

Responsive polyelectrolyte multilayers

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Abstract

In this review we present selected recent developments of responsive multilayers formed by layer-by-layer assembly of oppositely charged polymers, with particular emphasis on the preparation of temperature- and pH-sensitive systems. We discuss the influence of the architecture and of the nature of the polyelectrolytes used on the responsive behavior of the films. Different strategies based on polyelectrolyte shells or films incorporating stimuli-responsive polyelectrolytes are reviewed as well as the entrapment of stimuli-responsive polymer into hollow capsules.

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1. Introduction

Among the methods developed to prepare thin films, the layer-by-layer (LbL) deposition of polyelectrolytes has aroused considerable attention due to its simplicity and versatility [1,2]. In addition this technique has the advantage of enabling nanoscale control of the thickness, the structure and the composition of the films. Beside the preparation of polyelectrolyte multilayers (PEMs) on flat substrates, the LbL technology has been extended to produce well-defined hollow capsules [3]. These microcontainers made by layer-by-layer deposition of oppositely charged polyelectrolytes onto colloid templates and subsequent removal of the core, are particularly attractive due to their promises for microreactors, microsensors, and drug-delivering systems [4]. Recent developments and potential applications of polyelectrolyte films and hollow microcapsules are described in details in various past reviews [5–10].

One of the significant research interests emerging recently from the PEMA area is the development of environmental responsive devices due to their potential applications in medicine, cosmetics, pharmaceuticals and textile industry [11]. Here, the challenge is the preparation of thin films or shells showing a predictable response of their functional properties such as wettability, adhesivity or porosity when an external condition is varied. A common approach to produce such systems consists in using the propensity of some polyelectrolytes to change their macromolecular characteristics following a variation of external stimuli such as pH, temperature, ionic strength, magnetic field or light. The present review focuses on our recent work on the preparation and characterization of PEM films and microcapsules showing a variation of their characteristics in response to external stimuli, with emphasis placed on the influence of the structure and nature of the polyelectrolytes on their responsiveness.

The first part of this paper is dedicated to the preparation of thermoresponsive multilayers. The most developed approach to produce such systems is to use derivatives of poly(*N*-isopropylacrylamide) (PNIPAM). PNIPAM is a polymer that at room temperature is water soluble through strong hydrogen bonding with water [12]. However, above 32 °C the hydrogen bonding is disrupted and water no longer acts as a suitable solvent. As a consequence, above this temperature called lower

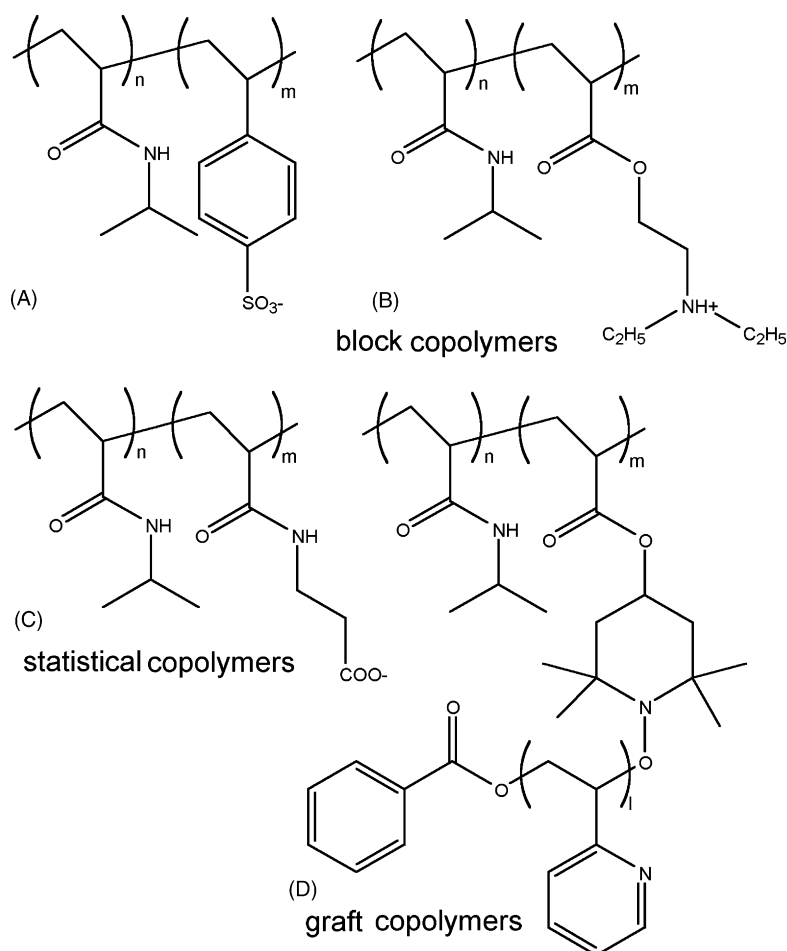
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critical solution temperature (LCST), PNIPAM chains undergo a coil to globule transition where they preferentially make hydrophobic bonds with neighboring polymer chains [12–14]. Due to its LCST close to physiological temperature, PNIPAM is a very attractive candidate for biomedical applications [15]. The first approach to introduce PNIPAM into multilayers is to prepare hydrogen-bonded self-assemblies. Caruso et al. found that multilayers of hydrogen-bonded PNIPAM and poly(acrylic acid) could be reversibly loaded with a dye and subsequently emptied by varying the temperature [16]. However, such systems disintegrate when the pH exceeds a certain value. For this reason, other approaches using charged derivatives of PNIPAM were also tested. Different charged PNIPAM derivatives differing by their structure and their composition, were successfully synthesized and incorporated within polyelectrolyte assemblies [17–22]. However, the responsiveness of the resulting assemblies was shown to strongly depend on the microstructure of the polyelectrolyte used. This aspect will be discussed here by considering the thermosensitive behavior of different systems based on mono- or multilayers and incorporating charged copolymers of PNIPAM of various structures (Scheme 1). Moreover, the preparation of microcapsules filled with a high molar mass PNIPAM is outlined as an alternative approach to prepare thermoresponsive devices.

