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Thermoresponsive surfaces by spin-coating of PNIPAM-*co*-PAA microgels: A combined AFM and ellipsometry study

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Abstract

Thermosensitive coatings are fabricated by spin-coating of microgels consisting of the cross-linked copolymer poly(*N*-isopropyl acrylamide-*co*-acrylic acid) (P(NIPAM-*co*-AA)) on silicon wafers. The microgels were synthesized with two different cross-linker molar ratios and the thin films were prepared at pH 2. At this pH the particles are negatively charged only due to the starter used for the polymerization. Scanning force microscopic (AFM) images indicate a dense packing of the particles and a strong flattening in the adsorbed state. This effect is stronger for microgels containing less cross-linker. Coatings consisting of these microgel particles show a reversible thermoresponsive swelling/shrinking in the region of the lower critical solution temperature (LCST) of NIPAM. For the ellipsometric study of this process a standard setup was modified in order to allow temperature dependent measurements of the optical thickness in a liquid cell. The temperature induced transition is sharper in the case of microgels with lower amount of cross-linker and smears out with increasing amount of cross-linker. No significant desorption of the particles occurs at pH 2, which was shown by AFM of the dried films before and after the ellipsometric measurements. In the dry state the average thickness of the prepared films is approximately 30 nm and a thickness of about 400 nm is reached in the swollen state.

Keywords: Microgel; Responsive material; Surface coating

1. Introduction

Smart surfaces and surface coatings are of great importance in a lot of applications like e.g. in enhanced water repellency [1,2] or sensors [3]. Therefore, a growing number of publications on this subject can be found in the literature.

The present work introduces a new approach for the preparation of thermoresponsive surfaces. Here, we focus on the thermoresponsive surface coatings having e.g. tunable reflectivities or thicknesses by simply changing the temperature. A rather straightforward approach for realizing such surfaces is the use of coatings based on polymers exhibiting a lower critical solution temperature (LCST). A well known polymer with this property is poly(*N*-isopropyl acrylamide) (PNIPAM) and also copolymers containing NIPAM blocks. Responsive surface layers were already prepared with this material using the rather demanding technique of plasma polymerization [4].

It would be very appealing to achieve this kind of surface coating by simple self-assembly approaches. In order to obtain PNIPAM based thermosensitive surface coatings anionic diblock copolymers of PNIPAM and polystyrene sulfonate (PSS) and polycations were adsorbed alternately on solid substrates [5,6] applying the so-called layer-by-layer method [7]. However, using this approach the obtained change in thickness was small (below 10%) and more importantly irreversible, which rules out to use this kind of surface for sensoric applications.

As a reason for the only small deswelling effect and its irreversibility the strong interdigitation between polycations and

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polyanions in these thin films was assumed. A conclusion from this work was to separate the thermosensitive part of the structure from the stabilizing "matrix" in future work. A possibility to have small fast-reacting thermosensitive regions is offered by embedding PNIPAM microgels in a polymer matrix [8,9] or to form the whole coating of microgel particles [10–12]. In these studies copolymer microgels containing chargeable groups were used to increase the adsorption by means of electrostatic interaction. Several PNIPAM copolymer particles with mainly COOH containing co-monomers were already synthesized [13–18].

Recently, the influence of a solid interface on the volume transition of a single ionic PNIPAM copolymer microgel particle was studied by in situ AFM measurements [19,20]. In these works it was found that even in the adsorbed state the temperature induced volume transition of the microgels is reversible and the magnitude of the size change is still sufficiently large to use attached particles as actuators or to sense their environment. This also corresponds to the findings by Vincent and co-workers for microgel films obtained by dip coating [10].

