Synthesis and Characterization of Poly(vinylcaprolactam)-Based Microgels Exhibiting Temperature and pH-Sensitive Properties

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ABSTRACT: Novel temperature- and pH-responsive microgels based on poly(vinylcaprolactam-*co*-acetoacetoxy methacrylate) (VCL/AAEM) functionalized with vinylimidazole (VIm) has been prepared in aqueous medium using simple batch dispersion polymerization procedure. Obtained microgel particles are characterized by narrow particle size distribution and their hydrodynamic radius can be varied from 200 to 500 nm (pH = 6, T = 20 °C). The T- and pH-sensitivity of obtained particles can be easily tuned by the variation of the Vim content in the copolymer structure. Increase of VIm content in the microgel structure led to increased swelling of the microgels in acidic medium and strong shift of the volume phase transition temperature to higher temperatures. It has been found that sedimentation behavior of obtained microgels is strongly pH-dependent, and this effect can be used for controlled particle separation.

Introduction

Recently colloidal microgels became an important subdivision of polymer colloids and numerous synthetic microgel systems have been developed. The preparation and characterization of microgel particles has been described in the reviews of Park and Hoffman[1] and Pelton[2] providing an excellent overview over the microgel field as well as basic understanding of the microgel particles, their synthesis and behavior in dispersed media. Most of the microgel particles operating in aqueous medium are based on poly(*N*-isopropylacrylamide) (PNIPAAm),[2−4] poly(*N*-vinylcaprolactam) (PVCL)[5,6] or other water-soluble polymers such as poly(acrylic acid) (PAA),[7,8] poly(methacrylic acid) (PMA),[9] or poly(2-(diethylamino)ethyl methacrylate) (PDEA).[10] The special interest in PNIPAAm- or PVCL-based microgels is dedicated to their temperature-sensitivity what enables fabrication of “switchable” or “stimuli-responsive” materials. Recently PEO-grafted sterically stabilized PVCL microgel particles have been prepared by macromonomer approach.[11] The comparison of the colloidal stability of electrostatically, sterically and electrosterically stabilized PVCL microgels shows that incorporation of the PEO macromonomer increases microgel resistance to the high electrolyte concentrations especially at temperatures above volume phase transition.[12]

The temperature sensitivity of microgels was also combined with pH sensitivity by incorporation of ionic monomers such as acrylic acid, vinylimidazole, 4-vinylpyridine, etc. into the PNIPAAm[13−18] or PVCL[5,19,20] microgel structure. In this way preparation of stimuli-responsive colloidal particles with defined size, functionalized surface and enhanced colloidal stability has been achieved. The multifunctionality of microgels resulted in some interesting applications such as preparation of hollow thermosensitive microgel capsules,[21] colloidal crystals,[22] microlens arrays,[23] specific targeting of cancer cells and drug delivery.[24−26] The key factor for the successful utilization of microgel particles is their chemical composition which determines location of functional groups within swollen cross-linked particles providing targeted adsorption or grafting of small molecules, polymers, proteins, etc.

With regard to this phenomenon the synthesis of new microgel systems with tailored properties is still a big challenge. The aim of present work was preparation of reactive microgel particles with tunable swelling degree and modulated separation properties as smart enzyme carriers. Herein we describe synthesis of poly(*N*-vinylcaprolactam)-based microgel particles which exhibit T- and pH-sensitive behavior. In the present system vinyl caprolactam (VCL) (main monomer) was copolymerized with acetoacetoxyethyl methacrylate (AAEM) and vinylimidazole (VIm) by simple batch polymerization procedure in aqueous medium leading to the formation of colloidally stable multifunctional microgel particles. Obtained PVCL-based microgels are temperature-sensitive, reactive β-diketone groups (originating from AAEM units) are able to react with biomolecules, and VIm units can be reversibly protonated/deprotonated by changing pH of the aqueous medium.

Experimental Section

Materials. *N*-Vinylcaprolactam (VCL), acetoacetoxyethyl methacrylate (AAEM), and vinylimidazole (Vim) (Aldrich) were purified by conventional methods and then distilled under vacuum. Initiator 2,2′-azobis(2-methylpropyonamidine) dihydrochloride (AMPA) and cross-linker *N,N*′-methylenebis(acrylamide) (BIS) (Aldrich) have been used as received.

Microgel Preparation. The synthesis of VCL/AAEM microgels has been reported elsewhere.[6] In this study, we used a similar procedure but additional monomer (VIm) was introduced into the reaction mixture. The substances used for the microgel preparation are shown in Figure 1.

