



Ultra-thin films of cationic amphiphilic poly(2-(dimethylamino)ethyl methacrylate) based block copolymers as surface wettability modifiers

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ABSTRACT

Ultra-thin films of cationic amphiphilic block and statistical copolymers were applied on silica surfaces from aqueous solutions through electrostatic interactions, and the resulting modification in the wettability of the surfaces was studied. A copolymer series from 2-(dimethylamino)ethyl methacrylate with methyl methacrylate and butyl methacrylate was polymerized by ATRP. Subsequently, the conformation of the polymers in aqueous solutions was studied by surface tension measurements, dynamic light scattering, ¹H NMR and cryogenic transmission electron microscopy. Unimeric conformation, equilibrium micelles or frozen micellar structures were observed, depending on polymer composition and the ionic strength of the solution. The polymers were applied on silica from aqueous solutions by either spin coating or adsorption. The formed ultra-thin film surfaces were studied by AFM and water contact angle measurements. The spin-coated surfaces were highly hydrophilic with rapidly dropping contact angles, whereas the surfaces prepared by adsorption had stable water contact angles between 30–60°, depending on polymer. The difference between the spin-coated and adsorbed surfaces is explained by the formation of a monolayer in the adsorbed surfaces.

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1. Introduction

Water-soluble amphiphilic block polyelectrolytes, consisted of a charged hydrophilic block and hydrophobic block, have attracted increasing interest. On one hand this is due to their ability to form interesting self-assembled structures, e.g. in aqueous solutions and on various interfaces [1,2]. On the other hand, easily applicable methodologies for the synthesis of block copolymers by controlled radical polymerization have been developed recently [3].

Polyelectrolytes can be adsorbed on surfaces of opposite charge as ultra-thin films through electrostatic attraction [4]. Adsorption of water-soluble amphiphilic block polyelectrolytes could potentially be utilized to modify the wetting properties of charged surfaces. The polyelectrolyte block can be adsorbed onto the surface from aqueous solution, and the surface wettability could subsequently be modified by the hydrophobic block, given that during

the modification process the hydrophobic block finally ends on the uppermost layer of the modified surface.

Similar approach could also be achieved with water-soluble amphiphilic statistical copolymers instead of block copolymers. In both cases, the modification could be done in an environmentally friendly aqueous environment and therefore used in applications where such environment is necessary, e.g. in papermaking [5]. Practical consideration of such applications can lead to relatively high polymer concentrations within the adsorption solutions (ca. 1 w/v-%) due to the necessity to limit the amount of water in the process. However, only a very small amount of polymer is expected to be needed for the actual modification, due to the nanoscale thickness of the polymer films.

When dissolved in water, amphiphilic block polyelectrolytes often form micellar aggregates, which can be either equilibrium structures or kinetically frozen structures [1]. There have been several studies on the preparation of ultra-thin amphiphilic block polyelectrolyte films on surfaces of opposite charge from aqueous solutions. The properties of the films have been studied both in contact with the polymer solution and after rinsing and drying [6–11]. The effect of various adsorption parameters to the surface morphology and adsorbed amount has been studied, including

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solution pH, ionic strength, polyelectrolyte charge density and polymer concentration. Micellar structures were often present on surfaces, even though their characteristics were not necessarily the ones seen in solution. One commonly encountered phenomenon was relaxation and stretching of the polyelectrolyte block on the surface due to strong electrostatic interactions between the substrate and the polyelectrolyte. The surfaces from micellar aggregate solutions were also often featureless, depending on conditions.

Few studies of block polyelectrolyte ultra-thin films have examined the wetting properties of the films [9,10]. Instead, several studies have been published on the effect of polyelectrolyte multilayers on surface wettability [12–15]. They indicate that the surface wetting properties are dependent on the nature of the top-most polyelectrolyte layer, where especially the surface charge density is significant.

2-(Dimethylamino)ethyl methacrylate (DMAEMA) is a monomer with a cationic character in neutral and acidic aqueous solutions. The amine group of DMAEMA can also be quaternized, leading to pH independent charge. The synthesis of block copolymers requires controlled polymerization techniques, of which ATRP has been one of the most widely applied [16,17]. The synthesis of DMAEMA homopolymer and block copolymers by ATRP has been studied extensively [18–24].

In this paper we have studied, how the wettability of charged hydrophilic surfaces can be modified by ultra-thin films of amphiphilic block or statistical polyelectrolytes. The polyelectrolytes were applied on the surfaces from aqueous solutions (Scheme 1). A series of DMAEMA copolymers with varying architectures and chemical compositions was synthesized by ATRP. The

polymers were dissolved in water at relatively high concentrations (1 w/v-%) and the structures formed in the resulting solutions were studied by several methods. The polymers were then applied onto silica surfaces from the aqueous solutions by either adsorption or spin coating method. The effect of the polymer composition and surface modification method on the structure and wettability of the modified surfaces was studied.

2. Experimental

2.1. Materials

2-(Dimethylamino)ethyl methacrylate (DMAEMA) (98% Aldrich) was stored under molecular sieves. It was purified by passing it through a basic alumina column and freshly distilled before use. Methyl methacrylate (MMA) (99% Aldrich) and butyl methacrylate (99% Merck) were stored under molecular sieves and passed through basic alumina before use to remove the inhibitor. *p*-Toluenesulfonyl chloride (TsCl) (99% Fluka), CuCl (99% Aldrich), 1,1,4,7,10,10-Hexamethyltriethylenetetramine (HMTETA) (97% Aldrich), bipyridine (BiPy) (99% Aldrich), iodomethane (MeI) (99% Fluka) and ethyl 2-bromoisobutyrate (EBiB) (98% Aldrich) were used as received. Methanol, toluene, anisole, THF and hexane were of analytical grade and used as received. The SiO₂ surfaces used as base substrates were oxidized silicon wafers supplied by Okmetic Oy, Espoo (Finland). The silicon wafers were cut into slides and then hydrophilized by cleaning first for 15 min in a boiling mixture of NH₄OH and H₂O₂, and then for 15 min in a boiling mixture of HCl and H₂O₂. Slides were rinsed with water after both steps, and dried with nitrogen gas in the end.

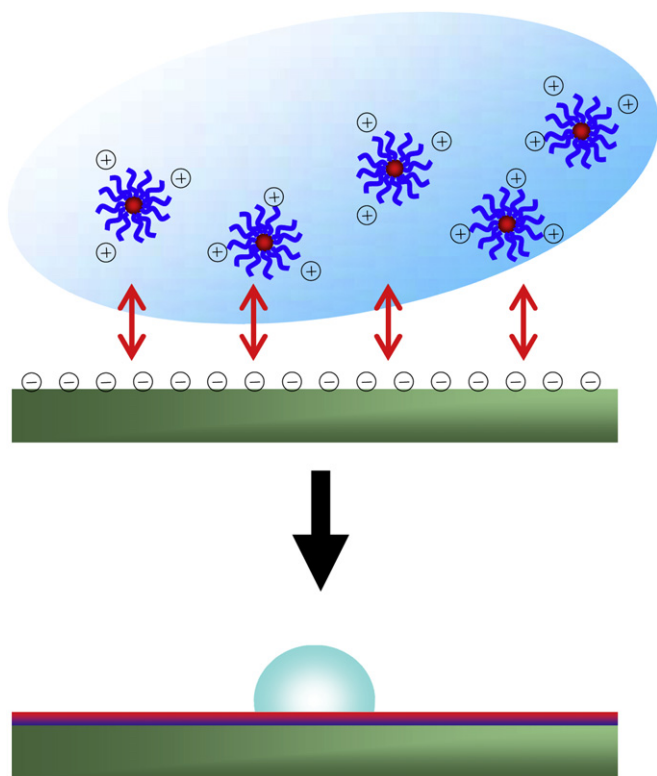
2.2. Syntheses

2.2.1. Homopolymerization of PDMAEMA

The PDMAEMA homopolymer was prepared by applying a catalyst/solvent system described by Mao et al. [19]. The polymerizations were done with a [M]:[CuCl]:[HMTETA]:[initiator] ratio of 75:1:1:1 and they were conducted as follows: CuCl (0.392 g, 4 mmol) was added to a dry, 250 ml Schlenk flask equipped with a magnetic stirring bar. The flask was evacuated and back-filled with argon three times. Degassed DMAEMA (40 ml, 297 mmol), HMTETA (1.08 ml, 4 mmol), degassed methanol (10 ml) and degassed distilled water (5 ml) were added with argon-flushed gas-tight syringes. The mixture was immersed to a thermostated 25 °C water bath and stirred for a few minutes. Finally TsCl (0.755 g, 4 mmol) dissolved in degassed DMAEMA (10 ml, 0.059 mol) was added with an argon-flushed gas-tight syringe. During polymerization, samples were withdrawn with argon-flushed gas-tight syringes to determine the conversion (by NMR) and molecular weight (by SEC). The polymerization was continued for 150 min, until ca. 40% conversion was reached. The polymerization was quenched by exposing the polymerization mixture to air. The mixture was diluted with 50 ml of THF and passed through a column of basic alumina to remove the catalyst. The mixture was concentrated with a rotary evaporator. The polymer was precipitated from a large excess of hexane and further purified with two repeated dissolutions in THF and precipitations from hexane. The product was dried in vacuum overnight.