The second part of this review deals with the pH-responsive PEMs. Due to their pH sensitivity, weak polyelectrolytes were extensively exploited to prepare responsive films and shells. Indeed, the variation of the pH induces a change in the charge density of the chains which affects the interactions between the polyelectrolytes and results in a change of the morphology or of the permeability of the films. Reversible swelling and porosity transitions in multilayers, tuned by pH changes, have been described in the case where poly(allylamine hydrochloride) (PAH) was associated to the strong polyanion poly(sodium styrene sulfonate) (PSS) [23]. The reversible formation of pores is crucial for the control of loading and release of substances. Others pH-sensitive membranes have been described, containing always at least one weak polyelectrolyte such as poly(acrylic acid) (PAA) [24], poly(methacrylic acid) (PMA) [25] or others weak co-polymers [26]. The thickness and the stability of the films were always determined by the pH of the dipping solutions. Stable films have been obtained after crosslinking the multilayers, due to the formation of strong covalent bonds [27]. A particular interest is in the preparation of responsive capsules whose permeability can be tuned with pH for drug delivery applications [28–30]. The preparation of such devices will be discussed here. In addition, a second approach which consists in embedding a polypeptide



Scheme 1. Structure of the PNIPAM derivatives used in this study.

showing a change of its conformation with pH will also be described.

2. Temperature-responsive PEMs incorporating PNIPAM

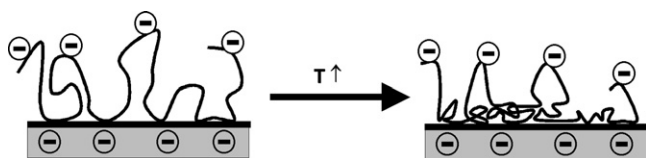
2.1. Responsive behavior of PNIPAM copolymers adsorbed in monolayers

An interesting question is how the phase transition properties of thermoreversible polymers would change in adsorbed layers on solid surfaces, and how electrostatic interactions would affect them. The phase transition of uncharged PNIPAM adsorption layers was studied by temperature-dependent dynamic light scattering (DLS), where a transition with a pronounced hysteresis occurred. The occurrence of the hysteresis was interpreted as a kinetically unstable ‘extended brushlike conformation’ [31]. On the other hand, at very low surface coverage on silica, no transition was detected at all [32].

For incorporation into multilayers, in addition to interfacial constraints, charges on the PNIPAM chain are required for electrostatic coupling. In solutions, co-monomers are known to influence the phase transition considerably: hydrophobic co-monomers lower the LCST, while hydrophilic or charged ones raise it, or might even prevent it [33–35].

A co-monomer containing carboxylic acid (Scheme 1C), where the influence of the charged group is compensated by a C₂-spacer was designed [35,36]. The LCST in solution does not change until the co-monomer content exceeds 10 mol%, as confirmed by DSC, ¹H NMR and PFG-NMR diffusion [36,37]. This copolymer is thus a promising compound with an optimized co-monomer architecture. In spite of the negative charge on the co-monomer groups, this polymer adsorbs to silica surfaces with a low negative surface charge at neutral pH conditions (Scheme 2). For monolayers adsorbed to colloidal silica the segmental mobility was monitored by spin relaxation. Here, restrictions of mobility lead to enhanced relaxation: at room temperature, two components of different mobility were detected which were attributed to segments of intermediate mobility, and mobile loops and tails, respectively, while the trains relaxed too fast to be detected [38]. At high temperature, the overall signal decreases, since mobile segments solidify and are not detected any more.

A parameter monitoring the phase transition is thus the signal integral in liquid type ¹H spectra. In this way the collapse of loops and tails was followed for different mixing ratios of poly-



Scheme 2. Proposed model of partial collapse in the interfacial phase transition of negatively charged PNIPAM copolymer: charged segments are repelled from the negatively surface and remain liquid above the phase transition temperature.

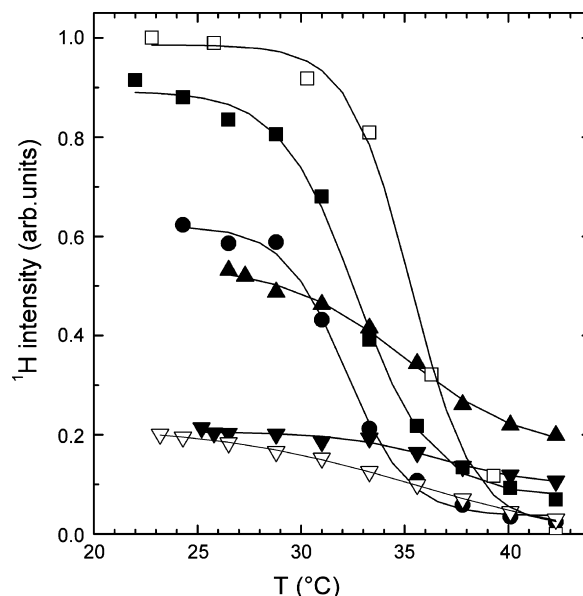


Fig. 1. Liquid state methyl ¹H signal of PNIPAM (open symbols) and Co-PNIPAM (solid symbols) in a monolayer. Polymer/silica weight ratio: 1 (squares), 0.85 (circles), 0.5 (triangles), 0.25 (upside down triangles). The lines are fits to the data as described elsewhere [38].

mer and silica (Fig. 1). A quantitative analysis shows that the width of the transition increases with decreasing polymer coverage, which was confirmed by DSC measurements. In addition, the transition temperature increased at low coverage [38]. It can thus be concluded that shorter loops formed at low coverage are more confined, leading to a broader, enhanced transition temperature, while longer loops exhibit transition properties more similar to free chains.