The polymerization procedure can be described as follows. Appropriate amounts of AAEM, VCL, VIm, and cross-linker (3 mol %) were dissolved in deionizer 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 under continuous purging with nitrogen. After that, the 5 mL aqueous solution of initiator was added under continuous stirring. Reaction was carried out for 8 h. Microgel

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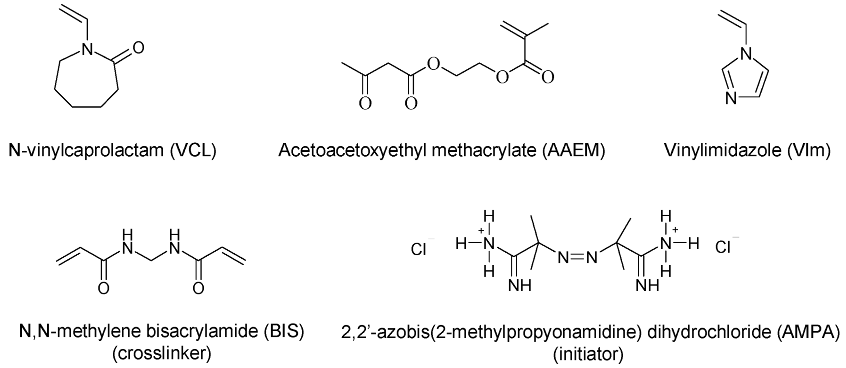

Figure 1. Substances used for microgel synthesis.

Table 1. Amounts of Reagents Used for the Microgel Synthesis

sample	VCL, g	AAEM, g	VIm, g	BIS, g	AMPA, g	water, g	pH	VIm, mol %	SC,[a] %
VCL/AAEM	1.877	0.338		0.06	0.05	150	3.96	0	1.45
VCL/AAEM/VIm(0.9%)	1.858	0.335	0.014	0.06	0.05	150	6.22	0.90	1.57
VCL/AAEM/VIm(1.85%)	1.839	0.331	0.028	0.06	0.05	150	6.30	1.85	1.51
VCL/AAEM/VIm(2.88%)	1.820	0.328	0.043	0.06	0.05	150	6.30	2.88	1.45
VCL/AAEM/VIm(3.92%)	1.801	0.325	0.057	0.06	0.05	150	6.23	3.92	1.48
VCL/AAEM/VIm(4.91%)	1.783	0.321	0.071	0.06	0.05	150	6.45	4.91	1.59

[a] SC = solid content.

dispersion was purified by dialysis with Millipore Dialysis System (cellulose membrane, MWCO 100 000). The amounts of ingredients used for polymerization process as well as some important microgel characteristics are shown in Table 1.

Particle Characterization. Static light scattering (SLS) experiments were performed using modified FICA 50 (SLS Systemtechnik G. Baur, Denzlingen, Germany) with He−Ne-laser (wavelength of 632.8 nm) in the scattering angle range between 15 and 145°. The refractive index increment (*dn*/d*c*) was estimated using differential refractometer DR 1, (SLS Systemtechnik G. Baur, Denzlingen, Germany) with He−Ne laser ($\lambda_0 = 632.8$ nm) as the light source.

Dynamic light scattering DLS measurements were performed using commercial laser light scattering 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. The DLS experiments were carried out in the range of scattering angles $\theta = 30-90°$. All solutions were filtrated using a 5.0 μm membrane filter before measurements.

Electrophoretic mobility of microgel particles has been measured with a Zetasizer 2000, Malvern Instruments. pH was adjusted by addition of 0.01 M NaOH or 0.01 M HCl. Average value of at least 10 measurements was adopted as electrophoretic mobility of particles at certain pH value.

Stability measurements of microgel dispersions were performed with separation analyzer LUMiFuge 114 (LUM GmbH, Germany). Measurements were made in glass tubes at acceleration velocities from 500 to 3000 rpm. The slope of sedimentation curves was used to calculate the sedimentation velocity and to obtain information about stability of the samples.

SEM images were taken with Gemini microscope (Zeiss, Germany). Samples were prepared in the following manner. Microgel dispersions were diluted with deionized water, dropped onto cleaned glass support and dried at room temperature. Samples were coated with thin Au/Pd layer to increase the contrast and quality of the images. Pictures were taken at a voltage of 4 kV.

FESEM images were obtained with LEO Gemini microscope equipped with field emission cathode at voltage 2 kV. Diluted microgel dispersions were placed onto Al substrates and dried at room temperature.

Results and Discussion

The preparation of thermosensitive microgels by copolymerization of VCL and AAEM has been introduced first in our earlier publication[6] and the use of VCL/AAEM microgels as carrier for polypyrrole,[27,28] magnetite,[29] ZnS,[30] and Ag[31] nanoparticles has been reported recently. It has been found that in the batch dispersion polymerization process the VCL:AAEM ratio determines size of microgels below phase transition temperature due to regulation of cross-linking (swelling), but only slightly influences the size of collapsed particles. The microgels possess core−shell structure (AAEM-rich core and VCL-rich shell) due to fast consumption of more reactive methacrylic monomer. Because of the presence of AAEM in copolymer structure the phase transition temperature of the PVCL-rich shell is shifted to ca. 28 °C as compared to reported 32 °C for pure PVCL. In present study we introduced different amounts of additional monomer (vinylimidazole) into the reaction mixture by keeping the ratio between VCL and AAEM as well as cross-linker and initiator concentrations constant (see Table 1 for details). The incorporation of VIm into the microgel structure was confirmed by potentiometrical titration and results are summarized in Table 1. The determined VIm contents in the microgel structure indicate that the incorporation efficiency was around 90−95%.