PNIPAM microgels are colloidal particles consisting of a swollen polymer network internally. The network can be swollen with water or other polar solvents. The great interest in microgels made of *N*-isopropyl acrylamide (NIPAM) stems from their responsive characters giving them potential with respect to a large variety of advanced applications [21,22]. Moreover, they combine properties of colloids (e.g. crystallization [23–25] or glass formation [23]) with the properties of smart responsive polymer systems. A majority of the publications on this subject focus on their response upon changes in temperature [23,26–32] but some works also treat size changes of these particles induced by changes of pH [13,14,16,17], ionic strength [13,16,33], or solvent quality [34]. The internal structure of these smart particles was already studied in several small-angle neutron scattering studies [32,35–37] and by neutron spin-echo spectroscopy [38].

Also core–shell structures with a styrene core and responsive shell of PNIPAM [36,39–41] or with two different polymers both comprising a volume phase transition [42] were already synthesized.

In industrial applications PNIPAM microgels are already used e.g. to modify the surface properties of paper. Further future applications of PNIPAM are removal of heavy metal ions from waste water [43], in microgel controlled catalysis [44] and new optical materials [45–48].

Given the finding that microgels still swell and collapse in a reversible way when attached to a surface and given the large variety of properties, which can be realized with these particles, it seems to be straightforward to use microgels for the preparation of thermoresponsive surface coatings. However, the layer-by-layer technique (lbl) was already applied to microgels but led to a rather low surface coverage in one case [8]. In another work using this dip coating approach a very high coverage was obtained [10]. Simple drying of microgel suspension on a solid substrate also leads to high coverage [12], but the process is not well controlled and also formation of multilayers is possible.

In the present work an easy way to achieve good control of the film formation and at the same time high coverage by spin-coating will be presented. The approach is similar to the one used in Ref. [9]. The obtained microgel layers are characterized by atomic force microscopy in the dry state and by ellipsometry when covered with water.

2. Experimental section

2.1. Synthesis

The microgel synthesis was done in a conventional precipitation polymerization as described elsewhere [51]. After dissolving 55 mmol NIPAM, a mixture of 500 ml de-ionized water (MILLI-Q) and 5.5 mmol BIS (BIS 10%) and 1.1 mmol BIS (BIS 2%) was added followed by heating to 70 °C under nitrogen atmosphere. Then, 40 mg of potassium persulfate dissolved in 1 ml water was added to start the polymerization. The reaction proceeded for 24 h at constant temperature. Thereafter, the microgel suspension was cooled down slowly to room temperature (4 h) under continuous stirring. The final step of the preparation comprises extensive washing of 250 ml of the reaction solution in an ultra-filtration cell (Millipore, 350 ml) using a cellulose acetate filter (Satorius, pore size 0.45 μm). In each washing cycle 300 ml water was added and almost completely removed. Some of the water inevitably remained in the hydrogel particles. For the last two washing cycles the conductivity of the out-flowing water was constant at 3 μS/m. After carrying out five washing cycles in total, the particles' suspension is freeze dried (Yield: ≈85%).

2.2. Dynamic light scattering (PCS)

Intensity time auto-correlation functions were recorded at a constant scattering angle of 90° using an ALV goniometer setup with an Nd:YAG laser as light source (wavelengths $\lambda = 532$ nm). The output power was 150 mW, constantly. Measurements were done at different temperatures in a temperature range between 20 °C and 40 °C controlled by a thermostated toluene bath. The correlation functions were generated using an ALV-5000/E multiple τ digital correlator and subsequently analyzed by inverse Laplace transformation (CONTIN [52]).

2.3. Spin-coating

The microgel layers were prepared using a standard spin-coater. About 200 μl of a microgel suspension (0.5 wt%, adjusted to pH 2 using conc. HCl) was dispensed on the wafer (1 × 1 cm; at zero rotation), followed by spinning up to a rate of 1000 rpm. After the wafer was left spinning for 5 min the liquid is completely evaporated and the particles are regularly deposited on the substrate.

2.4. AFM

AFM imaging of the dry microgel layers was performed in air on a NanoScope IIIa instrument (Veeco Instruments, Santa

Barbara, CA) in tapping mode. Commercial silicon probes were used with a nominal force constant of 42 N/m at a resonance frequency of about 330 kHz (PPP-NCHR, Nanosensors, Switzerland).