The effect of charged co-monomers is an incomplete transition (see the high temperature plateau for solid symbols in Fig. 1). This was attributed to electrostatic repulsion of the charged segments from the silica surface. Thus, a liquid-like mobility is retained for a fraction of segments even at high temperature. In Scheme 2 a conformation is suggested taking electrostatic repulsion into account. Though the repulsion causes an immobilization of the polymer conformation on a long-range scale, the charged segments remain hydrated and mobile on the length scale of local bonds, which is the relevant length scale of dynamics monitored in the NMR experiment. The incomplete phase transition occurs at low surface coverage only. At high coverage segments, which are repelled from the surface, can collapse laterally by interaction with neighbouring loops instead of interaction with surface bound trains.

In the above discussion, the length of the loops appears to be a crucial parameter. Thus, for a complete phase transition to occur under simultaneous interfacial and electrostatic constraints, the chains should exhibit long loops of the thermoreversible component. Aiming at multilayer build-up from thermoreversible copolymers, these results suggest that a large layer thickness is favourable over a flat adsorption. Alternative types of copolymers, such as diblocks or graft-copolymers, are thus preferable over statistical copolymers.

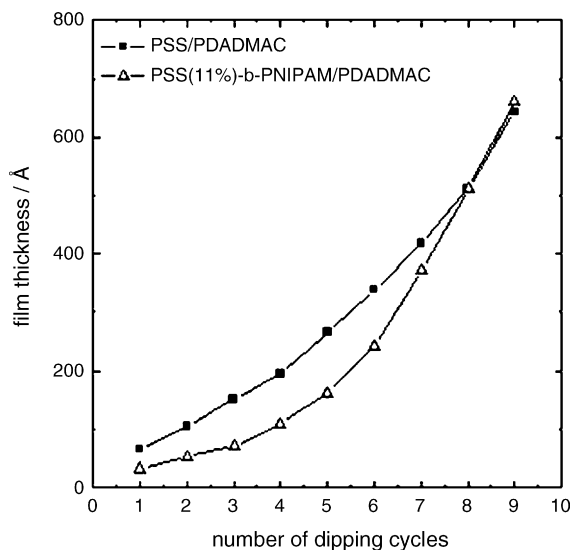


Fig. 2. Thickness of polyelectrolyte multilayers in dependence on the number of adsorbed polycation/polyanion double layers: PSS(11%)-b-PNIPAM/PDADMAC vs. reference system.

2.2. PEMs with block copolymers incorporating PNIPAM

In order to enhance the thermosensitivity of PEM, thermoresponsive block copolymers of PNIPAM showing a LCST of about 30 °C [19] were incorporated. The question then arises whether the volume phase transition is affected by spatial confinement in multilayers. The challenge is to generate a stable matrix (by charged polymers) including thermosensitive compartments, which are not disturbed by the charged units of the matrix. Hence, the molecular architecture and charge distribution might be very important. One route is to incorporate PNIPAM in the multilayer via block-copolymers which consist of a large PNIPAM block and a short highly charged anchor (either positively or negatively charged). Fig. 2 shows an example for the layer formation with a block-copolymer. It contains PNIPAM, where 11% of the segments were styrene sulfonate, concentrated in the anchor (Scheme 1A). PSS(11%)-b-PNIPAM and poly(diallyldimethylammonium chloride) (PDADMAC) were adsorbed sequentially by the layer-by-layer technique. The film thickness determined by ellipsometry increases monotonically with increasing number of double layers and is in the same order of magnitude as of the PSS/PDAMAC multilayer.

It was shown previously that a minimum charge density is required for building up the multilayers. The charge threshold required for the growth of PSS/(statistical copolymers of PDADMAC) systems varies between 10% and 70%, depending on the growth conditions and comonomer unit used to dilute the charge [39–41]. Therefore, it is not surprising that a continuous growth is observed here since the copolymer PSS(11%)-b-PNIPAM contains a highly charged anchor. Until now the conformation of the PNIPAM block is unclear as is the way in which the oppositely charged polyelectrolyte is adsorbed onto this diblock.

Fig. 3 shows neutron reflectometry spectra of PSS(11%)-b-PNIPAM/PDADMAC against D₂O at different temperatures. The experiments were carried out in a liquid cell, as described

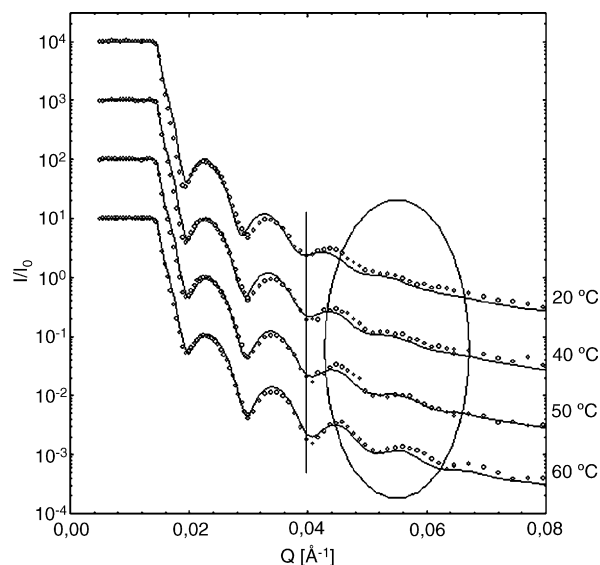


Fig. 3. Neutron reflectometry spectra of [PSS(11%)-b-PNIPAM/PDADMAC]₁₀ for different temperatures.

