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pH-Responsive Microgel Particles Comprising Solely Basic or Acidic Residues

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Summary: pH-responsive microgel particles with a diameter between 200 and 600 nm, comprising either basic or acidic moieties, have been synthesized by emulsion polymerization. Basic microgels were prepared by the polymerization of the hydrophobic monomer 2-(diethylamino)ethyl methacrylate (DEAEMA), while *t*-butyl methacrylate (*t*-BuMA) was used as the protected ester monomer to obtain methacrylic acid (MAA)-based microgel particles following acid hydrolysis of the ester groups. These microgels exhibit reversible swelling in water in response to changes in the solution pH. Thus, when ionized, the microgel particles are swollen due to the electrostatic repulsions between the charged monomer repeating units and the osmotic pressure created within the microgel particles by the presence of the counterions to the charged monomer units. The solution properties of the polymer microgels were investigated as a function of the solution pH by potentiometric titrations, and the effective ionization constant (K_α) of the microgels was determined. Dynamic light scattering was used to characterize the swelling behavior of the microgels as a function of the degree of ionization of the monomer residues. The tertiary amine-based microgels swell at low pH upon protonation of the amine units, while the PMAA microgels are swollen at high pH when the acid groups become neutralized. A change of the solution pH above or below a critical value (the effective pK_α of the protonated monomer repeating units) leads to the formation of collapsed PDEAEMA or PMAA latex particles, respectively. Transmission electron microscopy was used to confirm the shape and size of the microgel particles while their morphology was also characterized by scanning electron microscopy. These pH-responsive microgels can be used as colloidal templates for the in-situ synthesis of inorganic nanoparticles at high loadings and in controlled drug delivery.

Keywords: degree of ionization; emulsion polymerization; microgels; stimuli-sensitive polymers; swelling

Introduction

Responsive microgels are lightly cross-linked latex particles of submicrometer size that can become highly swollen in response to certain external stimuli.[1] Stimuli-responsive microgel particles have attracted great attention due to their potential applications as thickeners, as the stationary phase in liquid chromatography and in waste removal.[2–5] The synthesis of either thermo-responsive or pH-responsive microgels has been reported in the literature,[6] while complex microgels that exhibit both thermo-responsive and pH-responsive character have also been synthesized.[7] Temperature-sensitive microgels are usually based on poly(*N*-isopropylacrylamide) (PNIPAM). Their thermosensitive properties are due to the lower critical solution temperature of PNIPAM in aqueous solution. pH-sensitive microgels[8] are based on

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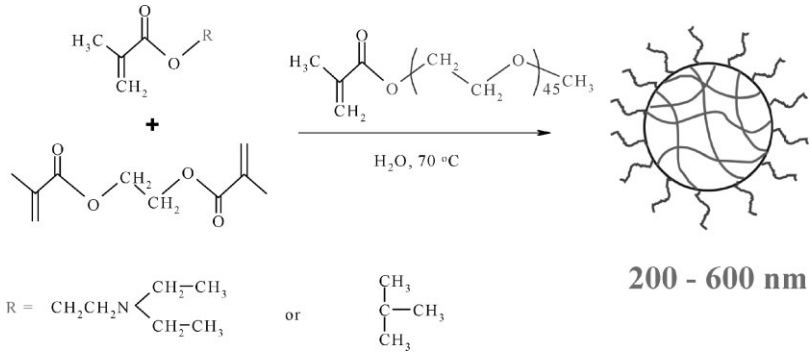
either weakly acidic or weakly basic monomer repeating units and are particularly attractive for use in biomedical and biotechnological applications such as protein adsorption, drug delivery, immobilization of biomolecules and in sensor technology, membrane filtration and catalysis.[9–12]

However, in most studies so far the fraction of pH-sensitive moieties within the gel phase was limited to a few percent, resulting in a weak pH-responsive behavior and a swelling behavior that is strongly influenced by the distribution of the pH-sensitive comonomer.[13–21] Only recently have the preparation of pH-responsive microgels based solely on pH-sensitive monomers been reported[22–27] and their use as recoverable catalyst supports in organic chemistry and drug-delivery vehicles been suggested.[28–30] The binding capacity and accessibility of the microgel sites for the active species are important properties for such applications.[31] Polyampholytic microgels have also been synthesized by the copolymerization of methacrylic acid and different amine-based methacrylates as anionic and cationic monomers, respectively.[32,33] The pH-induced volume collapse of these particles occurred at their isoelectric point, while the particles were swollen at both low and high pH.

