Diverse 2D structures obtained by adsorption of charged ABA triblock copolymer on different surfaces

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ABSTRACT

In the larger context of 2D polymeric structures, the morphologies obtained by adsorption and subsequent drying of charged, ABA type amphiphilic triblock copolymer of poly[2-(dimethylamino)ethyl metacrylate] (PDMAEMA) and poly(propylene oxide) (PPO) were investigated with atomic force microscopy and X-ray photoelectron spectroscopy as well as in situ adsorption analysis with quartz crystal microbalance with dissipation monitoring. Hydrophilic silica and hydrophobic polystyrene (PS) were used as substrates for adsorption. The structures emerging from the self-assembly of adsorbing polymer were profoundly influenced by composition of the aqueous solution and the choice of substrate. When adsorbed from dilute polymer solution where the concentration is so low that the polymer does not yet show surface-active behavior, the triblock copolymer unimers associated on hydrophilic silica surface forming large, irregular clustered aggregates, with sizes increasing with electrolyte concentration of the solution. On a hydrophobic PS substrate, on the other hand, unimers spread much more evenly, forming clear surface patterns. The roughness of these patterned structures was tuned with the electrolyte concentration of the solution. Adsorption from a more concentrated polymer solution, where the surface-activity of the polymer is perceptible, resulted in the formation of a smooth film with complete coverage over the hydrophilic silica substrate when the electrolyte concentration was high. On PS, on the other hand, nucleation of evenly scattered globular, disk-like micelles was induced. Besides the dry film morphology, the even distribution of the irreversibly adsorbed polymer over the PS surface was likely to serve as an optimal platform for the build-up of reversible hydrophobically bound multilayers at high electrolyte concentration. The multilayer formation was reversible because a decrease in the electrolyte concentration of the solution re-introduces strong electrostatic repulsion between the multilayered polymer coils which results in breakdown of the layer.

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1. Introduction

Supported 2D structures from polymers have gained burgeoning interest because of their potential in novel applications such as electronic sensors [1], antireflective coatings [2], smart materials [3], platforms for controlled drug release [4], and scaffolds for nanoparticle growth [5]. In case of polymers, there are a number of different ways to implant various nano- and microscale structures on a substrate: spin coating [6], Langmuir–Blodgett deposition [7], various lithographic techniques [8], and controlled dewetting [9,10], to name but a few. Adsorption from a solution is an especially simple and effortless method for building polymeric surface structures as the process is completely defined by the chemical interactions between the polymer, the solvent, and the surface. As the self-assembly during adsorption is based on reaching the thermodynamic equilibrium, the obtained structures are stable. The use of block copolymers instead of homopolymers for preparation of nanostructured templates for various functionalities typically results in formation of more elaborate structures [11]. However, adsorption of block copolymers and the resulting 2D structures are increasingly difficult to predict. In this paper, we have investigated the fundamental dry morphologies obtained by adsorption and subsequent drying of charged, ABA type amphiphilic triblock copolymer of poly[2-(dimethylamino)ethyl metacrylate] (PDMAEMA) and poly(propylene oxide) (PPO) on two chemically different surfaces.

There are numerous studies on adsorption of amphiphilic diblock copolymers [12–14]. Fundamental studies exist also on the adsorption of neutral, nonionic amphiphilic triblock copolymers, mainly composed of poly(ethylene oxide) (PEO) and PPO (Pluronics) [15]. Neutral ABA triblock copolymers have lately been found to form outstandingly diverse morphologies when physically forced on a substrate by spin coating [16,17]. From a fundamental point of view, it is relevant to understand also films
and submonolayer structures resulting from chemical deposition. Bringing electrostatically charged groups into the structure of an ABA block copolymer provides the possibility for tuning the conformation and subsequent morphological patterns upon adsorption by varying the charge density and the electrolyte concentration. Despite their potential, systematic research on structures formed by charged amphiphilic ABA triblock copolymer number in few [18]. This study concentrates on morphological structures obtained by adsorbing charged PDMAEMA–PPO–PDMAEMA on hydrophilic silica and hydrophobic polystyrene surfaces from aqueous solution. Influence of salt and polymer concentrations are also examined. The focus is set on morphologies in the dry state, followed by atomic force microscopy (AFM), because of their application potential. In addition, a study of solution properties and in situ monitoring of adsorption with quartz crystal microbalance (QCM-D) were conducted in order to complement the ex situ AFM data and to provide understanding of polymer self-assembly on a fundamental level.