2.2.2. Block copolymerization of PDMAEMA-*b*-PMMA

The block copolymers were synthesized by using the previously prepared PDMAEMA homopolymers as macroinitiators. For example: To a dry 100 ml Schlenk flask equipped with a magnetic stirring bar, 4 g of PDMAEMA (*M_n* 9500 g/mol, 0.42 mmol), 36 mg of CuCl (0.36 mmol) and 113 mg of BiPy (73 mmol) was added. The



Scheme 1. Amphiphilic polyelectrolytes are applied from aqueous solutions to a surface of opposite charge, forming an ultra-thin film of nanoscale thickness. The conformation of the polyelectrolyte in aqueous solution can be micellar aggregates, as pictured, or unimers. After drying, the surface wettability has been modified by the polymer film, as depicted by the water droplet.

flask was evacuated and back-filled with argon three times. 4.27 ml of degassed MMA (40 mmol) and 8.54 ml of degassed anisole were added through argon-flushed gas-tight syringes. The mixture was stirred for few minutes and then immersed to a thermostated 90 °C water bath. During polymerization samples were withdrawn with argon-flushed gas-tight syringes to determine the conversion (by NMR) and molecular weight (by SEC). The polymerization was continued for 180 min. The polymerization was quenched by exposing the polymerization mixture to air. The mixture was diluted with 20 ml of THF and passed through basic alumina to remove the catalyst. The polymer was precipitated from a large excess of hexane and purified by repeated dissolution in THF and precipitation from hexane. The product was dried in vacuum overnight.

2.2.3. Block copolymerization of PDMAEMA-*b*-PBMA

PDMAEMA-*b*-PBMA polymer was polymerized otherwise as PDMAEMA-*b*-PMMA polymers, but toluene was used as a solvent instead of anisole. After polymerization, the polymerization mixture was diluted with THF and passed through basic alumina to remove the catalyst. The product was precipitated from water in order to remove the unreacted PDMAEMA macroinitiator and purified by dissolution in THF and precipitation from hexane. The product was dried in vacuum overnight.

2.2.4. Random copolymerization of PDMAEMA-*co*-PMMA

To a dry 100 ml Schlenk flask equipped with a magnetic stirring bar, 67 mg of CuCl (0.68 mmol) and 213 mg of BiPy (1.36 mmol) were added. 5.7 ml of degassed DMAEMA (34 mmol), 3.6 ml of degassed MMA (34 mmol) and 9.4 ml of anisole were added with argon-flushed gas-tight syringes. The flask was immersed to a thermostated 90 °C water bath. Finally, 0.1 ml of EBiB (0.68 mmol) was added. During the polymerization, samples were withdrawn with argon-flushed gas-tight syringes to determine the conversion (by NMR) and molecular weight (by SEC). The polymerization was continued for 120 min and it was quenched by exposing the polymerization mixture to air. The mixture was diluted with 20 ml of THF and passed through basic alumina to remove the catalyst. The product was precipitated from a large excess of hexane and purified by repeated dissolution in THF and precipitation from hexane. The product was dried in vacuum overnight.

2.2.5. Quaternization

Quaternization of the amine groups of PDMAEMA was done by applying a method described by Baines et al. [25]. For example: 1 g of PDMAEMA-*b*-PMMA block copolymer (3.6 mmol of amine groups) was dissolved in 100 ml of THF. A three-fold excess of MeI was added (0.7 ml, 11 mmol). The reaction was left stirring at room temperature overnight. The precipitated product was isolated with centrifugation and purified by soxhlet extraction with THF. The product was dried in vacuum overnight.

2.3. Characterizations

2.3.1. Polymer composition

¹H NMR spectra were recorded on a Varian Gemini 2000 300-MHz spectrometer in *d*-chloroform and D₂O. The molecular weights from the NMR spectra of the polymers were calculated by comparing the end-group peak at 7.6–7.8 ppm (2H) to the repeating unit peaks.

Size exclusion chromatography (SEC) was conducted with respect to polystyrene standards at room temperature. The system was equipped with four Waters Styragel columns (10², 10³, 10⁴ and 10⁵ Å) and a Waters 410 differential refractometer. THF containing

2 v/v-% of triethylamine was used as an eluent and was delivered at a flow rate of 1 ml/min.

2.3.2. Solution properties

Surface tension was measured with a Kibron AquaPi tensiometer by the Du Nouy maximum pull force method. The polymer samples were directly dissolved at 1 w/v-% concentration in water containing 0.0001 M NaCl. The solutions were stirred overnight. A concentration series was prepared from the 1 w/v-% polymer solutions by diluting with 0.0001 M NaCl. The samples were equilibrated in saturated atmospheric humidity for 24 h to ensure equilibrium between the air/water interface layer and the bulk solution. The surface tension probe was cleaned by flaming before each measurement.

Dynamic light scattering (DLS) measurements were conducted with a Malvern Zetasizer Nano ZS instrument operating at a scattering angle of 173° and a wavelength of 633 nm. The 1 w/v-% polymer solutions were prepared by direct dissolution in water with 0.0001 M NaCl and stirred overnight. The samples for measurements in 0.1 M NaCl were prepared from the low ionic strength samples by adding a small amount of concentrated NaCl solution (polymer concentration remained practically constant at 1 w/v-%), followed by measurement after 1 h. All salt solutions were filtered with 0.25 μm filters before the addition of the polymer.

For cryogenic transmission electron microscopy (cryo-TEM) analysis, 1 w/v-% polymer solutions were prepared by direct dissolution in water containing 0.0001 M NaCl. The salt solution was filtered with 0.25 μm filter before the addition of the polymer. The solutions were left stirring overnight. A small amount (6 μl) of sample solution was placed on a Quantifoil holey carbon copper grid with a hole size of 2 μm. With use of a Tecnai Vitrobot the samples were blotted at 100% humidity and plunged into liquid ethane of temperature –175 °C. The vitrified samples were maintained at about –180 °C and transferred into the microscope with a Gatan 910 cryotransfer holder for imaging. The cryo-TEM analysis was conducted with a Tecnai 12 Bio Twin transmission electron microscope in bright field mode.

2.4. Properties of the polymer films on silica

Polymers were deposited on the silica substrates by adsorption and spin coating methods. In adsorption, the substrate was first immersed for 15 min in 1 w/v-% polymer solution. The sample was then rinsed extensively with water and dried at room temperature by allowing the solvent to evaporate. In spin coating, the 1 w/v-% polymer solution was deposited on a static substrate and spin-coated at 2800 rpm for 1 min, with an acceleration rate of 2000 rpm/s.

Advancing contact angles were measured with CAM 200 (KSV Instruments Ltd, Helsinki, Finland) contact angle goniometer. The software delivered by the instrument manufacturer calculates the contact angles based on a numerical solution of the full Young-Laplace equation. Measurements were performed at room temperature with water. The contact angle was measured for at least on three parallel samples, and on the bare substrates.

AFM experiments were conducted with a Nanoscope IIIa Multimode scanning probe microscope (Digital Instruments Inc., Santa Barbara, CA, USA). The images were scanned in tapping mode in air using silicon cantilevers. No image processing except flattening was done. Thicknesses were studied by scratching the samples with a needle and determining the z-directional difference between the bottom of the scratch and the intact areas of the film. The thicknesses were determined on at least four different spots on each sample.

Table 1
The polymer series.