In the present work, we describe the synthesis of pH-responsive microgels based solely on weakly basic or weakly acidic monomer repeating units by the emulsion polymerization of 2-(diethylamino)ethyl methacrylate (DEAEMA) or *t*-butyl methacrylate (*t*-BuMA), respectively. Ethylene glycol dimethacrylate (EGDMA) was used as the cross-linker in both cases. PDEAEMA microgel particles of different cross-link densities were prepared by varying the amount of cross-linker used during synthesis. The P(*t*-BuMA) microgels were subsequently deprotected by acid hydrolysis to obtain the poly(methacrylic acid) (PMAA) cross-linked particles. Potentiometric titrations and dynamic light scattering were used to characterize the microgel solution properties and their swelling behavior as a function of the solution pH and, consequently, of the degree of ionization of the monomer repeating units. The size and shape of the microgels was confirmed by transmission electron microscopy (TEM) and scanning electron microscopy (SEM).

Experimental Part

The microgel particles were prepared by emulsion free-radical copolymerization of a suitable hydrophobic monomer with a bifunctional cross-linker, EGDMA, in water using a monomethoxy-capped poly(ethylene glycol) methacrylate ($M_n = 2000$) stabilizer (see Scheme 1). DEAEMA was used as the monomer for the preparation of the basic microgels while *t*-BuMA was employed for the synthesis of the acid-based microgels followed by acid hydrolysis of the ester groups to give the MAA moieties. After their synthesis, the microgels were purified by ultrafiltration to remove any unreacted monomers and stabilizer. The *t*-BuMA microgels were deprotected by acid hydrolysis using trifluoroacetic acid in dichloromethane and were next transferred in water. The aqueous solution behavior of the microgel particles was investigated as a function of the solution pH by potentiometric titration at a microgel concentration $c = 0.1\,wt\%$ while their swelling behavior was studied by dynamic light scattering using an ALV spectrophotometer and a Nd-YAG laser with $\lambda = 532\,nm$. The hydrodynamic radius R_h of the diffusing moieties was calculated by the Stokes-Einstein Equation $R_h = k_B T/(6\pi\eta D)$. A microgel concentration of 0.005 wt% was used for the DLS measurements to avoid multiple scattering events and light absorption by the sample. TEM images were recorded with a JEOL JEM-100C instrument at an electron accelerating voltage of 80 kV. Specimens were prepared by drying a drop of a diluted microgel dispersion ($c = 0.05\,wt\%$) on a carbon-coated copper grid in air overnight. SEM images were obtained using a JEOL JSM 7000F field emission instrument at an accelerating voltage of 15 kV. The samples



Scheme 1.
Schematic representation of the synthetic procedure followed for the preparation of the pH-responsive microgel particles.

were prepared by drop casting a 0.02 wt% dispersion of the microgels particles on a glass slide and allowing the sample to dry overnight before the measurement.

Results and Discussion

Four PDEAEMA microgels were prepared in which the amount of cross-linker used for the synthesis was varied systematically between 0.5 and 3 wt % with respect to the monomer. Figure 1a shows the potentiometric titration curve for the PDEAEMA microgel particles prepared with 1 wt% EGDMA cross-linker. The appearance of a plateau region around pH 6.0 signifies the protonation of the DEAEMA units upon lowering the solution pH by the addition of HCl. The effective pK_α of the microgels was calculated from this plateau region plotted as the pH versus the effective degree of ionization, α_{eff} $(0 < \alpha_{eff} < 1)$ of the DEAEMA moieties, as the pH at 50% ionization (see inset). The effective pK_α for the PDEAEMA particles prepared with 1 wt% EGDMA was found 5.9. Figure 1b shows the effective pK_α values calculated for the four PDEAEMA microgels as a function of the degree of cross-linking. The effective pK_as of the DEAEMA units in all conetworks are significantly lower than the intrinsic dissociation constant of the DEAEMA monomer (pK_a 8.6) due to the polyelectrolyte effect. Moreover, the effective pK_αs were found to decrease from 6.0 to 4.9 as the cross-link density of the microgels increased from 0.5 to 3 wt % EGDMA suggesting that the protonation of the DEAEMA units is progressively

