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Layer-by-Layer Assembly of Polyelectrolyte Multilayers on Thermoresponsive P(NiPAM-*co*-MAA) Microgel: Effect of Ionic Strength and Molecular Weight

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ABSTRACT: The layer-by-layer assembly of polyelectrolyte multilayers of poly(diallyldimethylammonium chloride) (PDADMAC) and poly(sodium styrenesulfonate) (PSS) on soft and porous thermoresponsive poly(*N*-isopropylacrylamide-*co*-methacrylic acid) (P(NiPAM-*co*-MAA)) microgel was studied by dynamic light scattering and electrophoretic measurements. Polyelectrolyte multilayers were prepared from solutions of polyelectrolytes in different salt concentrations of sodium chloride and from polycations of different molecular weights in order to analyze the influence of the ionic strength and the polyelectrolyte chain length, respectively, on the properties of the polyelectrolyte-coated microgels. We show that the latter retain their thermoresponsive property and that the swelling and deswelling processes are nearly reversible. There is an "odd−even" effect of the hydrodynamic radius of the coated microgel depending on the type of polyelectrolytes in the outermost layer: PSS-terminated microgels are more swollen and more temperature-sensitive than PDADMAC-terminated microgels. Upon assembly of a strong polyelectrolyte shell around the pH-responsive microgel core, the ensemble is no longer pH-responsive. The core−shell microgel shows a clear increase of the size with increasing salt concentration from which the layer (shell) is being deposited, although no strong dependence of the size on the polycation molecular weight has been found. The electrophoretic mobility results reveal charge reversal after each layer deposition and the magnitude of which decreases with increasing number of layers as well as with increasing salt concentration in the depositing polyelectrolyte solutions.

Introduction

In the early 1990s, Decher[1,2] developed a simple and yet extremely powerful approach to the formation of controlled architecture multilayer polymer films based upon the layer-by-layer (LbL) assembly of oppositely charged polyelectrolytes on a charged surface, irrespective of the shape and size of the substrate. Extensive research was focused on parameters that influence the formation and growth of polyelectrolyte multilayers, such as type of polyelectrolytes, salts,[3−5] ionic strength,[6,7] pH,[8,9] degree of charge,[10−12] etc. Once thought to be exclusively electrostatically driven through charge reversal, polyelectrolyte multilayers formation has also been achieved through secondary cooperative interactions[13] such as van der Waals, hydrophobic−hydrophobic interaction, H-bonding, etc. Linear and exponential growths[14,15] were identified as the two major modes of film growth, with both modes yielding extremely interdigitated layers.[16] The immense success of LbL assembly of polyelectrolytes on flat and rigid substrates was extended to three-dimensional hard colloidal particles, which became the precursor route for the fabrication of hollow capsules.[17,18] The use of porous colloidal particles such as $CaCO_3$[19,20] and mesoporous silica[21,22] with interfaces characterized by a large surface-to-volume ratio wherein encapsulated biomacromolecules can retain their activity suddenly became attractive new type of templates for LbL. Recently, the challenge has been to perform LbL assembly on soft and porous templates in the submicrometer size range.[23−32] Templates that are deformable and into which the polyelectrolytes may or may not interpenetrate constitute a real challenge.

Smart microgels are stimuli-responsive 3D soft and porous polymeric networks[33] which swell and contract in response to external stimuli such as temperature, pH, ionic strength, light, electromagnetic field, etc. Poly(*N*-isopropylacrylamide) (PNiPAM) is a well-studied smart microgel.[34−39] Thermoresponsive microgels are characterized by the so-called volume phase transition temperature (VPTT), at which temperature the microgel undergoes a transition from a swollen to a collapsed state during heating. The swelling of a neutral microgel is due to a balance of osmotic and elastic forces. Introducing ionic groups into the neutral PNiPAM network gives rise to what can be assimilated to polyelectrolyte microgels. In such microgels there is an additional osmotic contribution to the swelling due to the higher concentration of mobile ions within the network as a consequence of the Donnan equilibrium.[40]Polyelectrolyte microgels can be multistimuli-responsive.[37,38] In a copolymer such as poly(*N*-isopropylacrylamide-*co*-methacrylic acid) P(NiPAM-*co*-MAA), the principal monomer, NiPAM, lends thermosensitivity to the system while the comonomer, methacrylic acid, allows for pH tunability (hence charge and different swelling behavior).[37−39] Core−shell microgels can also be built with the core and the shell having different VPTT[41] or charges located in either the core or the shell,[24] hence with a different ability to respond to various external stimuli. In other words, microgels, unlike conventional hard and rigid substrates, provide a wide range of templates whose architectural design is in itself a parameter to consider.[24]

The striking simplicity of the LbL technique makes it an attractive process to impart new thermoresponsive properties to microgels, depending on the internal architecture of the latter.[24,30] Depositing polyelectrolyte multilayers onto polyelectrolyte microgels gives rise to microgel systems that contain both negative and positive charges within the ensemble, analogous to the so-called polyampholyte microgels.[38,42] Such polyelectrolyte−microgel systems are very interesting systems as multiple interactions can act in parallel with or against each other within the ensemble. The properties of microgel particles can be tailored, or their stability improved, by depositing a shell of polyelectrolyte multilayers. Proper choice of the polyelectrolyte pairs, number of layers, and assembly conditions can

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govern the transport of substances into and out of the microgels. By controlling the trafficking of macromolecules across the diffusion barrier, one can achieve selective permeability as well as sustained release simply through the LbL surface engineering. With soft and porous templates such as microgels, layer thickness, mechanism of multilayer growth, and the surface conformation of polyelectrolyte multilayers are no longer independent of the underlying substrate size and topology.[24,30] Additionally, the surface roughness and homo- and heterogeneity of the deposited layers are also influenced by the ionic strength of the polyelectrolyte depositing solutions, chemical nature of the polyelectrolytes, the pH of the solutions,[43] and the amount of time spent in the polyelectrolyte solutions. Although the LbL assembly of polyelectrolytes on charged microgels is largely electrostatically driven, secondary cooperative interactions such as hydrophobic−hydrophobic interaction are not negligible with uncharged microgels. Furthermore, the thermal behavior of polyelectrolyte multilayer microcapsules has recently been reported.[44−49] Confining polyelectrolyte multilayer films onto thermoresponsive microgels can lead to very interesting behavior resulting from antagonistic effect of the polyelectrolyte multilayer wanting to swell while the microgel wants to collapse.

Very few groups have attempted the LbL assembly on microgels,[23−30] and so far, no systematic study of the influence of the above-mentioned parameters has been really undertaken. With the increasing popularity of smart microgels and their potential applications in a wide range of fields, there is a need for a thorough study of parameters influencing the formation and growth of polyelectrolyte multilayers on soft and porous templates, to identify challenges microgels present as building block, and to understand the similarities and differences between their being used as depositing layers and their being used as depositing templates. A crucial issue about whether multilayer assembly of polyelectrolytes can be done on such deformable, penetrable, and water-swollen submicrometer size templates has already been qualitatively[29] as well as quantitatively[50] demonstrated. The present work is essentially devoted to the systematic study of the parameters that govern the buildup of polyelectrolyte multilayers, and herein, the LbL assembly of two strong polyelectrolytes on a charged microgel is investigated. We focus on the influence of ionic strength of the polyelectrolyte depositing solutions as well as the molecular weight of the polycation on the thermoresponsive properties of the coated microgels. The LbL-coated microgels were shown to be stable while retaining their reversible thermoresponsive properties. An "odd−even" effect was observed on the hydrodynamic radius, R_h, of the coated microgels dictated by the nature of the polyelectrolyte layer in the outermost layer. Upon assembly of strong polyelectrolyte multilayer shell around the pH-responsive microgel core, the ensemble is no longer pH-responsive. These microgels with varying number of polyelectrolyte layers in the shell may find applications from storage and transport of drugs for controlled release delivery to externally triggered sensors.