Sample	Average composition (NMR)	DMAEMA content (mol%)	M_n (g/mol) (NMR) ^a	M_n (g/mol) (SEC)	M_w/M_n
<i>Homopolymers</i>					
D1	P(DMAEMA ₆₈)	100	10600	8700	1.11
D2	P(DMAEMA ₇₃)	100	11400	9800	1.10
QD1	P(META ₆₈)	100	10600/20200	8700 ^b	1.11 ^b
<i>Block copolymers</i>					
B1(D ₇₆ M ₁₇) ^c	P(DMAEMA ₇₆ - <i>b</i> -MMA ₁₇)	82	13600	13300	1.08
B2(D ₈₁ M ₂₁) ^c	P(DMAEMA ₈₁ - <i>b</i> -MMA ₂₁)	79	14900	13600	1.09
B3(QD ₇₆ M ₁₇)	P(META ₇₆ - <i>b</i> -MMA ₁₇)	82	13600/24400	13300 ^b	1.08 ^b
B4(QD ₆₁ M ₇₉)	P(META ₆₁ - <i>b</i> -MMA ₇₉)	44	17500/26100	17400 ^b	1.10 ^b
B5(QD ₆₆ B ₇₆)	P(META ₆₆ - <i>b</i> -BMA ₇₆)	47	21100/30500	20800 ^b	1.17 ^b
<i>Statistical copolymer</i>					
C1(QD ₆₀ M ₆₂)	P(META ₆₀ - <i>co</i> -MMA ₆₂) ^d	49	–	15600 ^b	1.19 ^b

^a Before/after quaternization.^b Before quaternization.^c B1(D₇₆M₁₇) and B2(D₈₁M₂₁) samples were approximated in this study to behave identically. B1(D₇₆M₁₇) was used in the surface studies and B2(D₈₁M₂₁) was used in the solution studies.^d Estimated from the SEC result.

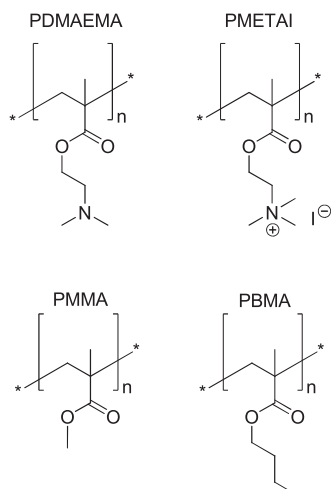
3. Results and discussion

3.1. Synthesis of the polymer series

A series of water-soluble, amphiphilic polyelectrolytes was synthesized for the surface studies. The series consisted of block and statistical copolymers where hydrophilic monomer was either DMAEMA or its quaternized form, [2-(methacryloyloxy)ethyl] trimethyl ammonium iodide (META), of which META is more hydrophilic. Methyl methacrylate (MMA) and butyl methacrylate (BMA) were used as hydrophobic monomers in the copolymers, of which BMA is more hydrophobic. In addition, PDMAEMA and PMETA samples were studied as homopolymer references. The properties of the polymers are presented in Table 1 and the applied repeating unit structures are presented in Scheme 2.

The polymer series was constructed in a way that allows studying the effect of various composition parameters to the properties of the modified surfaces. The parameters under study were

1. *The effect of quaternization.* The block copolymer B1(D₇₆M₁₇) had a relatively short PMMA block and was therefore water-soluble already before quaternization. It was present in the series both as non-quaternized and quaternized versions:

**Scheme 2.** Chemical structures of the repeating units used in this study.

B1(D₇₆M₁₇) (or closely corresponding B2(D₈₁M₂₁)) and B3(QD₇₆M₁₇), respectively.

2. *The effect of hydrophobic block length.* The samples B3(QD₇₆M₁₇) and B4(QD₆₁M₇₉) differed in the length of the PMMA block.
3. *The effect of the hydrophobicity of the hydrophobic block.* B4(QD₆₁M₇₉) and B5(QD₆₆B₇₆) were both block copolymers with similar block lengths, but they differed in the chemical constitution of the hydrophobic block (PMMA and PBMA, respectively).
4. *The effect of polymer architecture.* Block copolymer B4(QD₆₁M₇₉) and statistical copolymer C1(QD₆₀M₆₂) had similar monomer compositions but different chain architectures.

The block copolymers were prepared by first polymerizing PDMAEMA homopolymer by ATRP and then using it as a macro-initiator in the polymerization of the hydrophobic block. In DMAEMA polymerizations, we used the solvent/catalyst system described by Mao et al. [19]. The DMAEMA homopolymer blocks prepared by this method had low polydispersities, approximately 1.1 in all the polymerizations. However, the molecular weights were approximately two times higher than what was theoretically expected. The polymerization mixtures turned deep blue immediately when the reaction was initiated, indicating that large amount of Cu(II)Br was formed at the beginning of the reaction due to termination by radical-radical coupling. This provided some challenges to the predictability of the reaction, but the macro-initiators prepared by this method were of good quality.

The prepared PDMAEMA homopolymers were used as macro-initiators in the polymerization of the block copolymers. The SEC curves of the polymers are presented in Fig. 1. The molecular weight distributions were narrow in all the copolymers. In the block copolymerizations (a, b and c in Fig. 1) the molecular weight clearly shifted to a higher value when compared to the homopolymer macroinitiator. Significant macroinitiator traces were not visible in the curves.

3.2. Solution properties of the polymers in water

The behavior of the polymer samples in aqueous solutions was studied by surface tension measurements, ¹H NMR, DLS and cryo-TEM. Typically, 1 w/v-% polymer was dissolved in low ionic strength aqueous solution (0 M or 0.0001 M NaCl). DLS measurements were conducted both at low (0.0001 M) and at high (0.1 M) NaCl concentrations. The solutions of the polymer samples containing DMAEMA units were measured to have pH values between 9.0–9.3.

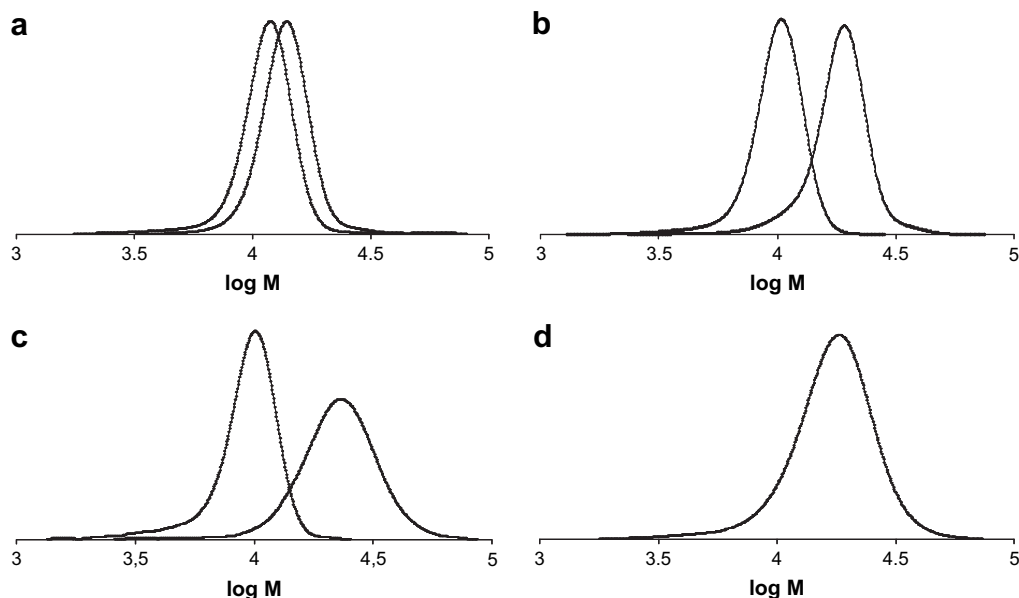


Fig. 1. SEC curves of the copolymers. In the curves of the block copolymers the macroinitiator curve is presented as well (the left curve). (a) B1(D₇₆M₁₇) (b) B4(QD₆₁M₇₉) (before quaternization) (c) B5(QD₆₆B₇₆) (before quaternization) (d) C1(QD₆₀M₆₂) (before quaternization).

PDMAEMA has a pK_a value of 7.4–7.8 in water [26].¹ Therefore, the PDMAEMA containing polymers were only weakly charged in the solutions. By contrast, the quaternized samples containing METAI repeating units were strong polyelectrolytes independent of pH. The quaternization considerably enhances the water solubility of the polymers. The surface tensions of the polymer solutions are presented in Fig. 2, the ¹H NMR spectra are presented in Fig. 3, and the DLS results are presented in Table 2. The conformations of the polymers under aqueous conditions, based on the combined results of all the measurements, are also presented in Table 2.