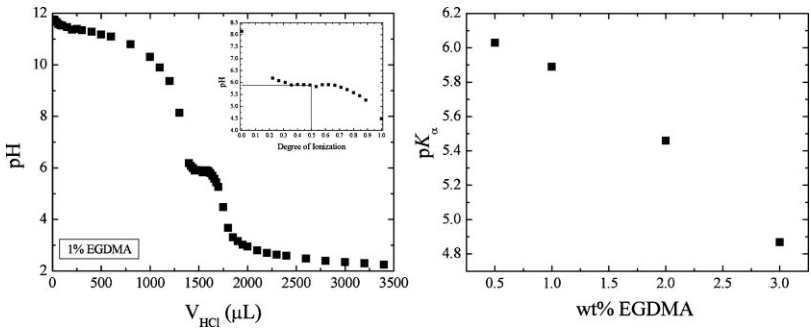


Figure 1.
Potentiometric titration curve for the PDEAEMA microgel with 1 wt% cross-linker (a) and effective pK_α values for the PDEAEMA microgel particles as a function of the degree of cross-linking (b).

hindered by the increase of the cross-link density of the microgel. This is attributed to the polyelectrolyte effect and to the Donnan equilibrium between the gel phase and the external solution where the pH is measured. Donnan equilibrium becomes more important as the degree of cross-linking increases.[34,35]

Figure 2 shows the potentiometric titration curves for the P(*t*-BuMA) microgel prepared using 1 wt% EGDMA before and after the acid hydrolysis of the ester groups. Before deprotection, the *t*-BuMA moieties do not participate in the hydrogen ion equilibrium, and, therefore, their titration curve is very similar to that of water. However, after deprotection, a new sigmoidal portion is observed in the titration curve of the microgel at around pH 7 signifying the presence of the methacrylic acid groups which possess a weak acid character and thus participate in an acid-base equilibrium. The presence of the plateau region verifies the successful deprotection of the ester groups and the formation of the PMAA microgel particles. The effective pK_α value for the acidic microgel particles was calculated from this plateau region as the pH at 50% ionization and was found to be 7.2. This value is significantly higher than the effective dissociation constant of a PMAA homopolymer (pK_a 5.5) and this is again attributed to the polyelectrolyte effect and the Donnan equilibrium which hinder the neutralization of the MAA units within the gel phase, as discussed above for the PDEAEMA microgels.

The variation in the hydrodynamic size of the microgel particles with the solution pH was followed by dynamic light scattering. To ensure that potentially strong interparticle interactions will not affect the light scattering results, the concentration of the microgels was kept sufficiently low for these measurements. Figure 3 shows the hydrodynamic radii of the PDEAEMA microgels as a function of the effective degree of protonation of the tertiary amine groups. For all microgels the hydrodynamic radius was found to increase with the degree of ionization of the monomer repeating units. This swelling is attributed to the increase of the hydrophilicity of the polymer upon ionization of the DEAEMA moieties and the electrostatic repulsive forces among the charged monomer repeating units which allow water to enter into the microgel particles. Besides, ionization creates an osmotic pressure within the microgels due to the counterions to the charged monomer repeating units and causes the microgels to further swell. Moreover, as seen in Figure 3, the degree of swelling progressively decreases as the degree of cross-linking of the microgels

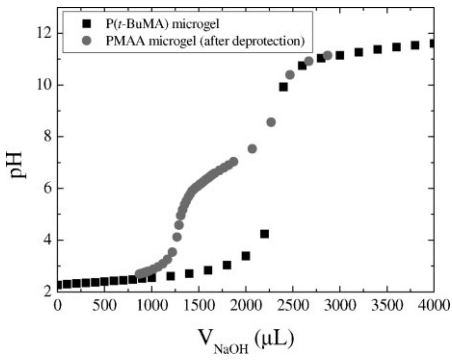


Figure 2.
Potentiometric titration curves for the P(*t*-BuMA) microgel with 1 wt% cross-linker before (black squares) and after (red circles) deprotection.

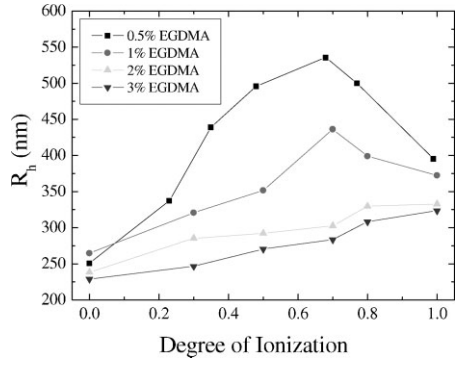


Figure 3.
Hydrodynamic radii of the PDEAEMA microgel particles as a function of the degree of ionization of the monomer repeating units. The lines are guides to the eye.

