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Buildup of Multilayers Based on Amphiphilic Polyelectrolytes

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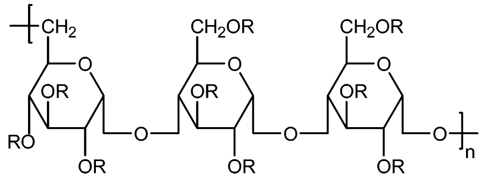
ABSTRACT: We report on the preparation of layer-by-layer (LbL) assemblies based on anionic hydrophobically modified polysaccharides and different polycations. We systematically investigate the influence of the effect of the hydrophobicity of the polysaccharide derivatives on the multilayer buildup. We provide clear evidence that the presence of hydrophobic interactions contributes strongly to stabilize the adsorbed layers. In addition, the correlation between the study of the multilayer growth and of the solutions properties of the amphiphilic derivatives shows that the thickness of adsorbed layers is directly determined by the conformation of amphiphilic chains in solution. These results are in agreement with the presence of hydrophobic microdomains in the films.

Introduction

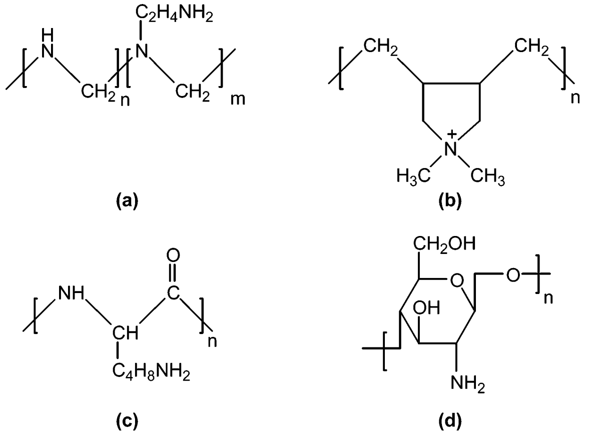
The layer-by-layer (LbL) assembly of polyelectrolytes introduced by Decher and co-workers[1,2] consists of the alternating adsorption of polycations and polyanions at solid charged surfaces, resulting in the formation of thin films. This technique is particularly attractive due to its simplicity and versatility. So far, a large variety of charged materials such as biomacromolecules, inorganic particles, dyes, and conductive polymers have been successfully included in these multilayers to prepare optical or electrochemical devices, biosensors, separation membranes, catalytic systems, etc.[3−6]

The multilayering process has been explained by the overcompensation of charge at each adsorption step. Hence, the electrostatic interaction between the surface and the polyions in solution is usually considered as the driving force for multilayer formation. The adsorption behavior of polyelectrolytes is influenced by a number of factors such as the charge density,[7−11] the ionic strength or the pH of the solutions, and the solvent quality.[12−14] However, recent theoretical[15,16] and experimental[17−20] reports suggest that nonelectrostatic short-range interactions also play an important role in the multilayering process. Among these secondary interactions, a particular case is the hydrophobic interaction. Only a few studies[17−21] have been devoted to their effect in LbL, and their role is not yet fully understood. Here, we use anionic amphiphilic polysaccharides of varying hydrophobicity to investigate this effect. These amphiphilic polysaccharides (Scheme 1) are obtained by grafting alkyl chains on carboxymethylpullulan (CMP), an anionic flexible polysaccharide. In contrast with the previously used synthetic polyelectrolytes,[17−21] the backbone of CMP is highly hydrophilic; therefore, the hydrophobicity of our amphiphilic derivatives results only from the grafted alkyl groups. These hydrophobically modified CMP's were previously shown to develop spontaneous inter- and/or intramolecular interactions in aqueous solutions, depending on the content and the length of grafted alkyl chains.[22,23] It is interesting to explore how these different solution behaviors affect the multilayer growth.

Scheme 1. Anionic Polysaccharide Derivatives Used in This Study: R = H or $CH_2COO^-Na^+$ for Carboxymethylpullulan Precursor and R = H or $CH_2COO^-Na^+$ or $CH_2C(O)OC_nH_{2n+1}$ for Hydrophobically Modified Carboxymethylpullulans



Scheme 2. Cationic Polyelectrolytes Used in This Study: Poly(ethylenimine) (a), Poly(diallyldimethylammonium) (b), Poly(L-lysine) (c), and Chitosan (d)



In this paper we report on the LbL assembly of these amphiphilic CMP's with polycations of different nature such as poly(ethylenimine) (PEI), poly(diallyldimethylammonium) (PDDA), poly(L-lysine) (PLL), and chitosan (Scheme 2). We systematically investigate the effect of the content and of the length of the alkyl chains grafted on the CMP backbone on the multilayer buildup.