2. Materials

2.1. Quaternized PDMAEMA–PPO–PDMAEMA triblock copolymer

An ABA type triblock copolymer qDMAEMA34–PO34–qDMAEMA34 (the subscripts indicate the number of repeats) was synthesized by oxyanionic polymerization of PPO macroinitiator and 2-(dimethylamino)ethyl metacrylate (DMAEMA) monomer and then quaternized (q) into a permanently cationic form (PqDMAEMA–PPO–PqDMAEMA). The triblock copolymer chain is terminated at both ends simply with a proton. The detailed synthesis procedure is described in ref. [19] and the quaternization in ref. [20]. The molar weight of the PDMAEMA block was \(~\sim\) 3.7 kDa (equivalent to 24 DMAEMA units) and the PPO block 2.0 kDa (equivalent to 34 PO units). The chemical structure of the qDMAEMA34–PO34–qDMAEMA34 is presented in Fig. 1.

After synthesis, the polymer was purified from salt residues by dialyzing with Spectra/Por regenerated cellulose dialysis membranes with a molecular weight cut off value 6.0–8.0 kDa.

2.1.1. Polymer solutions

Aqueous 20 g dm\(^{-3}\) stock solution was prepared by heating and stirring mixture of polymer and water in \(~\sim\)70 °C for 30 min. After this, stirring was continued overnight at room temperature. The pH of the solutions was \(~\sim\)6.5.

2.2. Other chemicals

Milli-Q water (resistivity 18.2 MΩ cm) was used throughout the study. NaCl of analytical grade was supplied by Merck (Darmstadt, Germany) and used without further purification.

2.3. Substrates

The QCM-D crystals used as substrates for adsorption were AT-cut quartz crystals supplied by Q-Sense AB, Gothenburg, Sweden, with thickness 0.3 mm, fundamental resonance frequency \(f_0 \approx 5\) MHz, and sensitivity constant \(C = 0.177\) mg m\(^{-2}\) Hz\(^{-1}\).

2.3.1. Silica substrates

The AT-cut quartz crystals were coated by the supplier with silica by means of vapor deposition. Before the QCM-D measurements, crystals were cleaned in a UV/ozoneator (Bioforce Nanosciences, Ames, Iowa) with 28 mW cm\(^{-2}\) at 254 nm wavelength for 20 min and rinsed with water to remove any organic contaminants and to induce the formation of hydroxyl groups on the surface. An AFM image of a silica surface is presented in Fig. 2a.

2.3.2. Polystyrene substrates

AT-cut quartz crystals that were coated with gold by the supplier were used as substrates for polystyrene (PS) films. PS was deposited on gold surface by spin coating from 10 g dm\(^{-3}\) toluene solution at spinning speed of 4000 rpm. AFM image of a PS surface is presented in Fig. 2b.

3. Methods

3.1. Solution properties

In order to study the behavior of qDMAEMA\(_{34}\)–PO\(_{34}\)–qDMAEMA\(_{34}\) in aqueous solution, series of 11 solutions with different concentrations (from 0.0001 to 10 g dm\(^{-3}\)) and 10 mM NaCl was prepared by diluting the 20 g dm\(^{-3}\) stock solution with water and 0.1 M NaCl.

3.1.1. Dynamic light scattering (DLS)

DLS measurements were conducted with a Malvern Zetasizer Nano ZS instrument operating at a scattering angle of 173° and a wavelength of 633 nm. All DLS sample solutions were filtered with 0.2 μm filters before the measurement. Temperature of the solutions was maintained at 25 °C. Reported values of light scattering intensities are averages of three measurements. In addition to scattering intensity values, the data on particle sizes in 20 g dm\(^{-3}\) solution with 0.1 M and 0.5 M NaCl were examined.

3.1.2. Surface tension measurement

Surface tension was measured with a Kibron AquaPi tensiometer by the Du Nouy maximum pull force method. The sample solutions were equilibrated in saturated atmospheric humidity and constant temperature (25 °C) for 24 h to ensure equilibrium between the air/solution interface layer and the bulk solution. The surface tension probe was cleaned by flaming before each measurement. Reported values are averages of three measurements.
3.2. Adsorption

Polymer solutions for QCM-D measurements were prepared in two different concentrations, 0.05 g dm$^{-1}$ and 0.5 g dm$^{-1}$, based on the data received from the solution property studies. Three different electrolyte concentrations were used: 1 mM, 10 mM, and 100 mM NaCl.