Experimental Section

Materials. Poly(sodium 4-styrenesulfonate) (PSS), MW = 70 000 g/mol, and poly(diallyldimethylammonium chloride) (PDADMAC), MW = 100−200 000 g/mol, were purchased from Sigma-Aldrich (hereafter denoted as $\text{PDADMAC}_{100-200\,000}$). PDADMAC with MW = 1000 g/mol (hereafter denoted as PDADMAC_{1000}) was generously supplied by Kemira Oyj (Finland). The monomer *N*-isopropylacrylamide (NiPAM) was purchased from Acros Organics, and methacrylic acid (MAA) was purchased from Lancaster. Potassium peroxodisulfate (KPS), *N*,*N*′-methylenebis(acrylamide) (BIS), and sodium chloride (NaCl) were purchased from Merck. All chemicals from commercial origin were used without further purification. Ultrapure water obtained from double-distilled Milli-Q water (resistivity ≥18 MΩ·cm) was used to prepare all solutions.

Table 1. Summary of the pH of the Solutions at Various Stages during the Buildup of the First and Second Layer of Polyelectrolytes (in Aqueous Solutions) on the Microgel

sample in water	pH
P(NiPAM-*co*-MAA) microgel (MG)	4.44
PDADMAC	4.72
PSS	6.42
MG + excess PDADMAC	3.87
MG/PDADMAC (1 L-coated)	5.25
MG/PDADMAC + excess PSS	6.11
MG/PDADMAC/PSS (2 L-coated)	6.40

Synthesis of P(NiPAM-*co*-MAA) Microgel. The P(NiPAM-*co*-MAA) microgel was synthesized by dispersion polymerization. In summary, polymerization was performed in a 1 L reaction vessel equipped with a mechanical stirrer, reflux condenser, thermometer, and gas inlet. 7.545 g of NIPAM, 0.143 g of the cross-linker BIS, and 0.734 g of MAA were dissolved in 0.75 L of water at 70 °C and purged with nitrogen for at least 1 h. Polymerization was initiated with 0.230 g of KPS dissolved in 5 mL of water and carried out for 6 h under a nitrogen stream and constant stirring at 400 rpm. The dispersion was passed through glass wool in order to remove particulate matter and further purified by three centrifugation cycles at 50 000 rpm and 25 °C.

LbL Assembly on Microgel. The assembly of polyelectrolytes was done[24] by slowly adding 3 mL of an aqueous dispersion of the microgel (0.02 wt %) to 12 mL of an aqueous 1 g/L solution of the polyelectrolytes in either water or different NaCl concentrations (0.10, 0.25, and 0.5 M). The microgel being negatively charged, the first layer is always a polycation. The mixture was kept under constant stirring, overnight in the case of aqueous polyelectrolyte solutions and for 2−4 h in the case of polyelectrolytes in salt solutions. The excess of the polyelectrolytes was removed by using three ultracentrifugation cycles at 50 000 rpm and 25 °C, followed at each step by decantation and redispersion in water by vigorous shaking during at least 4 h. This sequence was repeated until the desired number of layers was achieved. Throughout this work, the pH was not adjusted (unless specifically stated). The pH of the various components at each stage of the assembly is summarized in Table 1. Before any characterizations, *the coated microgels were always redispersed in water* overnight and then filtered through a 1.20 μm Minisart hydrophilic filter in a laminar-flow box.

Dynamic Light Scattering. The R_h was determined by dynamic light scattering (DLS) performed on highly diluted aqueous solutions of the sample using an ALV goniometer equipped with an avalanche photodiode. Temperature was increased from 293 to 313 K in steps of 2 K and then decreased again to 293 K, in order to get a complete cycle. The samples were allowed to equilibrate for 20 min before each temperature, and three sets of recordings were measured at each temperature. Scattered light was detected at 60° with an integration time of 120 s and computed with a digital ALV 5000E autocorrelator using an ALV Software version 5.3.2. The particle size was calculated by cumulant fits.

Electrophoretic Measurements. The electrophoretic mobility (μ) measurements were performed with a Malvern Zetasizer 3000HSA. For each layer, a temperature dependence study was performed (heating from 293 to 313 K and cooling down to 293 K, with a temperature increment of 2 K). Each point is the average of 10 measurements, and the sample was allowed to equilibrate for 10 min for each temperature. Although zeta potential (ζ) is a more common notion to quantify surface charge on hard and rigid particles, no attempt has been made to convert the mobility values (μ) into ζ because microgels are soft, porous, and solvent-penetrable particles[51] that do not conform to the usual hard-sphere model hypothesized in standard theories relating μ to ζ.

Scanning Electron Microscopy. Scanning electron microscopy (SEM) micrographs were obtained using a JEOL 5600 LV to study the morphology of uncoated as well as LbL-coated microgels. Samples were prepared on Al supports, dried at room temperature, and coated with a mixture of Pd and Pt prior to measurements.

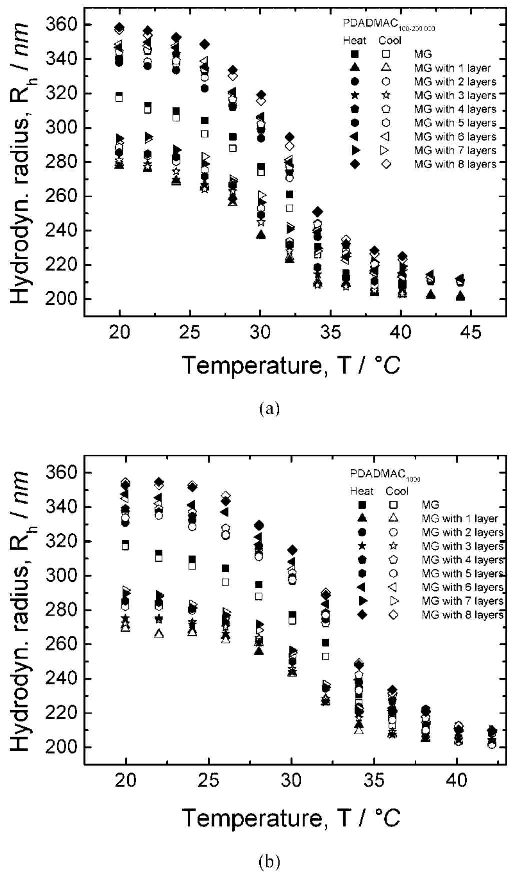


Figure 1. Thermoresponsive behavior of (a) PDADMAC$_{100-200\,000}$/PSS- and (b) PDADMAC$_{1000}$/PSS-coated microgels as monitored by the R_h for different number of layers as a function of temperature. Assembly was carried out from polyelectrolyte solutions with 0.25 M NaCl, washed, and finally redispersed in water.