Experimental Section

Materials. Branched poly(ethylenimine) (M_w = 750 000 g mol^{-1}), poly(diallyldimethylammonium chloride) (M_w = 100 000−200 000 g mol^{-1}), and poly(L-lysine) (M_w = 62 140 g mol^{-1}) were purchased from Sigma-Aldrich. Chitosan (M_w = 150 000−400 000 g mol^{-1} (86% deacetylated) and pullulan (M_w

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Table 1. Characteristics of the Hydrophobically Modified CMP's Used in This Study

sample	alkyl chain	grafting deg (%) (±0.5)[a]
CMP-13C_4	butyl	13
CMP-8C_6	hexyl	8
CMP-8C_8	octyl	8
CMP-2C_{10}	decyl	2
CMP-7C_{10}	decyl	7
CMP-14C_{10}	decyl	14
CMP-18C_{10}	decyl	18
CMP_L-18C_{10}[b]	decyl	18
CMP-9C_{12}	dodecyl	9

[a] The grafting degree is expressed as the number of alkyl chains per 100 anhydroglucose units and was determined by gas-phase chromatography measurement of alcohol obtained after alkaline hydrolysis of CMP derivatives according to the procedure described in ref 23. [b] L referred to a sample of low molar mass obtained by ultrasonic degradation.

= 320 000 g mol^{-1}) were supplied by FMC BioPolymer (Norway) and Hayashibara Biochemical Laboratory (Japan), respectively, and were used without further purification. Carboxymethylpullulan (CMP) (Scheme 1) with a substitution degree in carboxymethyl groups of 0.9 ± 0.05 and M_w = 235 000 g mol^{-1} [24] was prepared from pullulan according to a procedure already described.[25] A sample of carboxymethylpullulan with a low molar mass (CMP_L) (M_w = 24 000 g mol^{-1})[24] was obtained by ultrasonic degradation of the CMP precursor according to the procedure previously described.[23] Hydrophobically modified carboxymethylpullulans (Scheme 1) were synthesized by grafting alkyl chains on carboxymethyl groups of the CMP through ester linkage as reported previously.[26] Briefly, the acidic form of CMP was neutralized by tetrabutylammonium hydroxide [$(C_4H_5)_4N^+,OH^-$] up to 7. After freeze-drying, 5 g of the resulting CMP salt was dissolved in 30 mL of dimethyl sulfoxide (DMSO) at 40 °C. Alkyl bromide (butyl, hexyl, octyl, decyl, or dodecyl) was slowly introduced, and the reaction was continued at 40 °C under magnetic stirring for 12 h. A concentrated aqueous solution of NaCl (12% w/w) was then added to convert hydrophobically modified CMP obtained into the sodium salt form which is precipitated in the bulk. The precipitate is removed by filtration, washed with 400 mL of ethanol, and dried. The resulting hydrophobically modified CMP was then purified by dialysis against pure Milli-Q water and freeze-dried. Different hydrophobically modified CMP derivatives were obtained by varying the length (from 4 to 12 carbon atoms) and the content of grafted alkyl chains. The characteristics of the different CMP derivatives used in this study are summarized in Table 1. Hydrophobically modified CMP will be denoted CMP-xC_n in the sequel with x the number of grafted alkyl chains per 100 anhydroglucose units and n the number of carbon atoms in alkyl chain.

Solutions of Polyelectrolytes. The solutions of polyelectrolytes were made by dissolving the polymer in 0.1 M NaCl with a concentration of 2 g L^{-1}. The pH of the solutions was set to 4, 4.5, 7.4, and 8.0 by adding HCl 0.1 M or NaOH 0.1 M for PEI, chitosan, PLL, and CMP derivatives, respectively. All solutions were filtered through a 8 μm Millipore membrane before use.

