulum</td>
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<td></td>
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<td>2.5</td>
<td>0.025[**]</td>
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<tr>
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<td>0.3**</td>
<td>180</td>
<td>92.06</td>
<td>4.52</td>
<td>59.50</td>
</tr>
</tbody>
</table>

* - Na$_2$S$_2$O$_8$; ** - 2,2’-azobis(2-methylpropionamidine) dihydrochloride (AMPA); *** - AIBN
# - DVB; ## - DEGMA

5.3.2.2 Characterization of PS-PEGMA core

Measured surface tension values of stable PS latexes decrease with increasing PEGMA content in the system indicating that more PEGMA is grafted onto particle surface. According to Fig.5.3.1 PEGMA shows certain surface-active properties, however its surfactant properties are rather poor. This behaviour is not surprising since PEGMA molecule has no defined hydrophobic part, which is typical for conventional surfactants. However, one can see two break points on $\sigma - c_{\text{PEGMA}}$
dependency, which can be related to the formation of some aggregates in solution. The PEO chain in PEGMA structure provides good solubility in water and the presence of OH-groups can result in appearance of hydrogen bonds. These hydrogen bonds can be a reason for aggregation in water and formation of “classical” micelles in water solution is not in this case.

The failed experiments with AIBN as initiator indicate that there is no stabilization effect from PEGMA if the polymerization is initiated in monomer droplets. Contrary, with water soluble initiators stable dispersions were prepared even at very low PEGMA content. Of course, in this case we should also take into consideration the presence of ionic sulphate groups on the particle surface, which can improve the stability of particles.

A surprising effect can be observed when the average hydrodynamic radii of obtained particles prepared with Na₂S₂O₈ as initiator are plotted as the function of the PEGMA concentration in reaction mixture (Fig.5.3.1).

**Fig.5.3.1:** Dependency of surface tension and final $<R_h>$ (DLS) of obtained dispersions from the PEGMA concentration in the system (a). The ratio of $<R_g>/<R_h>$ calculated by using DLS and F-FFF-MALLS (solid symbols) or SLS (open symbols) (b).
Fig. 5.3.1a indicates that the size of latex particles decreases when PEGMA amount in reaction mixture increases. This behaviour is typical also for low molecular weight (LMM) surfactants, since increase of the stabilizer amount allows system to increase the total surface area, e.g. particle size decreases. However, particle size suddenly starts to rise up when the PEGMA concentration in reaction mixture is close to the end of first plateau on $\sigma - c_{\text{PEGMA}}$ curve, reaches the maximum and decreases again with decrease of the surface tension. This effect can be speculatively explained by appearance of organized structures in solution at ca. 8 g/l which can increase the solubilization of monomer and consequently the final dimensions of particles. Static light scattering measurements indicate that $<R_g>$ of measured samples behaves similar to $<R_h>$. The ratio $<R_g>/<R_h>$ calculated for experimental data from F-FFF-MALLS and SLS measurements seems to be not dependent on PEGMA concentration and is close to the theoretical value for spherical particles (see Fig. 5.3.1b), so the effects discussed above do not change the particle morphology.

**Fig. 5.3.2:** Experimental F-FFF-MALLS data: a) elution intensity vs time diagram for sample prepared at 5 wt.% PEGMA; b) $<R_g>$ as the function of cummulative mass fraction for samples prepared with different PEGMA contents.
F-FFF-MALLS measurements indicate that by using PEGMA as reactive surfactant nearly monodisperse particles can be obtained. Fig.5.3.2a shows the intensity-elution time diagrams of sample prepared at 5 wt.-% PEGMA as a function of the scattering angle. First peak in the elutgram corresponds to the void peak, second signal is related to the intensity of scattered light by particles when they pass the measuring cell. For large particles typical increase of the scattered intensity at lower angles can be observed.

Cumulative mass distribution curves for some selected samples presented in Fig.5.3.2b indicate that particle size distribution (PSD) did not change with PEGMA content up to 7,5 wt.-% PEGMA. Latex prepared at 10 wt.-% PEGMA shows broadening of PSD. Tab.5.3.2 shows the PSD values of PS/PEGMA dispersions calculated from F-FFF-MALLS and SEM experimental data.

<table>
<thead>
<tr>
<th>Sample</th>
<th>PEGMA, [wt.-%]</th>
<th>(R_{90}-R_{10})/R_{50}</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>0.015</td>
<td>1.005</td>
</tr>
<tr>
<td>2</td>
<td>1.5</td>
<td>0.016</td>
<td>1.006</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>0.014</td>
<td>1.004</td>
</tr>
<tr>
<td>4</td>
<td>2.5</td>
<td>0.015</td>
<td>1.005</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>0.022</td>
<td>1.006</td>
</tr>
<tr>
<td>6</td>
<td>5.85</td>
<td>0.0023</td>
<td>1.007</td>
</tr>
<tr>
<td>7</td>
<td>7.5</td>
<td>0.027</td>
<td>1.014</td>
</tr>
<tr>
<td>8</td>
<td>8.55</td>
<td>0.040</td>
<td>1.041</td>
</tr>
<tr>
<td>9</td>
<td>10</td>
<td>0.039</td>
<td>1.034</td>
</tr>
<tr>
<td>10</td>
<td>12</td>
<td>0.047</td>
<td>1.057</td>
</tr>
<tr>
<td>11</td>
<td>15.5</td>
<td>0.051</td>
<td>1.084</td>
</tr>
</tbody>
</table>

Note that increase of the PSD with increase of PEGMA content correlates with the inversion point which was observed in Fig.5.3.1. We suppose that the homogeneous nucleation mechanism is dominant in present system at low PEGMA concentrations. Broadening of the PSD can be attributed to the increased influence of micellar nucleation mechanism if indeed some aggregates are formed in water at this concentration.
Fig. 5.3.3: SEM images of particles prepared at different PEGMA contents: (a) 1wt.-%, (b) 1.5wt.-%, (c) 2.5wt.-%, (d) 5wt.-%, (e) 7.5wt.-%, (f) 10wt.-%, (g) 12wt.-%, (h) 15.5 wt.-%. AFM image (j) of sample prepared at 1 wt.-% PEGMA: height profile is taken along the line shown on the top view image (size: 4 × 4 µm).
SEM images presented in Fig.5.3.3 indicate the regular spherical shape of obtained particles. It is clear that particle size decreases if the amount of PEGMA in the system increases. At 10 wt.-% PEGMA particle size increases again and this is in accordance with DLS measurements. Up to 7,5 wt.-% PEGMA the particle size decreases without change of polydispersity. Small particles appear in the image when the PEGMA content is 10 wt.-% (see arrows), and this correlates with F-FFF measurements. It is also good to see that starting from this PEGMA concentration particles are slightly deformed in the image and look like soft spheres. When PEGMA concentration reaches 15,5 wt.-% particle surface is completely deformed in the image and PSD is really broad.

AFM image of sample prepared at 1 wt.-% PEGMA and corresponding height profile indicate the uniform particle size (510 nm), which can be measured from the average distance between two adjacent triangles that indicate the particle sides. At higher magnifications the surface of the particles appears relatively smooth both in SEM and AFM images (Fig.5.3.4). It is also interesting to note that particle surface is not really hard and neighbour particles are connected with bridges. We believe that particle surface consists of PEGMA-rich copolymers with styrene, which have much lower glass transition temperature than polystyrene.

![AFM image](image)

**Fig.5.3.4:** SEM (a) and AFM (b) images of particles prepared at 1 wt.-% PEGMA.

As a summary, particle size measurements with different methods are presented in Fig.5.3.5. It is good to see that there is a good correlation between experimental data obtained by different methods. Sudden increase of the particle size after 7,5 wt.-% PEGMA seems to be not a measurement mistake and not the result of particle aggregation.
Fig.5.3.5 shows an excellent correlation between experimental $<R_g>$ data from MALLS detector coupled to F-FFF and SLS. Particle radii obtained from SEM measurements are considerably smaller than $<R_h>$ from DLS measurements indicating the shrinkage of the hydrodynamic shells around particles during drying process.

Since the initiator concentration was kept constant in every run, the particle size and morphology are determined by the concentration of PEGMA in reaction mixture. Additionally it should be noted that up to 5 wt.-% PEGMA obtained particles are completely soluble in THF. GPC measurements indicate extremely broad distribution ($M_w/M_n \sim 6$) and molecular weight increases with increasing PEGMA content in the system. At higher PEGMA contents the particles are not soluble even if no crosslinker was used. This effect is due to the high tendency of PEGMA to chain transfer reactions [150], which leads to the crosslinking of PEGMA-rich surface layer of the particles. As it will be shown later, this crosslinking effects influence strongly the properties of particles.

- Thermal behaviour

The surprising feature of obtained particles is their thermal sensitivity. The particle size of obtained samples was measured by means of DLS at elevated temperatures (Fig.5.3.6). At every temperature samples were measured 10 times and the average value was determined.
Sample prepared at 1 wt.-% PEGMA shows slight decrease of the particle size after 25 °C and rapid decrease after 45 °C. Around 50 °C the sample is losing stability in water. Sample prepared at 2.5 wt.-% PEGMA shows rapid decrease of the particle size in range of 25 – 45 °C. Then a kind of plateau is reached and from 55 °C particle size decreases again. It should be noted, that during this measurements the PSD remains nearly constant, so samples are quite stable and no aggregation was observed. Contrary, sample prepared at 10 wt.-% PEGMA shows no changes of the particle size with temperature. Crosslinked sample was prepared at 2.5 wt.-% PEGMA by adding the crosslinker (DVB) to the monomer. In this case obtained particles were considerably smaller if to compare with similar sample prepared without DVB. The particle size in this case is also not temperature sensitive as it can be seen in Fig.5.3.6. If we assume, that obtained particles possess core-shell structure and compare all samples in Fig.5.3.6, the crosslinking of the PS-rich core and crosslinking of PEGMA-rich shell leads to the disappearance of thermal sensitivity. Wu et al. [151, 152] observed the collapse of the PEO chains grafted onto PNIPAM particles. This transition was detected at 33 °C after total collapse of the PNIPAM core and explained in terms of \( n \)-clustering attractive interaction model at higher grafting densities [153].

Another interesting observation is that the cooling run of the same probe results in remarkably higher particle diameters, however in range 10 – 25 °C detected particle sizes are similar for both heating and cooling runs (see Fig.5.3.7a).
Fig. 5.3.7: Temperature dependence of a) $\langle R_g \rangle$; $\langle R_h \rangle$ for sample prepared with 2.5 wt.-% PEGMA and b) correspondent ratio $\langle R_g \rangle / \langle R_h \rangle$ for heating run.

The $\langle R_g \rangle$ measured by SLS is nearly not influenced by the temperature and cooling-heating cycle. This leads to the increase of $\langle R_g \rangle / \langle R_h \rangle$ values, (see Fig. 5.3.7b) and at elevated temperatures $\langle R_g \rangle / \langle R_h \rangle$ ratio is much higher than 0.774 predicted for nondraining and uniform sphere. It seems, that we observe the shrinkage of highly swollen hydrodynamic shell around particles with increasing temperature which changes partially the particle morphology.

Tab. 5.3.3 shows the results of DLS measurements of different samples performed at 20 and 60 °C and calculated shrinkage of the particle diameter ($\Delta D$). Samples prepared at PEGMA content lower than 2 wt.-% showed aggregation at high temperature. Samples prepared at higher PEGMA contents were quite stable and $\Delta D$ decreases gradually as PEGMA content is rising up. When DVB (5 % to ST) was
used as crosslinker, we observed no changes of the diameter with heating. Contrary, when DEGMA was added to the reaction mixture (5 % to PEGMA) $\Delta D$ value is still high, but slightly lower if to compare with sample prepared without any crosslinker. When the water-soluble azo- initiator was used instead of persulphate, smaller particles were obtained and $\Delta D$ was also considerably high.

<table>
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<th>PEGMA, [wt.-%]</th>
<th>Initiator type</th>
<th>Crosslinker type</th>
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<th>$D_h$ &lt;sub&gt;60°C&lt;/sub&gt;, [nm]</th>
<th>$\Delta D_h$, [nm]</th>
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<td>aggr</td>
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<td>219,1</td>
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It is expected, that the rheological properties of investigated dispersions can be also influenced by the temperature. Shrinkage of the particle size at elevated temperatures will reduce the effective volume fraction and interparticle distance at constant particle number in the system. This will reduce particle interactions and viscosity of the dispersion when the stability of particles is high enough to avoid aggregation. Some effects of the particle size distribution on the rheology of investigated dispersions can be excluded for samples prepared at lower PEGMA contents which show narrow PSD. Temperature-dependent measurements were performed at constant shear stress in temperature range 20-70 °C. At elevated temperatures dispersions behave like non-Newtonian liquids. Samples prepared at PEGMA contents lower than 2 wt.-% coagulated at higher shear rates with increasing the measurement temperature. Fig.5.3.8 shows the change of the viscosity of dispersion with temperature as a function of shear stress for sample prepared at 2,5 wt.-% PEGMA.

Fig.5.3.8 indicates that the experimental viscosity data decreases gradually with the temperature. Obtained viscosity-temperature dependencies are similar to the change of $<R_h>$ with temperature (compare with Fig.5.3.7). Experimental curves indicate no
aggregation effects and this is in accordance with our light scattering experiments. Fig.5.3.8 indicates that the viscosity decrease follows nearly linear dependency. It is good to see that the plateau of constant viscosity is shifted to lower temperatures when measurement is performed at higher shear stress. This can be explained by enhanced possibility of the interparticle interactions and formation of organized particle structures in solution at higher shear stress. To our surprise, similar measurements performed at constant shear stress with dispersions prepared at different PEGMA contents show no dramatic influence of the particle size on viscosity-temperature curves.

The unusual thermal behaviour of PEGMA-functionalized particles can be explained in following way. First of all it is necessary to consider the mechanism of this batch polymerization process. A two-step mechanism for similar monomers was proposed by Kawaguchi et al. [154,155]. Pichot et al. [156,157] confirmed this mechanism for system styrene-NIPAM. At lower PEGMA concentrations in presence of water soluble initiator the polymerization in water phase proceeds probably via homogeneous nucleation mechanism, because the functional monomer has a low ability to form defined micelles in water. Considering much higher reactivity of PEGMA if to compare with styrene, in initial stages of polymerization formed oligo-radicals will contain more PEGMA units. This will lead to the enhanced heterogeneity of the copolymers formed in water. Further addition of styrene units can provide formation of amphiphilic polymer chains which can effectively stabilize the polymerization of
residual styrene in the core of formed nuclei. So, the final particle consists, probably of PS-rich dense core and more diffuse PEGMA-rich shell. It can be also assumed, that the structure of the polymer chains close to the particle surface is brush-like (hydrophobic main chain and short hydrophilic branches). These brushes can be stretched due to the repulsion between the negatively charged initiator groups which are incorporated in polymer structure and their solubility in water is maintained by short PEGMA-branches. Schematically this structure is presented in Fig.5.3.9. If the temperature increases, the PEO segments lose partly their solubility in water \[^{158}\] and this induces the brush-like surface layer to shrink, and when there is no sufficient PEGMA amount on the particle surface coagulation takes place.