in [42]. The thickness decreases slightly (visible by the vertical line) and the Kiessig oscillation at higher q -values becomes more pronounced with increasing temperature. The enhancement of oscillation is a hint for a higher film quality (less defects, lower roughness) which is due to an annealing process. Both effects are irreversible and do not vanish, when the multilayer is re-cooled. The latter effect is also detectable for multilayers of non-thermosensitive polyelectrolytes [20]. It is assumed that the enhancement of Kiessig oscillations originated from an irreversible decrease in scattering length density of the solvent-swollen film and a decrease in rms-roughness at the substrate/film interface.

The decrease in thickness of the adsorbed planar film was below 10% and irreversible [20] as shown in Fig. 4. For 3d microgel particles the volume transition is reversible and the reversible volume effect is by factor 10 or even larger [43]. However, a factor of 1.8 was found for the thermosensitive PNIPAM layer of core-shell latex particles in solution [44]. One reason for the decreased volume effect at interfaces, is a restriction in one to two dimensions, depending on the connection to the interface. Especially in the case of polyelectrolyte multilayers the strong interdigitation between adjacent layers leads to an additional restriction of the chain dynamics. This effect becomes even more pronounced after heating. A further proof that the interdigitation between polyelectrolytes and microgels reduces the sensitivity was found for microgel particles based on PNIPAM and coated with polyelectrolyte multilayers [45].

To increase the thermosensitivity of these systems, a combination of two oppositely charged diblock copolymers incorporating PNIPAM and 34% and 24% of cationic and anionic anchors, respectively (Schemes 1B and A), were successfully used to fabricate flat films and hollow capsules [19]. By combining confocal microscopy and FRAP measurements, it was shown (Fig. 5) that the diameter and the permeability of the capsules decrease upon heating in aqueous solution. However, this process is only partially reversible upon cooling, limiting

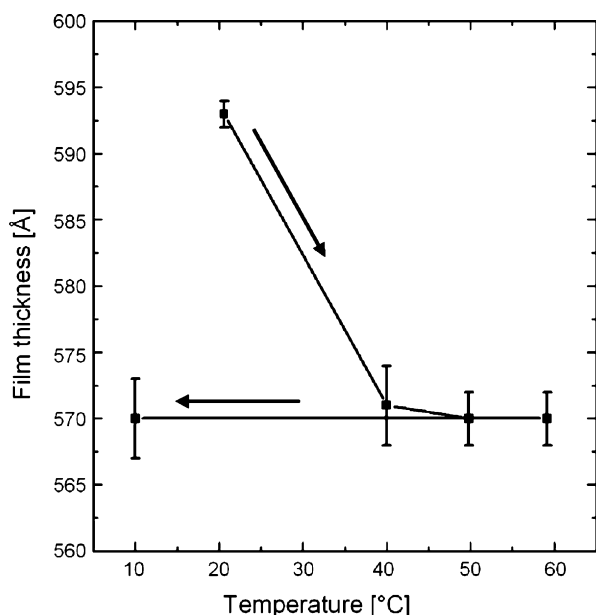


Fig. 4. Thickness of [PSS(11%)-b-PNIPAM/PDADMAC]₁₀ during heating and cooling cycle.

the thermoresponsive behavior of the capsules. Although similar thermal behaviors were reported for multilayer capsules devoid of PNIPAM, they were observed only for higher temperatures [46]. As a consequence, the higher thermosensitivity of systems based on diblock copolymers was attributed to the presence of PNIPAM segments which tend to collapse with temperature. However, the presence of numerous electrostatic associations within the films contribute to slow down the disentanglements of the PNIPAM segments upon cooling and consequently decrease the responsiveness of the films.

2.3. PEMs with graft copolymers incorporating PNIPAM

A further advanced approach to prepare thermosensitive PEM consisted of employing graft copolymers with a PNIPAM back-

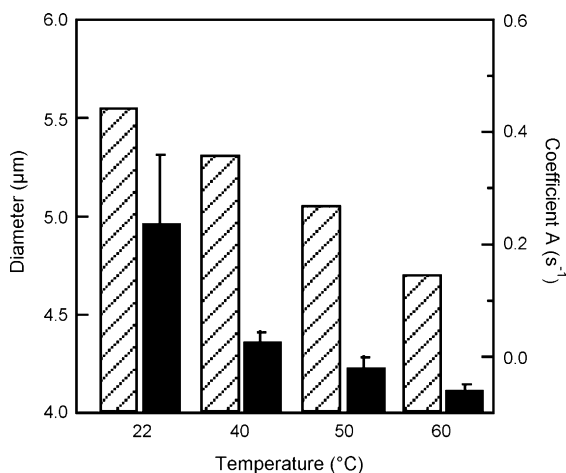


Fig. 5. Variation with temperature of the diameter (hatched bars) and of the coefficient A (proportional to the shell permeability) (solid bars) of eight-layer capsules based on diblock PNIPAM copolymers.