Solution Properties. The macromolecular characteristics of the hydrophobically modified CMP's in aqueous solution were investigated by using a symmetrical flow field−flow fractionation (F4) system coupled on-line with multiangle laser light scattering (MALLS) and differential refractive index (DRI) detectors. This technique is described in detail elsewhere.[22,27] Briefly, F4 is a separating technique in which the separation takes place in a thin, open channel through which the sample is transported by a laminar flow of carrier showing a parabolic flow profile. An external solvent flow applied perpendicularly to the channel flow partitions the various components of the sample into regions of different velocities. As a result, the components of a smaller hydrodynamic volume are eluted faster than the larger ones. The simultaneous measurements of the light scattering intensity and the concentration of the different eluted fractions allow us to compute the molar mass distribution and the average molar mass of the sample. Unlike the size exclusion chromatography (SEC), the open channel geometry of F4 without stationary phase is particularly suited to the fractionation of amphiphilic polymers which show a complex associating behavior in solution.[22,23,27] Experimentally, we used an universal F4 fractionator model F-1000 from PostNova (Munich, Germany) piloted by Flow 160 software and coupled on-line with a DAWN-F (DSP) photometer from Wyatt Technology Inc. (Santa Barbara, CA) and a differential refractive index ERC 7515A detector from Erma CR Inc. (Tokyo, Japan). The carrier used was 0.1 M $LiNO_3$ + 0.02% NaN_3 filtered through a 0.22 μm Millipore membrane and continuously degassed with Gastorr 154 from Flom (Tokyo, Japan). The sample-injected volume consists of a 100 μL full loop. The samples were prepared as described below and analyzed according to the following running procedure: The channel flow rate was held at 0.5 mL min^{-1} during all the analysis; the cross-flow rate was first held at 1 mL min^{-1} for 5 min, then exponentially decreased until 0.3 mL min^{-1} for 10 min and held at 0.3 mL min^{-1} for 20 min, and finally held at 0.05 mL min^{-1} until the end of the elution of the sample.

Preparation of Multilayered Films. The substrates used for multilayer growth were one-side polished (100) silicon wafers (ACM, France) cut into rectangles 3 cm by 1 cm. The wafers were first cleaned by treatment in a hot piranha solution (H_2O_2 (35%):H_2SO_4 (98%) 1:1 v/v) for 20 min (caution: piranha solution is extremely corrosive) and then thoroughly washed with pure Milli-Q water. Multilayers were grown by alternately dipping the substrate in aqueous solution of polycation (PEI, PDDA, PLL, or chitosan) and polyanion (CMP or CMP-xC_n derivatives) for 20 min each. Between each deposition step, the substrate was rinsed by dipping 10 times in three different beakers of pure Milli-Q water and blown dry with a stream of pure air. In the case of films prepared with chitosan, a precursor cationic PEI layer was deposited onto silicon wafers to promote the subsequent multilayer deposition. A film prepared with N bilayers of polycation and CMP derivative (CMP-xC_n) will be named [polycation/CMP-xC_n]$_N$ in the sequel.

Characterization of Multilayers. The multilayer growth was monitored by a null ellipsometer from Multiskop instrument (Optrel, Germany) at a fixed angle of 70° and fixed wavelength of 6328 Å. For each sample, between five and eight spots were measured and averaged. A model consisting of an isotropic film deposited on a flat isotropic substrate was used to analyze the data. The refractive index of the silicon was taken to be 3.882-j0.019.[28] The effective refractive index of the film was obtained from the ellipsometry data by fitting trajectories in the (ψ, Δ) plane corresponding to samples of increasing thickness. A typical refractive index of 1.52 was obtained by this procedure. The thickness of the native oxide layer atop the silicon substrate (∼15 Å) was not subtracted from the computed total thickness of the film.

Results

Solution Properties. We investigated the macromolecular characteristics of the unmodified CMP and CMP-xC_{10} derivatives by the F4/MALLS technique to get a better understanding of their behavior in aqueous solution. Whereas only one population was obtained for the CMP precursor, two populations were observed for the modified CMP's: a main one, which represents 80−95% of the sample according to the DRI detector and which is eluted at low elution volumes, and a second one eluted at high elution volumes, which corresponds to large aggregates of very high molar mass. The variation of the apparent number-average molar mass (M_n) of the main fraction of the CMP-xC_{10} samples is reported as a function of the grafting degree in Figure 1. We observed a continuous increase of M_n when x increases up to 14%. For a *larger* grafting degree, the apparent molar mass decreases.