2.5. Ellipsometry

An Optrel Multiskop Ellipsometer (Optrel, Berlin, Germany), which has been extensively described elsewhere [53], was modified to allow for measurements in liquid (see Fig. 1) as described by Benjamins et al. [54]. Windows mounted at the end of the laser and detector arm were adjusted in such a way that the beam goes through the air–quartz–water interface at an angle of 90°. In this configuration the ellipsometric measurement is not biased by the transition of the beam from air to water. The windows possess an anti-reflection coating to reduce errors due to multi-beam reflections. To avoid birefringence due to mechanical stresses a rubber ring was placed in the window fittings.

The error of the setup was determined by measuring the two ellipsometric parameters Δ and Ψ for an oxide layer on silicon of known thickness. Over the whole range of temperatures the deviation of the parameters from the ideal value did not exceed 0.2° and 0.4° for Ψ and Δ, respectively. A stainless steel measuring cell with a length of 80 mm and a width of 13 mm allows measurements in an angle of incidence (Φ_{in}) interval of $30° < \Phi < 64°$. To allow temperature variation of the liquid cell we used external Peltier elements connected to a Eurotherm 2408 programmable controller, capable to regulate the temperature within ±0.1 K. A temperature ramp was used between 20 °C and 42 °C at a rate of 0.5 °C/min. The temperature was read by a PT100 temperature sensor positioned directly in the liquid (see Fig. 1). In order to prevent temperature differences between sample and liquid the sample is placed on two Teflon bars, with the aim of avoiding direct contact to the bottom of the cell where most of the heat is exchanged. Aluminum foil was used as a heat conductor to heat and cool the liquid cell more evenly. The foil connects the Peltier module and the walls of the liquid cell. This reduces convection of the liquid in the cell, which would be caused by strong temperature gradients in the cell.

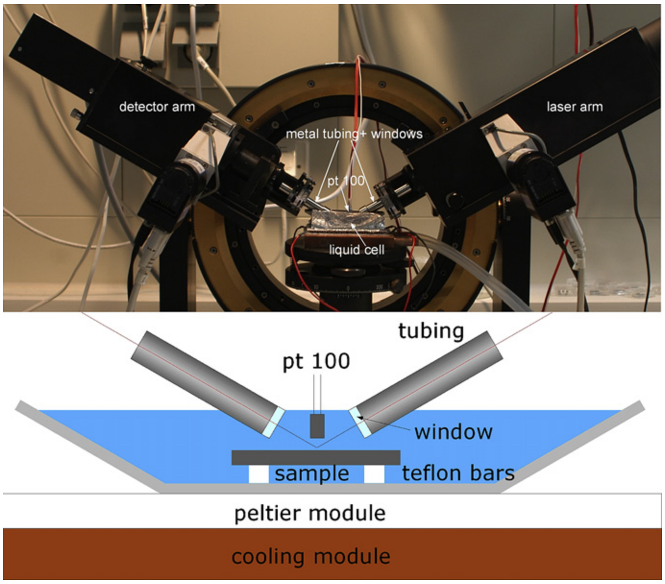

Fig. 1. Photograph and scheme of the ellipsometric setup used. In comparison to conventional setups the laser light is going through tubes immersed in the liquid above the microgel layer. This kind of setup was introduced by Benjamins et al. [54] and avoids problems with the refractive index of the entrance windows of a conventional liquid cell. Temperature control is achieved using a Peltier system.

3. Results and discussion

Two types of copolymer microgels were synthesized using precipitation polymerization. In the first synthesis 2 mol% of the cross-linker BIS was used, whereas the second particle type contains 10 mol% BIS, nominally.

Both contained 5 mol% of acrylic acid as comonomer. This allows to control the charge of the particles by changing the pH value. All temperature dependent experiments were performed at pH 2. This means that all carboxy groups of the acrylic acid comonomer are protonated and the particles only have some surface charges introduced by the initiator during the synthesis (surface potential -0.5 ± 1 mV).