Figure 2 shows the influence of Vim content on the particle size of microgels at pH = 6 and $T = 20$ °C. Figure 2 indicates that the hydrodynamic radii of microgels increase with linear order if larger VIm amounts are introduced into the microgel structure. At the same time the polydispersity index of obtained microgels remains unaltered (proved by DLS measurements) what indicates that introduction of VIm does not induce the formation of secondary particles in the aqueous phase.

These observations lead to the conclusion that incorporation of small amounts of VIm increase strongly the hydrophilicity of the particles leading to better solvatation by water molecules and higher swelling in continuous medium. This results finally in the increase of hydrodynamic radii of microgel particles with gradual increase of VIm content.

The morphology of microgels has been studied by different microscopy techniques. SEM images presented in Figure 3a,b indicate that VCL/AAEM microgels and their analogues with 2.9% VIm are spherical particles which are slightly deformed and shrunken after water removal. Comparing images a and b in Figure 3, it is obvious that VCL/AAEM/VIm(2.9%) particles

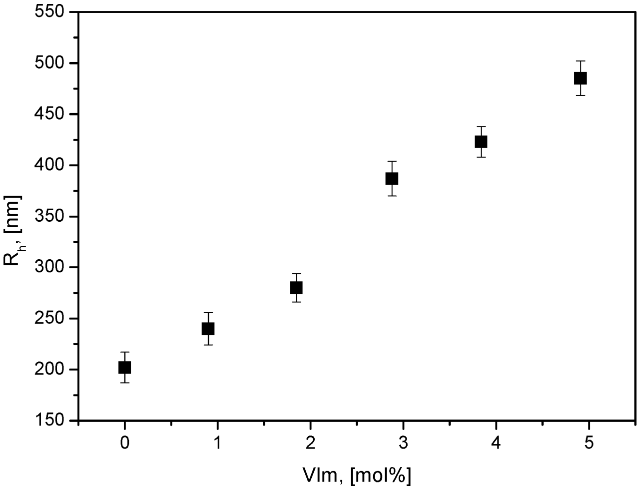

Figure 2. Hydrodynamic radii of microgel particles prepared at different VIm contents ($T = 20$ °C; pH = 6).

are larger than VCL/AAEM microgels what supports light scattering measurements. A closer look by FESEM technique on the microgel morphology reveals some interesting effects. FESEM images presented in Figure 3c,d indicate that VCL/AAEM/VIm(2.9%) microgels exhibit a corona-like shell which is hardly visible in the case of the VCL/AAEM particles.

The average particle size in the dry state determined from the FESEM images can be used to determine the size ratio between dry and swollen state for two microgel samples and compare them. Interestingly, the radius ratio for VCL/AAEM and VCL/AAEM/VIm(2.9%) is 1:1,92 (in the swollen state) and 1:2 (in the dry state). This similarity indicates that the effects visible in FESEM images picture partly the situation in the swollen state, so the observed increase of microgel size by introduction of VIm units correlates well with our light scattering data.

As expected, the pH of the aqueous phase influences the dimension of the microgel particles. Figure 4 shows the hydrodynamic radii of different microgel samples as a function of pH (light scattering data). The R_h−pH dependencies for all samples containing VIm exhibit maximum at pH = 4 what correlates with maximum ionization pH of VIm units. This effect leads to the swelling of microgel particles due to the strong electrostatic repulsion between the charged VIm groups. Figure 4 indicates also that the swelling at pH = 4 increases gradually with increase of the VIm content in the microgel structure indicating that the repulsion forces within the microgel particle became stronger at higher concentration of charged VIm groups. The decrease of the R_h values at pH > 4 is attributed to the increase of the ionic strength by excess of HCl and screening of the electrostatic repulsion within microgel particles. By performing the measurement at constant ionic strength (using buffer solution for the adjustment of the pH value) one can avoid such effect and R_h values should remain constant at pH < 4.

Contrary, the hydrodynamic radius of VCL/AAEM microgels is not influenced by the pH indicating that microgels contain less amount of ionizable groups. The experimental results presented in Figure 4 demonstrate that by incorporation of small amounts of VIm groups into VCL/AAEM microgels, it is possible to prepare highly pH-sensitive particles and the maximum swelling degree can be easily controlled by the amount of ionizable groups in the polymer network.