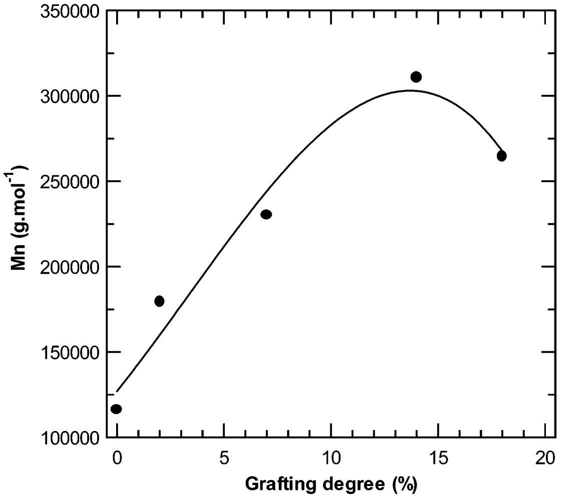


Figure 1. Variation of the number-average molar mass (M_n) of CMP-xC$_{10}$ derivatives vs grafting degree determined by F4/MALLS. The line is drawn as guide for the eye.

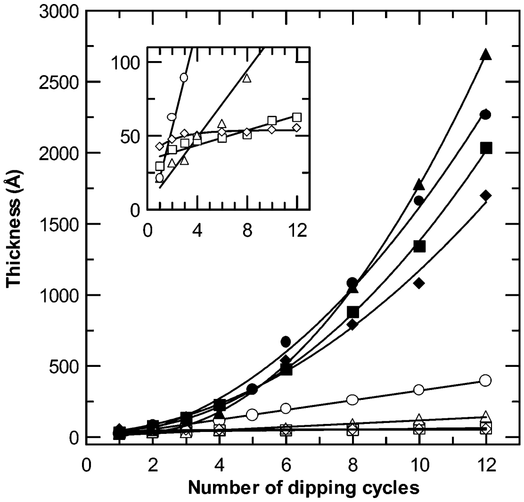


Figure 2. Thickness of multilayers based on [polycation/CMP] (open symbols) and [polycation/CMP-18C$_{10}$] (closed symbols) vs number of dipping cycles. Polycation nature: PLL (◇, ◆), PDDA (□, ■), chitosan (○, ●), and PEI (△, ▲). Inset: zoom-in of the data obtained for the films based on unmodified CMP. The lines are fit to the data.

Polyelectrolytes Multilayers. Nature of the Polycation. Several polycations were selected for assembly with amphiphilic CMP derivatives to investigate the influence of their nature on multilayer growth. The variations of thickness with number of dipping cycles measured for samples based on CMP-18C$_{10}$ assembled with PEI, PDDA, PLL, and chitosan are displayed in Figure 2. The results obtained for the films prepared in the same conditions with the unmodified CMP precursor are added for comparison. A linear increase of the thickness with number of deposited layers is detected for samples based on the unmodified CMP, except for PLL for which the multilayer growth stops after three deposited bilayers. In contrast, films prepared with the CMP-18C$_{10}$ derivative show an exponential growth and are largely thicker than the ones prepared with the unmodified CMP precursor. In both cases, the thickness of the films increases from PLL to PDDA, PEI, and chitosan. Interestingly, thicker films based on the amphiphilic CMP, obtained for a large number of dipping cycles, were found to be cloudy, suggesting increased roughness or possible phase separation in the film.

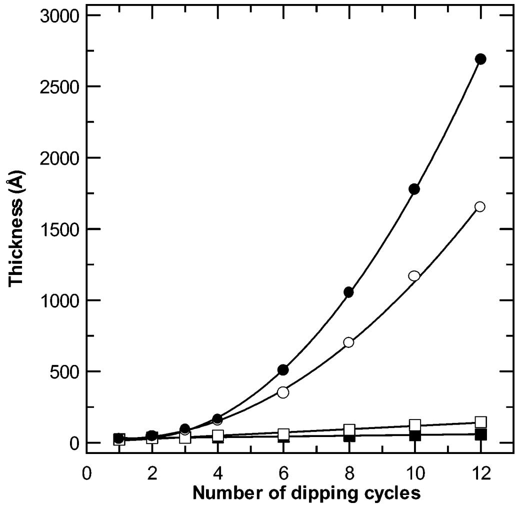


Figure 3. Variation of the thickness of [PEI/CMP-18C$_{10}$] (●), [PEI/CMPL-18C$_{10}$] (○), [PEI/CMP] (□), and [PEI/CMPL] (■) LbL films vs number of dipping cycles. The lines are fits to the data.