When particles were prepared at high PEGMA concentrations, the PEGMA-rich surface layer is crosslinked and this decreases the mobility of the chains leading to no significant change of particle dimensions with heating. TEM image in Fig.5.3.10 indicates clearly the presence of PEGMA-rich shells (light areas) surrounding dark polystyrene cores. Particles prepared at high PEGMA amounts remain stable at elevated temperatures, because no real phase separation on the surface occurs.

![Fig.5.3.9: Schematic representation of the internal structure of PEGMA-functionalized particles.](image-url)
Fig.5.3.10: TEM image of sample prepared at 7.5 wt.-% PEGMA.

Fig.5.3.11a demonstrates that the particle size of PS-PEGMA particles can be effectively varied by fleet-ratio ($W_p/W_m$) or the macroscopic weight ratio of polymeric stabilizer PEGMA ($W_p$) to monomer ST ($W_m$).

![Graph a](image)

![Graph b](image)

Fig.5.3.11: Fleet-ratio ($W_p/W_m$) dependence of the hydrodynamic radius ($R_h$) of the PS-PEGMA particles (a); Plot of $[RW_p/(W_m + W_p)]^{1/2}$ vs $1/R_h$ on the basis of Eq.5.3.1 (b).
Fig. 5.3.11a indicates that by adding more PEGMA molecules larger particle surface can be stabilized, which means the decrease of the particle size and increase of particle number in dispersion. Recently Wu’s group reported structural model for surfactant/monomer microemulsion \(^{[159]}\) and surfactant-free macromonomer/monomer emulsion \(^{[160,161]}\) systems which presents quantitative relation between the particle size and the fleet-ratio. This model described by Wu and co-workers suggests that for a given type of stabilizer and monomer, the surface area \((s)\) occupied by each stabilizer molecule is a fundamental parameter for the control of the particle size. The relation between stabilizer/monomer fleet-ratio \((W_p/W_m)\) and surface area \((s)\) is expressed by following equation:

\[
\left\{ \frac{R_h W_p}{W_m + W_p} \right\}^{1/2} = \left[ s \frac{N_A \rho}{3 M_p} \right]^{-1/2} \left( 1 - \frac{b}{2 R_h} \right)
\]

Eq. 5.3.1

where \(R_h\) is hydrodynamic radius of particles; \(N_A\) is Avogadro’s constant; \(\rho\) is the average density of microspheres; \(M_p\) is molar mass of stabilizer; and \(b\) is the thickness of the stabilizer shell layer. Analysing Eq. 5.3.1 it is clear that if \(s\) is constant \(\left( RW_p/(W_m + W_p) \right)^{1/2}\) will be also nearly constant in case if \(b << 2R_h\). This situation was observed in \(^{[161]}\) for PS microspheres stabilized by poly(ethylene oxide) macromonomers. Applying Eq. 5.3.1 to our system we can conclude from Fig. 5.3.11b that surface area occupied by PEGMA molecules on particle surface is not constant. Increase of \(\left( RW_p/(W_m + W_p) \right)^{1/2}\) when PS-PEGMA particles became smaller indicates that according to Eq. 5.3.1 \(s\) should decrease indicating that PEGMA molecules should be more densely packed on the particle surface. This will induce increase of the surface layer thickness \(b\) and when \(R_h\) continuously decreases condition \(b << 2R_h\) will be not satisfactory. So, from these theoretical considerations we can conclude that in present system particle size of PS-PEGMA particles can be varied by stabilizer/monomer fleet-ratio \((W_p/W_m)\) and the thickness of PEGMA-rich shell increases gradually when \(R_h\) decreases.
Calculated total surface area of polymeric particles in different samples indicates again that adding more macromonomer can stabilize more particle surface, resulting in smaller microspheres. The special feature of PS-PEGMA system is that decrease of the particle size is followed by increase of hydrophilic PEGMA-rich shell. This fact is extremely important if we consider PS-PEGMA particles as templates for deposition of other material e.g. polypyrrole. It is expected that PEGMA-shell should play an important role in successful incorporation of conducting polymer and morphology of composite particles.

5.3.3 Composite PS-PEGMA-PPy particles

5.3.3.1 Preparation of PS-PEGMA-PPy particles

Polypyrrole was deposited onto PS-PEGMA particle surface by oxidative pyrrole polymerization directly in presence of pre-formed polymeric cores. Tab.5.3.4 summarizes details of preparation of composite particles. The values of loaded polypyrrole (PPy\(^T\)) were determined by elementary analysis. Comparison with theoretically expected values presented in Tab5.3.4 indicates that in all cases pyrrole polymerization was characterized by high yield. Samples prepared with FeCl\(_3\) and H\(_3\)PMo\(_{12}\)O\(_{40}\)-29H\(_2\)O show low PPy loads because reaction was terminated before all pyrrole molecules were consumed (more explanations will be
given in later discussion). In first set of samples (S-1 – S-7) different polypyrrole amounts were deposited onto PS-PEGMA particles containing 2,5 % PEGMA ($R_b = 240,7 \text{ nm}$). Similarly, samples (Mo-13 – Mo-17) are prepared by using Molybdate as the oxidant and with different polypyrrole deposition amount. In second set (S-8 – S-11) loaded pyrrole amount was constant but particles with different PEGMA contents (from 1,5% to 12,5%) and different dimensions were applied as core material. Finally, a few reactions were performed with similar core particles but different oxidation agents. Samples Fe-12 and Mo-13 can be directly compared with sample S-9. Last three reactions have been performed to study the polymerization kinetics and in this case loaded PPy amount was increased by reducing amount of core particles in the system.

**Tab.5.3.4:** Preparation of composite particles.

<table>
<thead>
<tr>
<th>N</th>
<th>$R_b$, [nm]</th>
<th>PEGMA, [wt.-%]</th>
<th>Latex, [g]</th>
<th>Pyrrole, [g]</th>
<th>Oxidant, [g]</th>
<th>Water, [g]</th>
<th>Load PPy$_T$, [%]</th>
<th>Load PPy$_P$, [%]</th>
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<tr>
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<td>1,70**</td>
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<td>0,96***</td>
<td>20</td>
<td>15</td>
<td>2,10</td>
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</tbody>
</table>

* - Na$_2$S$_2$O$_8$; ** - FeCl$_3$; *** - H$_3$PMo$_{12}$O$_{40}$.29H$_2$O
First two reaction sets should show the influence of the deposited polypyrrole amount, total surface area of PS-PEGMA particles and the thickness of PEGMA layer on properties of final composites. By changing the oxidant we can control the kinetics of the pyrrole polymerization and change the thickness of PPy shell and nature of dopant anion.

5.3.3.2 Characterization of PS-PEGMA-PPy particles

Qualitatively deposition of polypyrrole on PS-PEGMA particle surface can be observed by FTIR spectroscopy. Fig.5.3.13 shows part of FTIR spectra (1500 – 400 cm\(^{-1}\)) of samples S-2 and S-3 with loaded 4.5 % and 6.41 % PPy, respectively as well as spectrum of PS-PEGMA core.

![FTIR spectra of PS-PEGMA core (1) and composite particles with loaded 4.5 % (2) and 6.41 % (3) polypyrrole.](image)

Presence of PPy in composites results in characteristic signals which can be observed in IR spectra of composite particles (signals marked with arrows in Fig.5.3.13). The band of the C-N stretching vibration in the ring should appear at 1459 cm\(^{-1}\), but is overlapped by the doublet of the C-H bending vibration of polystyrene. The broad band from 1400 to 1275 cm\(^{-1}\) is attributed to the C-H or C-N in-plane deformation modes (maximum located at 1322 cm\(^{-1}\)). The broad signal from 1250 to 1140 cm\(^{-1}\) corresponds to breathing vibration of the pyrrole ring (maximum located at 1200 cm\(^{-1}\)). In-plane deformation vibration of N\(^+\)H\(_2\) which is formed due to the protonation of PPy chains shows peak at 1100 cm\(^{-1}\)\[^{[162]}\]. Peaks at 1037 and 910 cm\(^{-1}\) corresponds to N-H in-plane and C-C out-of-plane ring deformation vibration, respectively. It can
be also observed that typical polystyrene doublet signals at 1495.3 - 1453 cm\(^{-1}\) (C-H bending vibration) and 754.9 - 699.1 cm\(^{-1}\) (C-H out-of-plane bending) appear smaller if PPy load increases.

The morphology of composite particles was investigated in details by SEM and AFM. SEM images of samples prepared at different PPy loads (samples S-1 – S-7) are presented in Fig.5.3.14. It can be clearly observed that increase of PPy content increases the surface roughness of composite particles. Additionally, at higher PPy loads (starting from 11.06 %) formation of secondary polypyrrole particles was detected. These secondary particles are not attached to the PS-PEGMA core surface and cause partial destabilization of colloidal system by formation of flocks in water solution. Similar tendency has also been observed for the morphology of PPy composite particles prepared by using H\(_2\)PnMo\(_{12}\)O\(_{40}\)·29H\(_2\)O as the oxidant (see in Fig.5.3.15).

**Fig.5.3.14:** SEM images of PS-PEGMA particles coated with different PPy amounts (a – 2.28%; b – 4.5%; c – 6.41%; d – 9.38%; e – 11.06%; f – 19.29%) (2.5% PEGMA) by using Na\(_2\)S\(_2\)O\(_8\) as the oxidant.

**Fig.5.3.15:** SEM images of PS-PEGMA particles coated with different PPy amounts (a – 0.84%; b – 1.2%; c – 4.02%) (5% PEGMA) by using H\(_2\)PnMo\(_{12}\)O\(_{40}\)·29H\(_2\)O as the oxidant.
This observation leads to conclusion that the PEGMA-rich layer on the particle surface is able to stabilize effectively certain amount of PPy and when some critical value is reached large polypyrrole domains are formed in the system. More detailed microscopy study was performed by combination of SEM and AFM techniques. Microscopy images for samples S-1, S-2, and S-3 are shown in Fig.5.3.16.

Fig.5.3.16: SEM micrographs (1st layer) and AFM images made in tapping mode (height images – 2nd layer; phase images – 3rd layer; and 3D height images – 4th layer) for samples S-1, S-2, and S-3 (from left to right). The height, phase, and 3D height scales are 0 – 500 nm, 0 – 40°, and 0 – 800 nm respectively.
In this case PPy amount on particle surface increases gradually from 2.28 to 6.41 (see Tab.5.3.4). It is also obvious to see that the surface roughness of the composite particles increases, which indicates that more and more PPy inclusions appear on the particles surface. PPy is deposited in form of very small “islands” which are located on the certain distance from each other if the PPy load is low (see sample S-1) and then become packed more tightly at high PPy loads. So, actually this polypyrrole shell possesses a complex structure of self-assembled PPy nano-particles. It can be also observed that at higher PPy loads the size of PPy domains increases. This effect can be connected with the direction of the shell grows: at low PPy loads its inclusions spread on the PS-PEGMA particle surface and further increase of PPy domains will induce more and more compact packaging of PPy inclusions.

When particle surface is completely covered with first layer of PPy domains, shell will start to grow in direction perpendicular to particle surface. In these conditions it is possible that polypyrrole particles can form larger aggregates which are clearly visible in microscopy images of sample S-3 inducing increase of the surface roughness of composite particles.

![SEM images of samples S-8 (a), S-2 (b), S-9 (c), S-10 (d), and S-11 (e).](image)

Fig.5.3.17: SEM images of samples S-8 (a), S-2 (b), S-9 (c), S-10 (d), and S-11 (e).

Fig.5.3.17 presents SEM images of the samples prepared at similar PPy load but PS-PEGMA particles with different size have been used as a template.
Microscopy pictures indicate that the particle morphology can be influenced by particle size (number) of PS-PEGMA template or the total particle surface area in the system. According to Fig.5.3.12 smaller PS-PEGMA particles possess much larger surface area in certain volume of dispersion if to compare with larger microspheres. It is obvious from images presented in Fig.5.3.17 that if we increase total particle surface area in the system and load identical PPy amount the morphology of the PPy layer changes from more or less compact to “patchy”. It was also mentioned before that the thickness of PEGMA layer on particle surface should increase for smaller PS-PEGMA particles.

Tab.5.3.5: PPy shell thickness of composite particles.

<table>
<thead>
<tr>
<th></th>
<th>N</th>
<th>PEGMA, [wt.-%]</th>
<th>( R_{\text{SEM}}^{c} ), [nm]</th>
<th>( R_{\text{SEM}}^{c_s} ), [nm]</th>
<th>( h ), [nm]</th>
<th>Load PPy(^{p}), [%]</th>
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</table>

Tab.5.3.5 shows particle radii of PS-PEGMA and corresponding composite particles measured by analysis of SEM pictures. Increase of PPy load (samples S-1 – S-7) provides formation of thicker shell. This result is in good agreement with Fig.5.3.14 and 5.3.16. In case of samples prepared at similar PPy loads but using core of different size (samples S-8, S-9, S-10, and S-11), the shell thickness increases gradually if the particle size decreases. This result also correlates with microscopy
investigations presented in Fig.5.3.17, because increase of the surface roughness in case of smaller particles leads to somewhat larger $h$ values.

It should be noted that shell thickness values presented in Tab.5.3.5 should be treated with much care since measured difference in the particle size of PS-PEGMA cores and corresponding composite particles is rather small and must be proved in the future by TEM measurements.

- **Control of shell thickness by oxidant nature**

To demonstrate the alternative way to control the thickness of polypyrrole shell on PS-PEGMA particle surface different oxidants were selected because polymerization of pyrrole in presence of different oxidants will be characterized by different reaction speed. We select FeCl$_3$ $^{[20,23,163]}$ and H$_3$PMo$_{12}$O$_{40}$$^{29}$H$_2$O $^{[164]}$ as rather common oxidant for pyrrole.

![Temperature profile](image1)

![pH change](image2)

**Fig.5.3.18:** Temperature profile of the exothermic oxidation of pyrrole in presence of PS-PEGMA particles (a); and pH change during formation of composite particles (b) in presence of different oxidants (1 – Na$_2$S$_2$O$_8$ (sample S-18); 2 – FeCl$_3$ (sample Fe-19); 3 – H$_3$PMo$_{12}$O$_{40}$$^{29}$H$_2$O (sample Mo-20)).
Fig. 5.3.18a shows the exothermic profiles of pyrrole oxidation process. It is interesting to note that in case of pyrrole polymerization in presence of Na$_2$S$_2$O$_8$ temperature increases very rapidly and after PPy has been produced, the reaction mixture slowly cools. Similar temperature profiles were reported by Stejskal et al. \cite{127, 165} for aniline polymerization. In above mentioned studies polymerizations were also completed in 5 - 7 min. Contrary, reactions performed with FeCl$_3$ and H$_2$PMo$_{12}$O$_{40}$·29H$_2$O exhibit totally different temperature profile. In this case temperature increases monotonically as the polymerization proceeds and it seems that polymerization speed is much lower if to compare with Na$_2$S$_2$O$_8$-initiated reaction. The pH measurements can also monitor the progress of polymerization \cite{166, 167} (see Fig. 5.3.18b). The locally increased concentration of protons at the electrode surface is responsible for the overshooting to low pH values and for observation of the minimum. When polymerization is completed, the concentration of protons equilibrates and pH increases slightly and then remains constant. It can be observed that minimum of pH value correlates with maximum temperature in case of polymerization initiated by Na$_2$S$_2$O$_8$. In case of reactions performed with FeCl$_3$ and molybdate these minima are not clearly pronounced probably due to much slower oxidation process.