3.2.1. Solution properties of the homopolymers D2 and QD1

The conformation of the homopolymer samples D2 (PDMAEMA homopolymer) and QD1 (PMETAI homopolymer) in aqueous solution can be expected to be unimeric. Accordingly, the scattering intensities of the 1 w/v-% homopolymer solutions were very low (Table 2). Both homopolymer samples were surface active decreasing the surface tension of water (Fig. 2). However, the non-quaternized D2 was clearly more surface active than QD1.

3.2.2. Solution properties of the block copolymers B2(D₈₁M₂₁) and B3(QD₇₆M₁₇)

When comparing the block copolymers with the lowest molar contents of MMA, which are the non-quaternized B2(D₈₁M₂₁) and quaternized B3(QD₇₆M₁₇), the non-quaternized sample is clearly more surface active according to the surface tension measurements (Fig. 2). Similar surface tension behavior has previously been observed for same kind of non-quaternized and quaternized PDMAEMA–PMMA block copolymers [25,27]. The turning points of the surface tension curves can often be attributed to critical micelle concentrations (cmc) of the polymers. However, it is obvious that the surface tension curve of B2(D₈₁M₂₁) is closely similar to the surface tension curve of pure PDMAEMA homopolymer, indicating that the surface tension behavior was actually dominated by the PDMAEMA block, which forms the majority of the polymer. Therefore it seems unlikely, that the turning point of the B2(D₈₁M₂₁) curve is associated with the cmc.

Previously, de Paz Báñez et al. [28,29] have observed similar surface tension behavior for non-quaternized PDMAEMA homopolymer and various block copolymers. They attribute the surface tension behavior to the efficiency of packing of the polymer on the surface instead of giving information on cmc. Likewise, we believe that it is not possible to make quantitative conclusions about the critical micelle concentrations or even verify the absence or presence of micellar structures in B2(D₈₁M₂₁) and B3(QD₇₆M₁₇) samples based on only surface tension studies. However, it seems likely that the non-quaternized sample is more prone to form aggregates.

More information on the properties of B2(D₈₁M₂₁) and B3(QD₇₆M₁₇) in low ionic strength solutions was obtained from the ¹H NMR experiments. When comparing the spectra of B2(D₈₁M₂₁) in D₂O, which is a selective solvent for the hydrophilic block (a1 in Fig. 3), and in *d*-chloroform, which is a good solvent for both blocks (a2 in Fig. 3), especially the methoxyl peak of PMMA was highly broadened in the D₂O spectrum. The methoxyl peak was broad in the D₂O spectrum of B3(QD₇₆M₁₇) (b in Fig. 3) as well. Broadening indicates decreased mobility and aggregation of the hydrophobic PMMA block in D₂O. However, it is not possible to distinguish, whether this aggregation was intramolecular (unimeric molecules with PMMA block collapsed to a tightly packed globule) or intermolecular (micellar aggregates).

Finally, the differences between B2(D₈₁M₂₁) and B3(QD₇₆M₁₇) were studied by DLS (Table 2). In addition to the previous

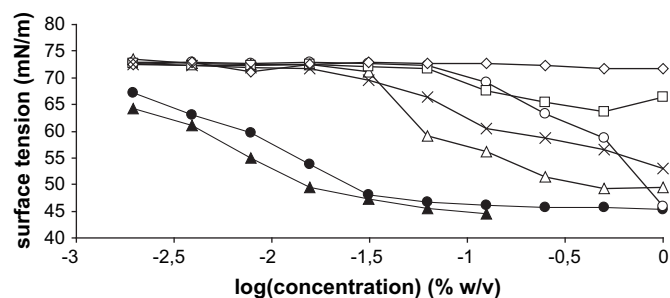


Fig. 2. Variation of surface tension with polymer concentration (0.0001 M NaCl solutions). ● D2, ○ QD1, ▲ B2(D₈₁M₂₁), △ B3(QD₇₆M₁₇), □ B4(QD₆₁M₇₉), ◇ B5(QD₆₆B₇₆), × C1(QD₆₀M₆₂).

¹ Measured for 0.2–0.3 w/v% polymer solution with 0.15 M NaCl.

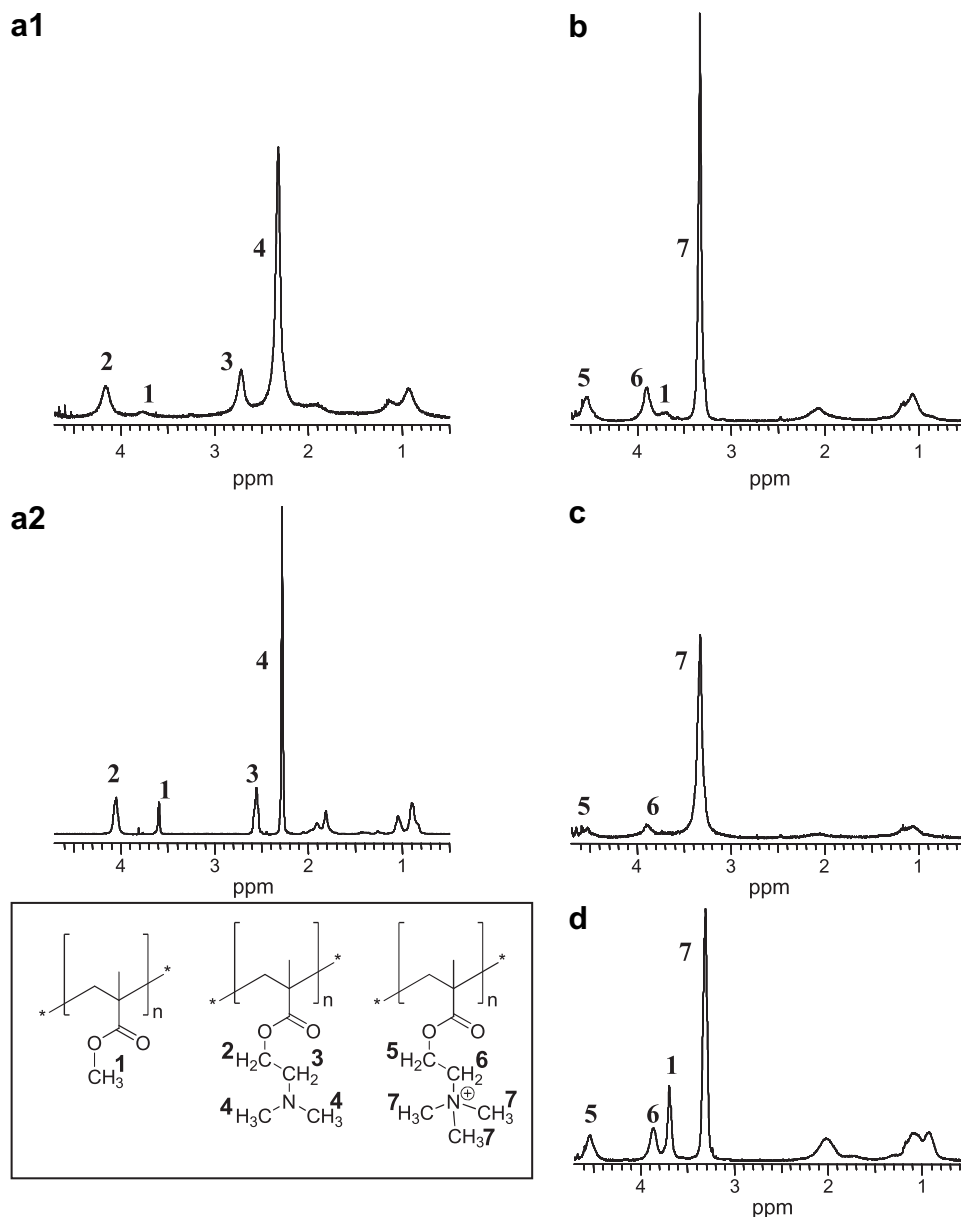


Fig. 3. NMR spectra of the sample series. (a1) B2(D₈₁M₂₁) in D₂O. (a2) B2(D₈₁M₂₁) in CDCl₃ (b) B3(QD₇₆M₁₇) in D₂O. (c) B4(QD₆₁M₇₉) in D₂O. (d) C1(QD₆₀M₆₂) in D₂O. 1 w/v-% samples, no salt added.

measurements, which were done at low NaCl concentrations, these measurements were conducted both in 0.0001 M and in 0.1 M NaCl. In DLS measurements the strong electrostatic interactions within the quaternized samples need to be screened by a sufficiently high salt concentration, otherwise the dynamics of the solutions are

determined by the electrostatic interactions, and no information concerning particle size can be obtained from the data [30]. The samples for measurements in 0.1 M NaCl were prepared from low ionic strength samples by adding a small amount of concentrated NaCl solution.