3.1. PNIPAM-co-AAC microgels in bulk solution

The swelling curves of the two investigated types of microgel as shown in Fig. 2 were obtained using photon correlation spectroscopy (PCS) at a fixed scattering angle of 90°. It was possible to fit the intensity time auto-correlation functions with single exponential functions. This already indicates the low polydispersity of the synthesized microgels. However, the data given in Fig. 2 are based on the relaxation rates obtained by Laplace inversion of the functions.

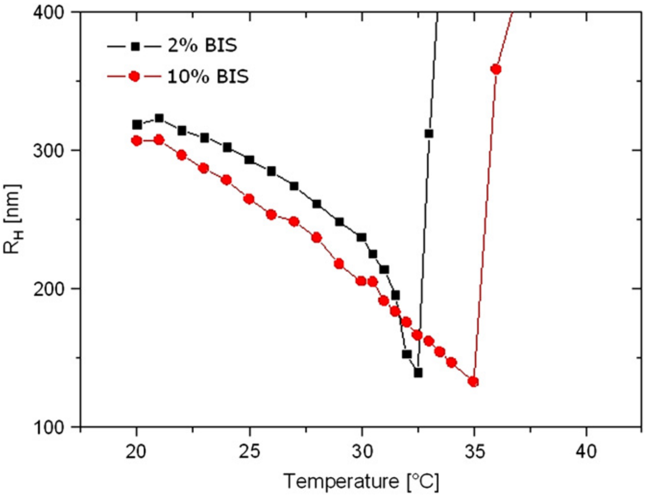

Fig. 2. Swelling curves of the investigated microgels measured at pH 2 using photon correlation spectroscopy (scattering angle = 90°). Due to the low pH the COOH groups of the acrylic acid are fully protonated and hence, beyond the LCST the microgel particles partly lose their colloidal stability and start to form large aggregates.

The observed swelling behavior in the present work is similar to the swelling behavior found in previous works on PNIPAM-*co*-poly(acrylic acid) [13–16,49].

Also in some of these works the copolymer microgels were studied at low pH. Under these conditions the particles were found to reversibly form aggregates in bulk solution at temperatures beyond the LCST of NIPAM. Only for intermediate pH values no aggregation occurs since then the collapsed particles are still stabilized electrostatically due to the under these conditions charged COOH groups.

3.2. Thin films of PNIPAM-co-AAc microgels

3.2.1. Dry state

A straightforward way to prepare thin layers on solid substrates is spin-coating. Since the synthesized microgels were negatively charged it was necessary to use a positively charged substrate. This can be achieved using the deposition of hyperbranched polyethylene imine (PEI) on a silicon substrate. The PEI layer also leads to an increase of the surface roughness and allows for the formation of entanglements with the dangling ends on the microgel surface. On these coated Si wafers the microgel suspension was then spin-coated leading to densely packed microgel monolayers on top of the PEI covered wafer.

In the present work PNIPAM-*co*-poly(acrylic acid) particles were used because at higher pH these particles were expected to have a stronger attractive interaction with the substrate. However, finally only the behavior at pH 2 is of interest, since the prepared films were found to be stable only at this pH. This is shown in Fig. 3. At the pH of de-ionized water (approx. pH 5) and above the films are unstable and more than half of the material is desorbed. This is different compared the observations reported by Vincent and co-workers where also PNIPAM-*co*-poly(acrylic acid) copolymer particles were used [10]. In the case of the spin-coated films investigated here the increasing repulsion between the like charged particles, which grows with pH leads to desorption when the produced films are placed into solutions with higher pH values. Hence, the binding of layers obtained by dip coating apparently seems to be stronger compared to spin-coated ones.