Totally different kinetics of pyrrole polymerization with different oxidants demonstrated in Fig. 5.3.18 can be used for control of polypyrrole shell thickness on PS-PEGMA surface. For example reaction processes shown in Fig. 5.3.18 have been terminated after 40 min and composite particles with different PPy load can be obtained (see Tab. 5.3.4: samples S-9, Fe-12, and Mo-13 possess PPy load 4,69 %; 3,5 %; and 1,2 % respectively and samples S-18, Fe-19, Mo-20 exhibit PPy load 12,83%; 8,83 %; and 2,10 % respectively). Additionally, polypyrrole chains in every case are doped with different anions without any strong changes in particle morphology. SEM images presented in Fig. 5.3.19 indicate that PS-PEGMA cores are homogeneously coated with polypyrrole independently on the oxidation agent. The thickness of polypyrrole layer deposited onto core surface increases gradually with PPy load (see samples S-18, Fe-19, and Mo-20 in Tab. 5.3.5). Shell thickness for samples Fe-12 and Mo-13 was not possible to determine due to very low PPy load.
Stability of composite particles

The sedimentation of PS-PEGMA particles with deposited PPy shells was investigated by method developed by Lerche et al. [168]. In special centrifuge an integrated optoelectronic sensor system allows spatial and temporal changes of light transmission during the rotation to be detected. In contrast to other approaches [169] the local transmission is determined over the entire sample length simultaneously. Throughout the measurement, transmission profiles are recorded and sedimentation process can be depicted as a time course of the relative position of the boundary between supernatant and sediment (resolution better than 100 µm) or of the transmission averaged over the entire or a chosen part of the sample length. On the basis of the obtained data the sedimentation constants, the packing density, etc., can be derived.

The transmission-time curves for particles bearing different polypyrrole amounts (samples S-1, S-2, and S-3) are presented in Fig.5.3.20a. The transmission increases with centrifugation time since particles move to the bottom of the cell. When PPy amount on PS-PEGMA particles increases the sedimentation process is accelerated. The slope of the transmission-time curves was used to calculate the sedimentation velocity (Fig.5.3.20b).

The fact that PPy deposition decreases stability of core particles is not surprising. Incorporation of polypyrrole into PEGMA-rich shell will lead initially to partial “immobilization” of PEGMA chains by formation of hydrogen bonds. Later when shell layer is saturated and PPy amount is still increasing PEGMA chains will be totally blocked by polypyrrole. Since PS-PEGMA particles are stabilized mostly by
sterical mechanism effects mentioned further increase of PPy amount above must reduce considerably stability of composite particles.

**Fig.5.3.20:** Sedimentation curves for samples with different PPy loads (1- no PPy, 2 – 2.28 %; 3 – 4.5 %; and 4 – 6.41 %) at 2000 rpm (a); and calculated sedimentation velocity \( v \) as a function of loaded PPy (b).

- **UV-characterization**

Deposition process of polypyrrole on the surface of PS-PEGMA particles was followed by changing of the colour of dispersion. Originally PS-PEGMA dispersions are white, but just after addition of oxidant and beginning of pyrrole polymerization dispersions became coloured. It was observed that dependent on experimental conditions always different colour appears brown, magenta, navy-green etc. **Fig.5.3.21** shows a photograph of dried composite particles which were pressed to form a tablet.
Fig.5.3.21: Photograph of coloured composite particles. Core size increases from left to right: $R_h = 118; 130; 193; \text{ and } 211 \text{ nm}$. Due to the photograph reproduction, some of the colours exhibit different nuances of the true colours.

It has been observed qualitatively that the change of the colour is connected with the particle size of the PS-PEGMA core. After drying polymeric particles show the same colour as original dispersion independently from the water removal technique from the latex samples (drying at room temperature, freeze-drying or spin-coating). This indicates that the colour is intrinsic property of obtained composite particles which depends on the particle morphology, dimensions and polymer nature.

Fig.5.3.22: UV-spectrum of composite particles (sample S-7) (a), and positions of peaks 1 and 2 as a function of the core particle size (samples S-2; S-4 – S-7) (b).
To investigate more in details the origin of the colour UV-spectroscopy measurements were performed. Fig.5.3.22a shows a typical UV-spectrum of sample S-7 ($R_b = 130$ nm) and two peaks maxima at 366.3 and 557.7 nm can be clearly distinguished. Similar measurements were performed for samples S-4, S-2, S-5, and S-6. In this set similar PPy amounts were loaded on particles of different size. The peak maxima 1 and 2 (see Fig.5.3.22a) were plotted vs. particle size of the original PS-PEGMA core particles. It is interesting to note that this results in linear dependency and increase of the particle size shifts both peak maxima 1 and 2 to higher wavelength.

To explain the physical nature of unusual optical properties of composite particles it is necessary to consider that the origin of colours in case of monodisperse particles is often attributable to Mie scattering $^{[170]}$ by individual particles or Bragg diffraction from three-dimensional particle arrays (colloidal crystals) $^{[171,172,173]}$. The second possibility requires organization of microspheres in 3-D lattice by special methods, and as it was demonstrated above by microscopy investigations such organized structures are not present in dried samples of PS-PEGMA particles coated with polypyrrole. In the standard Mie theory, the incident and scattered fields, as well as the fields inside a spherical particle are developed into series of transverse electric and magnetic multipols. Depending on the size and complex refractive index of the particles, resonances are observed as a function of wavelength, which arise from the poles of the various multipolar contributions in the series. Obviously, the number of resonances in the visible range and their magnitudes and halfwidths depend on the optical properties of the particle material as well as on size and composition of the particles. For very small particles, i.e. in the Rayleigh limit, only the dipolar contribution is relevant. In this case resonances occur when the complex dielectric function of the particle material approaches certain negative real values, which are in general related to bulk excitations. For larger particles so-called morphology-dependent resonances occur, which are not related to bulk excitations and do not require negative values of the dielectric function, but are determined by the size and shape of the particles. Following this approach numerous investigations have been performed in order to coat polymeric or silica particles with thin layer of material, which exhibits a negative dielectric function such as silver, gold, TiO$_2$ etc. $^{[174,175,176]}$ to obtain composite particles with special tailored optical properties. In our case composite particles consist of two materials with similar refractive indices.
(n_D=1.591 for polystyrene \textsuperscript{[177]} and n_D=1.55 for polypyrrole \textsuperscript{[178]}) what is normally not satisfactory for photonic effects. However, Bailey et al. \textsuperscript{[179]} reported the changes of refractive index for thin polypyrrole film in range 1.35 – 1.7 and this effect is still not understood. As it was already mentioned before, the refractive index of PPy can be changed with some changes in oxidation state of this conducting polymer. From this point of view, even small difference in refractive index of core and shell can lead to special optical effects if to consider that PS-PEGMA core size is in the range of the visible light. It has been also reported by Taranekar et al. \textsuperscript{[180]} that if polypyrrole is not completely in oxidized or reduced form the $\lambda_{\text{max}}$ of the neutral polymer for the $\pi \rightarrow \pi^*$ transition can be observed in UV spectrum at 334 nm. At the same time absorption maximum of $n \rightarrow \pi^*$ transition (bipolaron transition) is observed at 502 nm. When we assume that peaks observed in our UV-spectra correspond to intrinsic property of polypyrrole as material, comparison of above mentioned absorption maxima with our UV-measurements reveals the strong red shift with increasing of the core size. Since data reported in \textsuperscript{[180]} were obtained for planar well-organized PPy containing thin films the changes in UV-spectra must be connected with the dimension of the PS-PEGMA template. It has been reported by Chen et al. \textsuperscript{[181]} that characteristic absorption bands of PPy prepared in presence of sulfopropyl ether of $\beta$-cyclodextrin were shifted to higher values due to the higher degree of ordering and better coplanar characteristics. It has been assumed that $\beta$-cyclodextrin forms a hydrophobic cavity which induces self-assembly of PPy chains and provides improved molecular organization. Similar effect can be expected in present system if we consider the morphology of the PS-PEGMA particle surface layer. It can be assumed, that deposition of PPy chains into defined domains of grafted PEGMA-rich shell of the polymeric template leads to strongly directed layer growth followed by special orientation of conjugated chains. Similar effect was observed by Martin et al \textsuperscript{[182,183]} by polymerization of pyrrole in membrane inside of defined polymeric channels. The organized spherical PPy domains on the PS-PEGMA particle surface can’t be destroyed during cleaning or water evaporation since PEGMA chains are covalently bonded to the PS-core surface and no desorption processes takes place as in case of water-soluble polymeric stabilizers. Similar investigations performed by group of S. Armes \textsuperscript{[147,184]} (micrometer-large poly(N - vinylpyrrolidone) - stabilized polystyrene spheres were coated with polypyrrole shells) resulted in excellent uniform PPy coatings but no special optical effects were reported. This indicates that principally
such core-shell particles can be prepared with latex templates possessing different stabilizing surface layer, but morphology of the surface layer plays a dominant role in organization of polypyrrole chains. Formed PPy macromolecules possess positive charge in oxidized state which is counterbalanced by anions from oxidizing agent and can form small nano-domains visible in SEM due to the partial phase separation on the latex particle surface after water removal (see Fig.5.3.23 top).

**Fig.5.3.23:** Schematic representation of the surface layer on particle surface (top) and morphology development with increased PPy load (bottom).

Based on microscopy investigations presented in Fig.5.3.14 it is possible to suggest that increase of PPy load will induce the shell growth in lateral direction (Fig.5.3.23a) which results in formation of more or less compact layer on particle surface. During this step the shell thickness is not increased. After saturation point is reached PPy shell will start to grow in perpendicular direction (Fig.5.3.23b) and the surface roughness and shell thickness is rising up. Finally, if the stabilizing capacity of PEGMA layer is reached at high PPy loads secondary particles appear in the system.
Following the discussion above and morphology development presented in Fig.5.3.23, the thickness of the PPy shell at constant core size should influence the optical properties of composite particles. Fig.5.3.24 shows the positions of peak 1 and 2 for samples S-1 – S-7 as a function of PPy load.

![Fig.5.3.24: Shift of absorption bands in UV spectra (a, b) and change of the PPy shell thickness (c) of composite particles prepared with different PPy amounts.](image)

Fig.5.3.24 indicates that increase of PPy load results in more intensive and deep colours and absorption bands in UV-spectra exhibit a slight blue shift. At low PPy loads (up to 7.5 %) there is no considerable shift of absorption bands. When layer thickness increase is more pronounced the obvious blue shift can be observed (up to 15 % loaded PPy). Later the shift of absorbance peaks becomes less pronounced and this effect is connected with saturation of the PEGMA-brush layer, so no effective increase of the PPy layer is possible but secondary particles appear. Experimental results presented in Fig.5.3.24 are in good agreement with microscopy investigations and proposed morphology development shown in Fig.5.3.23. From this we can conclude that the optical properties of obtained composite particles depend also on the thickness of PPy shell.

Additional measurements have been performed to evaluate the influence of the oxidation state of PPy chains on the particle surface on the optical properties of composites. In this simple experiment composite particles prepared at 6.41 % PPy (sample S-3) were kept in water solutions with different pH-values for 24 hours. pH was adjusted to 6, 10 and 12 by adding small amounts of NaOH. After this treatment
particles were characterized by UV-spectroscopy. The peak maxima of absorption bands are shown in Fig.5.3.24.

Fig.5.3.25: Shift of absorption bands in UV spectra of composite particles after storage in water solution at different pH values.

Fig.5.3.26: Changes of polypyrrole structure induced by base/acid treatment.

Fig.5.3.25 indicates the red linear shift of absorption bands if the pH was adjusted to higher values. It is well known that PPy may be deprotonated by a base and turned into reduced state[58] as shown in Fig.5.3.26. In oxidized or doped state (initial pH=3) positive electronic charges of the PPy backbone are compensated by possibly solvated anions and therefore PPy layer on the particle surface reaches the state of maximal expansion. During reduction process (at higher pH) anions and solvent molecules are expelled, causing contraction of PPy shell[185] (see inset in Fig.5.3.25). This leads to conclusion that treatment at different pH values changes effectively the thickness of PPy shell on the particle surface at
constant PPy load. In other words, effect observed in Fig.5.3.25 is similar to situation presented in Fig.5.3.24, but the PPy shell thickness was varied in two different ways.

- Electro-properties of the composite particles

Fig.5.3.27 show the j-U characteristics of ITO/PS-PPy/Al sandwich samples prepared from core-shell type PS-PPy composite particles using molybdate, FeCl₃ and Na₂S₂O₈ as oxidants, respectively. The sample Mo-13 prepared by using phosphomolybdate as the oxidant shows five orders of magnitudes higher current, which may result from the reason that molybdate plays as an efficient dopant for the system. Due to the higher conductivity, we will study the influence of PPy content on the j-U characteristics of the PS-PPy particles prepared by using molybdate as oxidant.

![Fig.5.3.27: j-U characteristics of core-shell type PPy samples prepared by different oxidants](image)

Fig.5.3.27: j-U characteristics of core-shell type PPy samples prepared by different oxidants (Sample: S-2 by Na₂S₂O₈, Fe-12 by FeCl₃ and Mo-13 by molybdate).

Fig.5.3.28 shows the j-U characteristics of PS-PPy composite particles with different PPy content. Clear tendency can be found in Fig.5.3.28 that the conductivity of the composite particles also increases with the increase of PPy content in the system. And up to 4.02 wt.-% PPy was loaded the influence of increase of the PPy amount on the conductivity is not so strong, which indicates that 4.02 wt.-% PPy is enough to cover the whole insulating surface of PS core. After this point, more PPy content in the system will form secondary polypyrrole particles which are not attached on the PS-PPy particle surface and that is why it will not improve the conductivity of the composite particles obviously. This is also coincident with the results of the morphology of PS-PPy composite particles, which is shown in Fig.5.3.15.
Fig. 5.3.28: j-U characteristics of PS-PPy samples prepared with different PPy content. (a) Mo-14 (0.84 % PPy), (b) Mo-13 (1.2 % PPy), (c) Mo-15 (2.44 % PPy), (d) Mo-16 (4.02 % PPy), (e) Mo-17 (5.36 % PPy).

Photocurrent has also been measured for the PS-PPy samples prepared on glass surface. Fig. 5.3.29 shows the photocurrent for PS-PPy samples with different amount of PPy. It is interesting to see that the samples are slightly photoconductive. When the light is switched on, the photocurrent increased immediately and when the light is switched off, the photocurrent decreased again to the original value. Fig. 5.3.29(b) shows the maximum photocurrent of PS-PPy samples with different PPy load. Similar results can be got that at lower PPy load, the photocurrent increases fast with the increase of PPy load in the system, at higher PPy load, the photocurrent increases slightly with the increase of PPy load. This is in good agreement with the results we have observed for j-U characteristics of the samples.