Table 2

DLS results of 1 w/v-% polymer solutions, and the solution conformations of the polymers (based on results from all measurements).

	0.0001 M NaCl			0.1 M NaCl		
	Scattering intensity ^a (kcps)	D _H (nm)	Conformation	Scattering intensity ^a (kcps)	D _H (nm)	Conformation
D2	13		unimers	21	6	unimers
QD1	37		unimers	94		unimers
B2(D ₈₁ M ₂₁)	190	12	equilibrium micelles	340	22	equilibrium micelles
B3(QD ₇₆ M ₁₇)	28		unimers	121	21	equilibrium micelles
B4(QD ₆₁ M ₇₉)	4160		frozen micelles	4610	169	frozen micelles
B5(QD ₆₆ B ₇₆)	7690		frozen micelles	7940	100	frozen micelles
C1(QD ₆₀ M ₆₂)	79		unimers	92		unimers

^a From the DLS measurement.

From the scattering intensities it can be seen that in 0.0001 M NaCl solutions the scattering intensity of B2(D₈₁M₂₁) was almost one order of magnitude higher than the scattering intensity of B3(QD₇₆M₁₇). The scattering intensity of the B3(QD₇₆M₁₇) sample was on the same level with homopolymer samples, indicating that micelles were not present in these conditions. The hydrodynamic diameter of the B2(D₈₁M₂₁) micelles was 12 nm, but it could not be measured for the B3(QD₇₆M₁₇) due to the low NaCl concentration. The absence of micelles in quaternized samples and the micelle size of this order in non-quaternized samples have both been reported previously with similar PDMAEMA–PMMA block copolymers in similar conditions [25,31].

When salt was added to the solutions (0.1 M NaCl), both B2(D₈₁M₂₁) and B3(QD₇₆M₁₇) formed micelles with a hydrodynamic diameter of 21–22 nm. Again, similar result was obtained previously by Baines et al. [25,31]. The likely conformations of the samples in both salt concentrations are listed in Table 2.

3.2.3. Solution properties of the statistical copolymer C1(QD₆₀M₆₂)

The statistical copolymer C1(QD₆₀M₆₂) reduced the surface tension of water slightly more than the corresponding quaternized homopolymer QD1 in most of the measured concentrations (Fig. 2). In the ¹H NMR spectrum of the C1(QD₆₀M₆₂) in salt-free D₂O (d in Fig. 3) the methoxyl peak of PMMA was clearly visible and narrow. This strongly indicates that PMMA groups were not aggregated. The scattering intensity in 0.0001 M NaCl solution was relatively low (Table 2), and did not substantially increase when salt was added. Therefore, it is concluded that the conformation of C1(QD₆₀M₆₂) was unimeric in both 0.0001 M and 0.1 M NaCl concentrations.

3.2.4. Solution properties of the block copolymers B4(QD₆₁M₇₉) and B5(QD₆₆B₇₆)

The most hydrophobic block copolymers, B4(QD₆₁M₇₉) and B5(QD₆₆B₇₆) showed very little surface activity in the surface tension measurements (Fig. 2). In the DLS measurements at 0.1 M NaCl relatively large aggregates were observed; the hydrodynamic diameter was 169 nm for B4(QD₆₁M₇₉) and 100 nm for B5(QD₆₆B₇₆) (Table 2). The particle size distribution was broader for the sample B4(QD₆₁M₇₉), and therefore B4(QD₆₁M₇₉) solutions were likely to contain small particles as well as larger ones.

Cryo-TEM images were taken from B4(QD₆₁M₇₉) and B5(QD₆₆B₇₆) solutions in 0.0001 M NaCl (Fig. 4). The difference in the aggregate size distribution of the two samples is clearly seen also in the images. The B4(QD₆₁M₇₉) image contains a wide distribution of varying particles, whereas B5(QD₆₆B₇₆) image consists of clearly defined particles with diameters varying between 20–70 nm.

The solutions of B4(QD₆₁M₇₉) and B5(QD₆₆B₇₆) exhibited the highest surface tensions of all the samples being nearly completely surface inactive. The high surface tension values of aqueous solutions of amphiphilic block copolymers with highly hydrophobic core blocks has been reported recently by Théodoly et al. [32]. They attribute the surface inactivity to the frozen state of the particles formed in the solution.

Micellar aggregates can be frozen in water either due to the high interfacial tension between water and the hydrophobic block or due to the high glass transition temperature of the hydrophobic block, or for both reasons. Frozen micelles are non-equilibrium aggregates, and the solution properties are dependent on the dissolving method. In frozen systems, unimer-micelle equilibrium is not attainable since there is no unimer extraction from the aggregates [1]. It is further suggested [32] that the high surface tensions observed in such systems are due to the inability of the hydrophobic block to reach the interface, and the systems behave like colloidal suspensions of charged solid particles.

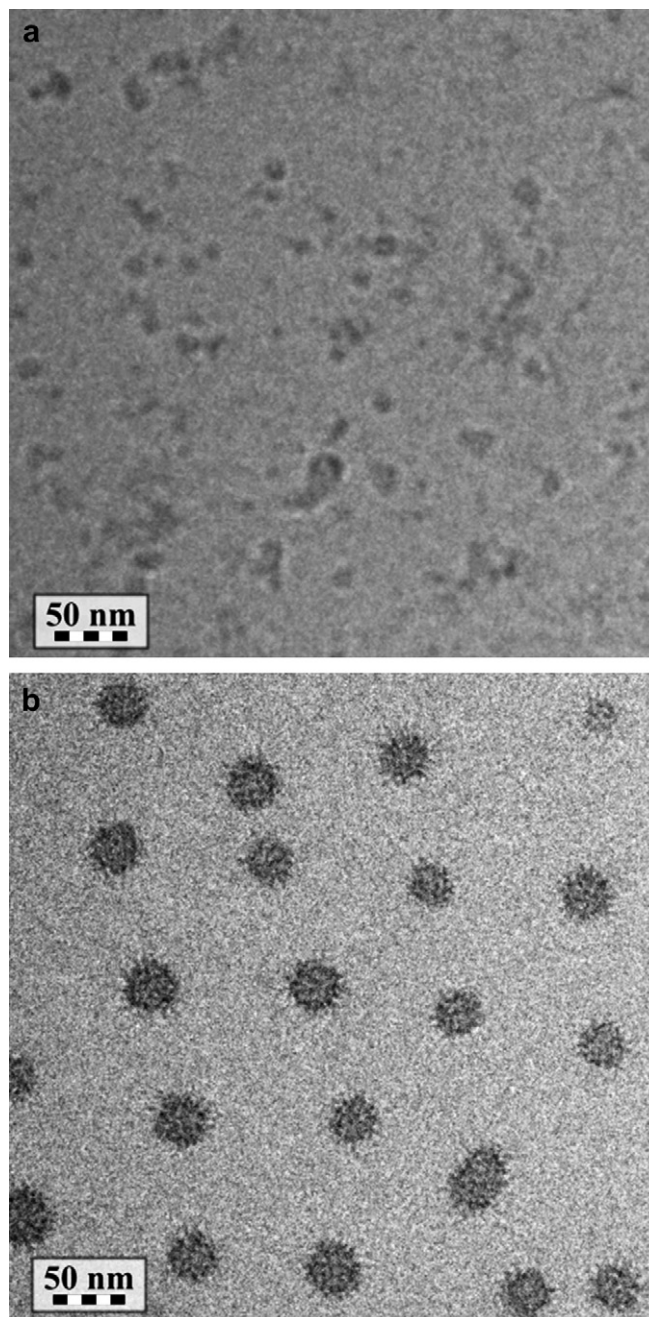


Fig. 4. Cryo-TEM images of (a) B4(QD₆₁M₇₉) and (b) B5(QD₆₆B₇₆), 1 w/v-% solutions in 0.0001 M NaCl.

Previously, Baines et al. [31] have observed, that the particle size of non-quaternized PDMAEMA–PMMA micelles was dependent on dissolving method when the PMMA content reached approximately 30 mol-%, indicating that the micelles were no longer able to reach equilibrium. When such block copolymers were directly dissolved in water, the formed aggregates were suspected to mirror the bulk structure, due to the inability of the hydrophobic block to dissolve. This memory effect is a well-documented phenomenon in block copolymer solutions prepared by direct dissolution [1,21].