In Fig. 4 AFM images of the prepared surfaces used for the ellipsometric experiments are shown. The images were obtained by scanning the dried microgel coated wafers in tapping mode. In both cases shown nearly densely packed monolayers of PNIPAM-*co*-poly(acrylic acid) were obtained. The averaged thickness of the microgel layers in the dry state was studied using a standard ellipsometric setup and was found to be 28 nm for the microgel with 2 mol% cross-linker and 30 nm for the microgel synthesized with 10 mol% cross-linker.

Related to the diameter of the used laser beam ellipsometric averages over an area of approximately 1 mm^2, which is by three orders of magnitude larger compared to the area investigated by AFM (shown in Fig. 4), the average height of the dry microgel particles is found to be between 60 nm and 100 nm for the two samples. This is significantly lower compared to the hydrodynamic diameter of the particles as measured with PCS, which is between 600 nm and 640 nm for the two types of particles. This is different compared to the work by Vincent and co-workers who reported a film thickness in the dry state for dip coated films which was still 25–30% of the diameter in the swollen state in solution [10]. Since the used particles are very similar in both studies, this might indicate that spin-coating produces real monolayers and dip coating might lead to double layer formation. However, this point still has to be further elucidated. The lateral dimension of the dry microgels is found to be of the order of 500 nm. Hence, shrinking mainly occurs perpendicular to the surface and not in the lateral

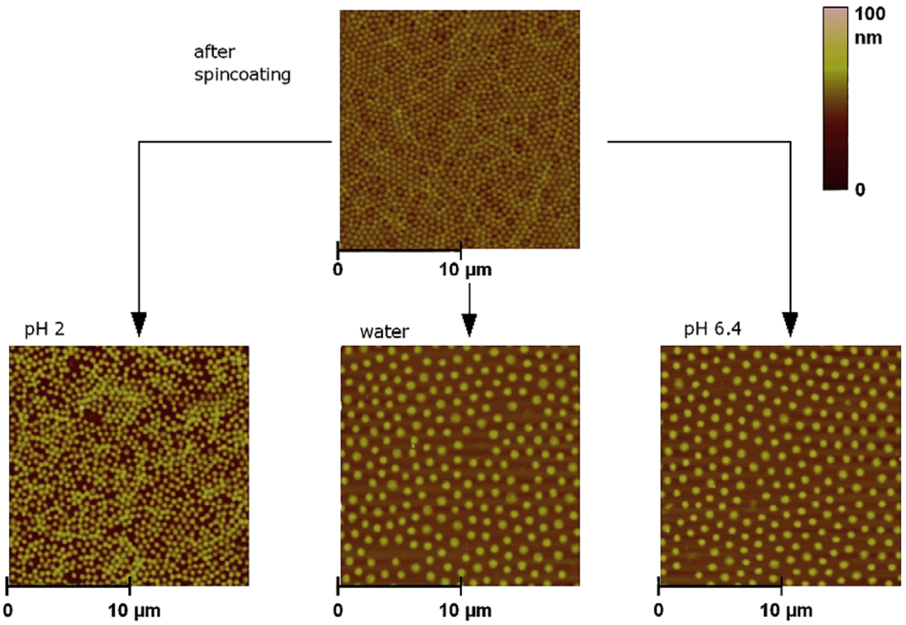

Fig. 3. AFM images of the films obtained by spin-coating after exposure to aqueous buffer solutions. The films are stable when immersed in water at low pH. However, in contrast to the findings by Vincent et al. [10] the microgel particles are desorbed from the surface at higher pH values.