3.2.1. Quartz crystal microbalance with dissipation monitoring (QCM-D)

Polymer adsorption and the characteristics of the adsorbed layer were studied with QCM-D (Q-Sense model E4, Gothenburg, Sweden) [21]. In this technique, the polymer-adsorbing QCM-D crystal is resonated in pulses, and the changes of resonant frequency $\Delta f$ and energy dissipation $\Delta D$ are measured simultaneously at the fundamental frequency and six overtones. Mass adsorbed on the crystal surface is directly proportional to the detected $\Delta f$ [22]. $\Delta D$ measures the exponential decay in oscillation that is proportional to the energy dissipated and stored during a period of oscillation. These data are attributed to the viscoelastic properties of the crystal and the adsorbed layer. If the adsorbed molecules form a thin, rigid, and homogenous layer ($\Delta D < 10^{-6}$) and the adsorbed mass is small compared to that of the resonating substrate, the mass of the adsorbed polymer can be calculated simply with Sauerbrey equation [22]:

$$\Delta m = -\frac{C \Delta f}{n},$$

where $n$ is the overtone number and $C$ is the sensitivity constant of the resonator. The principle of QCM-D has been described in more detail elsewhere [23].

In this study, the aqueous solution of qDMAEMA24−PO34−qDMAEMA24 was injected into the QCM-D cell as a continuous flow with the rate of 0.1 ml min$^{-1}$. The shifts in $f$ and $D$ were followed for 30 min, followed by rinsing first with aqueous NaCl solution with a concentration corresponding to that of the polymer solution, and then with pure water. Temperature of 25 °C was used throughout the study. In the reported experiments, results from the third overtone were used since these were more stable than those from the fundamental frequency.

3.3. Composition of the dry adsorbed films

After the adsorption experiments, the wet QCM-D crystals were removed from the QCM-D chamber and dried instantly with N$_2$ gas flow.

3.3.1. Atomic force microscopy (AFM)

A Nanoscope Illa Multimode scanning probe microscope (version V6.13 R1, Digital Instruments Inc., Santa Barbara, CA, USA) was used to determine the morphology of the dry polymer films. The images were scanned in tapping mode in air at 25 °C using silicon cantilevers. No image processing except flattening was done. At least three areas on each sample were measured.

Image analysis was performed with Nanoscope softwares and Scanning Probe Image Processor (SPIP) software (version 4.5.3, Image Metrology, Lyngby, Denmark). The surface coverage values were determined using the Grain Analysis module in SPIP with threshold algorithm.

3.3.2. X-ray photoelectron spectroscopy (XPS)

A Kratos Analytical AXIS 165 electron spectrometer with a monochromatic A1 Kα X-ray source was used to analyze the elemental and chemical compositions of the sample surfaces. All spectra were collected at an electron take-off angle of 90° from sample areas less than 1 mm in diameter and using 100 W irradiation [24]. The spectra were recorded at least from three different spots on each sample and the analysis vacuum was monitored during the experiments with an in situ reference sample.

The surface coverage of adsorbed polymer was calculated based on the intensity of N 1s emission, taking into account the atomic proportion of N of all the XPS-detectable elements in a polymer molecule. The theoretical proportion of N of the detectable atoms (C, O, and N) in the structure of a qDMAEMA24−PO34−qDMAEMA24 molecule (Fig. 1) was calculated to be 4.8%. Hence, if the intensity of N 1s emission (i.e., the percentage of N) detected from the sample surface would be, e.g., 0.5%, the percentage of polymer covering this surface would be 0.5/4.8 ≈ 10.4%. At least three measurements were taken and averaged from each sample.

4. Results and discussion

First, the concentration dependency of the intermolecular interactions of ABA type triblock copolymer qDMAEMA24−PO34−qDMAEMA24 in solution was investigated. Second, the adsorption process was monitored with QCM-D in two concentrations bearing different levels of surface-activity and also in different electrolyte concentrations. Third, the morphology of the dried adsorbed polymer films was studied.

4.1. Solution properties

Amphiphilic block copolymers are known to form micelles or less ordered aggregates in aqueous solution. ABA type block copolymers – ‘A’ denoting the hydrophilic and ‘B’ the hydrophobic sequence – typically form a micelle with a dense hydrophobic core and a corona of swollen hydrophilic chains [25]. Generally, the aggregation tendency of a neutral amphiphilic block copolymer increases with increasing proportion of the hydrophobic sequence in the polymer chain.