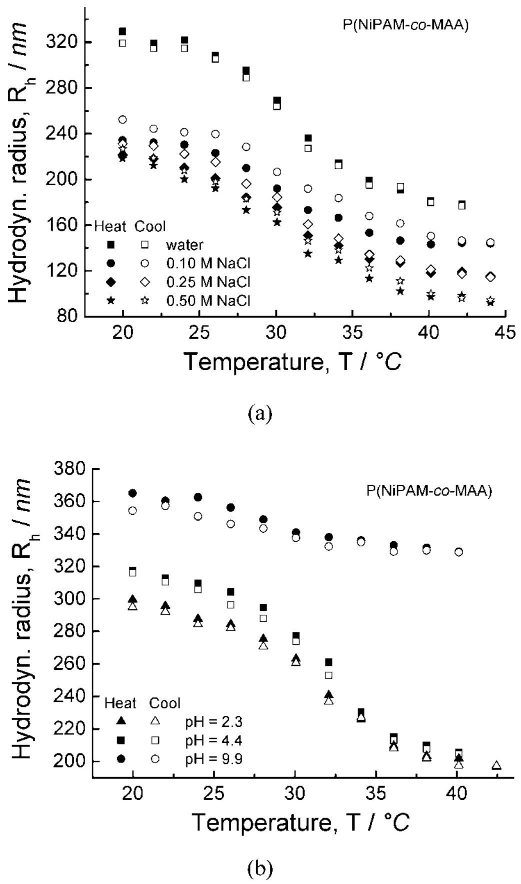


Figure 2. Influence of (a) salt and (b) pH on the thermoresponsive behavior of uncoated microgels as a function of temperature.

Images were taken at magnifications from 3000× to 10 000× with an accelerating voltage from 4 to 10 kV.

Results and Discussion

Effect of Molecular Weight. Multilayer thin films were prepared by the sequential assembly of PDADMAC and PSS for two polycations of different molecular weights (MW = 1000 and MW = 100 000−200 000 g/mol) denoted as PDADMAC$_{1000}$ and PDADMAC$_{100-200\,000}$. Figure 1 shows the thermoresponsive behavior of the LbL-coated microgel prepared from 0.25 M NaCl polyelectrolyte (Figure 1a: PDADMAC$_{100-200\,000}$/PSS; Figure 1b: PDADMAC$_{1000}$/PSS) solutions with different numbers of layers as a function of the temperature. One striking result is that, in spite of the extreme difference in MW, the R_h obtained for LbL-coated microgels with both MW polyelectrolytes are quasi-identical. The uncoated microgel (MG) in water, with no pH adjustment, has a pH of 4.44, a R_h of 320 nm, exhibits a VPTT around 32−33 °C, and collapses to about 200 nm. Upon adsorption of the first layer of PDADMAC there is a drastic decrease in the R_h from 320 nm to about 280 nm. The VPTT is unaffected by the presence of the PDADMAC layer, and the PDADMAC-coated microgel still collapses to around 200 nm. Upon adsorption of the second layer (PSS) there is now a dramatic increase in the R_h from 280 nm to about 340 nm. Again the VPTT is unaffected, and the R_h of the two-layer coated microgel in the collapsed state is slightly higher than that of the uncoated microgel. Upon further layer deposition, we observe systematically (T < VPTT) that each time the outermost layer is PDADMAC, there is a noticeable decrease of the R_h, and each time the outermost layer is PSS, there is a significant increase of the R_h. The thermoresponsive behavior of all LbL-coated microgels is fully reversible and reproducible. The size of PSS-terminated microgels is always larger than the uncoated microgel while that of PDADMAC-terminated microgels is always smaller. Furthermore, the temperature sensitivity of PSS-terminated microgels is higher than that of PDADMAC-terminated microgels.

It has been shown that negatively charged poly(*N*-isopropylacrylamide-*co*-acrylic acid) or P(NiPAM-*co*-AA) microgel particles, deposited as a monolayer, contract strongly onto the oppositely charged substrate surface[52] and irreversibly.[53] In the present case the microgel is the template onto which polyelectrolyte multilayers are being deposited. We have recently shown that LbL on soft and porous microgel is template-dependent depending on the location of charges.[24] The LbL assembly of polyelectrolyte multilayers on "neutral" PNiPAM,[24] whereby hydrophobic−hydrophobic interaction was mainly responsible for the buildup of layers, a slight increase in R_h was observed with increasing number of layers.[24] However, in the case of charged P(NiPAM-*co*-MAA) microgels, the drastic collapse in the R_h upon adsorption of the first positively charged polyelectrolyte layer on the negatively charged microgel is clearly indicative of a predominantly electrostatically driven interaction.

Since the polyelectrolytes used in this study are strong polyelectrolytes that are fully charged independent of the pH, we have undertaken some studies of the effect of salt and pH on the uncoated P(NiPAM-*co*-MAA) microgels. The P(NiPAM-*co*-MAA) microgel employed has a pH = 4.44 (without any adjustment of pH) in water. Various pK_a values of PMAA (between 4.5 and 6) have been reported depending whether salt is present or not.[8,9,54] Figure 2a shows the thermoresponsive curves as measured by DLS measurements for uncoated microgels in solutions of different NaCl salt concentration as a function of temperature. The VPTT of the uncoated microgel in salt solutions extends over a broader range of temperatures as compared to a relatively much "sharper" VPTT when they are in aqueous solution. This is similar to, and in accordance with, the effect of salt on the VPTT of P(NiPAM),[55] whereby the interaction between the microgel and water is weakened by the counterions present in the solution. Screening of the charges on the microgels by these counterions has also for effect to reduce the electrostatic repulsions (and a decrease in the osmotic pressure), and the uncoated microgel exhibits a smaller R_h (~240 nm) in the presence of salts than in their absence ($R_h \sim 320$ nm). With increasing salt concentrations the swelling ratio [$r = (R_h^{swollen}/R_h^{collapse})^3$] increases from 4.3, 7.2, to 13.2 in 0.1, 0.25, and 0.5 M NaCl, respectively. At high concentrations, more ions are available to neutralize or shield the charges in the polymer network. Figure 2b shows the thermoresponsive curves of the microgel in water at various pH. At pH = 10, the PMAA is fully deprotonated, and electrostatic repulsion between the charges and the osmotic contribution of the counterions make the microgel adopts a very swollen and extended conformation ($R_h \sim 360$ nm) which resists collapse ($R_h \sim 340$ nm) when heated above its VPTT. At pH = 2, the PMAA can be considered as fully protonated. From the negative electrophoretic mobility measured for an aqueous solution of P(NiPAM-*co*-MAA) microgel it can be assumed that, at pH = 4.44, the microgel is still partially charged.