Fig. 5.3.29: (a) Photocurrent for PS-PPy samples with different PPy content: (1) Mo-14 (0.84 % PPy), (2) Mo-13 (1.2 % PPy), (3) Mo-15 (2.44 % PPy), (4) Mo-16 (4.02 % PPy), (5) Mo-17 (5.36 % PPy), and (b) photocurrent dependence of PPy load for samples prepared on glass with Al electrodes distance 1 mm measured in vacuum at room temperature with 20 V light.
Conclusions

- Monodisperse PS-PEGMA particles were prepared in water medium by polymerization with sodium peroxydisulfate. Obtained particles possess hydrodynamic PEGMA-rich shell which can collapse at elevated temperatures. This effect may due to the brush-like structure of the particle surface layer which is formed during polymerization process.

- Monodisperse PS-PEGMA particles have been used as a template for deposition of polypyrrole (PPy). Obtained composite particles possess core-shell morphology where shell is composed out of small PPy nano-domains. The shell thickness can be varied by changing PPy load, controlling the overall template surface area in the system, and by influencing the pyrrole polymerization kinetics in presence of different oxidants. The last possibility provides also incorporation of different anions into polypyrrole shell.

- It has been established that obtained particles are intrinsically coloured and the colour can be changed by the PS-PEGMA core size. Increase of the core dimension leads to shift of the stop band to the higher wavelength. Additionally, it has been established that the shift of absorption bands can be induced by changing of polypyrrole shell thickness by reduction of conducting polymer or increase of PPy load.

- Conductivity measurement shows that PS-PPy composite particles prepared by using phosphomolybdate as the oxidant are much more conductive than particles prepared by the other two oxidants. The conductivity increases with the increase of PPy load in the system. Core-shell type PPy composite particles also show slight photoconductive property.
6 Applications of PPy - containing particles

6.1 Corrosion protection

6.1.1 Introduction

Corrosion is a natural process that has troubled human beings ever since the use of metals. It occurs when its potential has a value more noble than the reversible potential. The protection of oxidizable metals through the use of organic coatings is a quite ancient field of research. Among them, conducting polymer films became attractive since the first reported works by Mengoli et al. [186] then Deberry [187] on the corrosion protection of metals by inherently conducting polymers. The use of conducting polymer against corrosion in the case of iron, zinc, aluminium and magnesium has been investigated with some success [188,189,190]. Wei et al. [191] showed the corrosion protection effect of polyaniline coatings through a series of electrochemical measurements on the doped or undoped polyaniline-coated cold-rolled steel(CRS) under various conditions. Wessling [192] proposed a full mechanism by which the anticorrosion performance of polyaniline on steel was attributed to an increase in the corrosion potential and to the redox catalytic property of polyaniline in the formation of a passive layer of metal oxide. On the other hand, corrosion protection of electroactive heterocyclic polypyrrole had also attracted extensive research interest in the recent decade [193,194,195]. Most of them are focus on the electropolymserization of pyrrole on ion electrodes to produce uniform, strongly adherent and anticorrosive coatings [196]. Although this is a quick, easy to control and lower toxic method, the limitation on the shape and size of the treated metal sheet has prevented it from industrial application. Mixing conducting anticorrosive polymer dispersion with conventional coating is no doubt to be a more environmentally friendly, easier, economic way for preparation corrosion protection coatings. Truong et al. [197] has investigated the effectiveness of the corrosion protection of an acrylic paint containing electrically conductive polypyrrole for a magnesium alloy. The salt spray test results demonstrated that the paint containing PPy coated magnesium samples showed insignificant corrosion and little blistering in a salt spray chamber after 1000 h exposure.
The purpose of our work is to prepare corrosion protection coatings by using different kind of stable water-based polypyrrole dispersions as the additive for paint formulation \cite{198,199}. The compatibility and film formationability of these two components have been investigated. Two different kinds of metals, cold-rolled steel (CRS) and hot dip galvanizing (HDG) have been used for the corrosion test. Fig.6.1.1 shows the model for film formation of different polypyrrole dispersions on the metals.

**Fig.6.1.1:** Model for the film formation of different polypyrrole dispersions.

### 6.1.2 Core-type polypyrrole dispersion

Core-type polypyrrole dispersions prepared by different oxidants were used as the additive for the basis polymer. Tab.6.1.1 shows the detail information for the polypyrrole dispersions used in the corrosion test.

**Tab.6.1.1:** Recipe for preparation of core-type polypyrrole dispersion.

<table>
<thead>
<tr>
<th>Sample</th>
<th>PVME, [g]</th>
<th>Pyrrole, [g]</th>
<th>Oxiant, [g]</th>
<th>Water, [g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>WP1-1</td>
<td>0,1</td>
<td>0,1</td>
<td>0,5*</td>
<td>75</td>
</tr>
<tr>
<td>Mo-4</td>
<td>0,1</td>
<td>0,1</td>
<td>0,64**</td>
<td>75</td>
</tr>
</tbody>
</table>

* using Na$_2$S$_2$O$_8$ as the oxidant, ** using H$_3$Pmo$_{12}$O$_{40}$ as the oxidant.
Fig. 6.1.2: Photos for the dispersions (a) and films (b) prepared by the corresponding dispersions. (from left to right: basis polymer, Mo-4 dispersion and their mixture, respectively).

Fig. 6.1.2 show the photos of the polypyrrole dispersion used as the additive for the paint formulation and the films prepared from them. From Fig. 6.1.2 it is clearly to see that when we mix the black polypyrrole dispersion with the white basis polymer, mixture shows light blue color. And no phase separation was found even after weeks’ storage, which means that polypyrrole dispersion is compatible with the basis polymer. Furthermore, from Fig. 6.1.2(b) it can be found that polypyrrole dispersion alone cannot make homogeneous film, but film prepared by the mixture is transparent and homogeneous. This confirmed again the conclusion that polypyrrole dispersion is compatible with the basis polymer.

Fig. 6.1.3: AFM image for the film of pure basis polymer prepared by spinning coating on Fe: (a) height image and (b) phase image.
Fig.6.1.4: AFM image for the film of the mixture of Mo-4/Basis polymer=1:1 prepared by spinning coating at room temperature on Fe: (a) height image and (b) phase image.

Fig.6.1.3 and Fig.6.1.4 show the AFM images of the films prepared by basis polymer and the mixture of basis polymer and conducting polymer dispersion, respectively. AFM image of basis polymer shows very smooth surface topography. Moreover, Small spherical particles can be found in the AFM image of the film prepared by the mixture, which indicates that polypyrrole particles are homogeneously dispersed in the basis polymer.

**Tab.6.1.2:** Contact angle measurements of the films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Contact angle(M), [°]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basis polymer(RT)</td>
<td>77,7±1,41</td>
</tr>
<tr>
<td>Mo-4(10wt%) (RT)</td>
<td>72,0±0,64</td>
</tr>
<tr>
<td>Mo-4(50wt%) (RT)</td>
<td>71,4±1,04</td>
</tr>
<tr>
<td>Basis polymer(100°C)</td>
<td>74,5±1,24</td>
</tr>
<tr>
<td>Mo-4(10wt%) (100°C)</td>
<td>72,9±1,01</td>
</tr>
<tr>
<td>Mo-4(50wt%) (100°C)</td>
<td>72,2±0,86</td>
</tr>
</tbody>
</table>

Tab.6.1.2 shows the results of the contact angle measurements for the films. It is obvious to see that the differences of the contact angle between the films prepared by pure basis polymer and by the mixture is very less, which means the addition of
polypyrrole dispersion into the basis polymer did not influence the properties of final film no matter if the film is prepared at room temperature or at 100°C.

From Fig.6.1.5, it can be investigated that for both Fischer hardness and pedulum hardness measurements, the film prepared at 100 °C shows always better results than the films prepared at room temperature, which indicates that high temperature drying process is necessary for preparation of film with better property. Furthermore, it is also worth noting that with the increase of the polypyrrole dispersion amount in the basis polymer, the hardness of the film was improved. Especially when 40 wt-% polypyrrole dispersion was added in the system, there is an obvious jump for the increase of the hardness. This may due to the reason that hard polypyrrole particles play as a reinforcing agent in the system.
Fig. 6.1.6: Corrosion test for core-type polypyrrole dispersion prepared by different oxidants on (a) CRS, (b) HDG metal sheets. Blue and red line presents the corrosion test results for pure basis polymer on face corrosion and scribe corrosion, respectively.

Fig. 6.1.6 show the results of corrosion tests for polypyrrole dispersions prepared by different oxidant. Corrosion units (0 to 5) in the figure present different level of the corrosion on the metal sheet. “0” means there is no defect on the metal sheet after the corrosion test and “5” means the metal sheet has been totally corroded. From Fig. 6.1.6 it can be observed that polypyrrole dispersion oxidated by sulphate shows good results on face corrosion protection both on CRS and HDG metals, but shows no improvement or even worse results on scribe corrosion protection. By using molybdate as the oxidant, both face corrosion and scribe corrosion have been inhibited. And with the increase of polypyrrole dispersion amount added into the basis polymer, the improvement of corrosion protection is more obvious until 30wt-% of polypyrrole dispersion was used in the system.

Fig. 6.1.7: Kelvin-Probe study for core-type polypyrrole dispersion prepared by using Na$_2$S$_2$O$_8$ as the oxidant.
In order to understand the mechanism of the corrosion protection ability of polypyrrole dispersion prepared by different oxidants, delamination experiments were made with the use of Kelvin Probe. Fig.6.1.7 and Fig.6.1.8 show the changes of the potential of the delamination experiments for the film prepared by the mixture of basis polymer and polypyrrole dispersion on iron samples with the use of Kelvin Probe. Fig.6.1.9 shows model of the sample prepared for delamination experiment.

**Fig.6.1.9:** Kelvin-Probe study for core-type polypyrrole dispersion prepared by using phosphomolybdate as the oxidant.
From Fig.6.1.7 it can be seen that when Na$_2$S$_2$O$_8$ was used as the oxidant for pyrrole polymerization, the film prepared by the mixture of basis polymer and polypyrrole dispersion shows no potential increase either in the defect or at the delamination front which indicates that there is no passivation on the metal surface. While phosphomolybdate was used as the oxidant, it can be found from the delamination experiment results that the potential at the delamination front increases with time, which indicates passivation of the corroding iron. As a consequence of the potential increase at the delamination front, the potential difference between the intact polymer and delamination front decreases significantly (from -350 mV to -200 mV), as the result of that the delamination also slows down significantly. Furthermore, XPS analysis (see in Fig.6.1.10) showed that Mo anions can be found at the delaminated area under the film prepared by the mixture of basis polymer and PPy. As we know, there is no Mo in the basis polymer, so Mo can only come from the PPy dispersion, which were released free as a result of corrosion inhibition. All these results confirmed that molybdate can play as an effective dopant in polypyrrole dispersion which can be released during delamination and thus PPy dispersion works as a corrosion inhibitor for the metals.

Fig.6.1.10: XPS spectrum at the delamination area for the film prepared by the mixture of basis polymer and PPy dispersion.
6.1.3 IPN-type Polypyrrole dispersion

In this case polypyrrole composite particles, which were prepared by using poly(VCl-AAEM) microgel as the template, were used as the additive. Comparing the results of corrosion test for the samples prepared by the microgel with different amount of AAEM (in Fig.6.1.11), it is clearly to see that the corrosion protection of the samples was improved with the increase of the AAEM content in the system, especially for the scribe corrosion test. This may due to the interaction of the acetooacetate functional group of microgel with the metal which induces the good adhesion of the polypyrrole particles with the metal surface.

Fig.6.1.11: Corrosion test for IPN-type polypyrrole dispersions prepared by poly(VCL-AAEM) microgel with different AAEM content on CRS metal sheet.

Fig.6.1.12 shows the results of the corrosion test for IPN-type polypyrrole dispersions with different PPy content. It can also be found that when AAEM content is constant in the system, the increase of polypyrrole amount did not improve the corrosion protection properties of the samples either on CRS metals or on HDG metals.

Fig.6.1.12: Corrosion test for IPN-type polypyrrole dispersions prepared by poly(VCL-AAEM) microgel(2,5wt.-% AAEM) with different PPy content on (a) CRS and (b) HDG metal sheet.
6.1.4 Core-shell type polypyrrole dispersions

Copolymer poly(ST-co-BuA) with different Glass Transition Temperature (Tg) has been used as the core for pyrrole polymerization to prepare core-shell type polypyrrole dispersions. The detail information about the polypyrrole samples, which were used as the additive for corrosion test, has been summarized in Tab.6.1.3.

Tab.6.1.3: Recipe for preparation of core-shell type polypyrrole dispersions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>PEGMA, [%]</th>
<th>Core, [g]</th>
<th>ST: BuA</th>
<th>PPy, [g]</th>
<th>Na₂S₂O₈, [g]</th>
<th>Tg of the core, [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>NLP1</td>
<td>5</td>
<td>40</td>
<td>Pure styrene</td>
<td>0.2</td>
<td>1.0</td>
<td>90</td>
</tr>
<tr>
<td>CNL8.1</td>
<td>5</td>
<td>40</td>
<td>6:4</td>
<td>0.2</td>
<td>1.0</td>
<td>30</td>
</tr>
<tr>
<td>CNL11.1</td>
<td>5</td>
<td>40</td>
<td>2:2</td>
<td>0.2</td>
<td>1.0</td>
<td>60</td>
</tr>
</tbody>
</table>

Fig.6.1.13 and Fig.6.1.14 show the results of the corrosion test for core-shell type polypyrrole dispersions prepared by poly(ST-co-BuA) core with different Tg on CRS and HDG metal sheets, respectively. From Fig.6.1.13, first we can see that in all cases, addition of polypyrrole dispersion can improve the anti-corrosive ability of the basis polymer. Secondly, in case when the Tg of the core polymer is similar as that of basis polymer (around 40 °C) it shows better effect on the corrosion protection, which may due to the better film formation of the PPy dispersions coming from the lower Tg of the core particle (showing in Fig.6.1.1). Similar results have been found also for the corrosion test of HDG metals (see in Fig.6.1.14).

Fig.6.1.13: Corrosion test for core-shell type polypyrrole dispersions prepared by poly(ST-co-BuA) core with different Tg on CRS metal sheets.
Fig. 6.1.14: Corrosion test for core-shell type polypyrrole dispersions prepared by poly(ST-co-BuA) core with different Tg on HDG metal sheets.

**Conclusions**

- All types of polypyrrole dispersions show good compatibility with the basis polymer. The mixture can produce transparent homogeneous films.
- The results of corrosion test for CRS and HDG metals show that by using PPy dispersions as the additive of the paint, improvement can be achieved both in surface corrosion protection and scribe corrosion protection.
- Kelvin Probe and XPS study for the delamination experiments confirmed that when molybdate was used as the dopant for polypyrrole dispersion, passivation of the corroding iron was observed in the defect and at delamination front.
6.2 Absorption of amino acid

6.2.1 Introduction

Although conducting polymers (polypyrrole, polyaniline etc.) can be interesting molecular recognition systems, since they have an intelligent ability to control the ion exchange dependent on redox potential and pH in solution [200], they scarcely ever have been selected for molecularly imprinted polymer matrixes. It has been reported that a dopant determines the porosity of the polymer network (or network spacing), and this feature has been utilized for ion-selective electrodes to detect some inorganic anions [201,202]. An anion selectivity of a conducting polymer film has been studied by varying the size of the dopant anion and such layer has been used in potentiometric sensor for nitrate detection [202]. Preparation of poly(o-phenylenediamine) imprinted by glucose by electropolymerization has also been reported [203]. Recently Nagaoka’s group reported effective use of overoxidized polypyrrole in form of films [204] and colloidal particles [205,206,207] for enantioselective uptake of amino acid. A strategy used in this research requires initially doping of polypyrrole with L-glutamate or L-lactate during PPy synthesis. Further overoxidation step gives a possibility to remove the amino acid and create a cavity which shows very good enantioselectivity for L-acid over the D-enantiomer. It has been also demonstrated that such templated colloids can absorb different amino acids and the uptake efficiency is determined by the difference between molecular volume of the target molecule and volume of the templated cavity [207].