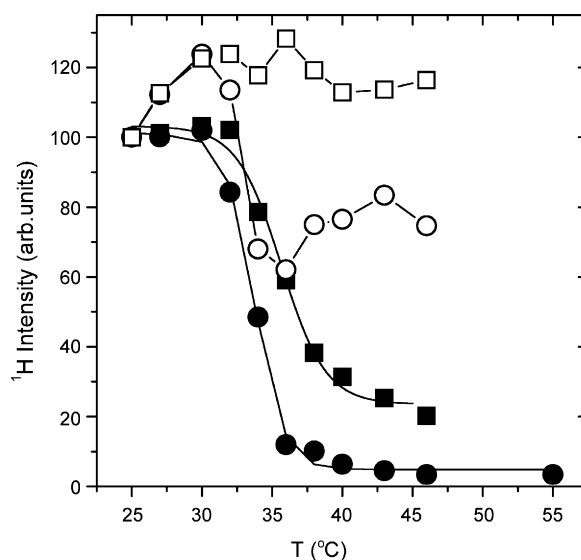


Fig. 6. Integrated ¹H NMR signal intensity of the main chain (solid symbols) and the grafted chains (open symbols) for the transition of graft-copolymers in solution [49]. Spheres: low grafting density, squares: high grafting density.

bone and charged grafted chains (Scheme 1D). The idea was to spatially separate the electrostatic functionality from the thermosensitive function, in order to minimize the effect of charges on the phase transition and to achieve a high flexibility of the main chain even in a stratified two-dimensional layer arrangement, since the electrostatic binding occurs only via the grafted chains. Copolymers carrying charged side chains of poly (2-vinylpyridine) (P2VP) grafted to a thermoreversible main chain of PNIPAM have recently been synthesized with high (PNIPY-H) and low (PNIPY-L) grafting density [47,48]. Their phase transition behavior was characterized in solution [47,49]: the collapse of the main chain is for example monitored by the ¹H signal decrease (Fig. 6, solid spheres), while the graft chains are only slightly immobilized (open spheres). For a polymer with a higher grafting density, the graft chains remain mobile due to electrostatic repulsion (open squares). However, here the transition of the main chain is not complete, as indicated by the liquid ¹H intensity at high temperature (full squares).

From these graft-copolymers, multilayers were formed on a precursor of strong polyelectrolytes by alternating adsorption with PSS [21,50]. X-ray reflectivity curves taken at 55% humidity show a slight decrease of the thickness of an internal PNIPY layer for temperatures above about 35 °C as expected for a collapse inducing water release. If the PNIPY layer is not an internal layer, but the terminating layer, a more pronounced thickness variation was found. Fig. 7 gives the thickness variation δ^5 of PNIPY in the system PEI/PSS/PDADMAC/PSS/PNIPY. The thickness of PNIPY-H depicted in Fig. 7a is lower than that of PNIPY-L (Fig. 7b), which is consistent with a detailed adsorption study, where this difference was attributed to the different charge density [21]. Layers of both polymers show a thickness decrease upon heating. However, neither for the terminating nor for an embedded (data not shown) PNIPY layer the thickness decrease is fully reversible. This is similar to the findings for block copolymers described above.

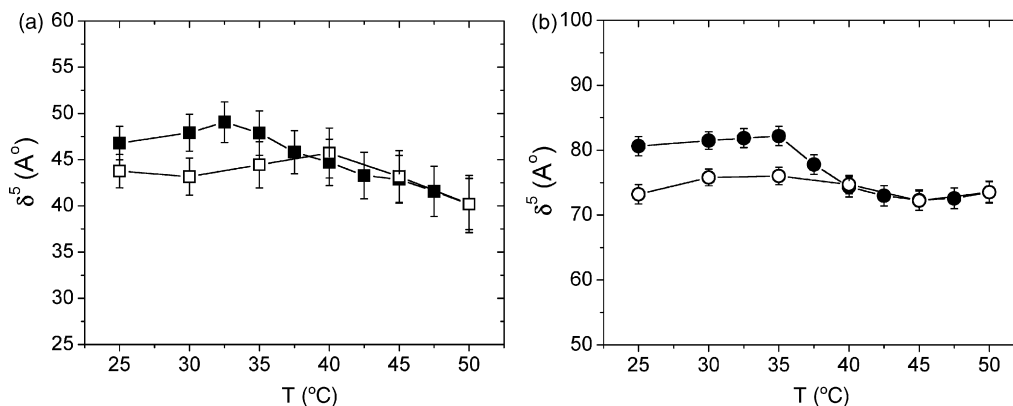


Fig. 7. Thickness δ^5 of PNIPY in the system PEI/PSS/PDADMAC/PSS/PNIPY at 55% humidity: (a) PNIPY-H and (b) PNIPY-L. Solid symbols: heating, open symbols: cooling. Data points are simply connected.

Multilayer formation could also be achieved by adsorption on colloidal templates. The adsorbed amount and the layer thickness per monolayer are highly dependent on the grafting density, thus the coverage with thermoreversible segments also varies [21]. The multilayers on colloidal templates were studied by solvent spin relaxation of the hydration water [50]. At high and low temperatures, a high mobility of the hydration water was found. Within a broad transition region strongly immobilized water was detected. In this temperature regime, hydration water becomes immobilized, until above the transition region it is expelled from the layer system and becomes mobile again.

The studies of the phase transition of PNIPY graft-copolymers in multilayers imply that in spite of providing long thermoreversible chains between the anchoring points of the graft chains, the electrostatic immobilization within the multilayer is still too strong for a fully reversible transition. Further optimisation of the polymer architecture remains necessary.