When the block A of an amphiphilic block copolymer is charged, the association gets more complicated as also the electrostatic factors affect the system. Charge reduces the hydrophobic effect and causes electrostatic repulsion, which weakens the driving force for aggregate formation. Association may be completely hindered if the charged block is long compared to the hydrophobic block [26]. Besides the chemical structure of the block copolymer, the ionic strength of solution has a straight correlation on the aggregation behavior in these kinds of systems [27].

Quaternized poly(dimethylaminoethyl metacrylate) (PqDMAEMA) carries a strong positive charge with constant charge density within the whole pH range. PPO, on the other hand, is thermoresponsive by its solubility [28]. Throughout this study, however, the PPO block has constant hydrophobic nature as the temperature is maintained at 25 °C.

Transitions in light scattering intensity and surface tension values correspond to changes in molecular arrangements in block copolymer solution. Surface tension data in Fig. 3 indicate that the critical micellization concentration (cmc) for qDMAEMA24−PO34−qDMAEMA24 in 10 mM NaCl is $\approx$10 g dm$^{-3}$. Above this concentration, the air/solution interface is saturated with polymer and polymer unimers in bulk solution start to form distinct and stable micelles in order to minimize the contact between the hydrophobic moieties and water.

The surface excess, $\Gamma$, at the air/solution interface at $\geq$cmc was obtained from the surface tension isotherm by the Gibbs adsorption equation for ionic surfactants

$$\Gamma = \frac{1}{2RT} \left( \frac{\partial \gamma}{\partial \ln c} \right)_{T},$$

as follows:

$$\Gamma = \frac{1}{2RT} \left( \frac{\partial \gamma}{\partial \ln c} \right)_{T},$$
4.2. Adsorption mechanism

The influences of the chemical composition of the substrate, the electrolyte concentration, and the polymer concentration on the adsorption were investigated.

4.2.1. Effect of electrolyte concentration

Ionic strength is widely known to affect solution properties and adsorption of polyelectrolytes [35]. In the studied systems, screening of the charges by addition of electrolyte affects in the system in two ways: (1) by decreasing the attraction between the cationic polyelectrolyte and the anionic surface and (2) by decreasing the repulsion between charges along polyelectrolyte chains.

4.2.1.1. Hydrophilic silica. The QCM-D results in Fig. 4a and c illustrate the dynamics of the process of the cationic qDMAEMA24–PO34–qDMAEMA24 adsorbing on silica from different NaCl concentrations. The recorded values of frequency shift ($\Delta f$) are directly proportional to the mass adsorbed on the surface, whereas the dissipation factor ($\Delta D$) is attributed to the viscoelastic properties of the adsorbed layer. The $\Delta f$ values increase upon increased electrolyte concentration (Fig. 4a). This is an expected phenomenon in polyelectrolyte adsorption: the presence of salt weakens the repulsive intramolecular electrostatic interactions along the polyelectrolyte chain, which leads to increased coiling of the molecule and thus enables more molecules to fit the surface [35]. The $\Delta D$ values increase slightly with electrolyte concentration (Fig. 4b), indicating increased softness of the adsorbed layer, but the values are nonetheless so low (<10$^{-6}$) that the layers can all be considered to be tightly bound and rather rigid. Despite the substantial screening of the charges, relatively high and irreversible adsorption of qDMAEMA24–PO34–qDMAEMA24 on silica indicates that the polymer still behaves like polyelectrolyte in 100 mM NaCl. The electrostatic interaction between the cationic PqDMAEMA block and anionic silica [36,38] silica surface is likely to be the major driving mechanism behind the adsorption [39,40]. Numerous studies exist on the charge density of silica surfaces under the influence of various electrolyte concentrations and pH values [36–38]. However, electrostatically driven polyelectrolyte adsorption neutralizes the charge because of its irreversible nature, which increases the dissociation level of the yet unoccupied hydroxyl groups [41]. In the theoretical limiting case where all surface silanols are ionized due to adsorption of the cationic polyelectrolyte the maximum density of charges is 3.1 sites/nm$^2$ [42], corresponding to an average distance of ~0.6 nm between the adjacent charges.