Because of the surface inactivity of B4(QD₆₁M₇₉) and B5(QD₆₆B₇₆) solutions, we believe that the solutions of these samples were in the frozen, non-equilibrium state. In addition, the ¹H NMR spectrum of B4(QD₆₁M₇₉) (c in Fig. 3) was highly broadened and the methoxyl peak of PMMA was completely missing,

indicating that the majority of the polymer was aggregated. The expected frozen conformation for these samples is listed in Table 2.

3.3. Properties of the spin-coated and adsorbed ultra-thin films of polymer samples on silica surfaces

For the surface studies, the polymers were directly dissolved in aqueous 0.0001 M NaCl solutions so that the polymer concentration was 1 w/v-%. According to the solution studies, the polymer samples had unimeric, equilibrium micelle or frozen micelle conformations in these conditions, depending on the polymer. From these solutions, the polymers were applied onto silica surfaces as ultra-thin films either through spin coating or through adsorption. The contact angles of the surfaces were measured to assess the changes in the wetting properties. The surface structures were further studied by AFM.

The aqueous contact angles were measured directly after the surface formation in the case of spin-coated samples and after overnight drying at room temperature in the case of adsorption samples. The contact angles were measured as a function of droplet contact time, and the results are presented in Fig. 5.

The contact angle of water on the spin-coated surfaces was 25–50° at the beginning of the measurement, but then quickly dropped to lower values as the droplet stayed on the surface (Fig. 5a). At the end of the measurement values corresponding to highly hydrophilic surfaces were measured. By contrast, on surfaces prepared by adsorption, the contact angles were relatively stable and values between 30–60° were measured, depending on the adsorbed polymer (Fig. 5b).

In order to understand the characteristics of the formed ultra-thin polymer layers, we analyzed the surfaces with AFM. We recorded an AFM image of each copolymer surface, and measured the thickness of the polymer layers by scratch method. The AFM images alongside with height profiles from the scratch experiments are presented in Fig. 6 (spin-coated surfaces) and Fig. 7 (adsorbed surfaces). In addition, the layer thicknesses measured by the scratch method are tabulated in Table 3. Of the smooth surfaces, a value describing the thickness is presented, and of the rough surfaces, the extreme values are presented.

The AFM images of the spin-coated surfaces indicate that the solution conformation of the sample had an effect on the appearance of the spin-coated ultra-thin films. The unimeric samples B3(QD₇₆M₁₇) and C1(QD₆₀M₆₂) formed very smooth polymer layers when spin-coated on silica, as apparent in the height profile curves in Fig. 6. The surface spin-coated from sample B1(D₇₆M₁₇), which had a solution morphology of small 11 nm equilibrium micelles, appeared smooth as well. On the other hand, the samples B4(QD₆₁M₇₉) and B5(QD₆₆B₇₆), which had a solution morphology of frozen micelles, formed significantly rougher surfaces, where the surface formations visible in the AFM images can be assumed to derive from frozen aggregates.

The AFM results of the adsorbed surfaces in Fig. 7 show, that in general, the adsorbed surfaces were significantly thinner than the spin-coated surfaces. Regardless of the solution conformation of the samples, majority of the surfaces were featureless. However, the B5(QD₆₆B₇₆) surface was an exception; it had a structure of 100–200 nm wide and 2–6 nm high formations separated by smooth areas. These surface aggregates can be argued to derive from the frozen solution aggregates of B5(QD₆₆B₇₆) (Fig. 4), which have relaxed and flattened during adsorption and drying. Since the aggregates were frozen, it can be expected that the rinsing step in the surface preparation did not disaggregate them. The two samples with frozen aqueous conformations, B4(QD₆₁M₇₉) and B5(QD₆₆B₇₆), had different aqueous conformations in the cryo-TEM images (Fig. 4) and these differences were mirrored in the adsorbed

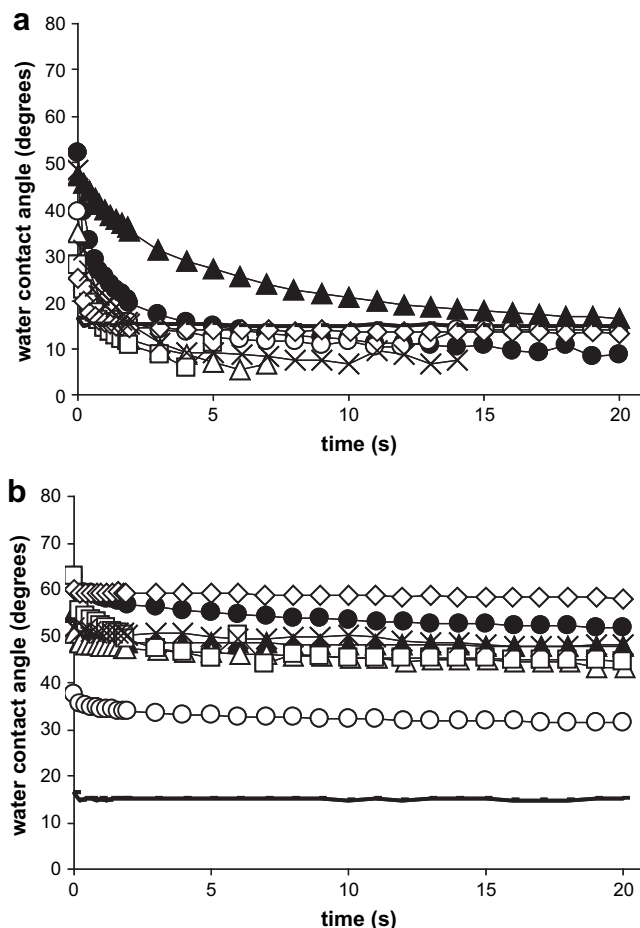


Fig. 5. Water contact angles of the polymer surfaces prepared by (a) spin coating and (b) adsorption. ● D1. ○ QD1. ▲ B1(D₇₆M₁₇). △ B3(QD₇₆M₁₇). □ B4(QD₆₁M₇₉). ◇ B5(QD₆₆B₇₆). × C1(QD₆₀M₆₂). — silica reference.

surfaces. Both in solution and on adsorbed surfaces, the B5(QD₆₆B₇₆) aggregates were clear and uniform and the B4(QD₆₁M₇₉) aggregates were not well-defined.

The adsorbed surfaces were formed from relatively concentrated solutions. Previously, Webber et al. [33] observed that when PDMAEMA homopolymer was adsorbed onto surface of opposite charge from concentrated solutions, adsorption was fast and sufficient relaxation of chains to achieve charge neutralization was not present. They also observed that fast adsorption of DMAEMA-MMA block copolymers could lead to featureless surfaces even if micelles were present in the solution. It is likely, that in our study the unimers or aggregates have adsorbed very quickly to the surface without significant relaxation, resulting in relatively smooth surfaces. In addition, of the samples with micellar solutions, the sample B1(D₇₆M₁₇) consisted of equilibrium micelles. This may have resulted in the adsorption of unimers, or if micelles were adsorbed, they may have disaggregated during the rinsing process. Only the B5(QD₆₆B₇₆) sample, which was formed of large frozen aggregates in the aqueous solution (Fig. 4), formed a surface where separate aggregates were present.