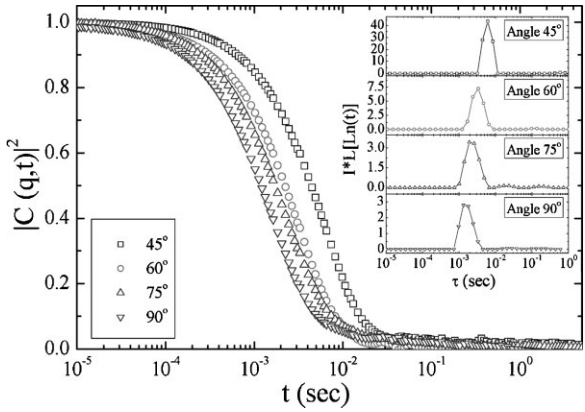


Figure 4.
Intensity autocorrelation functions of a 0.005 wt% P(*t*-BuMA) microgel solution for scattering angles 45° (□), 60° (○), 75° (△) and 90° (▽). Inset: distributions of relaxation times multiplied by the total scattering intensity (normalized to that of toluene) for the respective scattering angles.

increases, as expected. The decrease in the hydrodynamic size observed at high effective degrees of ionization for the microgels with 0.5 and 1 wt% EGDMA is attributed to the increase of the ionic strength of the solution upon the addition of acid. This causes screening of the electrostatic repulsive forces among the similarly charged DEAEMA units and results in the shrinkage of the microgels. Such a decrease in the degree of swelling is not observed for the microgels with 2 and 3 wt% EGDMA, possibly due to their lower degrees of swelling which result in a decrease in ion partitioning within the gel phase and thus in a less effective screening of the repulsion forces. From these swelling curves, the maximum volumetric swelling factors of the microgels were calculated as the cube of the ratio of the microgel diameter at maximum swelling when ionized to that of the collapsed hydrophobic latex particles at degree of ionization equal to zero. The volumetric swelling factor was found to decrease from 9.7 for the microgel with 0.5 wt% EGDMA to 5.8, 2.9 and 2.7 for the microgels with 1, 2 and 3 wt% EGDMA, respectively. This suggests that the microgels swell two and three times more when the cross-linker decreases by 2 and 4 times, respectively, below 2 wt%. For degrees of cross-linking above 2 wt% the effect of cross-linking on the degree of swelling is negligible.

The swelling process is accompanied by a change in the turbidity of the sample from milky-white in the collapsed state to clear-transparent for the swollen microgel. Furthermore, a change in the pH of the transparent solution to an effective degree of ionization equal to zero induces an increase in turbidity suggesting the reversibility of the swelling-deswelling process.

Figure 4 shows the intensity autocorrelation functions for a 0.005 wt% P(*t*-BuMA) microgel solution at different scattering angles. The inset shows the distribution of relaxation times from the inverse Laplace transformations of the correlation functions. A single process with very strong intensity and diffusive dynamics dominates the autocorrelation functions. From the distribution of relaxation times (see inset), the diffusion coefficient $D = \lim_{q\to 0}(\Gamma/q^2)$ for this process is $1.24 \times 10^{-8}\,\mathrm{cm}^2\ \ \mathrm{s}^{-1}$ and the corresponding hydrodynamic radius, R_h, is $177 \pm 2\,\mathrm{nm}$ attributed to the hydrophobic P(*t*-BuMA) latex particles.

Following acid hydrolysis of the ester groups, the PMAA microgels formed were characterized in terms of their swelling behavior as a function of the degree of neutralization of the acidic moieties by the