Molar Mass of the CMP Derivative. The growth of [PEI/CMP-18C$_{10}$] and [PEI/CMP$_L$-18C$_{10}$] samples based on large and low molar mass modified CMP derivatives, respectively, is displayed in Figure 3. The curves obtained for the films prepared with the corresponding unmodified CMP and CMP$_L$ are added for comparison. The decrease of the molar mass of the CMP precursor (by a factor of about 10) leads to a decrease of the thickness of the films based on CMP$_L$-18C$_{10}$ (by a factor of about 1.5). However, the linear and nonlinear growths observed for samples prepared with unmodified and modified CMP, respectively, are preserved.

Grafting Degree. The influence of the grafting degree x of CMP chains on the multilayer buildup was systematically studied for the [PEI/CMP-xC$_{10}$] system. The results presented in Figure 4a show that the thicknesses of the films are drastically affected by the content in alkyl chains. This effect appears more clearly by inspecting the variation with x of the thickness of [PEI/CMP-xC$_{10}$] films comprising 10 bilayers vs x (Figure 4b). Interestingly, the thickness of the multilayers reaches a maximum at a grafting degree comprised between 10 and 14%. A similar study performed on the [chitosan/CMP-xC$_{10}$] system gave the same behavior with a maximum reached between 14 and 18% (Figure 4b).

Length of the Alkyl Chain. Films based on PEI and CMP-xC$_n$ samples with x about 10% were studied for n varying from 0 to 12 (Figure 5a). In contrast to the linear variation of the thickness with number of deposited bilayers observed in the case of the films prepared with unmodified CMP, an exponential growth is seen for all the films based on hydrophobically modified CMP's. Moreover the grafting of alkyl groups on the CMP backbone results in a large increase of the thickness of the multilayers, even when the samples are based on a CMP modified by short butyl chains. The inspection of the variation of the thickness of 10-bilayer films based on CMP-xC$_n$ with x about 10% (Figure 5b) and n varying shows that the thickness continuously increases when n increases from 0 to 10 and seems to saturate for longer alkyl chains.

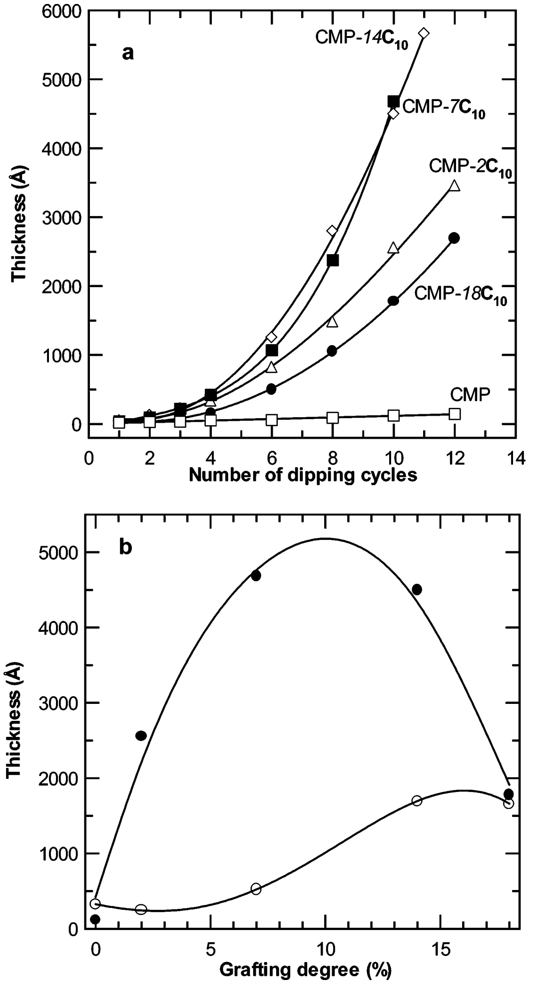


Figure 4. (a) Thickness of LbL films self-assembled from PEI and CMP-xC$_{10}$ derivatives vs number of dipping cycles: x = 0% (□); x = 2% (△); x = 7% (■); x = 14% (◇); x = 18% (●). (b) Variation of the thickness of 10-bilayer [PEI/CMP-xC$_{10}$] (●) and [chitosan/CMP-xC$_{10}$] (○) films vs the grafting degree x. The lines are drawn as guides for the eye.