While electrostatic attraction accounts for the drastic collapse of R_h of PDADMAC-coated microgels, several contributions could account for the drastic increase of R_h of PSS-terminated microgels. Coated microgels with an odd layer number have PDADMAC as the first and last layer and therefore possess one layer more than PSS, giving rise to an excess of positively charged polyions. Considering the first layer adsorbed the electrostatic attraction between the negatively charged microgel core and the positively charged PDADMAC is so strong that they pull on each other, causing the ensemble to contract. Upon approach of the negatively charged PSS to the positively charged surface of the PDADMAC-coated microgel, since the number (or density) of positive charges is constant, and that now they have to be shared between the microgel and the to-be-adsorbed PSS, one can visualize that the strengthening of the attractive interaction between the already deposited PDADMAC and the approaching PSS is done at the expense of the attraction between the microgel and the adsorbed PDADMAC. This has for effect to weaken the pulling attraction of the PDADMAC layer on the microgel which can consequently expand more. We previously reported[24] on similar behavior on a neutral P(NiPAM) microgel onto which was adsorbed a first layer of polyethylenimine (PEI) and a second layer of PSS. Upon adsorption of the PEI, a high MW and highly branched polyelectrolyte, the thermoresponsivity of the coated microgel is almost completely suppressed. However, upon addition of PSS, the thermoresponsivity of the microgel was recovered, clearly supporting the interaction between PEI and PSS is done at the expense of the interaction between microgel and PEI. Additionally, it was reported that elemental analysis performed on PDADMAC/PSS hollow capsules support the fact that for capsules with an even number of layers a nearly 1:1 ratio of the polyions were found while for an odd number of layers, this ratio is only 0.8, leaving ~20% of the positive charges uncompensated (on the basis of the total amount of excess polyelectrolyte).[46] Assuming the same stoichiometry in the microgel–polyelectrolyte system, the excess of negatively charged PSS (responsible for charge reversal) distribute themselves in such a way as to have maximum repulsion between the charges, contributing in the expansion of PSS-terminated LbL-coated microgels.

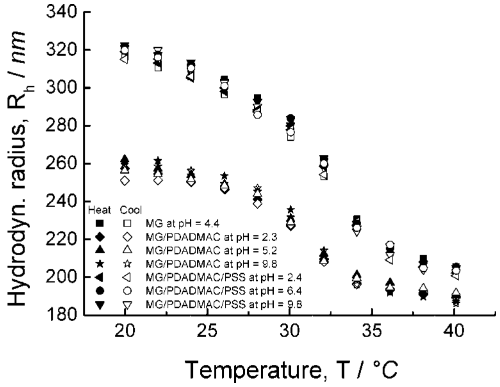


Figure 3. Influence of the pH on the thermoresponsive behavior of coated microgels in water as a function of temperature. LbL assembly was carried out from polyelectrolyte solutions in water, washed in water, and redispersed in water, and then the pH was adjusted to the desired value.

The above explanation alone could hardly account for the significant increase in size in PSS-terminated LbL-coated microgels. The LbL-coated microgels still exhibit a flexible network, and the "odd–even" effect is a clear indication that the temperature sensitivity of PSS-terminated microgels is higher than that of PDADMAC-terminated microgels (see Figure 1). It has been previously demonstrated, from contact angle measurement,[56] that PSS-terminated surfaces are more hydrophilic and consequently absorb more water than PDADMAC- or poly(allylamine hydrocholoride) (PAH)-terminated surfaces. The polyelectrolyte-coated microgel system *is* in aqueous solution, and for PSS-terminated coated microgel, more water can diffuse in and out of the outer layer than for PDADMAC-terminated coated microgel. The ability of PSS layer to contain more water leads to a decrease of entanglement of polyelectrolyte chains, and eventually of the microgel network, enabling the entire ensemble to adopt a more expanded conformation, hence an increase in the R_h as measured by DLS. Since our substrate is soft and porous, another plausible explanation (discussed more in detail in the section "estimation of bilayer thickness") could be that PSS can diffuse in and out, an effect which is generally encountered with the so-called "exponential growth" during the LbL deposition of polypeptides such as poly(L-lysine) or poly(L-glutamic acid) on hard and rigid substrates.[14,15] However, at this stage, specific contributions of all the above-mentioned effects to the "odd–even" effect observed is not trivial; nevertheless, our results clearly indicate a strong influence on the size of the coated microgels depending on the last polyelectrolyte adsorbed.

Figure 3 shows the pH sensitivity of one-layer and two-layer coated microgels (deposited from $PDADMAC_{100-200\,000}$ and PSS in water) as a function of temperature as monitored by DLS. Comparing the pH sensitivity of the uncoated microgel in Figure 2b with that of the coated microgels (either with one or two layers) in Figure 3, it can be seen that the resulting core–shell ensemble exhibits identical reversible thermoresponsive behaviors independently of the pH.[30] Upon assembly of strong polyelectrolyte multilayers shell on a pH-responsive microgel core, the resulting core–shell ensemble is no longer pH-responsive. This is a clear evidence of successful surface modification of the microgel with polyelectrolytes, hence proving the presence of the latter on the microgel. Therefore, the LbL technique provides a simple and effective way to modify the surface of microgels and renders pH-stimuli microgels insensitive to pH.

Figure 4 shows the electrophoretic mobility of the microgel measured at $T = 20$ °C as a function of the number of layers for both high and low MW PDADMAC (prepared from 0.25

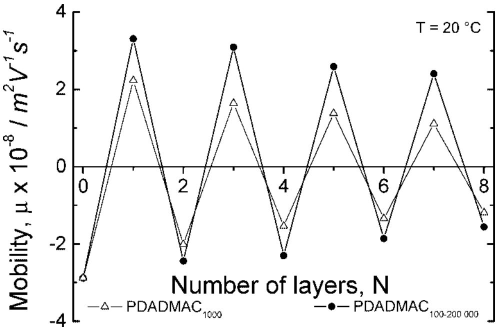


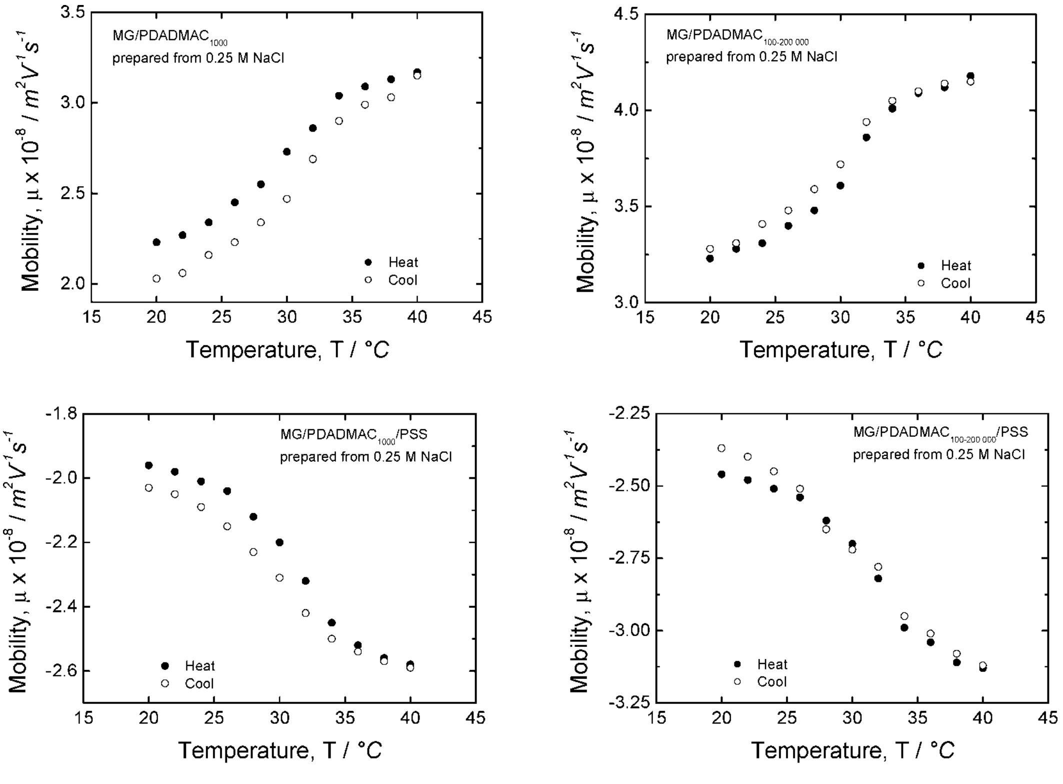
Figure 4. Influence of the molecular weight of PDADMAC on the electrophoretic measurements of the coated microgels as a function of number of layers. $N = 0$ is the uncoated microgel; an odd and even number indicates a PDADMAC- and PSS-terminated microgel, respectively. Error bars are within the size of the symbols.