As it was mentioned earlier, the VCL/AAEM microgels possess temperature-sensitive properties and the volume phase transition temperature was detected ca. at 28 °C. This phenomenon occurs due to the different solvatation of poly(vinylcaprolactam) chains by water molecules at the temperatures below and above the phase transition temperature (below 28 °C polymer is swollen and above 28 °C polymer is collapsed). The volume phase transition in the microgel occurs as a result of reduced hydrogen bonding between water molecules and the polymer and hydrophobic aggregation of the polymer. The temperature at which this occurs is dependent on the hydrophobic/hydrophilic balance of the polymer and consequently is tuned by the addition of solvents,[32,33] surfactants,[19] salts[5] or introduction of hydrophobic units[13] or charged groups[17] into the polymer structure. Therefore, the incorporation of VIm units into the VCL/AAEM microgels should influence considerably their volume phase transition temperature. As a consequence, pH becomes also an important parameter because it influences the charge of VIm units and the hydrophilic/hydrophobic balance within the microgel. To investigate the volume phase transitions of microgels the dynamic and static light scattering measurements have been performed at pH = 4 (VIm groups ionized) and pH = 6 (VIm groups deionized) to distinguish clearly the influence of the charges originating from protonization of VIm groups. The experimental results presented in Figure 5. show that incorporation of VIm units in microgel structure influences considerably the particle behavior at different temperatures. The change of the particle radii with temperature is completely reversible both at pH = 4 and pH = 6. Let us consider first the thermal behavior of hydrodynamic radius (R_h) for different microgel samples. Figure 5b shows clearly that at pH = 6 the incorporation of VIm units causes slight shift of volume phase transition temperature to higher values (probably due to the hydrophilicity of VIm) if compared with VCL/AAEM microgel. Additionally, the increase of VIm content led to the more pronounced swelling of the microgel at the temperatures below transition temperature and smaller increase of the R_h at temperatures above transition temperature.

The experimental R_h data determined for similar microgel samples at pH = 4 show totally different behavior. For VCL/AAEM sample similar values of R_h have been determined as for pH = 6. The increase of VIm content in the microgels led to the increased swelling degree and gradual shift of the volume phase transition temperature to much higher values than those of the native VCL/AAEM particles (Figure 5a). Both effects can be explained by the change of the hydrophilic/hydrophobic balance within the microgel by protonization of VIm units at pH = 4. Protonization of the VIm units results in increased electrostatic repulsion and better solvatation by water molecules therefore higher temperature is needed to destroy hydrogen bonds and cause the collapse of the polymeric network. Above mentioned effects increase dramatically the swelling of the microgels due to the electrostatic repulsion within the polymer network; however, the volume phase transition breath remains unaltered. It can be also observed from Figure 5a that above volume phase transition temperature all samples exhibit similar R_h values what may support the microscopy data discussed earlier leading to the conclusion that Vim units are distributed preliminary in the shell area of VCL/AAEM microgel particles.

The experimental data for radius of gyration (R_g) measured for the same microgel samples at two pH values show similar behavior to R_h (Figure 5c,d). At pH = 6 the slight shift of transition temperature to higher values is observed with increase of VIm content and at pH = 4 this effect is more pronounced. Interestingly, for VCL/AAEM microgel and VIm-containing samples R_g values are much weaker dependent on the temperature compared to hydrodynamic radii. Additionally the R_g data

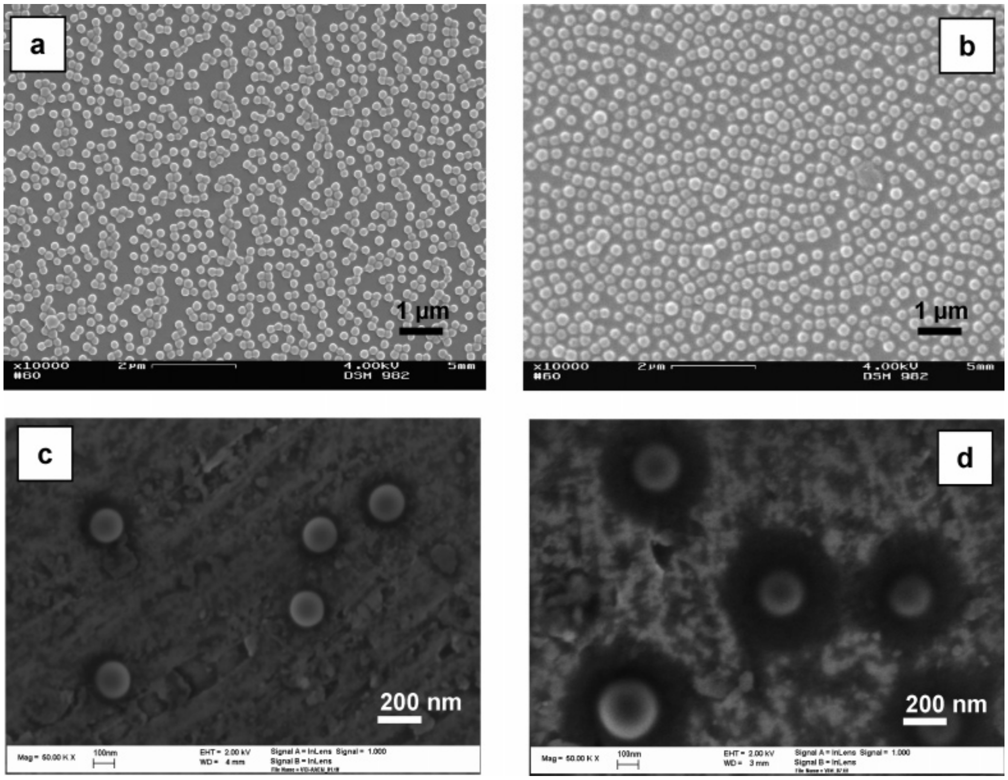

Figure 3. SEM (top) and FESEM (bottom) images of VCL/AAEM (a,c) and VCL/AAEM/Vim(2.9%) (b,d) microgels.