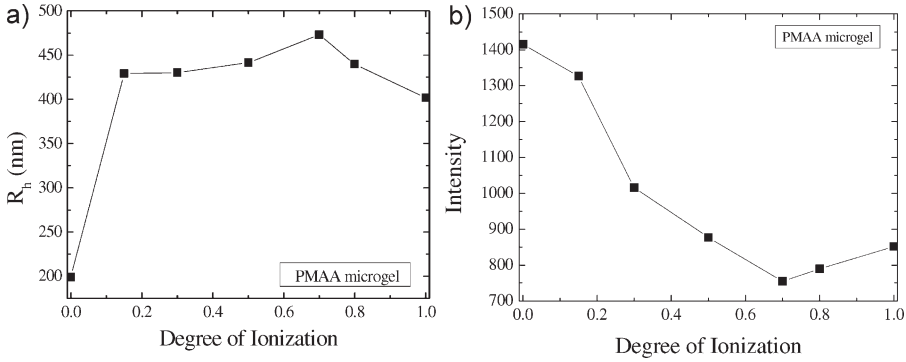


Figure 5.
Hydrodynamic radii (a) and scattering intensities at 45° scattering angle (b) for a 0.005 wt% PMAA microgel dispersion as a function of the degree of ionization of the monomer repeating units. The lines are guides to the eye.

addition of base (0.1 M NaOH). Figure 5 shows the hydrodynamic radii and the scattering intensities at 45° for the PMAA microgels vs. the effective degree of ionization of the MAA units. The size of the initial uncharged PMAA microgels was 200 nm (see Figure 5a) which is slightly higher than that found for the hydrophobic P(*t*-BuMA) latex particles (177 nm) This is attributed to the greater hydrophilic nature of PMAA compared to P(*t*-BuMA) which causes the swelling of the microgels. However, hydrogen bonding interactions among the protonated MAA units prohibit extensive swelling and result in the small particle size found at zero degree of neutralization. When the microgel becomes ionized the particle size increases abruptly upon neutralization of the MAA units (see Figure 5a). This is due to the electrostatic repulsive forces among the charged monomer units and the increase in the osmotic pressure created within the microgels due to the counterions to the charged monomer repeating units as discussed above for the PDEAEMA microgel particles. The observed decrease in the hydrodynamic size at high degrees of ionization is attributed again to the increase of the ionic strength of the solution which screens the electrostatic repulsions and causes the microgels to shrink. The maximum volumetric swelling factor calculated as the cube ratio of the microgel diameter at maximum swelling to that in the collapsed state at degree of ionization equal to zero was found to be 13.4 which is twice the value calculated for the respective PDEAEMA microgel particles prepared with 1 wt% EGDMA. This is attributed to the greater hydrophilic nature of the neutralized PMAA compared to that of the ionized PDEAEMA. Moreover, the PMAA microgels exhibit a much sharper swelling transition at lower degrees of ionization compared to the PDEAEMA microgels.

The scattering intensity shown in Figure 5b was found to decrease as the degree of ionization of the microgels increased and reached a minimum value at $\alpha = 0.7$ after which it increased again slightly. In order to explain the observed changes in the scattering intensity, which at first glance seem anomalous considering the increase in the particle (scatterer) size with the degree of ionization, a second effect should be considered. This is the decrease in the refractive index mismatch between the solvent and the water swollen polymer particles as solvent molecules enter the microgels upon swelling. The results suggested that the refractive index matching upon ionization dominated the scattering intensity and prevailed over the effect of the particle size. This is also consistent with the optical observation of

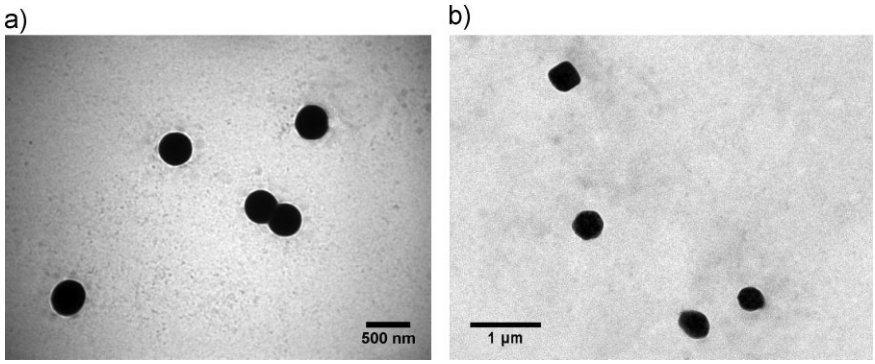


Figure 6.
TEM images of the PDEAEMA (a) and PMAA (b) microgel particles stained with potassium hexachroloplatinate and iron(II) chloride, respectively.

the change in the turbidity of the sample from milky-white in the collapsed state to clear-transparent for the swollen microgel.