Rigidity of the adsorbed qDMAEMA24–PO34–qDMAEMA24 layers seems reasonable from the following simple calculations: if the PqDMAEMA chain would be like a comb, all qDMAEMA side chains pointing to the same direction, the distance between adjacent cationic groups would be ~0.25 nm. In reality, however, the effective distance between charges along the polymer is undoubtedly longer because the qDMAEMA side chains are mobile and the distance of a cationic quaternionized amine from the polymer backbone is as long as ~0.6 nm. All in all, the same order of magnitude in the charge densities of the adsorbent and the adsorbate indicate – neglecting the potential conformational restrictions caused by the lack of affinity between the hydrophobic maximum 12 nm long PPO middle block and anionic silica – that flat adsorption with
rather efficient charge neutralization could be possible between the qDMAEMA block and silica. Rinsing the layers with pure water does not have a remarkable effect on the Δf. This confirms that the adsorption is irreversible, further supporting the assumption that the process is electrostatically driven.

4.2.1.2 Polystyrene. QCM-D data of the adsorption of the qDMAEMA_{24}–PO_{34}–qDMAEMA_{24} on PS from different NaCl concentrations are presented in Fig. 4b and d. Similar to silica, adsorption basically increases with increasing electrolyte concentration, as indicated by the Δf values (Fig. 4b). Also here, increased coiling of the polymer enables more polymer molecules to reach and attach on the surface. The ΔD values (Fig. 4d) were likewise analogous to those on silica, i.e., the adsorbed layers appeared relatively rigid. However, the adsorption kinetics differs from what was observed with silica, which must be connected with the different interaction mechanism between the polymer and the surface. As the PS substrate is hydrophobic and electrostatically neutral, ABA type amphiphilic block copolymers with PPO middle block have been generally assumed to adsorb from aqueous solution onto it via hydrophobic forces between anchoring PPO block, whereas the solvated hydrophilic head groups extend out into the solution as tails and loops [43-45].

At 100 mM NaCl concentration, the adsorption on PS does not appear to reach a plateau (Fig. 4b). In this electrolyte concentration, the repulsion between the charged polymer coils is screened to some extent, enabling a slow multilayer formation on a hydrophobic substrate as the attraction between the hydrophobic blocks within the polymers is emphasized. The fact that the layer formed at 100 mM NaCl is partially removed by rinsing with pure water (Fig. 4b and d), is also indicative of a multilayer formed. By contrast, at 10 mM NaCl concentration, the screening of the repulsion between the charged polymer coils is not intensive enough for multilayer formation to occur. However, the charge screening at 10 mM NaCl leads to coiling of the charged blocks, which appears to allow relatively fast adsorption kinetics as opposed to the system in 1 mM NaCl concentration where the polymers are still straight-chained and the adsorption is slow (Fig. 4b).

Overall, the QCM-D results (Fig. 4) indicate that the most distinct difference between the adsorption of the charged qDMAEMA_{24}–PO_{34}–qDMAEMA_{24} block copolymer on silica and PS is the reversible multilayer formation driven by intermolecular hydrophobic forces speculated to take place on PS. The reason why the multilayer structure does not occur on silica as well must be related to the differences between the structures of the first adsorbed layers on these substrates.

4.2.2 Effect of polymer concentration

To investigate the influence of the effective surface-activity on the morphologies of the adsorbed films, two polymer concentrations were selected for the adsorption experiments: one below the surface active region (0.05 g dm⁻³), and another in the surface active region (0.5 g dm⁻³), where the polymer enriches to the air/liquid interface and also some premicellar aggregation is expected to take place (based on the study of solution properties in Section 4.1). The salt concentration was kept constant (100 mM NaCl). The QCM-D curves – Δf and ΔD of the polymer adsorption on silica and PS from 0.05 g dm⁻³ and 0.5 g dm⁻³ are presented in Fig. 5.

Fig. 5a and c shows that the increase in polymer concentration seems to have only a minor effect on the adsorption on silica; there is only a slightly higher amount of water bound inside the layer adsorbed from 0.5 g dm⁻³ than there is in the case of the 0.05 g dm⁻³. At both concentrations, i.e., in the case of both unimers and the hydrophobically formed premicellar aggregates, the adsorption is electrostatically driven and irreversible. The main difference between the adsorbed layers is that rinsing with water causes a leap in – Δf and ΔD values for the layer adsorbed from 0.5 g dm⁻³ (Fig. 5a and c). The leap is attributed to water uptake that is probably an indication of electrostatically driven expansion
of the adsorbed polymer coils and hydrophobically formed pre-micellar aggregates caused by a sudden decrease of ionic strength from 100 to 0 mM NaCl. The fact that the leap occurs only in the case of 0.5 g dm$^{-3}$ indicates that there must be differences between the structural properties of these two adsorbed layers.