In previous chapter the synthesis and characterization of composite core-shell particles with polypyrrole layer on the surface has been described. The growth of the PPy shell was performed in highly swollen hydrophilic brush-like layer which was chemically grafted onto the core particle surface. Oxidative polymerization of pyrrole in such conditions leads to formation of well-defined conducting polymer layers on the surface of sub-micrometer monodisperse polystyrene particles. Schematically the structure of composite particles is shown in Fig.6.2.1.
The scope of this part of work is to determine the interaction of polypyrrole-containing core-shell particles with amino acids. As model amino acid the L- and D-alanine have been selected. The aim was to check the amino acid uptake for such particles as a function of the particle concentration in the solution, PPy load on the particle surface and nature of the dopant anion which was incorporated directly during pyrrole polymerisation [208].

### 6.2.2 Composite particles

Tab.6.2.1 shows a summary of most important properties of composite particles used in present study. Selected PS-PEGMA latex sample was used for preparation of core-shell particles. Composites have been prepared with different oxidants and PPy amount on the particle surface was varied.

Deposition of conjugated polymer provides formation of the shell around polystyrene core and increases the surface roughness considerably. In our previous chapter we demonstrated that no secondary PPy particle formation in the aqueous medium was observed up to 25 wt.-% PPy deposition.
Tab.6.2.1: Composite particles used in present study (polymerization pH=2).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Oxidant</th>
<th>PPy(^T), [%]</th>
<th>PPy(^P), [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Na(_2)S(_2)O(_8)</td>
<td>2,5</td>
<td>2,28</td>
</tr>
<tr>
<td>2</td>
<td>Na(_2)S(_2)O(_8)</td>
<td>5</td>
<td>4,5</td>
</tr>
<tr>
<td>3</td>
<td>Na(_2)S(_2)O(_8)</td>
<td>7,5(^*)</td>
<td>6,41</td>
</tr>
<tr>
<td>4</td>
<td>Na(_2)S(_2)O(_8)</td>
<td>10</td>
<td>9,38</td>
</tr>
<tr>
<td>5</td>
<td>Na(_2)S(_2)O(_8)</td>
<td>12,5</td>
<td>13,4</td>
</tr>
<tr>
<td>6</td>
<td>Mo</td>
<td>2,5</td>
<td>0,84</td>
</tr>
<tr>
<td>7</td>
<td>Mo</td>
<td>5</td>
<td>1,2</td>
</tr>
<tr>
<td>8</td>
<td>Mo</td>
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<td>2,44</td>
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<td>Mo</td>
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</tr>
<tr>
<td>10</td>
<td>Mo</td>
<td>20</td>
<td>5,36</td>
</tr>
<tr>
<td>11</td>
<td>Fe(_3)Cl(_3)</td>
<td>2,5</td>
<td>1,91</td>
</tr>
<tr>
<td>12</td>
<td>Fe(_3)Cl(_3)</td>
<td>5</td>
<td>3,49</td>
</tr>
<tr>
<td>13</td>
<td>Fe(_3)Cl(_3)</td>
<td>10</td>
<td>6,32</td>
</tr>
<tr>
<td>14</td>
<td>Fe(_3)Cl(_3)</td>
<td>15</td>
<td>11,63</td>
</tr>
<tr>
<td>15</td>
<td>Fe(_3)Cl(_3)</td>
<td>20</td>
<td>13,78</td>
</tr>
</tbody>
</table>

\(^*\) - PPy load at reaction pH=6 is 7,46
Mo - H\(_3\)PMo\(_{12}\)O\(_{40}\)·29\(\)H\(_2\)O.

6.2.3 **Investigation scheme**

It has been planed to investigate interaction of amino acids with obtained composite particles and in this case the chemical state of the polypyrrole chains on the particle surface should influence considerably above mentioned interactions. Scheme.6.2.1 shows that pyrrole polymerization can be performed at pH=2 leading to oxidized state of PPy shell. In this case PPy chains possess some positive charge which is counterbalanced by incorporated anions from oxidant. If pyrrole polymerization is performed at pH=6 it is possible to obtain overoxidized PPy \[^{207}\]. In this case the conjugated structure of PPy is destroyed as a result of introduction of the carbonyl group.
By NaOH treatment oxidized particles can be transformed into reduced state. This reversible process leads to neutral state of PPy chains and rejection of anions into water phase. In case of overoxidized particles no strong changes in the PPy structure can be expected after treatment with base. The treatment with NaOH does not change the core-shell morphology of composite particles. Fig.6.2.2 presents SEM images of composite particles before and after treatment with NaOH.

It is quite important to define the pH value for the investigation of the amino acid uptake by core-shell particles. In this case it is necessary to consider both the ampholyte behaviour of amino acids and structure of PPy layer on the particle surface. Scheme 6.2.2 indicates the acid/base equilibrium of alanine and it is clear that at pH<2 these molecules are positively charged, in the pH range 3-9 they are amphoteric.
and negatively charged in basic medium. Expecting electrostatic interactions with the colloids, all the uptake experiments were carried out at pH 1.0 to convert amino acids into cationic molecules.

\[
\begin{align*}
\text{COOH} & \quad \text{COO}^- \\
\text{H}_2\text{C} - \text{C} - \text{H} & \quad \text{H}_2\text{C} - \text{C} - \text{H} \\
\text{NH}_3^+ & \quad \text{NH}_3^+ \\
\end{align*}
\]

\[pK_a(\text{COOH}) = 2.3\]

\[pK_a(\text{NH}_3^+) = 9.7\]

**Scheme 6.2.2:** Acid/base equilibrium of alanine.

### 6.243 Uptake of amino acid

**- Uptake of L- and D-alanine as a function of particle concentration in the mixture**

In this set of investigations the particle concentration in the system was varied and the uptake of L- and D-alanine by composite particles has been determined. Fig.6.2.3 indicates that in all cases increase of the particle concentration leads to higher amino acid uptake. As expected, overoxidized particles (polymerization pH=6) show much higher amino acid uptake if to compare with composite particles modified with PPY in oxidized state. Fig.6.2.3 shows also that composite particles exhibit certain stereoselectivity of the amino acid uptake. It is interesting to note that particles treated with base show higher amino acid uptake and this effect is much stronger in case of D-alanine.
Fig. 6.2.3: Uptake of L- and D-alanine for composite particles prepared at different polymerization pH-values, (a) pH=2 and (b) pH=6 (PPy content 6.41% (SO$_4^{2-}$); $c_L$-alanine=$2.5\times10^{-3}$ M, pH=1).

This fact reduces strongly the selectivity of the amino acid uptake (ratio between L and D stereoisomer uptake) which is summarized in Tab. 6.2.3.

**Tab. 6.2.3:** Selectivity of alanine uptake by composite particles.

<table>
<thead>
<tr>
<th>Polymerization pH=2</th>
<th>Polymerization pH=6</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>b</td>
</tr>
<tr>
<td>Selectivity</td>
<td>4.3</td>
</tr>
</tbody>
</table>

a,c – no base treatment; b,d – treatment with base

Results summarized in Tab. 6.2.3 indicate also that uptake of alanine by oxidized particles is partly stereoselective (selectivity is much lower if to compare with
overoxidized particles) and treatment by NaOH increases the D-alanine uptake and reduces selectivity of the process.

- **Uptake of L- and D-alanine as a function of PPy content and dopant anion**

Since composite particles used in present study possess a PPy shell of defined thickness which is actually responsible for amino acid uptake, it is possible to check the influence of the PPy amount on the surface on uptake behaviour. In this case it is also important to consider the nature and size of the dopant anion, since it will determine to some extent the spacing of PPy network on the particle surface. The uptake of alanine by composite particles prepared with different oxidants (and doped by corresponding anions) has been investigated and experimental results are presented in Fig.6.2.4.

![Fig.6.2.4: Uptake of L-alanine as a function of PPy content on the particle surface: a) dopant sulphate; b) dopant chloride; c) dopant molybdate (c_{particles}= 2 g/l; c_{L-alanine}=2.5*10^{-3} M, pH= 1).](image)

The determined uptake of L- and D-alanine is plotted vs. loaded PPy amount on the particle surface. Uptake of amino acid increases linearly with increase of polypyrrole
content independently from the anion nature. This effect shows the attractive possibility to influence the amino acid uptake not only by particle concentration in the mixture, but also by the thickness of the PPy shell on the particle surface. All composite particles show higher affinity to L-alanine, but experimental data in Fig.6.2.4 indicate that amount of absorbed amino acid and selectivity of the L- and D-alanine uptake are quite different from three dopant anions used in this study. The calculated selectivity data are shown in Tab.6.2.4.

**Tab.6.2.4:** Selectivity of alanine uptake by composite particles.

<table>
<thead>
<tr>
<th>Anion</th>
<th>Cl⁻</th>
<th>SO₄²⁻</th>
<th>Mo</th>
<th>Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
<td>b</td>
<td>a</td>
<td>6.1</td>
</tr>
<tr>
<td></td>
<td>a</td>
<td>b</td>
<td>b</td>
<td>5.8</td>
</tr>
<tr>
<td></td>
<td>a</td>
<td>b</td>
<td>a</td>
<td>6.1</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>a</td>
<td>b</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>a</td>
<td>b</td>
<td>11</td>
</tr>
</tbody>
</table>

a – no base treatment; b – treatment with base

It is obvious that composite particles prepared with phosphomolybdate show extremely high selectivity if to compare with particles doped by chloride or sulphate. In all cases treatment with NaOH decreases selectivity of the process. If we compare the uptake values of L-alanine by different particles plotted vs. PPy amount on the particle surface (Fig.6.2.5) it is clear that uptake depends on the size of the dopant anion, and the particles prepared with phosphomolybdate exhibit much higher alanine uptake if to compare with their chloride and sulphate doped analogues with similar PPy content.

![Fig.6.2.5: Uptake of L-alanine as a function of PPy content on the particle surface](image)

From this we can conclude that indeed anion size plays important role in formation of the PPy layer on the particle surface and this influences the uptake of amino acid. The
open question is still the origin of this interaction forces between composite particles and alanine. In this experiment all particles have been prepared at pH=2, so they should be in oxidized state. The reason for this is that it is not possible to use phosphomolybdate as oxidant at pH=6, so no comparison with other oxidants can be made. As it was mentioned before, oxidized PPy layer should bear some positive charges and interaction with positively charged amino acids at pH=1 should be rather weak. But our experimental results indicate that there is sufficient alanine uptake and partly high selectivity to L- and D-isomers. This made an attempt to test uptake of other amino acids such as glycine and serine by composite particles doped by sulphate. Some experimental data are summarized in Tab.6.2.5.

Data in Tab.6.2.5 indicate that overoxidized composite particles show no serine uptake and particles treated with NaOH are not sensitive to glycine. So, it seems that prepared composite particles can’t be treated as effective absorbers for different amino acids and the system should be better optimized and better investigated in the future.

**Tab.6.2.5:** Uptake of different amino acids by composite particles(unit: mol).

<table>
<thead>
<tr>
<th>Amino acid</th>
<th>Polymerization pH=2</th>
<th>Polymerization pH=6</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
<td>b</td>
</tr>
<tr>
<td>Glycine</td>
<td>6.66*10^{-7}</td>
<td>0</td>
</tr>
<tr>
<td>L-alanine</td>
<td>1.76*10^{-6}</td>
<td>3.01*10^{-6}</td>
</tr>
<tr>
<td>L-serine</td>
<td>5.23*10^{-6}</td>
<td>4.23*10^{-6}</td>
</tr>
</tbody>
</table>

*a– no base treatment; b – treatment with base*

**Conclusions**

- PS/PEGMA/PPy composite particles can absorb quite high amounts of alanine and even show certain enantioselectivity. It has been found that the alanine uptake can be controlled by the particle concentration in the mixture as well as by the PPy amount on the particle surface. The uptake of alanine can be influenced by the size of dopant anion and the maximum value was detected for particles doped by phosphomolybdate.

- It has been established that the treatment of composite particles with NaOH (reduction of PPy shell) increases the alanine uptake but decreases the enantioselectivity.
6.3 Hydrogel/PPy composites

6.3.1 Introduction

Conducting polymers and hydrogels are two of the most promising types of polymers being used for new material development. Hydrogel can shrink/expand in water in response to stimuli such as pH [209], temperature [210], light [211] and even electric fields. Conducting polymers also undergo chemical and physical changes in response to electrical stimuli, such as ion exchange capacity, protein affinity, or enzyme bioactivity, conductivity etc [212, 213, 214]. Thus conducting electroactive polymer/hydrogel composites are extremely interesting structures, which can combine the properties of both classes of materials with potential application as electrical stimulated controlled release devices or artificial muscles [215, 216, 217, 218]. The research group of Wallace has done a lot of work in this field [219]. They synthesised conducting polymers inside a hydrogel support matrix by electrochemical method. And they found that the conducting polymer/hydrogel composites are electroactive and have high rehydration levels (80-90 %). A. G. Elie et al. [220] report the construction and application of novel polypyrrole-containing, p(HEMA)-hydrogel membranes in amperometric biosensors for three clinically important analytes; glucose, cholesterol and galactose. They found significant suppression of interference arising from the presence of the polypyrrole component in the composite membrane.

The aim of this part of work is to use PS/PEGMA particles as centres of polypyrrole deposition after they have been included into structure of hydrogel. As we know PS/PEGMA particles can be successfully used as templates for polypyrrole deposition in aqueous solution leading to formation of composite particles with dielectric cores and conducting shells, we expect that the combination of PS/PEGMA particles into the hydrogel matrix can provide controlled functionalization of hydrogels for conjugated polymer polymerization leading to formation of new polymeric materials.

Synthesis of composite gels was examined in two stages (see in Fig.6.3.1): first step is preparation of hydrogel sample which possesses PS/PEGMA particles integrated into polymeric network; and second step is selective deposition of polypyrrole during oxidative polymerization process both in chemical and electrochemical way.
6.3.2 Preparation and characterization of hydrogel template

PS-PEGMA particles have been entrapped in hydrogel matrix by means of disulfone reaction with hydroxyl groups which are present both on particle surface and in the polymer chains of the PVA and HPC. Generally, the preparation of composite PVA- and HPC-based hydrogels was performed in the way that the samples were prepared: a) with different particle contents; b) by using PS-PEGMA particles with different sizes; c) with different crosslinking degree (by varying DVS concentration). Tab.6.3.1 and 6.3.2 show the amounts of components for preparation of composite hydrogel template on HPC and PVA basis respectively.