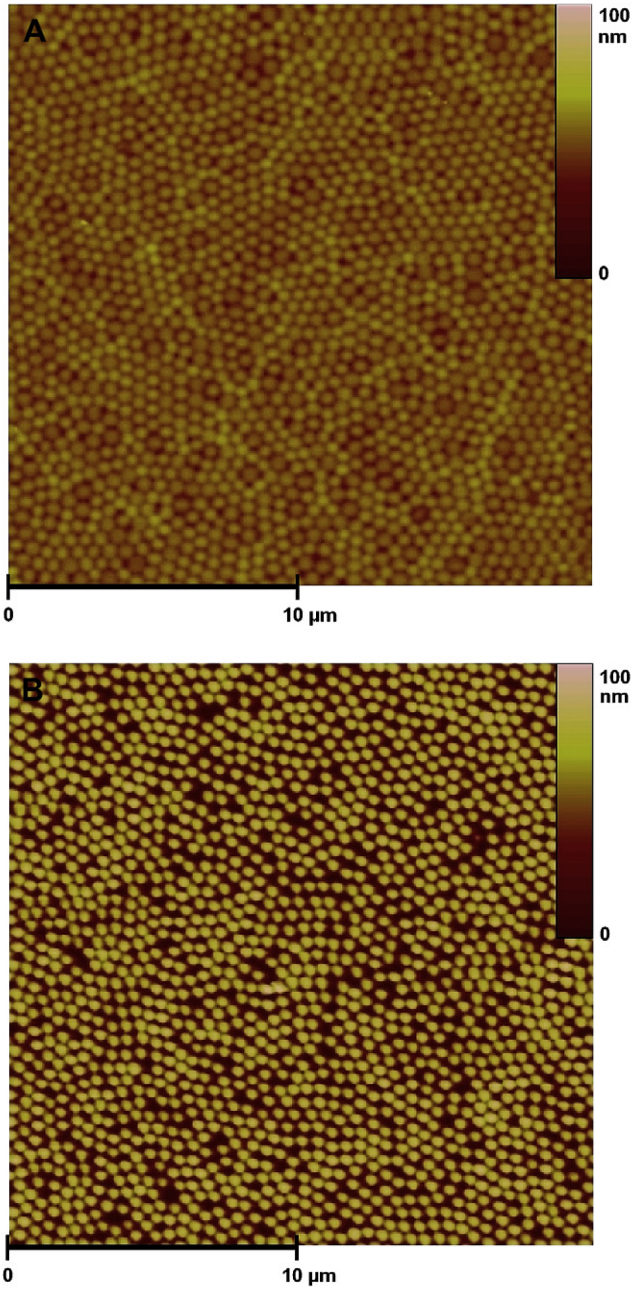

Fig. 4. AFM images of two different microgel coatings in the dry state before the ellipsometric experiments. Both types of microgels contain the same amount of acrylic acid co-monomers but different amounts of cross-linker ((A) 2% and (B) 10%). The images were obtained by scanning the dried wafers in tapping mode. The diameter of the deposited particles is about 500 nm in the case of the 2% BIS particles. This means that the microgels adopt a very flat form at the interface when dry.

direction. The same phenomenon was observed in an AFM study of single PNIPAM-*co*-poly(vinyl acetic acid) particles [19] and in a recent work by Lyon and Sorrell [9]. Obviously, the adsorption is rather strong and prevents in plane shrinkage. This is also in agreement with the results for dip coated layers [10].

3.2.2. Wet state

Ellipsometry also is an ideal tool for the determination of the thickness of a swollen microgel layer [50] when a liquid cell is used. When the cell has a precise temperature control also the temperature induced changes of the thickness can be followed with this technique. The coated wafers were placed into a water (pH 2) filled liquid cell (see Scheme in Fig. 1) and the thickness was followed as a function of temperature. Figs. 5 and 6 show the experimental results for a coating with a microgel containing 2 mol% cross-linker and for a second coating with a microgel containing 10 mol% cross-linker.

The thickness of both films changes nearly reversibly as a function of temperature and the obtained thickness vs. temperature curves are very similar to the bulk swelling curves found for several PNIPAM based systems [13,23,16,30]. Only small hysteresis effects occur during the first heating/cooling cycle. This can be attributed to the effects arising from the dangling ends on the surface of the particles. Also the refractive index change reveals the collapse of the microgels (increasing refractive index due to the expulsion of the water). At low temperatures when the particles are fully swollen the refractive index of the microgels is very close to the value of water, since in this state the particles consist of up to 90% of water. Under these conditions ellipsometry is less precise and the found decrease of the radius below 24 °C is probably an artifact related to this.