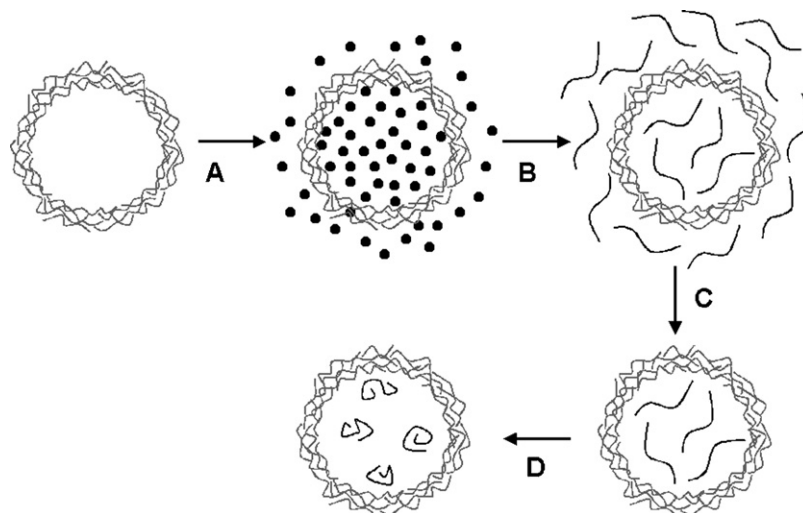
In summary, high quality films can be built from the charged derivatives of PNIPAM. All films show pronounced annealing (e.g. conformational changes and interface smoothing) during the course of the applied temperature cycles. The observed effect

is less pronounced than in 3d microgels. The structural changes found in the functionalized films are partially reversible or irreversible on the time scale of the experiments. This is not in line with the fully reversible phase transition observed for the 3d microgels. Further experiments are necessary to clarify the question of whether the temperature induced shrinkage of the PNIPAM multilayers is pre-dominantly due to an irreversible collapse of the functionalized part with elevated temperature or whether re-swelling is simply kinetically hindered.

So far the thermosensitive effect is quite small and works only for specific combinations. A challenge for future experiments would be to understand and to control the thermosensitive response of thin films.

2.4. PEM microcapsules filled with PNIPAM

An alternative approach tested to prepare thermoresponsive systems based on PEMs consists in incorporating free high molar mass PNIPAM chains inside of PEM capsules as described by Prevot et al. [51] (Scheme 3). The encapsulation of the PNIPAM inside the capsule was achieved by the polymerization of



Scheme 3. Encapsulation of PNIPAM: (A) addition of NIPAM monomer in a suspension of PEM capsules, (B) polymerization, (C) washing and (D) increase of the temperature above LCST.

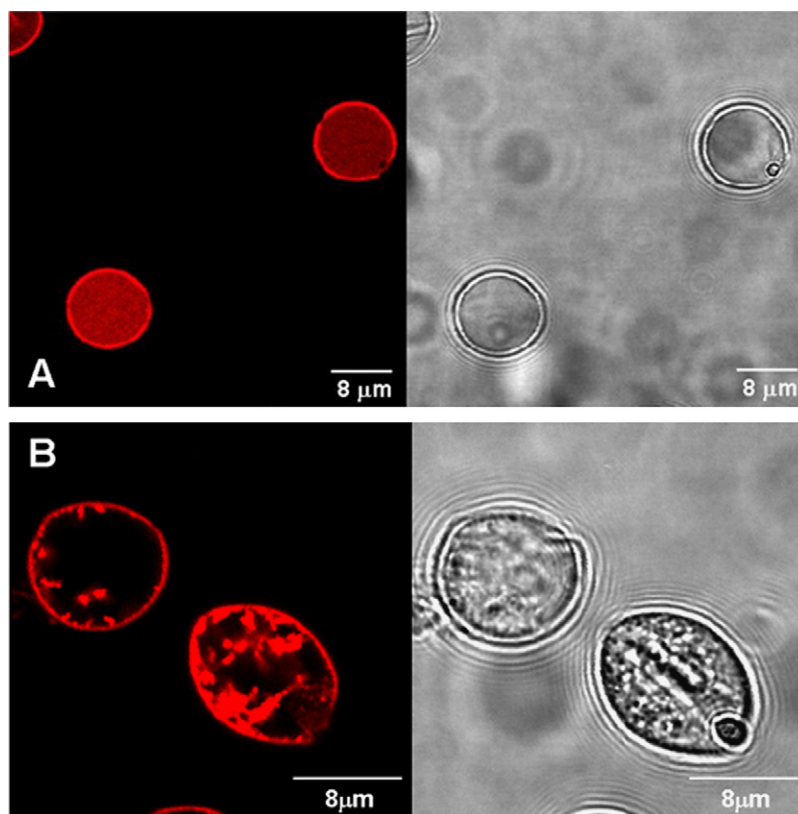


Fig. 8. (A) (PAH/PSS)₉ capsules with encapsulated PNIPAM in pure Milli-Q water (A) and 0.5 M NaF (B). All pictures were taken at room temperature. Left images are CLSM images, right images are optical micrographs.

NIPAM monomers inside a suspension of capsules in pure water [52]. The encapsulation of the PNIPAM inside of the capsule was proven with Raman spectroscopy, DSC (bulk LCST measurements), AFM (thickness change), SEM (morphology change) and CLSM (in situ LCST measurement inside of the capsules).