M NaCl). The microgel is negatively charged, and upon adsorption of polycation and polyanion, the net surface charge becomes positive and negative, respectively. We observe successful charge reversal at each adsorption step, indicating clearly buildup of multilayers of polyelectrolytes on soft and porous microgels.[23,26,30] From Figure 4 it can be seen that there is a bigger charge reversal when PDADMAC$_{100-200\,000}$ (+ 3.3 × 10^{-8} m^2 V^{-1} s^{-1}) is deposited as compared to PDADMAC$_{1000}$ (+ 2.2 × 10^{-8} m^2 V^{-1} s^{-1}). This could be accounted for by the fact that microgels are soft and porous templates, and the higher mobility of low-molecular-weight PDADMAC$_{1000}$ chains can diffuse and interpenetrate the templates to neutralize charges of the microgels otherwise not accessible by the high-molecular-weight PDADMAC$_{100-200\,000}$ chains. Even though DLS studies (Figure 1a,b) show that LbL-coated microgels with PDADMAC$_{1000}$ and PDADMAC$_{100-200\,000}$ are of comparable size, it gives no indication of the amount of PDADMAC adsorbed onto the microgel. PDADMAC$_{1000}$, being of smaller chain length than PDADMAC$_{100-200\,000}$, could interpenetrate more the microgel, neutralizing more charges, thereby conferring a lower surface charge density as revealed by the mobility. To our knowledge there is no reference in the literature about PDADMAC$_{1000}$ being used for LbL on hard and rigid particles, and therefore we cannot comment on any similarities or differences due to the nature of the templates. However, a clear difference with LbL deposition on hard and rigid particles, whereby the charge reversal is almost constant, is the systematic decrease in mobility (or net surface charge) with increasing number of layers deposited on soft and porous microgels, irrespective of the MW of the PDADMAC used.[30] LbL films are usually considered as ordered nonequilibrium arrangements, and the mobility of the polyelectrolyte chains within the multilayer during and after its construction is well-known. In contrast to polyelectrolyte films assembled on hard and rigid surfaces, microgels consists of a cross-linked network of chains and segments which impede the mobility of the chains and segments of the polyelectrolytes which are LbL-assembled onto the microgels. Breakage and reformation of ion pairs in all three dimensions occur not only between polycations and polyanions but also between polycations and microgels.

Figure 5 shows the electrophoretic mobility of one-layer and two-layer coated microgels prepared from polyelectrolytes of different MW in 0.25 M NaCl as a function of temperature. In Figure 5a we consider the system MG/PDADMAC$_{1000}$ and MG/PDADMAC$_{1000}$/PSS and in Figure 5b the system MG/PDADMAC$_{100-200\,000}$ and MG/PDADMAC$_{100-200\,000}$/PSS. It can be seen that the mobility of the coated microgels, in all cases, increases (in magnitude) with temperature. Similar results have been obtained before for PNiPAM[24,57,58] as well as P(NiPAM-*co*-AA).[24,52] The main reason the mobility increases with increasing temperature is simply due to the fact that the particles collapse, “squeezing out” the charges, causing the surface charge density to increase correspondingly. Particle swelling is entropy driven and depends on the hydrogen bonds between the microgel segments and water. An increase in temperature breaks the H-bonds, leading the microgel to deswell and collapse as water is expelled out. Above the VPTT, inter and intrachain hydrogen bonds and hydrophobic interactions are dominant. On cooling, water becomes again a good solvent and on reswelling, some trapped “frozen” segments become mobile again, and are able to reorient and reorganize as water flows into the microgel. The effect of the substrate (here, the microgel) on the polyelectrolyte chains, the enrichment of end-groups at the outer surface, a decrease or increase in the entanglement of the polymer chains with decreasing or increasing T, are but a list of effects that cause polymer chains to reorganize, and this might explain the hysteresis found in μ between the heating and the cooling curves. Figure 5 shows that this hysteresis is generally more pronounced for LbL-coated microgel with low MW PDADMAC. This is to be expected as shorter chains possess greater mobility and consequently a higher degree of freedom for rearrangement,[47] and in doing so, has a higher possibility of neutralizing charges in the microgel which were previously not accessible, and hence causing the effective charge at the surface to drop (in magnitude). This is confirmed by Figure 5a. With high-MW PDADMAC, only slight rearrangement is allowed; hence, the almost complete reversibility of the mobility curves versus temperature in Figure 5b.

It has been reported that heat[44−49] affects the polyelectrolyte multilayers in a manner similar to added salts.[59,60] Added salts swell the films through screening of the electrostatic forces that bind the layers together, causing dissociation of individual polycation and polyanion binding sites, thus promoting localized dissociation and increased conformational dynamics. While salt decreases the energy barrier and allows conformational changes, an increase in temperature supplies the kinetic energy necessary to overcome these barriers. Greater flexibility and fluidity of the polyelectrolyte chains imply increased mobility and interpenetration between layers, causing restructuring of layers within the film. Exponential growth[14,15] of film in weak polyelectrolyte systems is explained by an increase in interpenetration within the entire polyelectrolyte multilayers. In our case, while increasing the temperature has the above-mentioned effects on the polyelectrolyte multilayers, an increase in temperature has the opposite effect on the microgel which tends to collapse. While the osmotic pressure favors swelling, the elastic constant of the network (as influenced by the interaction of polyelectrolyte and microgel) restricts it, hence favoring deswelling. It could be that, at $T <$ VPTT, we have a swollen microgel with a thin polyelectrolyte shell, and at $T >$ VPTT, we have a collapsed microgel with a thick polyelectrolyte shell, analogous to incubating hollow PSS/PAH capsules for 24 h at 70 °C which resulted in a slight decrease in their diameter and accompanied by an increase of the wall thickness.[44] However this analogy is purely speculative and would need to be verified by contrast matching with neutron scattering experiments which is beyond the scope of the present work. On cooling, even though fluidity of polyelectrolyte layers may seem hindered, swelling of the microgel allows for breakage and reformation of new polyelectrolytes binding sites, and as previously discussed above, low-MW polyelectrolyte can interpenetrate more the microgel, neutralizing inaccessible charges, changing the equilibrium balance between electrostatic attraction and osmotic repulsion, causing rearrangement of the polymeric chains within the microgel, and hence causing a decrease (in magnitude) in the surface charge.