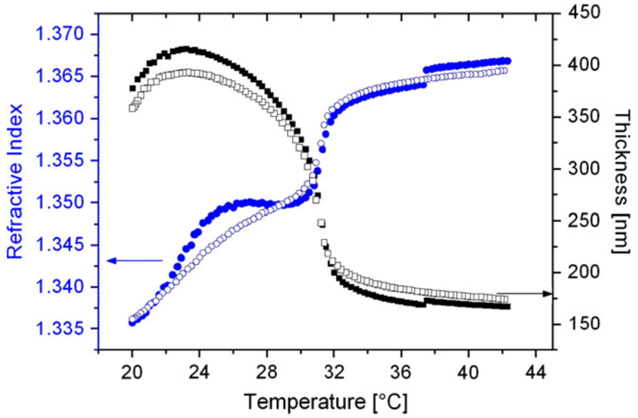

Fig. 5. Thickness vs. temperature and refractive index vs. temperature curves for the sample with 2% BIS.

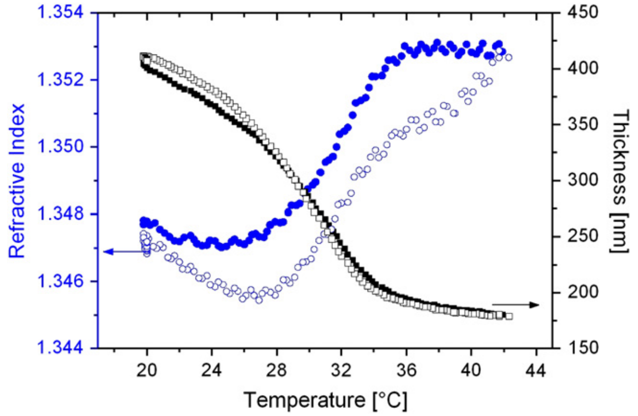

Fig. 6. Thickness vs. temperature and refractive index vs. temperature curves for the sample with 10% BIS. Full symbols indicate the heating curves and empty symbols stand for the data obtained during cooling.