As hydrogen bonds are affected by salt, the LCST of PNIPAM is influenced and can be tuned by salts. In fact, the addition of salt causes the LCST to decrease. Prevot et al. [51] showed that the addition of 1 M salt causes the precipitation of PNIPAM chains trapped inside (PAH/PSS) capsules, independently of the type of salt used. Fig. 8A shows fluorescently labeled (methacryloxyethylthiocarbamoyl rhodamine B)-PNIPAM encapsulated inside capsules. As fluoride is a more kosmotropic ion, the addition of NaF to achieve an overall concentration of 0.5 M led to the precipitation of PNIPAM as shown in Fig. 8B. In the other cases, where after salt addition the LCST was still above room temperature, the lowered LCST was determined by increasing the temperature until the precipitation was observed. Upon cooling below the LCST, the PNIPAM went from globule to coil transition. The process could be done multiple times, showing that the transition was not only reversible, but also repeatable.

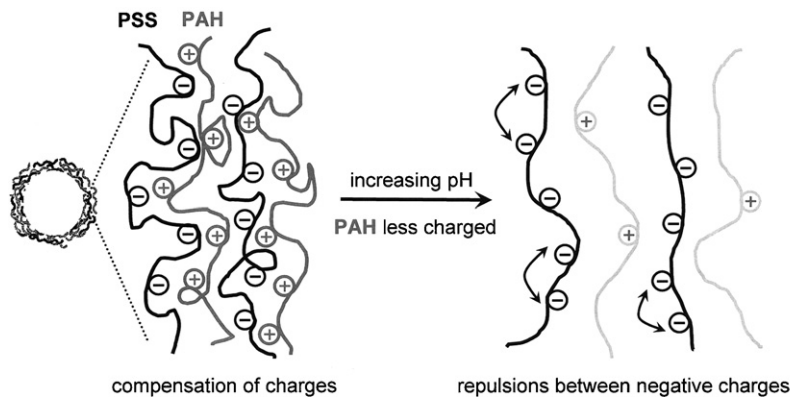
The PNIPAM inside the capsules remains thermo-sensitive because even though it is encapsulated, it is free to move or adopt a new conformation in response to the environment. As a consequence, the encapsulation of PNIPAM inside preexisting multilayers results in a reversible and stimuli-responsive system.

3. pH-responsive PEMs

3.1. Systems based on weak polyelectrolytes

Because the linear charge density along weak polyelectrolyte backbones is a function of pH, the electrostatic interaction within PEMs incorporating such polyelectrolytes can be easily tuned. This feature was widely exploited to trigger the properties of PEM films such as permeability, morphology or wettability. A particular interest is in the design of the capsules whose the shell permeability can be controlled for encapsulation and release procedures. Since the layer-by-layer (LbL) adsorption of polyelectrolytes has been developed on flat substrates [2] and later applied on colloidal particles for the fabrication of hollow polyelectrolyte microcapsules [53], a wide range of polyelectrolyte combinations have been explored.

The (PSS)/(PAH) pair is the most studied. While PSS is a strong polyanion, whose charge is fixed at any pH, PAH is a weak polycation and its charge density varies with the acidity of the aqueous solution. Its apparent pK_a in such multilayers has been determined to be about 10.8 [54]. Around this pH value, the charge density of the polymer decreases and the backbone becomes almost neutral in more basic solutions. As a consequence, many charges in PSS/PAH systems are not compensated any more and an excess of negative charges from PSS is present (Scheme 4). Furthermore, the multilayer swells because the polymer chains repel each other not only due to the electro-



Scheme 4. Swelling of (PAH/PSS) microcapsules in alkaline conditions due to the unbalanced electric charges.

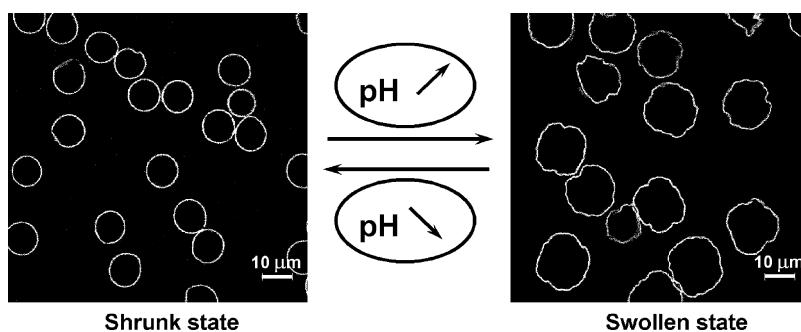


Fig. 9. Reversible pH-induced swelling of (PSS/PAH)₈ microcapsules below (left) and above (right) the threshold pH value 11.5.

static repulsions between negative charges but also due to the local increase of osmotic pressure created by the attraction of counterions by PSS. In the case of PSS/PAH capsules templated on various cores, increasing the pH above 11 led to a dramatic swelling of the structures and finally to their dissolution, but this swollen state could be stabilized after the use of organic solvents [55,56] (Fig. 9).

The swelling of these microcontainers in alkaline solutions is accompanied by an increase of the wall permeability and has been used for the controlled picogram dose encapsulation and release of macromolecules [57].

More complicated systems have then been developed which are made of two weak polyelectrolytes, responding both in acidic and alkaline regions. By replacing the strong polyelectrolyte PSS by the weak polyanion PMA in combination with PAH, new microcapsules have been described [58,59]. Following the mechanism involved in (PSS/PAH) capsules, (PMA/PAH) shells swell and then dissolve when PMA becomes less than 10% charged (pH below 2.7) and symmetrically when PAH loses most of its charges (pH above 11.5). In this case, a stable swollen state could be observed in a narrow acidic pH range (0.2 units), where hydrophobic interactions between PMA chains prevent the structure from dissolution. This system exhibits the most important features for multilayers with pH-switchable properties: a pH-tunable charge density and counteractive attractive and repulsive forces. In order to stabilize the swollen state at basic pH, PAH can be replaced by a much more hydrophobic polycation, the poly(4-vinyl pyridine) (PVP) which becomes insoluble and precipitates in water when pH decreases below

5. (PVP/PMA) capsules have been assembled and they exhibit pH-sensitivity both in acidic and basic solutions (Fig. 10) [60]. They show an interesting pH dependant behaviour, as they are stabilized by both electrostatic interactions and hydrogen bonding from pH 2 to 8. At both limit pHs, stable swollen states are observed due to counteracting hydrophobic as well as hydrogen-bonding interactions.

pH-responsive microcapsules could be prepared when using at least one weak polyelectrolyte in the LbL assembly. At a pH value that dramatically decreases the charge density of the weak polyion, a drastic swelling of the capsules was observed.