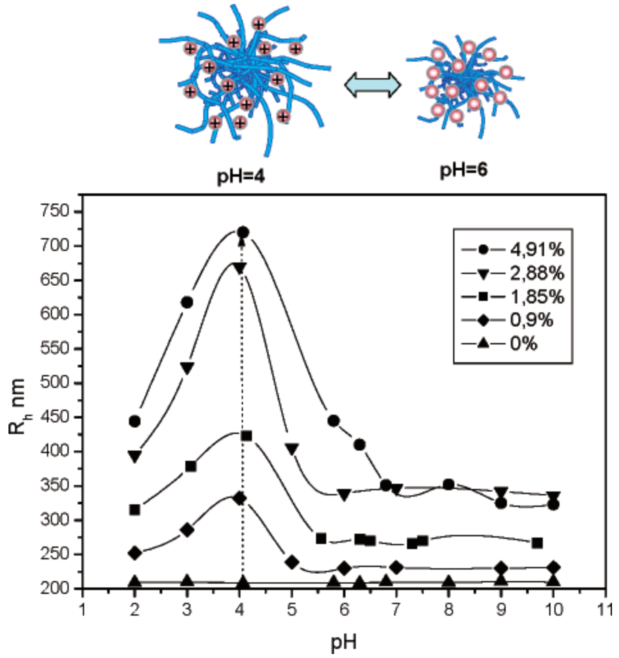

Figure 4. pH-dependency of hydrodynamic radii for different VCL/AAEM/Vim microgels ($T = 20$ °C).

shown in Figure 5c,d are nearly the same above and below volume phase transition temperature at pH = 4 and pH = 6 (e.g., no pH-dependency). These effects confirm that VIm units have been incorporated mostly in the outer region (shell) of the microgel particles leading to the formation of pH- and *T*-sensitive VIm-rich shell and compact AAEM-rich core. This conclusion is also supported by experimental data of hydrodynamic radii discussed earlier. The calculated ρ-parameter (ratio R_g/R_h) by using experimental results presented in Figure 5 a-*d* are shown in Figure 5e,f. The R_g/R_h ratio reflects the conformation of a polymer chain or the density distribution of a particle and thus gives valuable information about the internal structure of microgels. The typical ρ values for microgels in the swollen state have been reported in the range of 0.3−0.6[34,35] and the theoretically predicted ρ value for the homogeneous sphere is 0.775. Monitoring of ρ-parameter shows that with increasing of temperature mobility of PVCL chains decreases and a compact structure without internal motion is formed (Figure 5f). Up to now there are only a few observations of the transition from “soft” to “hard” sphere for thermosensitive microgels.[6,36] This transition occurs at pH = 6 in the same temperature region for all samples and as result, microgel exhibits hard sphere behavior above volume phase transition temperature (deviations from theoretical value are within experimental error). Contrary, at pH = 4 the transition from swollen microgel to hard sphere can be tuned by VIm content in the microgel structure (Figure 5e) because this parameter influences directly the amount of the charged units and, furthermore, the volume phase transition temperature.

The variations of the microgel dimensions by changing of pH and temperature did not cause the destabilization the colloidal system and no particle aggregation was detected. However, the swelling or collapse of the microgel particles should have considerable impact on the stability in aqueous phase and this might be important for specific applications which require fast separation of the polymer from continuous phase. The colloidal stability can be monitored by means of the analytical centrifuge where microgel particles are forced to precipitate under the action of centrifugal force and the sedimentation velocity is determined. The experimentally determined sedimentation velocity data for selected microgel samples are summarized in Figure 6a. In this case sedimentation experiments have been performed at pH = 6 and different rotation speeds. As expected measured sedimentation velocity values increase linearly with increase of the rotation velocity for all microgel samples (solid lines comprise linear fit for the experimental data points). It is obvious that if the increase of