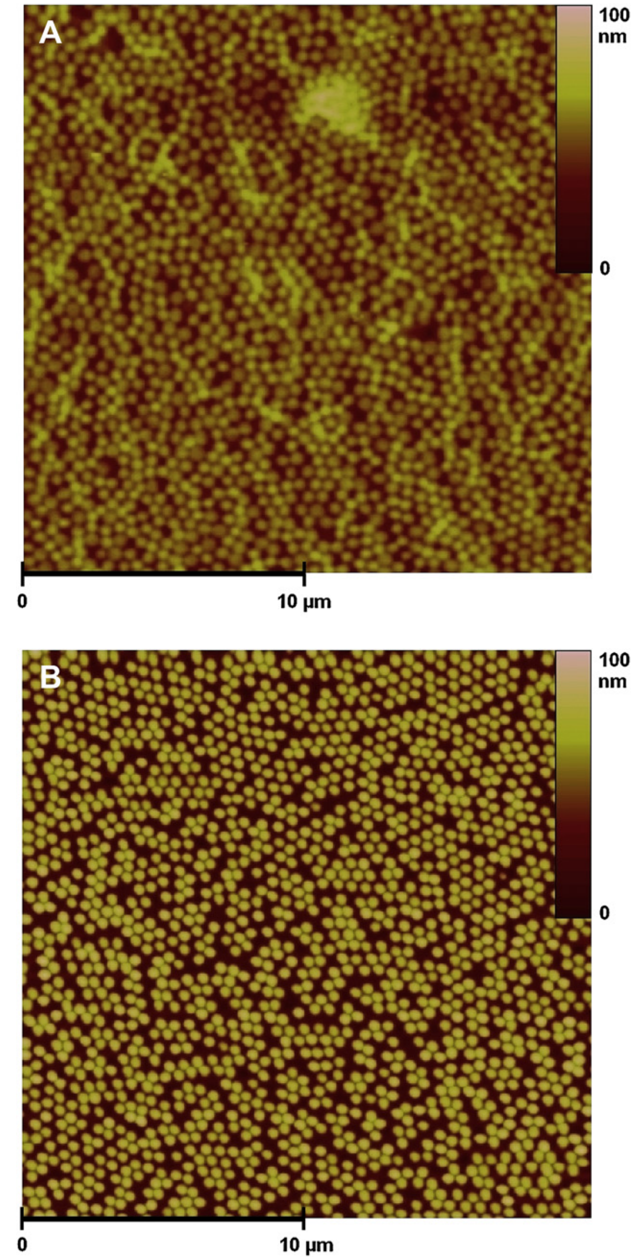

Fig. 7. AFM images of the two investigated microgel coatings in the dry state after performing the ellipsometric experiments. Compared to the images taken before the experiments only minor changes can be observed. Especially for the microgel with the higher content of cross-linker ((A) 2% and (B) 10%) no desorption occurs in the liquid cell of the ellipsometer. The images were obtained by scanning the dried wafers in tapping mode.

It is interesting that the higher cross-linker concentration leads to a broadening of the temperature interval where the transition in film thickness is observed. This is similar to the bulk behavior found for differently cross-linked microgels [30].

In bulk solution with increasing cross-linker content of the microgel the transition temperature is less well defined and the decrease in size is less steep.

The thickness decreases from about 400 nm to 165 nm for the microgel with 2 mol% cross-linker and from 420 nm to 180 nm for the sample with 10 mol% BIS.

After the ellipsometric experiments the microgel layers were dried and again examined with AFM. Only very small changes in packing were found (see images in Fig. 7) indicating that the layers are rather stable and nearly no desorption of microgel particles from the surface occurs when the layers are immersed in water during the ellipsometric experiments. In addition to the AFM experiments again standard ellipsometry was used to obtain the averaged thickness of the films in the dry state after the swelling/deswelling cycles. Within the experimental precision the same thickness values as for the freshly prepared films are found. This also clearly shows that no significant desorption occurs under the conditions chosen for the ellipsometric measurements.

4. Conclusion

Spin-coating offers the possibility to easily prepare nearly densely packed monolayers of PNIPAM based microgels of low surface charge. SEM images and ellipsometric data indicate a strong flattening of the microgels in the dry state at the substrate surface. The particles with a diameter of about 600 nm in solution (swollen state, determined with PCS) have a diameter of about 500 nm and a height of 60 nm in the dry state after adsorption. This flattening seems to be less pronounced in the case of microgels with a higher amount of cross-linker. Against water the microgel films have an average thickness of 400 nm. This means that they swell by approximately a factor of 7–10 perpendicular to the surface. Since the films were already tightly packed in the dry state, it is assumed that the swelling in lateral direction is partially suppressed and perhaps a lateral deformation takes place due to a tight contact between the particles.

Using a modified ellipsometer setup it was possible to show that these layers still respond to changes in temperature despite of confinement effects due to the adsorbed state. The reversible response indicates that no aggregation of the particles takes place above the LCST in contrast to microgels in solution. The aggregation in solution around the LCST makes a direct comparison of the amount of swelling/shrinking in solution and at the substrate surface impossible. The ellipsometric data might indicate a small shift (about 1 °C) of the transition temperature of the adsorbed particles compared to the bulk behavior. However, this effect remains to be studied more carefully.

Up to the LCST, the shrinkage behavior is the same in solution and after adsorption. The microgels containing 2 mol% of cross-linker show a sharp volume phase transition, while the increase to 10 mol% of cross-linker leads to a broadening of the volume transition. This might be caused by a larger inhomogeneity of the microgels due to the inhomogeneous distribution of the cross-linker within the microgels, which becomes more obvious at higher cross-linker content.

In the future the present work will be extended with respect to influences of the ionic strength and of the pH value on the layer thickness of spin-coated microgel films.

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