Effect of Ionic Strength. It is known that during multilayer formation polyelectrolyte chains adsorb irreversibly onto the



(a) (b)

Figure 5. Electrophoretic measurements as a function of temperature for a one-layer and two-layer LbL-coated microgel for two different molecular weights of PDADMAC: (a) PDADMAC$_{100-200\,000}$ and (b) PDADMAC$_{1000}$.

surface retaining their solution configuration, which depends on the ionic strength of the polyelectrolyte solution. One can speculate that ionic strength plays no significant role on the deposition of multilayers on a substrate that is made up of a network of cross-linked polymeric chains and segments that are perpetually rearranging themselves. During LbL assembly, aqueous microgel is exposed to an excess of the polyelectrolyte in salt solutions. This condition of deposition then implies that the microgel would also respond to the presence of salt in the solution (Figure 2a). This means that when PDADMAC/PSS multilayers are assembled onto the microgel from polyelectrolyte solutions in water, we are depositing on a template which is ~320 nm, while for those prepared from different NaCl concentrations (0.10, 0.25, and 0.50 M), we are actually depositing on a template which has a size of around ~240 nm. After removal of the excess polyelectrolyte (and the salt), the coated microgels are then washed (three times) with water and finally redispersed in water. The particle size was measured by DLS as a function of temperature.

Figure 6 shows a plot of the R_h of the LbL-coated microgels at two distinct temperatures (20 and 40 °C, below and above the VPTT, respectively) as a function of the number of layers deposited, for systems whereby PDADMAC$_{100-200\,000}$ was deposited from various salt concentrations. It is clear that the "odd−even" effect on the R_h is more pronounced in the swollen than in the collapsed state. Comparing identical number of layers deposited on the microgel from various NaCl concentrations during LbL assembly, we observe an increasing R_h of the coated microgel (in water) with increasing salt concentrations. For example, when one layer of PDADMAC$_{100-200\,000}$ is deposited on the microgel from water, 0.1, 0.25, and 0.5 M NaCl, the R_h of the coated microgel redispersed in water is 250, 270, 275, and 280 nm, respectively. Assembling from aqueous solutions, we observe a collapse in R_h of the uncoated microgel from 320 to 250 nm (coated microgel) due to the strong electrostatic attraction between the polycation and the negatively charged microgel, as discussed earlier. Assembling from salt solutions (assuming polyelectrolyte deposition is being made on a microgel of effective size ~240 nm in the presence of salt), the washing away of the counterions and the redispersing in water have for effect to increase the R_h of the coated microgel. During washing with water (in the presence of osmosis), the microgel is subject to an osmotic influx and thus an excessive internal pressure. The higher the salt concentration of the polyelectrolyte depositing solutions, the bigger is the osmotic flux and the greater is the internal pressure. The swelling of the

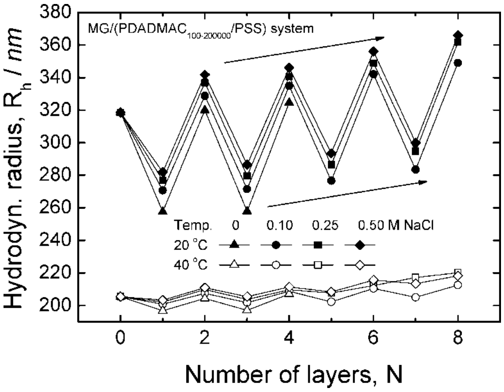


Figure 6. Influence of the ionic strength of the depositing polyelectrolyte solutions on the R_h of the coated microgels as a function of number of layers monitored at T = 20 and 40 °C. Arrows indicate regular increase in size of the microgel during coating of (PDADMAC$_{100-200\,000}$/PSS) and (PSS/PDADMAC$_{100-200\,000}$) bilayer onto PSS- and PDADMAC-terminated microgels, respectively. Assembly was carried out from polyelectrolyte solutions with or without salt but washed and finally redispersed in water. N = 0 is the uncoated microgel; an odd and even number indicates a PDADMAC- and PSS-terminated microgel, respectively.

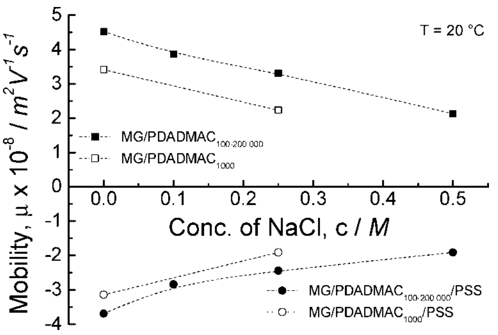


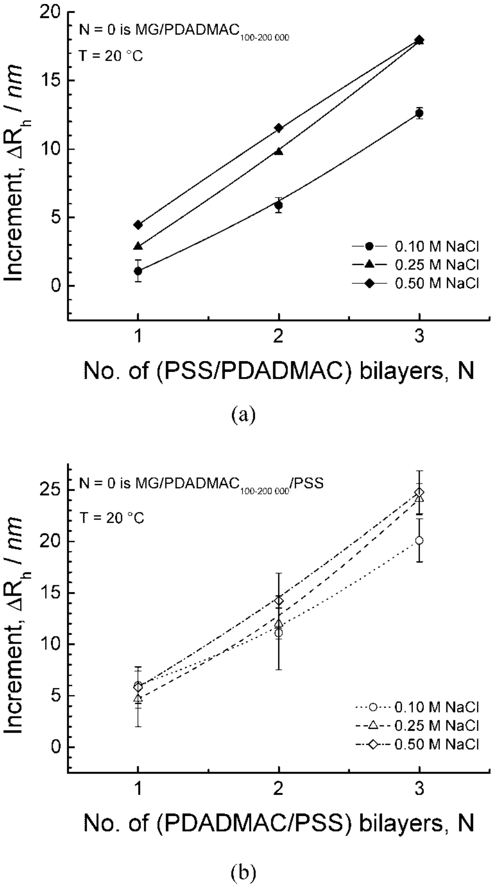
Figure 7. Influence of the molecular weight of PDADMAC on the electrophoretic measurements (at $T = 20$ °C) as a function of NaCl concentration used for the assembly of a one-layer and two-layer LbL-coated microgel. After the assembly the coated microgels were washed and finally redispersed in water. Error bars are within the size of the symbols.

ionic polymer network[61] is due to a balance of osmotic and elastic forces as well as osmotic contribution due to the ions within the network as a consequence of the Donnan equilibrium.[40] The final volume is reached when the osmotic pressure difference between the inside and the outside of the microgel is zero, and the latter is in equilibrium with its surrounding. The osmotic influx contributes to an increase of ~12, 15, and 17% in the R_{h} of coated microgels obtained from polyelectrolyte solutions containing 0.1, 0.25, and 0.5 M NaCl, respectively.

Under the assumption that the interaction between the microgel and the different deposited conformations, or different amount of polyelectrolytes adsorbed, all being equal, the increase in the R_{h} can be translated as an increase in the film thickness. In other words, the higher the salt concentration of the polyelectrolyte solutions used during the LbL assembly, the thicker is the film deposited. This is in agreement with what is commonly observed for deposition on hard and rigid substrates.[16] In aqueous or salt solutions of low ionic strength, the polyelectrolyte adopts a stretched conformation due to the repulsion of charges along the polyelectrolyte backbone, while in salt solutions of high ionic strength, charges of the polyelectrolyte are partially screened by counterions, thereby reducing both inter- and intramolecular repulsions, making the polyelectrolyte adopt a more coiled and compact conformation. Consequently, multilayers deposited at low ionic strength are thinner than those deposited at high ionic strength. A similar trend is also observed with PDADMAC$_{1000}$ (data not shown). However, the most important message from Figure 6 is that, on the whole, the deposition of layers, or more specifically of bilayers of (PSS/PDADMAC) or (PDADMAC/PSS) on PDADMAC- or PSS-terminated LbL-coated microgels, respectively, causes the size of the microgel to increase steadily—yet another confirmation of the successful LbL buildup of polyelectrolyte multilayers on microgels.