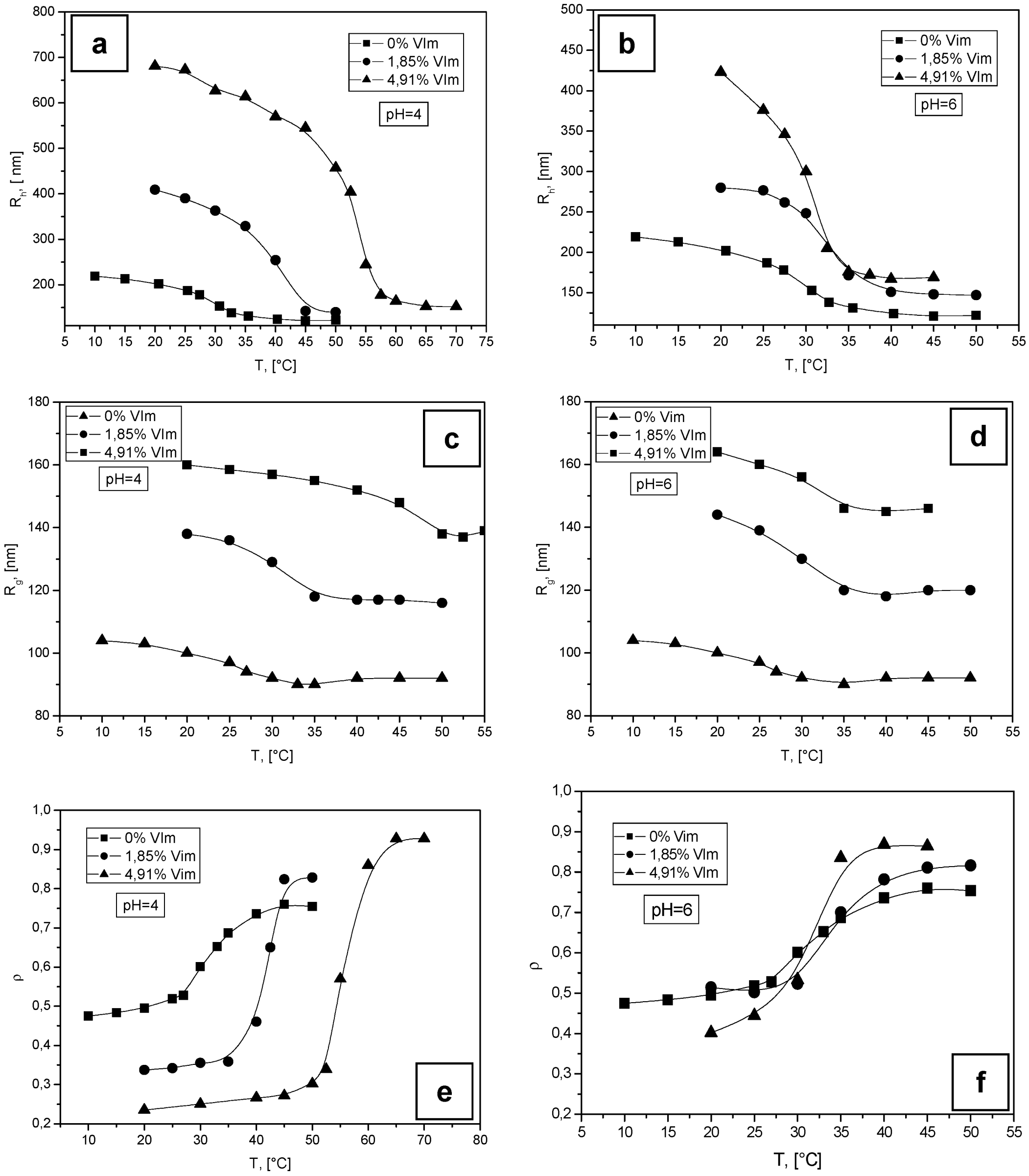

Figure 5. Hydrodynamic radii (R_h) (a, b), radius of gyration (R_g) (c, d) and ρ-parameter ($\rho = R_g/R_h$) (e, f) for microgels with different VIm contents.

VIm content in the microgels causes gradual decrease of the slope due to decrease of the sedimentation velocity values. This indicates that incorporation of hydrophilic Vim units provides additional improvement of the sterical stabilization for microgel particles at pH = 6.

Figure 6b shows sedimentation velocity data obtained at 3000 rpm for all microgel samples used in this study. It is obvious that incorporation of small VIm amounts led to the dramatic improvement of the microgel stability (sedimentation velocity decreases). However the microgel stability is less influenced by VIm content above 2.9% VIm.

Figure 7a shows the sedimentation velocity data for different microgel samples as a function of the pH. Figure 7a indicates that for VCL/AAEM microgel sedimentation velocity data are nearly not dependent on the pH. Contrary, all VIm-containig microgels show complicated picture. In this case the minimal sedimentation velocity (highest colloidal stability) has been detected at pH = 4 for all microgel samples containing VIm. Additionally, increase of the VIm content in the microgel structure shifts the sedimentation velocity to lower values. These observations are in a good agreement with DLS results presented in Figure 4 suggesting maximal ionization of VIm groups at pH = 4. As a consequence of the charge appearance microgel particles are much better stabilized in aqueous medium. As the pH increases VIm groups will be deprotonated and this provokes gradual increase of the sedimentation velocity. Unexpectedly, the sedimentation velocity increases even if pH value is higher than 7. Figure 7a indicates that maximal values of sedimentation velocity were detected at pH = 10 and in this pH region the sedimentation velocity increase with VIm content in the microgels. This behavior is difficult to explain at the moment. In the basic pH no change of the microgel dimensions was detected by DLS (Figure 4), so possible reason for the reduction of the colloidal stability of VIm-containing particles is the excess of OH^- ions and increase of the ionic strength due to the addition of NaOH. Similar effect can be observed at pH = 2 and 3 in Figures 4 and 7a where hydrodynamic radii decrease and sedimentation velocity increases respectively due to the increase of the ionic strength after addition of HCl. Figure 7b shows a summary of the experimentally determined sedimentation velocity data for all investigated microgel samples at pH values 4, 7, and 10. It is obvious that for obtained microgel