![Fig.6.3.1: Procedure for hydrogel/PPy composite preparation.](image)

### Tab.6.3.1: Reagents for preparation of HPC hydrogel template.

<table>
<thead>
<tr>
<th>Sample</th>
<th>HPC, [g/l]</th>
<th>PS, [g/l]</th>
<th>DVS, [g/l]</th>
<th>Water, [g]</th>
<th>PS:HPC, [wt:wt]</th>
<th>PEGMA, [wt.-%]</th>
<th>Solid content, [%]</th>
<th>Swelling</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>45,66</td>
<td>9,13</td>
<td>5,41</td>
<td>10</td>
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<td>5</td>
<td>5,7</td>
<td>66,66</td>
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<td>10</td>
<td>0,2</td>
<td>5</td>
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<td>49,27</td>
</tr>
<tr>
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<td>10,82</td>
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<td>5</td>
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<td>9,89*</td>
<td>8,38</td>
<td>10</td>
<td>0,2</td>
<td>2,5</td>
<td>6,41</td>
<td>27,57</td>
</tr>
<tr>
<td>3H</td>
<td>49,49</td>
<td>9,89**</td>
<td>8,38</td>
<td>10</td>
<td>0,2</td>
<td>7,5</td>
<td>6,41</td>
<td>25,38</td>
</tr>
</tbody>
</table>

* - NL4 (2,5% PEGMA); ** - NL3 (7,5% PEGMA)
Tab.6.3.2: Reagents for preparation of PVA hydrogel template.

<table>
<thead>
<tr>
<th>Run</th>
<th>PVA, [g/l]</th>
<th>PS, [g/l]</th>
<th>DVS, [g/l]</th>
<th>Water, [g]</th>
<th>PS:PVA, [wt/wt]</th>
<th>PEGMA, [wt-%]</th>
<th>Solid content, [%]</th>
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<td>5</td>
<td>5,59</td>
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<td>7,130</td>
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<tr>
<td>8P</td>
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<td>9,85***</td>
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<td>0,2</td>
<td>5</td>
<td>6,78</td>
<td>11,79</td>
</tr>
</tbody>
</table>

* - NL4 (2,5% PEGMA); ** - NL3 (7,5% PEGMA); *** - NL1 (5% PEGMA)

Fig.6.3.2 shows the photograph of composite hydrogels on PVA basis prepared at different contents of PS-PEGMA particles. It is obvious that step wise incorporation of the particles in hydrogel increases the turbidity of samples. Initially samples became opaque and later at higher particle concentrations white colour appears.

![Fig.6.3.2: Photograph of hydrogels prepared at different PS:PVA ratios (from left to right: blank PVA; 0,001; 0,01; 0,02; 0,1; 0,2; and 0,5).](image)
- Morphology of gels

SEM images of PVA-based hydrogels are presented in Fig.6.3.3. It can be observed that incorporation of PS-PEGMA particles increases considerably porosity of the hydrogels (samples a-d). Fig.6.3.3 e-g were taken at higher magnification to show that the PS-PEGMA particles are embedded into polymer network.

![SEM images of composite PVA hydrogels prepared at different PS/PVA ratios (a – no PS; b,e – 0.1; c,f – 0.2; d,g – 1).](image)

Similar effects have been observed for HPC-based hydrogels. SEM pictures presented in Fig.6.3.4 indicate that PS-PEGMA particles provoke induced porosity of the hydrogels (compare pictures a and b). Additionally it is clearly demonstrated by images b, c, and d that increase of the divinylsulfone concentration in the reaction mixture leads to the lower porosity of the composite hydrogels even if certain amount of PS-PEGMA particles is present.
This shows two principal independent possibilities for porosity variation of the composite hydrogels by incorporation of the polymer particles or variation of crosslinker concentration. This is quite important feature of the hydrogel template which should have a pronounced influence on the pyrrole polymerization process. It can be expected that the mobility of the pyrrole and oxidant molecules as well as newly formed PPy oligomer chains inside of the template will determine the polymerization kinetics and morphology of the PPy functionalized hydrogels.

- **Swelling in water**

The swelling of hydrogels in water was determined by gravimetric method. Fig.6.3.5 shows swelling degree of PVA-based hydrogels as a function of PS/PVA ratio and DVS concentration (Fig.6.3.5a and 6.3.5b respectively).
Fig.6.3.5: Swelling in water for samples 1 – 8 (left) and samples 4P; 5P; 6P; 7P; and 8P (right) (PVA matrix).

Fig.6.3.5 indicates that the swelling degree of PVA-based gels increases rapidly if the PS/PVA ratio is larger than 0.1. This result correlates with SEM images presented in Fig.6.3.3. The rapid increase of the swelling is related with some critical particle concentration in the system which prevents more intensive crosslinking of PVA chains. Since hard PS particles can’t be swollen and don’t correspond to the elasticity of the composite hydrogel, the integration of larger amount of polymeric particles into network leads to formation of highly porous material. On the other hand, if PS/PVA ratio is fixed and one changes crosslinker concentration it is possible to change effectively the crosslinking degree and swelling of the composite hydrogel. Fig.6.3.5b indicates that the swelling degree of hydrogels decreases in linear order if DVS concentration increases. The effects described above show two independent possibilities for the variation of the crosslinking degree in the hydrogel template.

Fig.6.3.6: Swelling in water for samples 1 – 6 (left), for samples 1P, 2P, 3P (PVA) and 1H, 2H, 3H (HPC) (right).
Fig. 6.3.6a indicates that also for HPC-based gels the swelling degree can be controlled easily by the DVS concentration in the reaction system. Fig. 6.3.6b indicates that the particle size has no strong influence on the swelling degree of the hydrogels. The slight decrease of the hydrogel swelling in this case can be attributed to higher amount of OH-groups on the PS-PEGMA particle surface and therefore more intensive crosslinking. It is also clear demonstrated in Fig. 6.3.6b that PVA-based gels exhibit much lower swelling degree if to compare with HPC-based gels prepared at identical conditions.

In summary, it has been demonstrated that composite hydrogels with entrapped polymeric particles can be easily prepared. These composite hydrogels combine properties of conventional bulk gels (high porosity, swelling in water) and polymeric particles (extremely high surface area, functionalized surface). As it is schematically shown in Fig. 6.3.7 polymeric particles are fixed in hydrogel matrix (see also SEM images) and can be considered as reactive centres for deposition of different materials (ZnS, magnetite, conducting polymers etc) or immobilization of different bio-molecules.

![Schematic representation of hydrogel template.](image)

It has been also demonstrated that the amount of entrapped particles in hydrogel sample can be varied in broad range. This influences strongly the swelling degree and porosity of the hydrogels. Independently from particle content swelling degree can be controlled by the crosslinker concentration. Polymeric particles can be fixed both in PVA and thermo-sensitive HPC matrix. Therefore HPC-based composite hydrogels
possess additional interesting feature, namely volume phase transition. This provides additional possibility to change the swelling degree (or hydrogel porosity) as well as the distance between particles in the network by simple change of the temperature.

6.3.3 Deposition of polypyrrole by oxidative polymerisation

Composite hydrogels on PVA and HPC basis have been used as templates for oxidative pyrrole polymerization. The ingredients used for these reactions are summarized in Tab.6.3.3 and Tab.6.3.4.

**Tab.6.3.3:** Deposition of PPy in PS:HPC hydrogel matrix.

<table>
<thead>
<tr>
<th>Run</th>
<th>Sample</th>
<th>PEGMA, [wt.-%]</th>
<th>PS/HPC, [wt/wt]</th>
<th>DVS, [g/l]</th>
<th>Py, [g/l]</th>
<th>PPy(^{D}), [%]</th>
<th>Preparation way</th>
<th>Swelling</th>
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<td>3,64</td>
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**Tab.6.3.4:** Deposition of PPy in PS:PVA hydrogel matrix.

<table>
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<tr>
<th>Run</th>
<th>Sample</th>
<th>PEGMA, [wt.-%]</th>
<th>PS/PVA, [wt/wt]</th>
<th>DVS, [g/l]</th>
<th>Py, [g/l]</th>
<th>PPy(^{D}), [%]</th>
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<td>Et/water</td>
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<td>Et/water</td>
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<td>-</td>
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<td>6,8</td>
<td>Et/water</td>
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Pyrrole polymerization process has been performed in composite hydrogels which were in equilibrium swelling state in water at room temperature. Cylindrical hydrogel samples were swollen directly in pyrrole or in solution in ethanol:water mixture containing certain pyrrole concentration. After this procedure gel samples were rinsed with water and immersed into aqueous solution of Na₂S₂O₈. The polymerization process can be easily observed by naked eye. Fig.6.3.8 and Fig.6.3.9 show photographs of the hydrogel samples immersed into aqueous oxidant solution taken at different reaction times.

Fig.6.3.8 and Fig.6.3.9 indicate that the pyrrole polymerization begins relatively fast. The appearance of black colour indicates polypyrrole formation in hydrogel matrix. From Fig.6.3.8 it is obvious that the pyrrole polymerization proceeds exclusively in hydrogel template and no polypyrrole formation in surrounding medium can be observed. This indicates that the hydrogel template offers sufficient amount of “domains” compatible with polypyrrole where effective PPy deposition takes place. It can be also observed from Fig.6.3.8 that pyrrole polymerization starts in the inner part of the hydrogel template and later expands to the outer side of the sample. Since oxidant molecules should penetrate into hydrogel template from the surrounding water medium the pyrrole polymerization can start faster on the outer parts of the hydrogel sample. But if we consider extremely high porosity of the hydrogel in swollen state and small size of oxidant molecules, then oxidant diffusion can take place extremely fast. If we assume that pyrrole molecules are adsorbed by numerous hydrophobic domains in form of PS-PEGMA particles inside of hydrogel sample then this is not surprising why polymerization takes place in the polymer network. In case when hydrogel template was directly immersed in pyrrole (Fig.6.3.9), polymerization proceeds in totally different way. Just from the beginning of polymerization process it is clearly seen that pyrrole polymerizes in hydrogel matrix and also in water solution. This intensive polymerization in water finally makes impossible observation of hydrogel sample after 5 min. This indicates that by direct swelling method excess of pyrrole was immobilized into hydrogel matrix. This leads to migration of formed water-soluble polypyrrrole oligomers into water phase followed by continuous polymerization and finally precipitation in form of black flocks. From this point of view this preparation way can lead to somewhat non-homogeneous distribution of
PPy in hydrogel matrix. Therefore swelling of hydrogel template in water:ethanol mixture containing pyrrole seems to be more suitable preparation way for next pyrrole polymerization step.

Fig.6.3.8: Top view of pyrrole polymerization in hydrogel matrix at different reaction times (on every picture hydrogel sample is immersed into water solution with added SPDS)(swelling of hydrogel in water/ethanol mixture containing pyrrole).

Fig.6.3.9: Top view of pyrrole polymerization in hydrogel matrix at different reaction times (on every picture hydrogel sample is immersed into water solution with added SPDS)(direct swelling of hydrogel in pyrrole).
Fig.6.3.10 shows the hydrogel sample before and after pyrrole polymerization immersed in oxidant solution (situation in Fig.6.3.8).

- Morphology of hydrogel/PPy composites

The PPy deposition in hydrogels changes strongly the morphology of samples. Fig.6.3.11 shows HPC-based hydrogels after deposition of ca. 4% polypyrrole. In this case hydrogel template was crosslinked with 8.38 g/l DVS and PPy was deposited by direct swelling method. Hydrogel in Fig.6.3.11a contains no PS-PEGMA spheres. In this case PPy is deposited in form of numerous non-spherical inclusions which form large domains in polymer network due to the lack of stabilization. Such domains increase of heterogeneity of gels and lead even sometimes to formation of micro cracks. Contrary, hydrogel template with entrapped polymeric particles seems to be more suitable for polypyrrole deposition. In this case PPy deposits on the PS-PEGMA particle surface, providing homogeneous distribution of the conducting polymer in the hydrogel sample (Fig.6.3.11b).
It has been determined that PPy deposition process in PVA-based hydrogels depends strongly on hydrogel characteristics and reaction conditions. Fig.6.3.12a indicates that amount of deposited PPy decreases monotonically if the crosslinking degree of the hydrogel template increases.

In this case hydrogel template was directly immersed into pyrrole. It seems that the diffusion of the pyrrole molecules into hydrogel template is limited at higher crosslinking of the polymer network. Comparing the swelling degree in water of the hydrogels prepared at different DVB concentrations and corresponding PPy modified samples (Fig.6.3.12b) it is clear that deposition of polypyrrole decreases the swelling degree of the polymer network.

Fig.6.3.12: PPy amount as function of crosslinker concentration (particles NL1 (5% PEGMA), direct swelling) (a); swelling degree in water (b) (1 – matrix; 2 – matrix + PPy).

This decrease is more pronounced in case of hydrogels with lower crosslinking degree and correspondent higher PPy loads. Principally, Fig.6.3.12 shows that PPy deposition depends strongly on crosslinking of the hydrogel template and modification by PPy leads to formation of composite gels with more hydrophobic character.

Fig.6.3.13 presents SEM images of composite gels functionalized by different PPy amounts by direct swelling method discussed above. In Fig.6.3.13 sample d – blanko; other samples contain PS/PVA=0,2 (5% PEGMA); samples a, b,and c prepared with 4,2; 8,38; and 12,5 g/l DVS respectively; blanko prepared with 8,38 g/l DVS.
It is obvious that PPy deposits not only on the particle surface but also forms large unorganized domains especially at high crosslinking degree of the hydrogel matrix (Fig.6.3.13c). This effect can be explained by bad diffusion of the pyrrole monomer into water-swollen hydrogel template and formation of concentration gradient inside of the hydrophilic polymeric network.

Alternative preparation way for composite hydrogels, namely by swelling in ethanol-water mixture containing pyrrole, shows other interesting effects. Fig.6.3.14a indicates possibility to change the PPy load in composite PVA-based hydrogels by the initial pyrrole amount in ethanol:water mixture. In this case the PPy load is linearly proportional to the pyrrole concentration in reaction medium. It is also obvious that introduction of conjugated polymer into hydrogels reduces step wise the swelling degree of the composites (Fig.6.3.14b).
The morphology of such composite gels is totally different from that of presented in Fig.6.3.13. Fig.6.3.15 indicates that polypyrrole deposits exclusively on the PS-PEGMA particle surface and increase of PPy load does not lead to formation of some domains in polymer network. In Fig.6.3.15 sample d – blanko; other samples contain PS/PVA=0,2 (7,5 % PEGMA); samples prepared at 8,38 g/l DVS.

This clearly indicates that initial swelling of hydrogel template in ethanol:water mixture containing pyrrole is much effective way to control the PPy deposition process and morphology of composite hydrogels. In this case pyrrole molecules are
soluble in ethanol:water mixture and can penetrate easily into hydrogel template providing smooth and well controlled polymerization/deposition process.

6.3.4 Deposition of polypyrrole by electro-chemical polymerization

Composite hydrogels on PVA basis have been used as templates for pyrrole polymerization by electrochemical way. The ingredients used for these reactions are summarized in Tab.6.3.5.