Figure 7 shows the electrophoretic mobility, measured at $T = 20$ °C, of one-layer and two-layer-coated microgels with both low and high MW PDADMAC as a function of the ionic strength of the polyelectrolyte solutions during LbL assembly. Comparing identical number of layers deposited on the microgels from various NaCl concentrations, we observe a decrease (in magnitude) of the electrophoretic mobility with increasing salt concentrations in the depositing polyelectrolyte solutions. For example, when one layer of PDADMAC$_{100-200\,000}$ is deposited on the microgel from water, 0.1, 0.25, and 0.5 M NaCl, the mobility of the coated microgels redispersed in water is $+4.5 \times 10^{-8}$, $+3.9 \times 10^{-8}$, $+3.3 \times 10^{-8}$, and $+2.1 \times 10^{-8}$ $\mathrm{m^2\,V^{-1}\,s^{-1}}$, respectively. This is in agreement with the notion of charges on the polyelectrolytes being more effectively screened at high salt concentration, and this could be a hint on the different conformations of the adsorbed poyelectrolytes onto the microgels. At an ionic strength of 0.5 M NaCl, the charges are screened and the polyelectrolytes adopt a coiled conformation, exposing fewer charges to the surface, as confirmed by electrophoretic measurements. Comparing between high and low MW for identical number of layers, we observe a decrease (in magnitude) of the electrophoretic mobility with decreasing MW: $+4.5 \times 10^{-8}$ and $+3.4 \times 10^{-8}$ $\mathrm{m^2\,V^{-1}\,s^{-1}}$ for a one-layer PDADMAC$_{100-200\,000}$ and PDADMAC$_{1000}$ coated microgel, deposited from water. We have shown, from Figure 1, that the extreme difference in MW has practically no effect in the R_{h} of the coated microgel. A layer of PDADMAC$_{100-200\,000}$ would then present more charges at the microgel surface than a layer of PDADMAC$_{1000}$. One would expect higher MW polyelectrolytes to be of longer chain length bearing more functional groups and charges. As mentioned earlier, the characterization techniques used in the present work do not allow for quantification of the amount of polyelectrolyte adsorbed. It could only be speculated that more of the PDADMAC$_{1000}$ would be adsorbed if PDADMAC$_{1000}$ could interpenetrate the microgel and neutralize charges otherwise not accessible to PDADMAC$_{100-200\,000}$. Indeed, we recently reported from titration studies that support our argument; namely, more low MW polyelectrolytes are needed to neutralize the charges on the microgels.[62]

Estimation of Bilayer Thickness. Because of the "odd−even" effect observed in the contraction and expansion of the LbL-coated microgels, together with the uncertainty of the exact location of the layer, a direct and precise determination of the thickness of each layer deposited is not accessible. However, taking into account the R_{h} of the microgel coated with the first layer (MG/PDADMAC) and the microgel coated with two layers (MG/PDADMAC/PSS) as denominators, one can get an estimation of the increment in the R_{h} of the LbL-coated microgel due to the deposition of a bilayer of (PSS/PDADMAC) on a PDADMAC-terminated and of (PDADMAC/PSS) on a PSS-terminated system, respectively. This increment in R_{h} provides an estimate of the thickness of bilayers on (MG/PDADMAC) and (MG/PDADMAC/PSS). From Figure 6 it can be seen that the "odd−even" effect of the R_{h} is more sensitive and pronounced in the swollen ($T < 32$ °C) than in the collapsed ($T > 32$ °C) state; therefore, the former state is chosen to estimate the thickness of bilayers, not only to minimize errors but also because it is the most realistic scenario since the LbL assembly has been carried out at room temperature. Figure 8 shows the thickness of bilayers as a function of the number of bilayers deposited on PSS- and PDADMAC-terminated systems for PDADMAC$_{100-200\,000}$. Figure 8a shows that the thickness of the first bilayer of (PSS/PDADMAC) deposited on MG/PDADMAC$_{100-200\,000}$ from a 0.10, 0.25, and 0.5 M NaCl solution is around 1, 2.5, and 5 nm, respectively, in agreement with the fact that the thickest layer was obtained from the polyelectrolyte solution with the highest ionic strength. Figure 8b shows that the thickness of the first bilayer of (PDADMAC/PSS) deposited on MG/PDADMAC$_{100-200\,000}$/PSS from a 0.10, 0.25, and 0.5 M NaCl solution are all around 5−6 nm. It is necessary to stress that these are all only an estimation of the thickness. These values are larger than what are usually reported for a dry bilayer of PDADMAC/PSS (for the corresponding ionic strength) on hard and rigid substrates. This can be rationalized as follows: considering that our system is soft and porous, polyelectrolytes not only interdigitate with each other but also, to some degree, can interpenetrate the microgel. Being in an aqueous medium, the polyelectrolyte layers are also fully swollen (and bound to a swollen microgel). So the value obtained is a good estimation of the thickness of a bilayer on microgel in water. From Figure 8, it appears that the addition of (PSS/PDADMAC$_{100-200\,000}$) onto MG/PDADMAC$_{100-200\,000}$



(a)

(b)

Figure 8. Estimation of the thickness of bilayers of (PSS/PDADMAC) and (PDADMAC/PSS) deposited on (a) MG/PDADMAC and (b) MG/PDADMAC/PSS microgels, respectively, from polyelectrolyte solutions with different salt concentrations during deposition. After the assembly the coated microgels were washed and finally redispersed in water. Lines are only guide for the eyes.

follows a linear growth while the addition of ($PDADMAC_{100-200\,000}$/PSS) onto MG/ $PDADMAC_{100-200\,000}$/PSS follows a "nonlinear" growth (similar to an exponential growth)—which could be an additional explanation to the significant increase in the R_h of PSS-terminated microgels, although for 0.1 M NaCl the growth is almost linear.

Storage Stability. For storage and application it is important to evaluate the storage or temporal stability of the LbL-coated microgels. This was done by monitoring any change in the R_h as well as in the thermoresponsive behavior as a function of time. Figure 9 shows the DLS curves of a two-layer LbL-coated microgel (MG/$PDADMAC_{100-200\,000}$/PSS) prepared from 0.5 M NaCl at $t = 0$, 15 days, 1 month, and 3 months. In between experiments the sample was stored at room temperature. At all of these defined periods, there are slight differences in the R_h of the coated microgel at 20 °C (before the heating cycle is applied). As can be seen in Figure 9, there is a perceptible increase in R_h with time, from 342 to 347 to 352 to 354 nm at 20 °C after $t = 0$, 15 days, 1 month, and 3 months, respectively. These values could be considered as almost constant. However, when the coated microgel is heated, independently of the size it reached (after time t), or in other words, irrespective of its history, it always collapse to the same size as when it was first coated ($t = 0$) and exhibit the same VPTT. On cooling, they all swell to about 340 nm, which is the original R_h of MG/$PDADMAC_{100-200\,000}$/PSS as on the day it was prepared ($t = 0$). We recently reported similar stability results on another system consisting of a core−shell microgel on which we deposited two layers of polyelectrolytes (polyethylenimine (PEI) and PSS).[24]