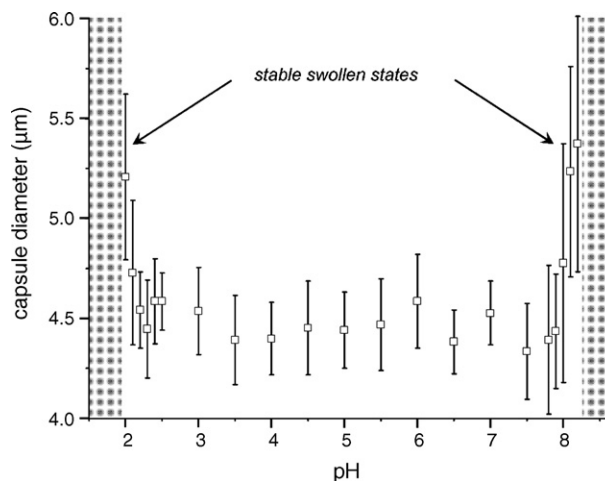
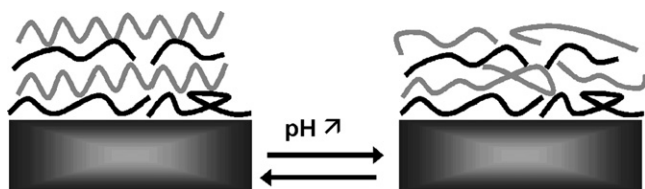


Fig. 10. Diameter of (PVP/PMA)₅ capsules as a function of the pH.



Scheme 5. Variation of the idealized internal structure of the (PAH/PGA) films under pH variation.

Without any stabilization, this swelling irreversibly led to the dissolution of the structure. However, stable swollen states were obtained by the help of hydrophobic interactions and hydrogen bonds; in these particular cases the swelling could be inverted by tuning back the pH to the initial value. Reversibility of the swelling is a key parameter for the application of those systems in such applications as encapsulation and release, or sensing.

3.2. PEMs based on structured polyelectrolytes

Some charged polypeptides such as poly(glutamic acid) (PGA) are well-known to display a reversible change of conformation with pH [61]. Indeed, PGA chains adopt different conformations mainly dominated by alpha-helical segments at low pH, while they are essentially random-coil above pH 10. This feature was exploited to prepare PEM films showing a change of their internal microstructure with pH (Scheme 5).

(PAH/PGA) multilayers were successfully prepared at pH 7.4 and subsequently stabilized by EDC/NHS crosslinking according to the method described by Picart et al. [27]. The inspection of the internal structure of these PEMs by circular dichroism (CD) revealed that PGA alpha-helical conformations are dominant within the films at pH 7.4 (Fig. 11). However, after exposure to high pH, a drastic variation of the CD spectrum was observed revealing a partial conformational transition of PGA macromolecules embedded into the films from helix to random coil

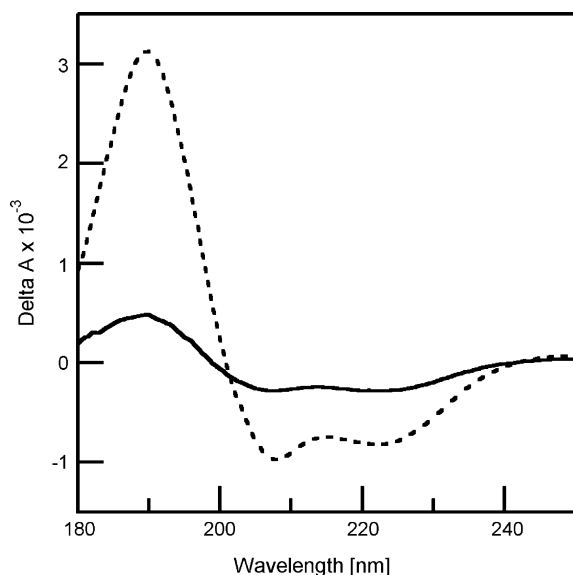


Fig. 11. Circular dichroism spectra of (PAH/PGA)₁₁ crosslinked films after exposure to pH 7.4 (dashed line) and 12 (solid line).

[62]. This partial characteristic of the conformational transition was attributed to the presence of crosslinks between PGA and PAH which tend to restrict the total reorganization of the macromolecules. However, even though this conformational change is partial, it was shown to be completely reversible upon decreasing the pH. Such a variation of the conformation of polyelectrolyte chains within the PEM films is expected to translate to different mechanical properties. Further work is in progress to evaluate the influence of these conformational changes on film properties.

4. Conclusion

This brief review of selected multilayers based on electrostatically interacting polymers illustrates the potential interests and pitfalls of LbL assembly for the preparation of responsive systems. Clearly, the knowledge accumulated on these systems is important, but we are still lacking a complete view of the dynamics of these systems, where the principles governing the rearrangement and motion of specific segments would be fully understood. This will be required before applications emerge, which can be envisioned in the fields of medicine, cosmetics and pharmaceuticals.

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