<table>
<thead>
<tr>
<th>Run</th>
<th>Sample</th>
<th>PEGMA, [wt.-%]</th>
<th>PS:PVA, [wt/wt]</th>
<th>DVS, [g/l]</th>
<th>Py, [mol/l]</th>
<th>PPy%</th>
<th>Preparation way</th>
<th>Swelling</th>
</tr>
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<tr>
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<td>-</td>
<td>8,38</td>
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<td>pyrrole/NaNO₃</td>
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<tr>
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Tab.6.3.5 indicates that the PPy amount in the hydrogel matrix can be varied by adjustment of initial pyrrole concentration in the reaction system. Another interesting observation is that hydrogel containing polystyrene particles contains much more PPy than the pure hydrogel after polymerization at similar conditions (compare sample 1EP and 4EP from Tab.6.3.5). This indicates that presence of polymeric particles inside of the hydrogel matrix improve the deposition process and provide sufficient stabilization for conducting polymer.

- Deposition process

It has been found that pyrrole polymerization can be successfully performed in hydrogel matrix which is fixed on Pt electrode. Fig.6.3.16 shows hydrogel samples fixed on the electrode after deposition of PPy. Increased PPy amount changes considerably the colour of the composite hydrogels from blue to dark-grey. In case of the pure PVA hydrogel electro-polymerization of pyrrole leads to appearance a black-coloured sample.
There was no polypyrrole deposition on the reactor walls or formation of the black precipitate during electropolymerization process indicating that this approach leads to controlled synthesis of conjugated polymer in the hydrogel sample attached to the electrode. The pyrrole polymerization process can be visualized by following changes in CV curves with polymerization time. Fig.6.3.17a shows selected CV curves (values indicate the circle number).

![Fig.6.3.17a: Cyclic voltammograms recorded for different reaction circles (scan rate 50 mV/s).](image)

It is obvious that initially current increases with polymerization time (see Fig.6.3.17b), then reaches a constant value after 30 min and after 70 min starts to decrease again. Initial increase of the current can be related to the increased amount of oxidized...
pyrrole molecules which participate in polymerization process and formation of conducting polymer layer on the electrode. Further increase of the PPy amount leads to increase of resistance and current drops down as polymerization proceeds. Similar behaviour was observed for samples prepared at different PPy loads indicating that this is a typical feature of the system.

-PPy incorporation and morphology of hybrid hydrogels

The morphology of obtained hydrogels was investigated by SEM. Fig.6.3.18 shows schematic representation of the profile of hydrogel sample and the areas investigated by electron microscope.

![Schematic representation of areas in hydrogel samples investigated by SEM: A – area close to the Pt electrode; B – internal area; C – surface area exposed to electrolyte solution.](image)

Fig.6.3.18: Schematic representation of areas in hydrogel samples investigated by SEM: A – area close to the Pt electrode; B – internal area; C – surface area exposed to electrolyte solution.

Fig.6.3.19 shows SEM images of composite hydrogels prepared at different initial Py concentrations (area facing Pt electrode surface). In all cases dense PPy layers have been formed and increase of PPy load leads to formation of more unorganized domains of conducting polymer.

![SEM images of area A for hydrogels prepared with different PPy loads: a) 4.07 %; b) 5.07 %; c) 9.09 %](image)

Fig.6.3.19: SEM images of area A for hydrogels prepared with different PPy loads: a) 4.07 %; b) 5.07 %; c) 9.09 %.

This result is not surprising, since highly porous hydrogel matrix can’t hinder the formation of the PPy layer directly on the electrode surface. Fig.6.3.20 shows microscopy images of composite hydrogels taken in the middle of the gel probe (area B).
Images in Fig.6.3.20 indicate clearly that inside of the hydrogel matrix PPy deposits on the PS particle surface in form of discrete domains. Increase of PPy content leads to complete coverage of the particle surface by conducting polymer. Very less PPy domains can be found beside particles indicating that polymeric spheres embedded into hydrogel matrix serve as deposition centres for PPy. Similar effects have been observed during oxidative Py polymerization with persulphate in presence of the same hydrogel samples.

Fig.6.3.21 shows SEM images depicting the surface morphology of composite hydrogels after PPy deposition. It is clear that despite PPy deposition composite hydrogels remain highly porous and conducting polymer is homogeneously distributed in the polymer network. Such typical open cell morphology for selected hydrogel sample is shown in Fig.6.3.22. Contrary, hydrogel prepared without PS particles exhibit lower porosity and large PPy domains of different size can be observed in microscopy images (see Fig.6.3.21d).
Fig.6.3.21: SEM images of area C for hydrogels prepared with different PPy loads: a) 4.07 %; b) 6.65 %; c) 9.09 %; d) 4.64 % (hydrogel without PS particles).

Fig.6.3.22: SEM image of area b for hydrogel prepared with 5.79 % PPy indicating highly porous structure.

Incorporation of PPy in hydrogel structure influences strongly the swelling properties of polymer network. Fig.6.3.23 shows that swelling degree decreases with linear order with loaded PPy amount.
Fig.6.3.23: Swelling of PVA/PS/PPy hydrogels composite prepared with different PPy amounts.

Similar results have been shown earlier for composite PPy-containing hydrogels prepared by means of oxidative polymerization in presence of persulphate. This indicates that the PPy deposition in such system is well-controlled process and the properties of the final hydrogel can be adjusted to certain values by changing the reaction parameters.

**Conclusions**

- PPy-functionalized gels can be prepared by two-step method: a) preparation of hydrogels by chemical crosslinking of poly(vinyl alcohol) (PVA) or hydroxypropyl cellulose (HPC) mixed with reactive PS/PEGMA particles in water solution; and b) deposition of polypyrrole onto surface of polymeric particles embedded into hydrogel matrix leading to complex structure schematically presented in Fig.6.3.24.
- Deposition of PPy can be achieved by electropolymerization process or by oxidative polymerization in presence of persulphate. It has been shown that polypyrrole deposits mostly on the surface of spherical polystyrene particles due to the special design of the surface layer.

- The polypyrrole deposition process as well as final properties of composite hydrogels can be effectively controlled by the adjustment of template parameters such as particle concentration, crosslinking degree etc. It has been shown that incorporation of PPy into hydrogels decreases the swelling degree of polymer network. Also, the crosslinking degree of the hydrogel template influences strongly the deposited PPy amount.
7. Experimental Methods

7.1 Experimental set up for polymerization

- Reactor set up

All the polymerizations were performed in double-wall glass reactor (Rettberg) with an effective volume of 250 ml. The reactor was equipped with stirrer, reflux condenser, and two inlets for nitrogen and the reagents. The temperature in the reactor was controlled by means of the thermostat (HAAKE DC1) operating in the temperature interval 20-400 °C. The schematic reaction set up is shown in Fig. 7.1.

![Fig. 7.1: Schematic representation of the reactor set up.](image)

- Electrochemical polymerization set up

Electrochemical polymerization was achieved using an EG&G Princeton Applied Research 273 potentiostat/galvanostat. Fig. 7.2 shows the electrochemical cell and
electrode arrangement used for the synthesis of the hydrogel-conducting-polymer. A divided two compartment cell connected with salt bridge was designed and constructed. The hydrogel was fixed on Pt electrode and it was the working electrode. Ag/AgCl (3 M KCl) reference electrode was positioned near the working electrode as indicated. And reticulated vitreous carbon (RVC) was used as the counter electrode in a separated cell.

Fig. 7.2: Electrochemical cell used for electrochemical deposition of PPy in the hydrogel matrix.

7.2 Reagents and solvents

- Monomers
Acetoacetoxyethyl methacrylate (AAEM) and styrene (ST) were obtained from Aldrich and were purified by conventional methods. N-vinylcaprolactam was obtained from Aldrich and purified by distillation. Pyrrole (Py) was purchased from Aldrich, distilled under vacuum, and stored in a refrigerator before use.

- Initiators and oxidants
Sodium peroxydisulfate (SPDS), Ferric chloride (FeCl₃) and phosphomolybdic acid (H₃PMo₁₂O₄₀·29H₂O) were obtained from Aldrich and used as received. 2,2’-azobis(2-methylpropioamidine), dihydrochloride (AMPA), AIBN was obtained from Aldrich and used as received.
- **Surfactants**

ω-hydroxy poly (ethylene glycol) methacrylate (PEGMA, Aldrich) with average $M_w=526 \text{ g/mol}$ was used as supplied. PVME was obtained as a 50 wt.% aqueous solution (BASF, Lutonat® M40) and was used as supplied. The molecular weight was determined by static light scattering in butanone to $M_w=46,000 \text{ g/mol}$. PVME microgels was crosslinked at T=50 °C and polymer concentration 1 g/l with radiation dose of 60 kGy.

- **Cross-linkers**

$N,N'$-methylenebisacrylamide (MBA) from Aldrich was used without further purification. Divinylsulfone (DVS) was received from Aldrich and used as commercially available.

- Sodium benzoate (Benzoate), potassium hydrogen phthalate (Phthalate) and sodium hydrogen succinate (Succinate) were obtained from Aldrich Chemical Corp. and were used as supplied.

- Basis polymer 884/2 was supported by Chemetal and used as supplied.

- Amino acids used were of reagent grade (Aldrich), and used as supplied.

- Deionized water was employed as polymerization medium. Ethanol (96 %) was obtained from Fluka.

**7.3 Polymerization of core-type polypyrrole**

PVME was dissolved in appropriate amount of water in a reactor equipped with stirrer. Then pyrrole was added to the stirred solution and reactor was purged with nitrogen for 15 min. Oxidant, which was first dissolved in water was then added by droplet and the polymerization was allowed to proceed for 24 hours. The resulting stable dispersions were cleaned by dialysis (Millipore membrane 100 000 MWCO) to remove oxidant and by-products.

**7.4 Polymerization of VCL/AAEM microgels**

The synthesis of VCL/AAEM microgels was described as follows. 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 carry out for 8 hours. The polymerization yield, determined gravimetrically, was around 80 %. The chemical structure of VCL/AAEM copolymer is presented in Scheme 7.1.

Scheme 7.1: Chemical structure of VCL/AAEM copolymer.

7.5 Polymerization of pyrrole using VCL/AAEM microgel as template
VCL/AAEM microgel was diluted with water or 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 hours. The polypyrrole content in composite microgels was determined by elementary analysis. Polymer dispersions were freed from monomer by dialysis. Latexes were dialysed against water using Millipore Amicon Miniplate membrane (MWCO – 10000).

7.6 Synthesis of PS/PEGMA core particles
Appropriate amount of PEGMA was dissolved in water and then the monomer was added to the stirred solution. Obtained pre-emulsion was stirred for 1 h. Double-wall glass reactor equipped with stirrer and reflux condenser was purged with nitrogen. Pre-emulsion was placed into reactor and the water solution of initiator was added under continuous stirring. Temperature was increased to 70 °C to start the polymerization process. Latexes were prepared at ca.10 % solid content.
7.7 Synthesis of core-shell PS/PEGMA/PPy particles
Diluted PS/PEGMA dispersions were placed into stirred reactor. Appropriate pyrrole amounts were injected by syringe and mixture was stirred for 15 min under nitrogen flow at 25 °C. Water solution of oxidant (FeCl₃) was added dropwise to start pyrrole polymerization. After 5-10 min dispersion became coloured (blue or dark red colour appears) indicating that pyrrole polymerization started. After 6 hours formed composite particles were removed from reaction vessel and cleaned to remove non-reacted pyrrole and all by-products.

7.8 Preparation of composite hydrogels
PS/PEGMA dispersion was mixed with appropriate water solution of PVA or HPC in glass tube. NaOH solution (0,1 M) was added to adjust pH to 9 – 10 followed by injection of divinylsulfone (DVS) into stirred solution. Samples were kept 24 hours at room temperature to ensure the complete reaction of DVS molecules with OH- groups. Obtained hydrogels were cleaned to remove non-reacted DVS, not grafted PS/PEGMA particles and residue of base.

7.9 Polypyrrole deposition in composite hydrogels
Chemical method
Hydrogel samples were cut into discs (d=1 cm and h= 0,5 cm).

a) Direct swelling in pyrrole
Gel samples were immersed into pyrrole for 1 hour. Later gel samples were washed by water 2-3 times and immersed into oxidant solution (Na₂S₂O₈ – 12,5 g/l). After 5-10 min dispersion became coloured indicating that pyrrole polymerization started. After 24 hours formed composite gels were removed from reaction vessel and cleaned to remove non-reacted pyrrole and all by-products.

b) Direct swelling in water/ethanol mixture containing pyrrole.
Water/ethanol mixtures (9:1) [wt:wt] were prepared with different pyrrole amounts (2,5; 5; 7,5; 10 and 12,5 g/l). Swelling and polymerization procedure is similar to direct swelling in pyrrole.
Electrochemical method
The hydrogel encapsulated electrodes were presoaked in the aqueous pyrrole monomer solutions, of varying concentrations, with 1 M NaNO₃ for 24 h. 1 M NaNO₃ was used as supporting electrolyte for the electropolymerization process.

7.10 Sample preparation and measurement conditions
Cleaning procedure for the metal sheets
First metal sheets were immersed in the Gardodean 854/5 solution (25 g/l) at 60 °C for 10 minutes. After sprung by distilled water, they were put into VE-water solution (1 g/l NH₃ H₂O) at room temperature for 1 minute. Then the metal sheets were dried in the oven at 100 °C for 5 minutes.

Preparation of conducting polymer film on the metal sheets
Conducting polymer dispersion was prepared by mixing colloidal polypyrrole dispersion with basis polymer (supplied by Chemetal) according to the recipe under stirring. The mixture was dropped onto the metal sheet surface and made a homogeneous layer on it by Lact with the thickness of 2 µm. The film was formed by drying the conducting polymer overlayer in the oven at 100 °C for 5 minutes or at room temperature for overnight.

Base treatment
Cleaned polypyrrole composite particles have been dried in the oven overnight at 40 °C and then were dispersed in aqueous 0,1 M NaOH with an ultrasonic homogenizer. The suspension was stirred overnight at room temperature and then purified by centrifugation at 8000 r/min for 15 min. The resulting sediment was rinsed several times with water.

Amino acid uptake
The uptake of amino acid in the colloidal particle was determined as follows: an 5 ml of aqueous solution (pH=1 adjusted by HCl) containing 0,0125 mmol amino acid and 0,01 g of particles was shaken vigorously for 24 hours and the colloidal particles were then removed by a membrane filter (0,45 µm). The pH of the filtered solution was adjusted to 7 with buffer solution. 2 ml of final solution was added to 0,4 ml ninhydrine reagent (0,1g Ninhydrin in 10 ml ethanol with water for 100 ml) and the mixture was heated in boiling water bath for 40 min. The solution shows typical blue colour which gives special UV absorbance at λ=570 nm. The peak intensity corresponds to the concentration of non-adsorbed amino acid which can be calculated
from calibration curve. The calibration curves have been determined separately for different amino acids.

**Light scattering (DLS)**

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. Static light scattering (SLS) measurements were performed with FICA 50 (SLS Systemtechnik G. Baur, Freiburg, Germany) using a light source (633 nm) at scattering angles 15 <\(\Theta\)< 145 and 25 °C.

**Flow-Field-Flow-Fractionation coupled with Multi-Angle-Laser-Light-Scattering**

Flow-Field-Flow-Fractionation coupled with Multi-Angle-Laser-Light-Scattering (F-FFF-MALLS) was used to characterize the particle size distribution. The fractionator F-100 (FFFractionation, Inc., Salt Lake City, USA) and DAWN-DSP light scattering photometer (Wyatt Technology Corp., Santa Barbara, USA) were used. Obtained data were interpreted by using ASTRA 4.50 software from Wyatt Technology Corp. Solvent for F-FFF-MALLS measurements was deionized water containing 0.02 % (w/w) SDS and 0.02 % (w/w) NaN3 as a bactericide. Samples were measured at constant cross flow rates. Scattering intensities are monitored continuously using a MALLS photometer with up to 18 detectors at fixed angles between 10 and 160 °.