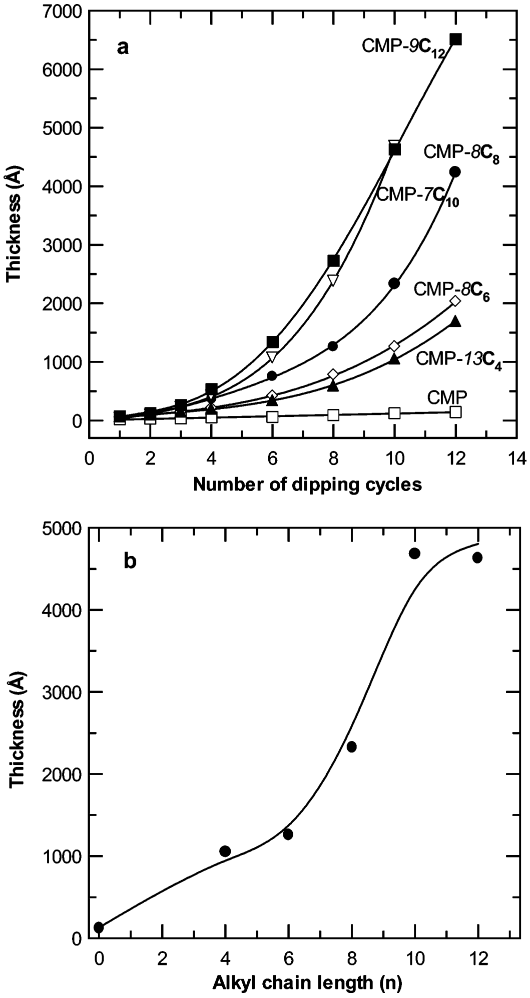


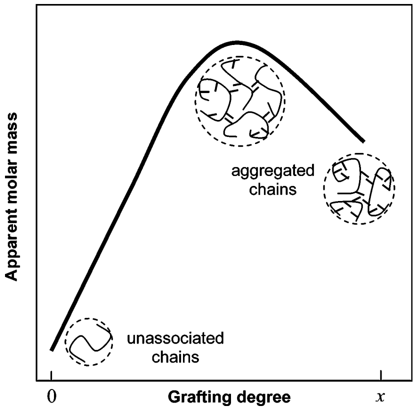
Figure 5. (a) Thickness of LbL films self-assembled from PEI and CMP-xC$_n$ derivatives (x ~ 10%) vs number of dipping cycles: CMP (□), CMP-13C$_4$ (▲), CMP-8C$_6$ (◇), CMP-8C$_8$ (●), CMP-7C$_{10}$ (▽), CMP-9C$_{12}$ (■). (b) Variation of the thickness of 10-bilayer [PEI/CMP-xC$_n$] films vs the length of alkyl chains (n) of CMP-xC$_n$ derivatives (with x ~ 10%). The lines are drawn as guide for the eye.

Discussion

We have systematically investigated the influence of the hydrophobic interaction on the multilayer assembly process using hydrophobically modified polysaccharides of varying hydrophobicity. The continuous multilayer growths obtained for these amphiphilic derivatives CMP-xC$_n$ assembled with different polycations (Figures 2, 4, and 5) provide the evidence for their robustness toward the LbL process. In contrast, the study of LbL assemblies based on unmodified CMP and the same polycations reveals that the multilayer buildup strongly depends on the nature of the polycation used. An interesting example is observed for PLL-based systems for which the multilayer formation stops after a few deposited bilayers using CMP and proceeds continuously using a hydrophobically modified CMP derivative (Figure 2). These results point to the fact that the LbL process may be driven by other interactions than simple electrostatics: The presence of secondary hydrophobic interactions between amphiphilic polysaccharides and polycations contributes to stabilize adsorbed polyelectrolyte layers and may be required to ensure film growth for some polyelectrolytes. This is supported by a recent Monte Carlo simulation showing a large increase of the amount of adsorbed polyelectrolyte and a higher stability of the film when nonelectrostatic parameters were taken into account.[15]