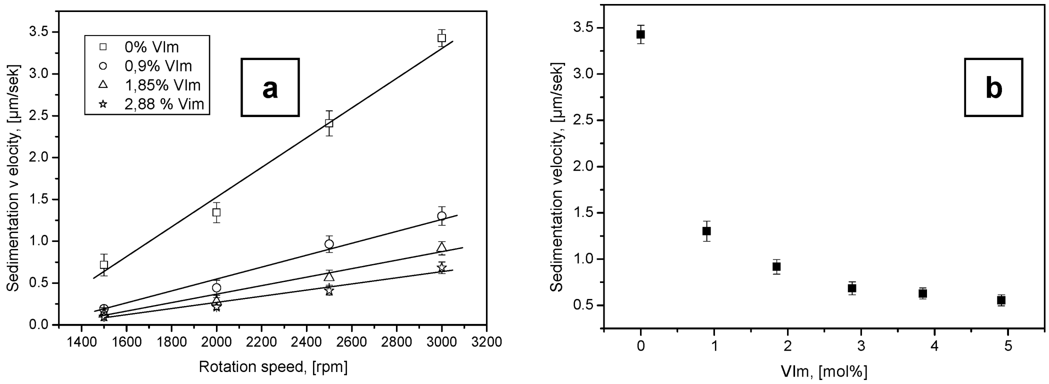

Figure 6. (a) Sedimentation velocity data as a function of rotation speed for selected microgel samples. (b) Sedimentation velocity as a function of VIm content in the microgels at 3000 rpm. (pH = 6; T = 20 °C.)

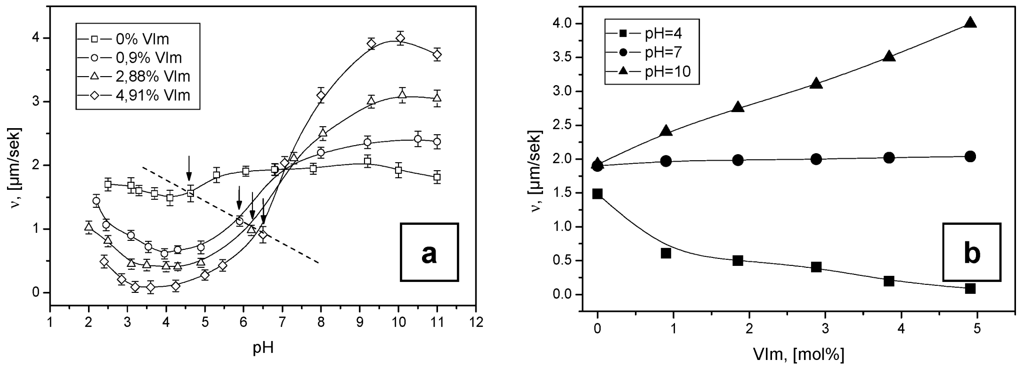

Figure 7. (a) Sedimentation velocity for microgels as a function of pH and (b) sedimentation velocity as a function of VIm content in microgels at pH 4, 7, and 10 (experimental data obtained at 3000 rpm).

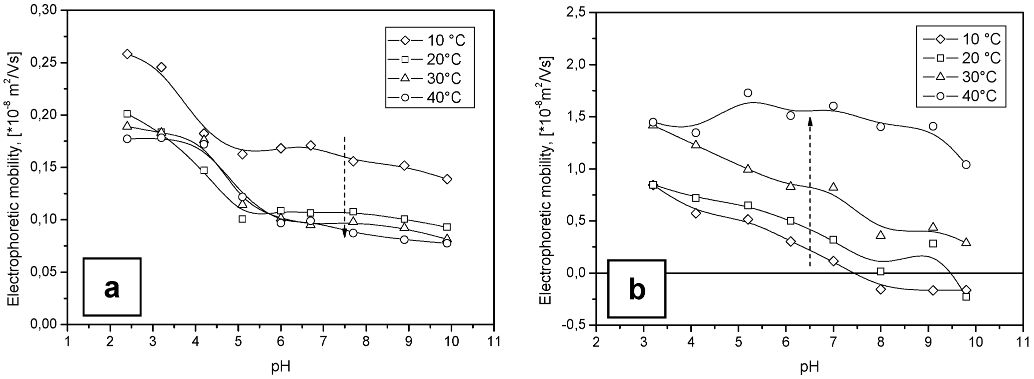

Figure 8. Electrophoretic mobility of VCL/AAEM (a) and VCL/AAEM/Vim(2.88%) (b) microgels as a function of pH (arrows indicate the shift of the experimental curves upon heating).

particles sedimentation process can be tuned by pH of the aqueous phase. The increase of VIm content in the microgel structure provides up to 4-fold reduction of the particle stability by changing the pH from 4 to 10 and this phenomenon can be used for the controlled separation of microgel particles.