When explaining the differences in contact angles between the spin-coated and adsorbed samples with the help of the AFM results, one thing to note is the clear difference in the layer thicknesses. The spin coating is a forced deposition method, where the layer thickness is governed by the spinning parameters and solution properties. On the other hand, adsorption is a method where only those polymer chains that have sufficient affinity to the

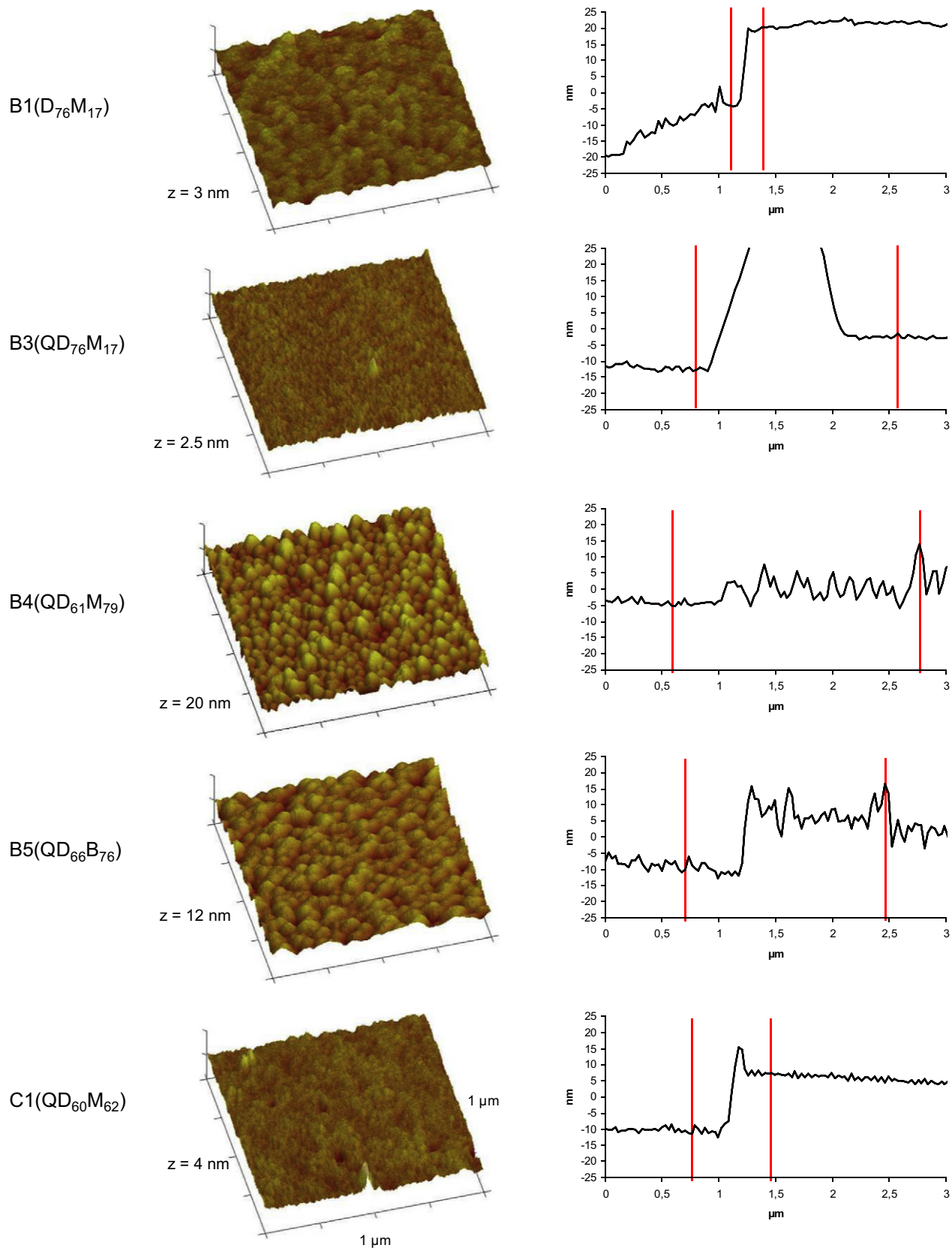


Fig. 6. The spin-coated surfaces. AFM images (not scratched, $1 \mu\text{m} \times 1 \mu\text{m}$) and height profiles with scratch. In the height profiles the vertical lines represent the points of highest film thickness.

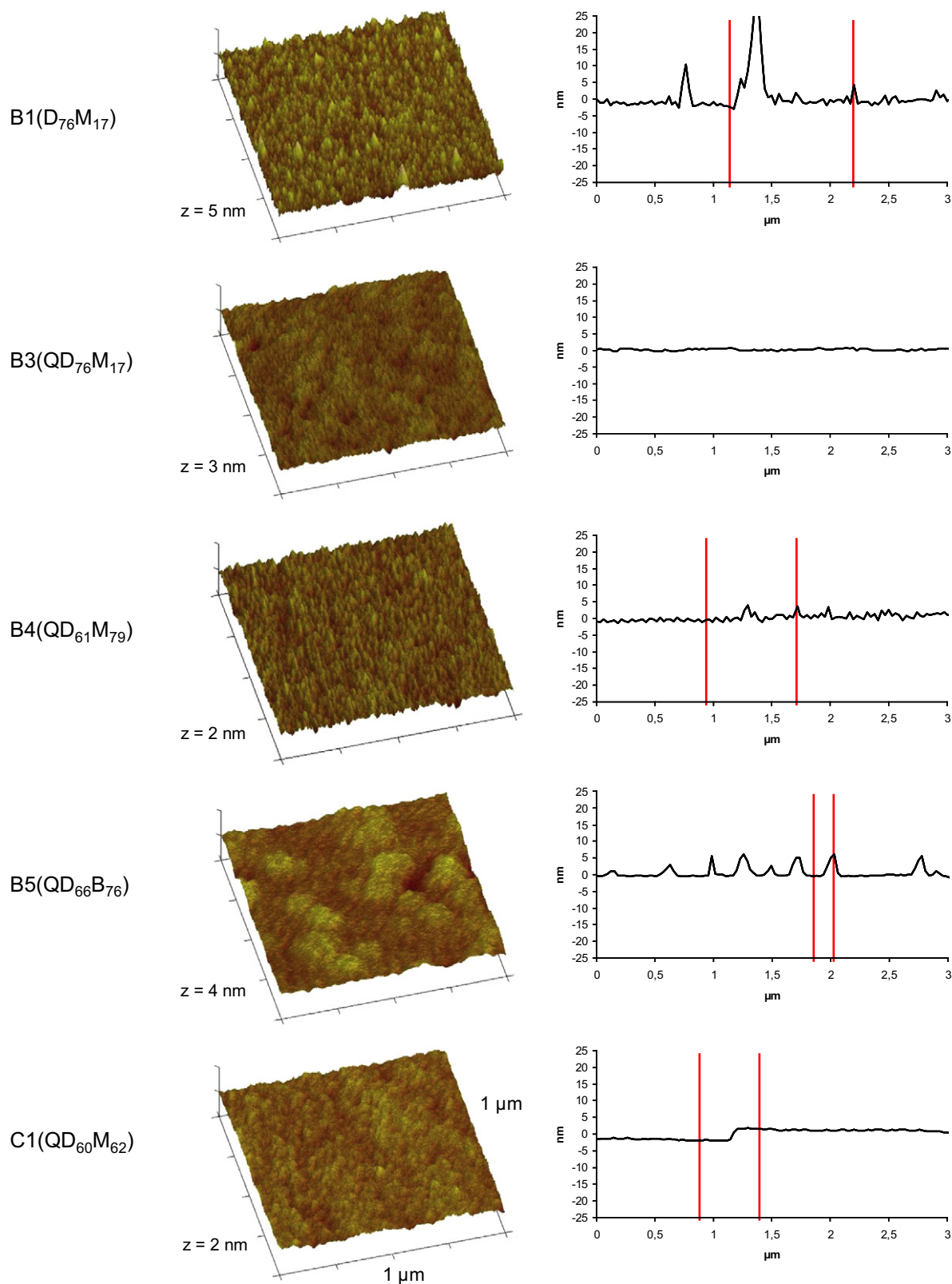


Fig. 7. The adsorbed surfaces. AFM images (not scratched, 1 μm × 1 μm) and height profiles with scratch. In the height profiles the vertical lines represent the points of highest film thickness.

surface are adsorbed and all the extra polymer chains are removed by the rinsing process. In the case of polyelectrolyte unimers, the well-known consequence is, that only a monolayer of chains is adsorbed.

Due to this difference, we expect that in the films prepared by adsorption, all the polymer chains were strongly attached to the silica surface through electrostatic attraction, whereas in the spin-coated surfaces only the lowest layer of polymer chains was attached

Table 3

Thickness of the polymer layers approximated from the AFM scratch experiments. For rough surfaces, the extreme values are presented.

	Layer thickness (nm), spin-coated	Layer thickness (nm), adsorbed
B1(D ₇₆ M ₁₇)	25	0–7
B3(QD ₇₆ M ₁₇)	10	Not available ^a
B4(QD ₆₁ M ₇₉)	20	0–5
B5(QD ₆₆ B ₇₆)	30	0–6
C1(QD ₆₀ M ₆₂)	20	3

^a No visible scratch mark.

to the surface and the top-most chains were free. Therefore, we expect that when the spin-coated surfaces are in contact with water, polymer chains or aggregates are able to dissolve. This would explain the rapidly dropping contact angle values as the measurement proceeded. The dissolved surface active polymer chains also lower the air-liquid interfacial tension of the measurement droplet, which could further decrease the contact angles. In addition, since spin coating is a rapid and forced deposition method, it is expected that the aqueous conformation of the polymer was retained on the surface, which exposed the most hydrophilic units of the polymer chain, further increasing the hydrophilicity of the surfaces.