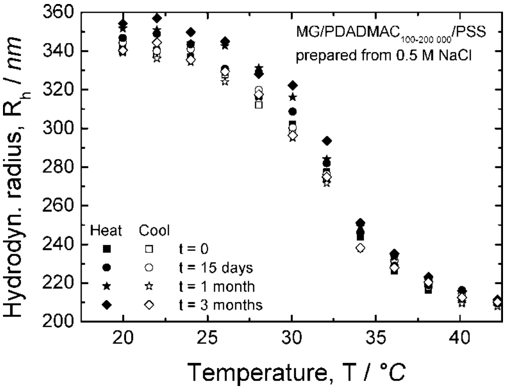
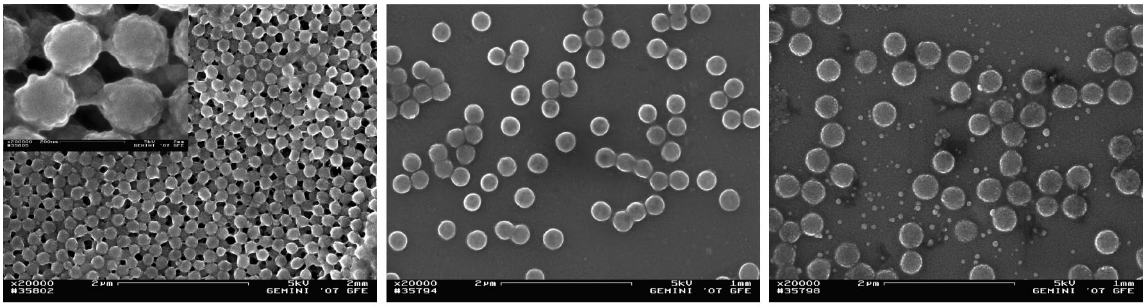


Figure 9. Temporal stability of MG/$PDADMAC_{100-200\,000}$/PSS microgels as monitored by DLS as a function of temperature.

When polyelectrolytes are adsorbed onto the microgel and subjected to a heating and cooling treatment, the interpenetration and interdigitation undergo reorientation, reorganization, and restructuring of the entanglement of the ensemble as water flows in and out (as already discussed above). When left standing over time, at room temperature, a likely explanation would be that, due to entropic reasons, relaxation of loose ends (ends group) or possibly collective sliding motion of the microgel and loops of the polyelectrolytes or a combination of both causes the latter to extend into the aqueous phase. This can be visualized as a hairy shell around the coated microgel explaining the increase in the R_h, and with increasing period of time, the hairy shell extends even further out, probably as the coiled chains adopt a stretched conformation. However, on heating and cooling, these chains "fold back", and the original size and thermoresponsive behavior of the LbL-coated microgel are restored, as shown in Figure 9. From a previous study using fluorescently labeled polyelectrolyte there is no indication that the polyelectrolyte desorbs with time (even after 3 months), clearly indicating that the LbL-coated microgels are very stable.[29]

SEM Micrographs. Figure 10 shows SEM micrographs obtained from the dried MG, MG/$PDADMAC_{100-200\,000}$, and MG/$PDADMAC_{100-200\,000}$/PSS. The dried uncoated and coated microgels shrunk during drying. However, unlike hollow capsules (templated from ~5 μm silica) that usually shrink to flat structures with creases and folds, microgels studied in this work keep their spherical shape upon drying (and with a low polydispersity in size).[46] It has been reported that at sizes below ~1.65 μm polyelectrolyte hollow capsules keep their spherical shape, just like the microgels. The authors explained this increase in stability of the capsules with decreasing diameter by a steadily increasing wall thickness.[46] Thicker shell also correlates with the decrease in permeability of low molecular weight dyes.[63]

From SEM, it can be seen that, in the dry state, MG, MG/$PDADMAC_{100-200\,000}$, and MG/$PDADMAC_{100-200\,000}$/PSS (layers deposited from 0.25 M NaCl) shrink to different sizes: diameter ~177, 265, and 365 nm, respectively. It has to be stressed that all samples are in the dry state, which is very different from being in aqueous medium in the collapsed state. The fact that the size of the dry MG/$PDADMAC_{100-200\,000}$/PSS microgels is significantly bigger than the dry MG/$PDADMAC_{100-200\,000}$ microgels is clearly indicative of the trend already observed when the microgels are in the swollen state in the solution. Although SEM micrographs do not allow for direct size comparison with that obtained with DLS, they provide a visual representation of the morphology of the samples (though



(a) (b) (c)

Figure 10. SEM micrographs of (a) MG, (b) MG/PDADMAC$_{100-200\,000}$, and (c) MG/PDADMAC $_{100-200\,000}$/PSS in the dry state. The inset in (a) is a magnification to show bridging between MG.

in the dry state). It should also be stressed that particle distribution on the support depends strongly on drying conditions to prepare the sample. However, the drying procedure employed to obtain all three samples were identical for consistency. Figure 10a shows a typical SEM image of the uncoated microgel where individual microgel is "interconnected" by sticking bridge, clearly visible in the inset. Figures 10b,c, obtained from a more dilute solution, show individual LbL-coated microgels clearly far more separated in the latter case (MG/PDADMAC$_{100-200\,000}$/PSS) than in the former case (MG/PDADMAC$_{100-200\,000}$). MG/PDADMAC$_{100-200\,000}$ tends to "attach" to a few (one or two) particles only, while MG/PDADMAC$_{100-200\,000}$/PSS tends to be more individual particles without any affinity to stick together. This could point to the fact that, as previously reported,[24] the surface coverage on soft and porous microgels is more efficiently achieved by PSS than PDADMAC, as further confirmed by the electrophoretic mobility studies above. MG/PDADMAC$_{100-200\,000}$ are likely to present regions that are partly uncovered by the PDADMAC, hence exhibiting a "local" negative charge that tends to bind with the PDADMAC-covered region of another MG/PDADMAC$_{100-200\,000}$ particle. SEM pictures not only provides visual proof of the coated microgels but also clearly shows (Figure 10) that the morphology of the LbL-coated microgels is very different to that of the uncoated microgels, which is a strong evidence of surface modification of the microgels, thereby confirming the presence of the polyelectrolyte layers on the microgel.

Conclusions

A thorough study of the conditions of the layer-by-layer assembly of polyelectrolyte multilayers of strong polyelectrolyte pairs, PDADMAC and PSS, on soft and porous thermoresponsive poly(*N*-isopropylacrylamide-*co*-methacrylic acid), P(NiPAM-*co*-MAA), microgel was undertaken by dynamic light scattering and electrophoretic measurements to see the influence of salt, ionic strength, and molecular weight on the thermoresponsive behavior of the coated microgels.

The hydrodynamic radius measurements demonstrate an "odd−even" effect of the size of the coated microgel depending on the type of polyelectrolytes in the outermost layer, that polyelectrolyte-coated microgels retain their thermoresponsive property, and that the swelling and deswelling processes are completely reversible. PSS-terminated microgels are more swollen and more temperature-sensitive than PDADMAC-terminated microgels.

Not much difference was observed in the size of the microgels coated with low and high molecular weight polyelectrolytes; however, electrophoretic measurements indicate microgels coated with low molecular weight are more prone to rearrangement.

The strong polyelectrolyte shell assembled around the pH-responsive microgel core is very effective in rendering the ensemble pH-insensitive.

The core−shell microgels show a clear increase of the size with increasing salt concentration from which the layer (shell) is being deposited. The electrophoretic mobility results reveal charge reversal after each layer deposition and the magnitude of which decreases with increasing number of layers as well as with increasing salt concentration in the depositing polyelectrolyte solutions.

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