The electrophoretic mobility measurements have been performed to characterize the influence of pH and temperature on the particle charge. The experimental data for VCL/AAEM and VCL/AAEM/VIm(2.88%) are summarized in Figure 8.

VCL/AAEM microgel shows positive values of electrophoretic mobility in the whole pH range. The determined electrophoretic mobility data are higher in acidic pH. The appearance of the weak positive charge can be explained by the presence of the positively charged initiator residues incorporated into the microgel structure during polymerization process. As temperature increases the electrophoretic mobility decreases probably due to the burying of the charged groups due to the collapse of VCL chains upon heating. The VCL/AAEM/VIm(2.88%) shows somewhat different behavior (Figure 8b). As expected the electrophoretic mobility values in this case are much higher if compared with VCL/AAEM sample due to the presence of VIm units in the microgel structure. Upon heating VIm-containing microgel shows opposite behavior to VCL/AAEM sample, namely the electrophoretic mobility increases with temperature increase. This phenomenon can be explained by the different charge distribution in VCL/AAEM/VIm(2.88%) sample. Upon heating the collapse of the polymer network is followed by the shift of the charged VIm units to the microgel outer layer what increases the electrophoretic mobility and partly improves particle stabilization. For VIm containing sample a gradual decrease of electrophoretic mobility with increase of pH was observed because less VIm groups are protonized. Unexpectedly, at pH > 8 the electrophoretic mobility approach zero and this effect is more pronounced at lower

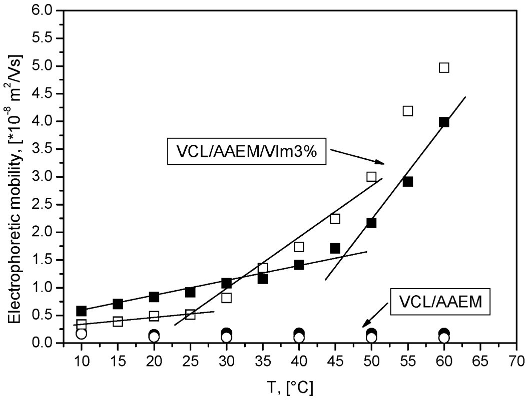

Figure 9. Electrophoretic mobility of VCL/AAEM and VCL/AAEM/Vim(2.88%) microgels as a function of temperature (solid symbols, pH = 4; open symbols, pH = 6) (solid lines are to guide the eye).

temperatures. However, this effect correlates with the fact that VIm containing samples exhibit maximal sedimentation velocity in the same pH region (Figure 7a).

The electrophoretic mobility data for VCL/AAEM and its VIm containing analogue as a function of the temperature at pH = 4 and pH = 6 are shown in Figure 9. The electrophoretic mobility of VCL/AAEM microgel particles does not change considerably with the temperature. Contrary, experimental data for VCL/AAEM/VIm (2.88%) microgel indicate clearly that the electrophoretic mobility increases rapidly if the measurement temperature approaches the phase transition temperature.

With further temperature increase electrophoretic mobility is by an order of magnitude larger as compared with data at low temperatures. Additionally, there is a similar trend as demonstrated in Figure 5a,b, namely the phase transition occurs at higher temperatures at pH = 4 (VIm groups fully ionized). The strong dependency of electrophoretic mobility on temperature has been first observed by Pelton et al.[37] for PNIPAAm microgels and confirmed in recent studies.[17,18] This phenomenon can be explained by the increase of the charge density within microgel particle due to the shrinkage of the polymer network and strong reduction of the microgel volume. However, it has been expected that at temperatures above volume phase transition electrophoretic mobility should reach a plateau value and do not change with further temperature increase, so this phenomenon will be a scope of our future work.

Conclusions

The incorporation of vinylimidazole (VIm) into the poly(vinylcaprolactam-*co*-acetoacetoxyethyl metacrylate) (VCL/AAEM) microgels has been achieved by simple batch polymerization process in aqueous medium. In this way monodisperse and colloidally stable microgel particles with variable VIm contents have been prepared. Obtained microgel particles exhibit both pH- and *T*-sensitive properties. It has been demonstrated that microgel particles swell at pH = 4 (complete ionization of VIm units) and the swelling can be controlled by the VIm content in the microgel. VCL/AAEM/VIm microgels possess temperature sensitive properties and the ionization of VIm units led to larger temperature response in the acidic medium, however the volume phase transition temperature was shifted toward higher temperatures with increase of VIm content in the microgel structure. The investigations of volume phase transition by light scattering methods indicate that VIm groups are located preliminary in the shell region of the microgels leading to the extreme swelling/deswelling of the polymer network as response to the variation of pH or temperature. The study of the colloidal stability by sedimentation centrifuge prove that the obtained microgel particles can undergo controlled pH-dependent separation process what is an important property for the cleaning or recycling of microgel/biomacromolecule conjugates. In summary, prepared microgel particles possess controlled dimensions, tunable *T*- and pH-sensitive properties, adjustable colloidal stability, and carry reactive β-diketone groups (originating from AAEM units) which can be used for the controlled immobilization of proteins.

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