By contrast, the adsorbed surfaces contained only chains firmly attached to the surface. Thus, dissolution or even significant readjustment of the chains was not possible during contact with the water droplet. Furthermore, it is expected that the aqueous wettability of the surface was decreased by the partial neutralization of charge between the polymer and the surface. We can conclude that in order to decrease the aqueous wettability of a hydrophilic surface significantly with water-soluble polyelectrolytes, the formation of a monolayer of polymer chains or aggregates is highly beneficial.

To further compare the properties of spin-coated and adsorbed surfaces, the spin-coated C1(QD₆₀M₆₂) and B5(QD₆₆B₇₆) surfaces, as an example, were immersed in water for 10 min and rinsed thoroughly. The water contact angles of the surfaces were measured before and after rinsing and the results are shown in Fig. 8. Before rinsing, the contact angles dropped rapidly to highly hydrophilic values, as described already in Fig. 5a, but after rinsing the values were rather stable and more hydrophobic. The difference is expected to derive from desorption of such polymer chains in the rinsing process, which were not electrostatically attached to the surface. This resulted in films consisting of only tightly attached polymer, as in the case of surfaces prepared through adsorption and rinsing (Fig. 5b).

The exact contact angle values between surfaces prepared by adsorption (with rinsing) or spin coating (with rinsing) were not the same, especially in the other example case, B5(QD₆₆B₇₆). After adsorption process, the water contact angle of B5(QD₆₆B₇₆) film stabilized to a value 58° during the measurement (Fig. 5b), whereas after spin coating and rinsing process the corresponding contact angle was 82° (Fig. 8), with even higher values obtained at the beginning of the measurement. The differences are expected to derive from the conditions of preparation: in the adsorption process the surface formation depends on the equilibrium formed on the solid-liquid interface, whereas spin coating is a forced process. To investigate the differences between the B5(QD₆₆B₇₆) films, we analyzed the films by AFM. The AFM images are presented in Fig. 9. The surface prepared by spin coating was significantly rougher than the surface prepared by adsorption, as apparent in Fig. 9, where both the AFM images are presented in the same scale. The surface prepared by spin coating and rinsing was also covered to a larger extent. It can be concluded, that different surface preparation methods may result in differences in wetting behavior, even if monolayers are formed.

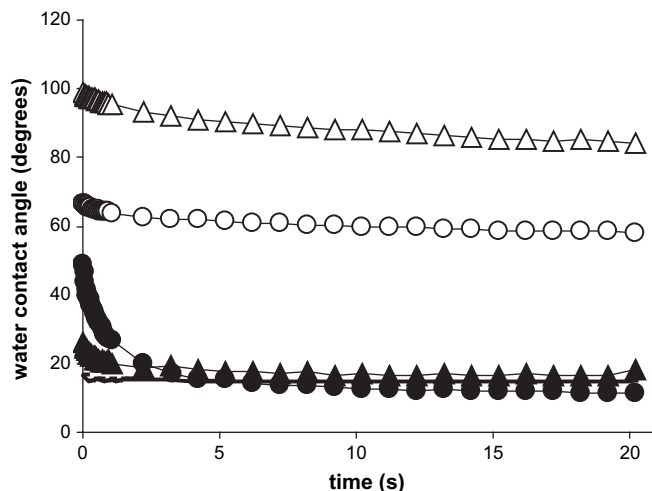


Fig. 8. Water contact angles of C1(QD₆₀M₆₂) and B5(QD₆₆B₇₆) surfaces prepared by spin coating, before and after rinsing. In the rinsing procedure, the surface was first rinsed with water, then immersed in water for 10 min, and finally rinsed again. ● C1(QD₆₀M₆₂), before rinsing. ○ C1(QD₆₀M₆₂), after rinsing. ▲ B5(QD₆₆B₇₆), before rinsing. △ B5(QD₆₆B₇₆), after rinsing. — silica reference.

When studying the differences between the contact angles of adsorbed samples with different polymer compositions, it can be seen, that the non-quaternized homopolymer D1 surface and non-quaternized block copolymer B1(D₇₆M₁₇) surface had equal contact angles, 47–54°, when taking account the error limits of the measurement. In the case of the quaternized samples, which were more amphiphilic in character, the homopolymer had a lower contact angle value, 31°, than the copolymers. The quaternized PMMA copolymers were equal within the error limits of the measurement, between 42–46°. The PBMA copolymer had the highest contact angle, 58°.

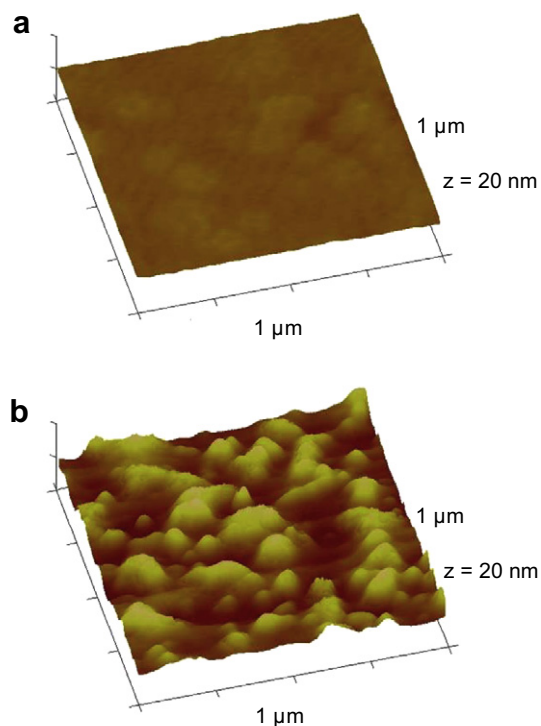


Fig. 9. AFM images of B5(QD₆₆B₇₆) prepared by (a) adsorption and rinsing (b) spin coating and rinsing.

When comparing these values to the polymer composition parameters, which were set under study in the design of the polymer series, we can conclude, that quaternization led to slightly more hydrophilic surfaces, whereas increasing the hydrophobicity of the hydrophobic block led to slightly more hydrophobic surfaces. In many cases, the differences were relatively small. The statistical and block copolymer samples of equal METAI/MMA ratio had equal contact angles, indicating that at least in this study the architecture of the polymer was not significant when considering the wettability of the adsorbed surfaces. For the surfaces prepared by adsorption, the contact angle values measured were lower than would be expected for pure PMMA or PBMA, which have been measured as 70° and 85°, respectively [34]. Annealing at high temperatures could further increase the hydrophobicity of the surfaces by increasingly exposing the hydrophobic monomer units towards air, and studies with annealed surfaces are currently conducted in our groups.

4. Conclusions

Amphiphilic polyelectrolytes applied from aqueous environment as ultra-thin films were studied for their potential in modifying the wettability of electrostatically charged surfaces. A polymer series consisting of non-quaternized and quaternized PDMAEMA homopolymers and block and statistical copolymers with PMMA and PBMA was synthesized. The polymers were dissolved directly in water, and varying structures were observed; unimers, equilibrium micelles and frozen micelles. These solutions were applied on silica surfaces by either spin coating or adsorption. Varying surface structures were observed by AFM. The water contact angles of spin-coated surfaces were unstable and decreased as a function of measurement time, and finally reached highly hydrophilic values. The adsorbed surfaces were less hydrophilic and the water contact angles were relatively stable as a function of time. We attribute the differences between the spin-coated and adsorbed surfaces to different surface structures; the adsorbed surfaces were monolayers of adsorbed unimers or aggregates firmly attached to the surface through electrostatic attraction, whereas spin-coated surfaces were thicker films where the top-most layer was free to readjust and dissolve. After the spin-coated surfaces were thoroughly rinsed, they exhibited stable water contact angles. We conclude that in order to get significant hydrophobization with water-soluble polyelectrolytes, the formation of monolayer is highly beneficial.

In the comparisons between the surfaces prepared by adsorption, we observed different contact angle values with different polymer compositions. To further increase the hydrophobizing effect of such systems, annealing at high temperatures in order to arrange the more hydrophobic groups to the top layer could be beneficial. The hydrophobicity of the modified surfaces could also

be increased by increasing the hydrophobicity of the hydrophobic monomer unit in the polymer structure. In addition, it might be beneficial to dissolve the polymers in a more controlled manner. Such studies are under way and they are the topic of a following paper.

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