**Stability measurements**

Stability measurements were performed with separation analyser LUMiFuge 114 (L.U.M. GmbH, Germany). Measurements were made in glass tubes at acceleration velocity 3000 rpm. The slope of sedimentation curves was used to calculate the sedimentation velocity and to get information about stability of the samples.

**\(\zeta\)-potential measurement**

\(\zeta\)-potential measurement was performed with Zetasizer 2000, Malvern Instrument. pH value was adjusted by adding diluted solution of NaOH and HCl to diluted dispersion. Samples are prepared at different pH starting from 2 to 12 with an internal of 0,5.
**Scanning electron microscopy (SEM)**

SEM images were taken with Gemini microscope (Zeiss, Germany). Samples were prepared in the following manner. Dispersions were diluted with deionized water, dropped onto aluminium support and dried at room temperature. Pictures were taken at voltage of 4 kV.

**Atomic Force Microscopy (AFM)**

Measurements were made with Dimension 3100 (Digital Instruments Inc.) using the tapping mode regime (set point ratio – 90%; integral gain – 0,2; proportional gain – 2,0; amplitude setpoint – 0,7 V; scan rate 0,901 Hz). Samples were prepared by spin coating technique (2000 rpm, 10 min) on previously cleaned glass supports.

**Transmission Electron Microscopy (TEM)**

TEM images were obtained with Zeiss Omega 912 at voltage10 kV. Polymeric particles were embedded into epoxy resin, crosslinked for 48 hours and microtomized. Ultra-thin cuts were placed onto carbon grids and stained with ruthenium tetroxide for 4 hours.

**Rheological measurements**

Rheological properties of polymeric dispersions were investigated with Bohlin CS Rheometer (Bohlin Instruments Inc.). The double gap measuring geometry was used. It consists of a hollow cylinder (outer diameter – 45,46 mm; inner diameter – 43,80 mm) which is lowered into a cylindrical groove in the outer cylinder (cylinder diameter – 50 mm; inner cylinder diameter – 39,82 mm). The sample is contained in the double annular gap between them.

**IR-Spectroscopy**

IR spectra were recorded with Mattson Instruments Research Series 1 FTIR spectrometer. Dried polymer samples were mixed with KBr and pressed to form a tablet.

**UV measurements**

UV spectra were recorded with PerkinElmer UV-VIS spectrometer Lambda 45. This device was equipped by RSA-PE-20 accessory which is an optical bench, including transfer optics, an integrating sphere and detector preamplification module. Samples were fixed between two quartz plates (layer thickness appr. 0,5 mm).

**X-ray photoelectron spectroscopy (XPS)**

The composition of the delaminated metal surface was examined by X-ray photoelectron spectroscopy (XPS) using a JEOL JPS-80 photoelectron spectroscopy.
Pass energies were set at 80 eV for survey and 40 eV for core line spectra. Peak position was calibrated against C 1s (285.0 eV).

**Constant Climate Test**

Constant Climate Test was made according to DIN 50017-KK. Metal sheets were put in the climate chamber at 40 °C with 100 wt.-% relative moisture under dewing for defined time.

**Delamination measurements**

Delamination measurements were performed by using of the micro Kelvin-probe. The vibrator is given by an extremely sharp Cr-Ni needle (tip diameter about 5 μ m), the vibration frequency being about 2 kHz. The vibrator is scanned over the sample by computer controlled step motors and the Volta potential is measured point by point using a specially built electronic circuit. Polymer films were prepared by spinning coating on Fe surface. The lacquer was removed on one half of the sample and a drop of 0.01 M KCl is deposited on top of the free metal surface just up to the intact metal/polymer interface. Thus the electrolyte may penetrate along the interface, causing delamination.

**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 dispersion on the electrode quantitatively and dried under vacuum for 24 hours. 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:

$$ \sigma = \frac{d}{R \times A} $$

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.

**Current-voltage (j-U) characteristics**

Current-voltage (j-U) characteristics were measured with Keithley 6517A electrometer. Sandwich samples were placed in vacuum chamber (10^{-5} Pa) with temperature adjustment system in the range from -30 to 100 °C. Fig.7.3 shows the Sandwich samples prepared for current-voltage characteristics.
Humidity sensitive measurements
Humidity sensitive measurements were done with home designed system and the relative humidity (RH) can be changed in the range of 2 ~ 98 % using nitrogen gas flow or 48 ~ 92 % using air flow. The RH value was calibrated using the comitial product. The AC and DC signal from samples were measured by HIOKI 3532-50 LCR HiTESTER and Keithley 6517A electrometer respectively.

Photoconductivity
Photoconductivity was measured with same Keithley 6517A electrometer under illumination by Quartz Halogen Lamp 200 combined with CORNERSTONE 130 Motorized 1/8 m monochromator. Fig.7.4 shows the surface samples prepared for photocurrent measurements.
**Swelling measurements**

Swelling degree \( (Q) \) in water \((W_s/W_d)\) in gel samples was determined by gravimetric measurements. The gel samples were dried and weighed to constant weight \((W_d)\). Later samples were immersed in a large amount of water and allowed to reach equilibrium before weighing \((W_s)\).

**Hardness measurements**

Measurements were performed with Fischerscope H 100 W Micro Hardness Control and Pendulum hardness tester “Gardner”. Polymer films prepared on previously cleaned glass plates were used directly for measurements of hardness.
8. Summary

We proposed the novel template oxidative polymerization method to prepare PPy composite particles with additional “value-added” properties. Water-soluble polymers, polymeric microgels, latex particles or bulk gels have been successfully used as the template. PPy composite particles with well-defined colloidal dimensions and morphology and controlled properties (such as biocompatibility, thermo-sensitivity and potential surface functionalization) can be obtained reliably.

In the case of uncrosslinked PVME being used as stabilizer, core-type polypyrrole spherical particles in the range of 50-100 nm were formed in both aqueous ethanol and water. Results of the elementary analysis, IR spectroscopy confirmed that the anionic salts can be incorporated in the PPy particles and play as the dopants. The presence of dopants in polypyrrole enhances the conductivity, especially in the case of sodium benzoate the conductivity of the final product has been improved by 3 orders.

Polymeric microgels were also applied as the templates for polypyrrole deposition. When crosslinked PVME microgels were used in the oxidation polymerization of pyrrole, large PPy fibrils (appr. 400 nm) were formed. Needle-like particles were formed due to the porous structure of microgels, which play a template role in the pyrrole polymerization process. When VCL/AAEM microgels were used as a template for oxidative polymerization of pyrrole, “raspberry-like” composite particles will be formed with PPy domains located in swollen hydrophobic particle shell.

Obtained stable composite microgels show similar thermal sensitivity as VCL/AAEM microgel particles with fully reversible collapse-swelling properties. 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.

Furthermore, monodisperse PS-PEGMA particles, which were prepared in water medium, have been used as a template for deposition of polypyrrole (PPy). Obtained composite particles possess core-shell morphology where shell is composed out of small PPy nano-domains. The shell thickness can be varied by changing PPy load, controlling the overall template surface area in the system, and by influencing the pyrrole polymerization kinetics in presence of different oxidants. The last possibility provides also incorporation of different anions into polypyrrole shell. The stability of composite particles decreases gradually if the deposited PPy amount increases. It has
been established that obtained particles are intrinsically coloured and the colour can be changed by the PS-PEGMA core size. Conductivity measurement shows that PS/PEGMA/PPy composite particles prepared by using phosphomolybdate as the oxidant are much more conductive than the particles prepared by the other two oxidants. The conductivity increases with the increase of PPy load in the system. Moreover, obtained polypyrrole composite particles have been tried for different applications. First, it can be used as the additive of the paint formulation. Corrosion protection tests show that by using PPy dispersions as the additive for the paint, improvement can be achieved both in surface corrosion protection and scribe corrosion protection. Especially when molybdate was used as the dopant for polypyrrole dispersion, passivation of the corroding iron was observed in the defect and at delamination front.

Secondly, PS/PEGMA/PPy composite particles have been used for amino acid absorption. It has been found that PPy composite particles can absorb quite high amounts of alanine and even show certain enantioselectivity. The alanine uptake can be controlled by the particle concentration in the mixture as well as by the PPy amount on the particle surface. The uptake of alanine can be influenced by the size of dopant anion and the maximum value was detected for particles doped by phosphomolybdate.

Finally, PPy-functionalized composite hydrogels can be prepared in two steps: (1) combination of PS/PEGMA particles into the hydrogel matrix and (2) deposition of PPy into hydrogel by both chemical and electrochemical methods. It has been shown that incorporation of PPy into hydrogels decreases the swelling degree of polymer network. The morphology and properties of final composite hydrogels can be controlled by particle concentration, PPy amount, crosslinking degree etc.

In summary, different morphologies are available: spherical, core-shell, raspberry, needle-like etc. The particle size range of obtained dispersions is from 50 nm to 1 µm. All polypyrrole products are stable water-based dispersions, which can be further used as additives for paint formulations, ion-separation or microelectronics. The most satisfying part of our work is that PPy composite particles with controlled morphology and properties can be successfully used in different areas. And we have no doubts that the excitement will continue to grow, as we go forward into the research of conducting polymers.
9. Future work

The future investigations can mainly focus on two directions: (1) to find new applications for obtained composite particles, and (2) to investigate new morphology and properties of PPy composites and some other conducting polymers.

For the first direction, it includes the applications for PPy composite particles with defined morphology. First of all, PPy-functionalized composite hydrogels are interesting multifunctional materials which combine both properties of hydrogels and conducting polymers. This unique combination can lead to successful application of such hydrogels in bio-sensory devices or different actuators. For example, the conjugated polymer actuators may find application in microfluidic pumps and valves for drug delivery or bioanalytical labs-on-a-chip. Fig.9.1 shows the principle how microvalve works. There is a large out-of-plane volume change which can be directly exploited to close a microchannel. The advantage of this configuration is that it has very little “dead volume”, which prevents remixing during chemical separations. A series of such actuators would result in a peristaltic pump.

![Diagram of microvalve](image)

**Fig.9.1:** Microvalve under development that utilizes out-of-plane volume change.
Secondly, for IPN type PPy/microgel composite particles, they can be used in protein and enzyme delivery systems because of their biocompatibility and hydrophilicity. VCL/AAEM microgels are an interesting group of particles with promising applications in nanotechnology due to their conspicuous fast response to external stimuli like temperature or electric field, which can undergo reversible volume phase transition between collapsed and swollen states as a result of the competition between repulsive intermolecular forces and attractive forces.

Furthermore, core-shell type PPy composite is also an interesting and promising system because it offers several advantages. Monodispersed spherical PS-PEGMA core particles possess bio-compatible surface and can be prepared within a broad size. Secondly, the thickness of the polypyrrole shell and nature of the dopant anion can be precisely adjusted by changing polymerization parameters or oxidant, respectively. Moreover, PPy chains on the particle surface are also well-organized due to the directed growth in the PEGMA-brush layer.

For example, it is interesting to perform the polymerization of poly(3,4-ethylenedioxythiophene) (PEDOT) or polyaniline (PANi) by using PS-PEGMA particles as the core to get conducting polymers with different morphology and properties.

![Fig.9.2: SEM images of PS/PEGMA/PEDOT particles prepared by using FeCl₃ as oxidant.](image)

Fig.9.2 shows the SEM images for core-shell type PEDOT composite particles by using PS/PEGMA as the core. Instead of traditional raspberry morphology, PS/PEGMA/PEDOT particles show special “tennis-ball” morphology. The possibility of controlling the morphology and property for PEDOT composite must be more deeply investigated.
Moreover, core-shell type polypyrrole composite particles are interesting for application as humidity sensors or potentiometric sensor. Some basic research has already been done in this direction. The changes of the resistance for relative humidity changes from 50% to 96% are presented in Fig.9.3.

![Fig.9.3: Changes of resistance of core-shell type polypyrrole composite particles during the change of relative humidity from 50% to 96.](image)

From Fig.9.3, it can be observed that fast change of the humidity during about 2 s was realized by the switching between dry and wet flowing nitrogen. The change of the resistance was more than four orders of magnitude (thickness of the film was ca. 200 nm); for thinner layers even larger changes could be detected. Similar changes were also observed in DC conductivity. It is also worth noting that the resistance changes were relatively stable and fully reproducible which indicates that it is possible to fabricate humidity sensors based on core-shell type PPy particles. Furthermore, it is interesting to point out that the magnitudes of the changes depend on the dopant. When phosphomolybdate was used as the oxidant, higher and more stable response for the humidity change was investigated. While FeCl₃ was used as the oxidant, the response was smaller and the signal was not stable and decreased with time. From this point of view, core-shell type polypyrrole composite particles have high guarantee to be used for humidity sensors, but more detail work should be done in the future to understand the mechanism how the humidity sensor works and how to control the response for the humidity change.
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Publications


**Presentations**


Acknowledgement

It is both a privilege and a pleasure to thank all the people who have kept me productive, sane and happy in Dresden in the last three years. First and foremost, my advisor Prof. Dr. Hans-Juergen P. Adler deserves all the credit for introducing me to the world of colloidal chemistry and making me feel at home in his institute. I thank him for showing me how to be a competent researcher and training us to be free-thinking independent scientists. I also have much appreciation for Dr. Andrij Pich for his valuable advising and introducing me to conducting polymers and methods for characterization. His patient remarks and suggestions clarify my understanding of conducting polymeric dispersions.

My sincere thanks to Prof. Meifang Zhu, who was always there to answer my questions. She is a real friend and a good teacher to me. I would be remiss if I did not acknowledge all the teachers, Prof. K.-F. Arndt, Prof. B. Voit, who taught me the courses and keeping my eyes, open to the (Materials) world beyond conducting polymers. I deeply appreciate the help of Prof. Nespurek with his group member, Dr. G. Wang for introducing me to the difficult world of electrical physics. I would like to thank Mr. V. Boyko for supplying the VCL-AAEM microgels and Mr. T. Schmidt for supplying the PVME microgels. I appreciate the help of Mrs. E. Kern for helping with SEM, Mrs. M. Dziewiencki for helping with FT-IR, Mrs. I. Poitz for helping with DSC and TGA, Mr. G. Busch for UV measurements, Mr. A. Mensch for TEM measurement, Mrs. C. Meissner for SLS measurements, Dr. C. Bellmann for ζ-potential measurement, Dr. S. Gao for AFM measurements, Dr. Y. Zhen and Ms. F. Li for conductivity measurements, Mrs. G. Paliwoda for KPS measurements and Ms. J. Schneid for the corrosion tests. I would like to thank all my group members: A. Musyanovch, A. Karad, J. Hain, N. Schiemenz our conversations, laughs and their help will always be fondly remembered. And also all the institute members: Dr. E. Jaehne, Dr. K. Potje-Kamlooth and Dr. D. Kuckling for helping and answering many of my questions. I express my sincere appreciation to all my Chinese friends and their kind words over these years with my homesickness. I would like to thank SFB 287 “Reactive Polymers“ (DFG) for the financial support.
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