The inspection of the influence of the content of hydrocarbon chains grafted on the CMP backbone on the multilayer growth (Figure 4) reveals a complex behavior which is slightly affected by the nature the polycation used for the assembly. This feature can be explained by considering the apparent molar mass of the components in solution. The existence of a maximum in the film thickness as a function of the grafting degree can be related to the maximum of the apparent molar mass observed in solution (Figure 1). A similar solution behavior was already observed for the amphiphilic CMP's bearing octyl chains.[22] It was ascribed to a transition from a random coil conformation to loose aggregates and then to more compact aggregates with increasing alkyl chain content, as sketched in Scheme 3. Such conformational transitions stem from the balance of intra- and intermolecular interactions between hydrophobic groups. The similarity between the increment of growth of the multilayers and the apparent molar mass of the components measured in solution indicates that the conformation and aggregation of the macromolecules is mainly kept upon adsorption on the surface. This contrasts with previous studies[17,20] per-

Scheme 3. Conformational Changes of CMP-xC$_{10}$ Derivatives as a Function of the Grafting Degree x in Alkyl Chains



formed with polyelectrolytes bearing chromophore and fluorophore groups, for which a complete disruption of hydrophobic associations present in aqueous solution were observed upon adsorption. This difference may be explained by the higher stability of intra/interassociations of alkyl chains grafted on a CMP backbone, which apparently resist adsorption on the solid surface.

A similar reason may be taken to explain the limited decrease of the thickness of the multilayers when the molar mass of the CMP precursor is decreased (Figure 3): the aggregation behavior is only little affected by the decreasing polymer molar mass, which results in limited perturbation of the adsorbed amount per cycle.

The increase of the length of hydrocarbon chains grafted on the CMP backbone also affects dramatically the multilayer growth (Figure 5): thicker films are obtained for longer alkyl chains. This behavior, which is observed even for CMP's modified by very short alkyl chains, is fully consistent with the reinforcement of the intermolecular hydrophobic interactions between CMP-xC$_n$ chains themselves and between CMP-xC$_n$ chains and the surface. The longer the length of grafted hydrocarbon chains, the higher and stronger the hydrophobic interactions. As a result, a larger amount of material is adsorbed after each deposition step, and the thickness of the films increases. However, this phenomenon is limited for long alkyl chains such as decyl groups. Indeed, as described above, the highly hydrophobic CMP-xC$_n$ macromolecules tend to associate in compact small aggregates due to numerous intramolecular interactions.

Another distinct difference between the samples based on unmodified and modified CMP's is the linear and exponential growths observed, respectively, for both systems (Figures 2–5). While the linear increase of the thickness with the number of dipping cycles is generally attributed to the constant amount of polyelectrolyte adsorbed after each deposition step, several models were proposed in the literature to explain nonlinear buildups. McAloney et al. suggested that such behavior is caused by the roughness of the film increasing with the number of deposited layers:[29] The macromolecules adsorbed in the initial layers adopt a flat conformation because of the strong interactions with the surface of the substrate; however, the influence of the substrate decreases with increasing number of deposited layers, and the polyelectrolyte chains start to adsorb in more loopy conformations, which results in an increasing surface area. Another way to explain the nonlinear multilayer growth is based on diffusion of free polyelectrolyte chains into the multilayer during each adsorption step.[30-32] In our case, both models can be considered, and a further investigation is required to fully understand the process involved in these systems.

Conclusion

We provided the evidence that the presence of hydrophobic interactions contribute strongly to stabilize adsorbed layers during the assembling process of LbL multilayers. In some cases, they happen to be decisive for the film formation. These results confirm previous simulations which consider that the hydrophobic interaction can be identified as an important factor for multilayer buildup. In addition, the thickness of adsorbed layers is directly determined by the conformation of amphiphilic polyelectrolytes in aqueous solution because most intra- and/or intermolecular hydrophobic interactions between macromolecules are preserved during the adsorption process. This indicates that a better understanding of the structures of polyelectrolyte solutions is of a crucial importance to understand fully the LbL mechanism. This behavior of amphiphilic CMP in the film allow us to think that hydrophobic microdomains are present in the multilayers. Such clusters are of a potential interest since they are expected to enhance greatly the loading capacity of the thin films for immobilization of hydrophobic drugs or biomolecules. Further research is underway to elucidate this point.

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