As for the adsorption of qDMAEMA$_{24}$–PO$_{34}$–qDMAEMA$_{24}$ on PS, polymer concentration has a substantial effect. Increase from 0.05 to 0.5 g dm$^{-3}$ results in significant addition in the amount of water bound inside the layer, as shown by clear increase in both $-\Delta f$ and $\Delta D$ in Fig. 5b and d. In both concentrations, the adsorption still continues after a fast initial phase, and replacing the NaCl solution with water leads to substantial desorption. These results indicate that a build-up of a hydrophobically bound multilayer structure occurs in both concentrations. The multilayer adsorbed from 0.5 g dm$^{-3}$ containing pre-micellar aggregates that are formed already in bulk solution is more loose and able to bind more water. Rinsing with water results in breakdown of these multilayers by re-introducing the strong electrostatic repulsion between the charges along PqDMAEMA chains. The breakdown effect is greater for the layer adsorbed from 0.5 g dm$^{-3}$ solution as suggested by a severe decrease in $-\Delta f$, which is probably an indication of heavy aggregates releasing from the layer. This type of monocomponent multilayer formation has been observed also during the desorption of a charged, highly hydorphobized copolymer from high polymer and electrolyte concentrations [46].

When the adsorbed layer is rigid ($\Delta D < 10^{-6}$) – which is the case in most experiments of this study – the mass of qDMAEMA$_{24}$–PO$_{34}$–qDMAEMA$_{24}$ adsorbed can be estimated with Sauerbrey equation (Eq. (1)). The maximum masses adsorbed on the solid/solution interfaces are in the range of 50–280 ng cm$^{-2}$, corresponding to packing of 0.03–0.18 molecules nm$^{-2}$. These values are much lower than the extent of surface coverage at the saturated air/solution interface (0.91 molecules nm$^{-2}$, see Section 4.1). This kind of denser packing at air/solution interface compared to solid/solution has been observed also by others when adsorbing qDMAEMA$_{24}$–EO$_{132}$–PO$_{50}$–EO$_{132}$–qDMAEMA$_{24}$ onto polypropylene and silica surfaces: the amount on the saturated solid/solution interfaces was $\sim 0.03$ molecules nm$^{-2}$ whereas the value for the air/solution was 0.81 molecules nm$^{-2}$ [40]. This kind of denser packing at air/solution interface compared to solid/solution interface is typically ascribed to the higher configurational entropic penalty during packing of the copolymers at a solid surface compared to packing at a more diffuse air/solution interface [47].

Also, general trends observed in this study for adsorption of the qDMAEMA$_{24}$–PO$_{34}$–qDMAEMA$_{24}$ were similar to those observed when adsorbing the qDMAEMA$_{24}$–EO$_{132}$–PO$_{50}$–EO$_{132}$–qDMAEMA$_{24}$ from the surface-active polymer concentration region with 100 mM NaCl: on hydrophobic surface, the adsorbed mass was higher than on silica and also the deformation of the polymer layer induced by rinsing with water was more substantial [40].

4.3. Morphology of the adsorbed layers

4.3.1. Effect of electrolyte concentration

AFM images of the dried qDMAEMA$_{24}$–PO$_{34}$–qDMAEMA$_{24}$ films adsorbed on hydrophilic silica from different NaCl concentrations are presented in Fig. 6. The films consist of aggregates or clusters of aggregates that cover the surface only partly. Generally, the aggregate size increases with electrolyte concentration. In case of 10 mM NaCl, however, the film appeared to be much more heterogeneous than the films adsorbed from 1 or 100 mM NaCl and thereby could not be represented by a single AFM image. Formation of increasing aggregates with increasing NaCl concentration is in agreement with the QCM-D analysis in Section 4.2 where the adsorption was found to increase with salt concentration. The presence of salt causes screening of electrostatic repulsion between the forming aggregates, which enables denser packing and formation of larger clusters on the surface.