The shape and the size of the microgels were investigated by TEM. Figure 6 shows TEM images for the PDEAEMA microgel particles prepared with 1 wt% EGDMA and stained with potassium hexachroloplatinate (Figure 6a) and the PMAA microgels with 1 wt% EGDMA stained with iron(II) chloride (Figure 6b). The metal species incorporated within the ionized microgels ($\alpha = 1$) at a monomer/metal = 2/1 molar ratio, cause their collapse[30] and provide the necessary contrast for the TEM imaging.

The PDEAEMA particles are spherical in shape with a mean TEM diameter of 383 ± 7 nm and have a very narrow size distribution as seen in Figure 6a. The diameter calculated by TEM is smaller than that found by DLS ($D_h = 528$ nm for $\alpha = 0$). This difference is attributed to the fact that DLS estimates a hydrodynamic size of the microgel in solution while TEM deals with a dried sample. Thus the former technique reports a hydrodynamic diameter that includes the thickness of the stabilizing layer and possible hydrodynamic interactions between the particles and thus tends to oversize relative to electron microscopy. Moreover, particle coalescence is minimal and individual PDEAEMA particles are observed by TEM despite the low T_g of PDEAEMA.[23] This is attributed to the ionization and the subsequent metallation of the microgel particles which are expected to increase the T_g of the polymeric material and thus prevent particle flattening and film formation. On the other hand, the PMAA microgels are

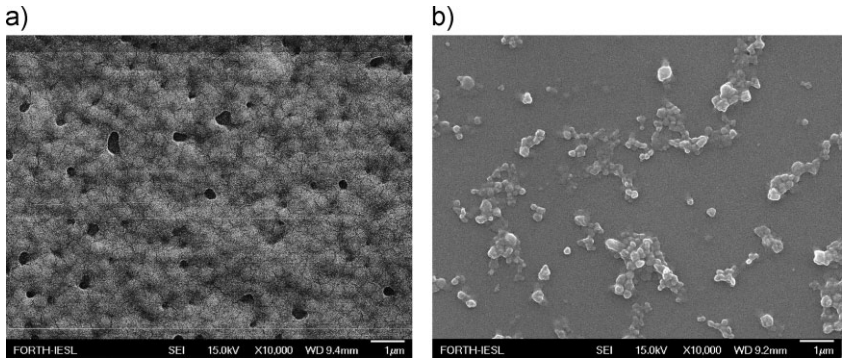


Figure 7.
SEM images of the PDEAEMA (a) and PMAA (b) microgel particles at degree of ionization equal to zero.

also spherical in shape and have a quite uniform size distribution as shown in Figure 6b. Their TEM diameter was calculated around 440 ± 20 which is in good agreement to that found by DLS ($D_h = 400$ nm at $\alpha = 0$).

The morphology of the microgel particles was also investigated by SEM. Figure 7 shows the SEM images for the PDEAEMA and PMAA microgel particles prepared with 1 wt% EGDMA at degree of ionization equal to zero. The soft nature and the film-forming properties of the non-metallated PDEAEMA microgels hindered their SEM visualization. Nevertheless, particles of a spherical shape with a diameter around 350 nm and a uniform size distribution are observed in Figure 7a. This result is in good agreement with the TEM data discussed above ($D = 383$ nm) and verifies the formation of uniform spherical PDEAEMA microgels. For the PMAA microgel the SEM study also indicated spherical particles with a broader size distribution as observed in Figure 7b. Moreover, large particle aggregates were found by SEM suggesting the high tendency of the particles to agglomerate due to their soft nature and this hindered their accurate size determination. Future work will involve the SEM investigation of the metallated particles which is expected to improve their visualization.

Conclusion

pH-sensitive microgel particles carrying solely weakly basic or weakly acidic residues were synthesized by emulsion polymerization. DLS measurements showed the reversible swelling-deswelling of the microgels in response to changes in the degree of ionization of the monomer repeating units. The degree of swelling was also influenced by the nature of the polymer and the crosslink density of the microgel particles. Thus, the PDEAEMA microgel particles exhibited upto a 10-fold increase in their volume, while the acidic microgels swelled more, exhibiting an increase in their volume by 13 times despite their higher degree of crosslinking. The spherical shape of the microgels, their size and narrow size distribution were confirmed by TEM. SEM also showed spherical particles for the PDEAEMA microgels in agreement with the TEM results, while spherical particles and large particle agglomerates were observed for the PMAA microgels. Such responsive colloidal particles are very attractive for application in drug delivery, sensor development, membrane filtration and catalysis.

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