At 0.05 g dm$^{-3}$ concentration, the polymer should be essentially non-aggregated in solution. However, the formation of aggregates
on the surface adsorbed from a solution consisting of free polymer chains is not an unusual phenomenon. There are both theoretical [48] and experimental [49] studies indicating that charged amphiphilic block copolymers or surfactants in solutions below their critical micellization concentration can associate at oppositely charged surfaces as the local concentration of charged unimers in the vicinity of an oppositely charged surface exceeds their bulk solution concentration. It has been observed before [50] that increasing the salt concentration of a dilute solution of charged block copolymer can lead to the formation of aggregate networks or clusters during adsorption onto different substrates.

Because of the detected heterogeneity of the polymer film adsorbed from 10 mM NaCl on hydrophilic silica (Fig. 6), the investigation was complemented with XPS measurements. The XPS data together with AFM image analysis data are presented in Fig. 7. As observed with AFM, films formed on hydrophilic silica do not fully cover the surface. According to both the XPS data and the AFM image analysis, surface coverage varies between ~5 and 20%, basically increasing with salt concentration. The dispersion of the detected polymer amounts on the film adsorbed from 10 mM NaCl is especially wide, supporting the conception that the film is particularly heterogeneous.

AFM images of the dried qDMAEMA24–PO34–qDMAEMA24 films adsorbed on PS are presented in Fig. 8. Also here, the films consist of aggregates with sizes increasing with salt concentration. In each of the films, however, aggregates are much more evenly shaped and distributed than those observed on hydrophilic silica (Fig. 6) and thus each film appears rather uniform. The film adsorbed on PS from 1 mM NaCl solution bears actually complete coverage over the substrate with an appearance very similar to deformed vesicles of a charged amphiphilic diblock copolymer poly(butadiene)140–poly(2-vinylpyridine)140 adsorbed on mica [51]. This kind of toroidal shape of a vesicle is explained to form when water escapes from the inner core of the vesicle during drying of the sample. In case of qDMAEMA24–PO34–qDMAEMA24 solution, however, vesicle formation seems unlikely [52] because the level of surface activity of the polymer is only moderate, as stated in Section 4.1. Instead, the surface structures on PS may have resulted from qDMAEMA24–PO34–qDMAEMA24 unimers adsorbing individually on top and besides each other via hydrophobic forces, with the degree of molecular coiling and thus the z-scale variation of the adsorbed layer increasing with salt concentration.

Figure 6. 7 μm × 7 μm AFM height images of dried qDMAEMA24–PO34–qDMAEMA24 films adsorbed on hydrophilic silica from 50 ppm solutions with (a) 1 mM, (b and c) 10 mM, and (d) 100 mM NaCl. The h values denote the height scale of the features on the surface. The two different images of the film adsorbed from 10 mM NaCl illustrate the poorer repeatability of the measurement.

Figure 7. qDMAEMA24–PO34–qDMAEMA24 amount on hydrophilic silica as calculated based on XPS and AFM data of the polymer films adsorbed on the surface from 0.05 g dm⁻³ solutions with different NaCl concentrations.
is likely to serve as an optimal platform for the build-up of multilayer structures. The silica surface with unevenly scattered clusters (Fig. 6d), on the other hand, would be too heterogeneous and rough for the purpose.

We emphasize that all AFM images illustrate the morphology in the dry state. It is the focus of this study because of the large application potential of dry polymeric 2D structures. Therefore, the link to the in situ QCM-D data is always indirect.

### 4.3.2. Effect of polymer concentration

AFM images of the dried qDMAEMA$_{24}$−PO$_{34}$−qDMAEMA$_{24}$ films adsorbed on hydrophilic silica and polystyrene from 0.05 g dm$^{-3}$ and 0.5 g dm$^{-3}$ solutions are presented in Fig. 9. The unimers adsorbing from 0.05 g dm$^{-3}$ on silica (Fig. 9a) form rather large clusters on the surface, as discussed already in the previous section. From 0.5 g dm$^{-3}$ (Fig. 9b), on the other hand, the film adsorbed is strikingly smooth (z variation ~6 nm) and seems to be fully covered with the polymer. (Note: z variation of vapor deposited silica surface is in the same range (~6 nm) but the morphology is different, see Fig. 2a.) Hydrophobic attraction between the PPO cores has, thus, overcome the electrostatic repulsion between the PqDMAEMA coronas of the aggregates as the aggregates have merged into a uniform film. Based on the QCM-D analysis in Section 4.2, the amount of polymer adsorbed from 0.05 g dm$^{-3}$ and 0.5 g dm$^{-3}$ solutions is approximately the same. The major difference between the two adsorbed layers detected by QCM-D was that rinsing with water induced strong swelling of the layer adsorbed from 0.5 g dm$^{-3}$ solution, whereas no such effect was seen in the layer adsorbed from 0.05 g dm$^{-3}$. This seems logical from the morphological point of view: a uniform film (Fig. 9b) is undoubtedly able to bind more water than the sparsely scattered clusters (Fig. 9a). Appearance of qDMAEMA$_{24}$−PO$_{34}$−qDMAEMA$_{24}$ in solution in these two concentrations and the structures adsorbed on silica are schematically illustrated in Fig. 10.

It seems based on AFM data that the formations adsorbed from the pre-surface-active concentration region on polystyrene (Fig. 9c) have spread over the surface rather evenly although the shapes of the structures are somewhat irregular. As speculated earlier, the formations may consist of qDMAEMA$_{24}$−PO$_{34}$−qDMAEMA$_{24}$ unimers adsorbed individually on top and besides each other via hydrophobic forces. The film adsorbed on polystyrene from the surface-active region (Fig. 9d) consists of globular and disk-like aggregates that have nucleated already in the solution state. The vicinity of the surface seems to have induced growing of the weak premicellar aggregates to more distinct and regular features. This hypothesis is in agreement with the general fact that the cmc tends to be lower on a surface than in bulk solution [53]. The assumption of micellization is supported not only by the regular shape of the observed features on the surface, but also by the fact that
the detected feature height value of ~5–9 nm is on the range of the aggregate sizes measured in solution state with DLS (~6 nm, reported in Section 4.1).

As discussed earlier in Section 4.2 based on the QCM-D data, it appears that both the unimeric coils (Fig. 9c) and premicellar or micellar aggregates (Fig. 9d) are able to pile up to form a soft and thick layer with a lot of water imbibed. The patterns seen in the Fig. 9c and d represent the state of the films after rinsing with water, i.e., after the loosely bound multilayer material has been removed from the surface. Extremely even distribution of surface patterns in both cases explains the ability for acting as platform for multilayers. These irreversibly adsorbed structures are schematically illustrated in Fig. 10.

In literature [54], micelles of nonionic surfactants (i.e., neutral diblock copolymers) adsorbed on hydrophilic and hydrophobic substrates are reported to form the structures of opposite type to what we found with the adsorbing (premicellar) aggregates of qDMAEMA24–PO34–qDMAEMA24: nonionic surfactants form glo- 
ular micelles on hydrophilic surface and laterally continuous layers on hydrophobic surface. It can be speculated that merging of the qDMAEMA24–PO34–qDMAEMA24 aggregates into more continuous film on the hydrophobic substrate is hindered by (i) the repulsion between the charges of coronal PqDMAEMA and (ii) their lack of affinity toward the hydrophobic surface and also (iii) the limited mobility of the aggregated ABA triblock chains compared to that of diblock copolymer chains. In the adsorption of ABA aggregates onto hydrophilic surface, on the other hand, such major conformational changes are not required for spreading of aggregates because of the high affinity between the coronal charges of the aggregates and the surface.

5. Conclusions

In this study, the cationic ABA type triblock copolymer qDMAEMA24–PO34–qDMAEMA24 was found to be a versatile molecule for preparation of tunable 2D morphologies emerging from the simple self-assembly upon adsorption. By tuning the adsorption conditions – electrolyte and polymer concentration and choice of the substrate – diverse morphologies were achieved: from smooth continuous films to conspicuous aggregates of varying sizes, shapes and regularity in appearance. At times, the adsorption led to loosely scattered aggregates with diameters on the order of 1 μm whereas other conditions resulted in more densely occurring surface features with circular cross sections and diameters of tens of nanometers. The formation of the morphologies was fundamentally explored with the theoretical aspects of polyelectrolyte and block copolymer adsorption, supported with experimental in situ data on adsorption kinetics.

This study presents fundamental aspects of 2D structure formation from qDMAEMA24–PO34–qDMAEMA24. It serves as a starting point for preparing diverse morphologies from similar triblock copolymers. Since this paper presents essentially dry morphologies, i.e., the state after the films have been removed from the aqueous environment, the possible uses for these materials are likely to involve functions that employ the structures in their dry state. However, also the wet state morphologies may find valuable applications with the structural rearrangements in the adsorbed layers imposed by changing the solution conditions in the surrounding aqueous medium. Naturally, tailoring the 2D structures for each functionality will require further tuning of the adsorption conditions.

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