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Stability and Cell Adhesion Properties of Poly(*N*-isopropylacrylamide) Brushes with Variable Grafting Densities

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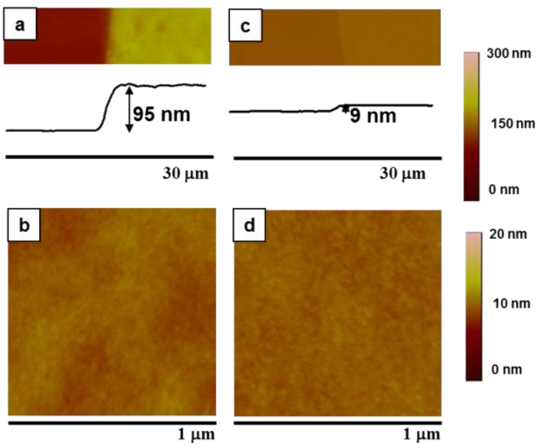

Fig. s1. Thickness images and surface morphologies of PNIPAM brushes (a, b) freshly prepared TB-MD brush and (c, d) freshly prepared TB-LD brush.

Analysis of ellipsometry spectra

The ellipsometry spectra, i.e. Ψ and Δ as a function of wavelength (275-827nm) at an incident angle of θ=63° (Fig. s2), were analyzed employing the package CompleteEASE (Woollam), using bulk dielectric functions for silicon, silicon dioxide and water.[54] The substrate is in all cases considered to consist of silicon with a 1.70nm thick silicon dioxide film.

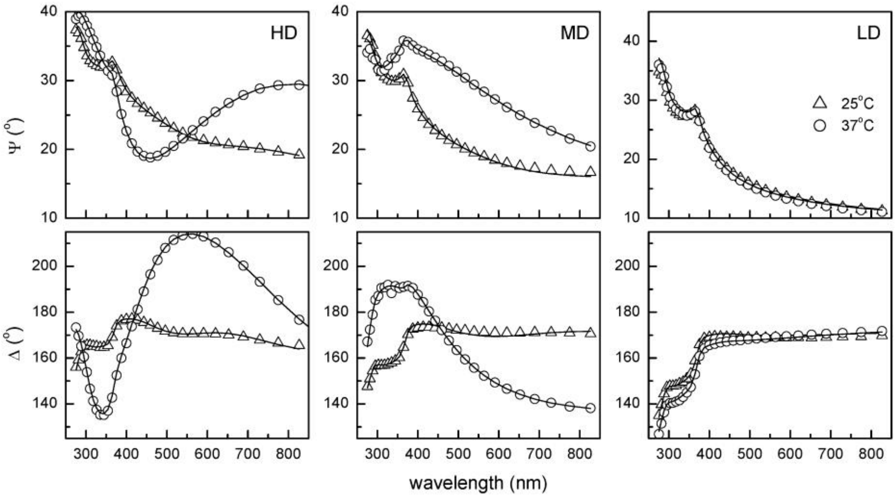

Fig. s2. Ellipsometry spectra for three different grafting densities (HD, MD and LD) at 25°C (triangles) and 37°C (circles). Solid lines represent fit results as discussed in the text.

For all spectra, the refractive index of the thin PNIPAM film is parameterized by the Cauchy dispersion relation given by

$$\lambda = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}$$

in which the wavelength λ is in microns. The quantities A, B and C represent fit parameters. In the analysis of our experimental spectra, we set C=0 since it does not yield improved fit results and often gives rise to large correlations with other fit parameter. Furthermore, in all cases we assumed the PNIPAM to be fully transparent, i.e. the refractive index is a real quantity (the imaginary part describing optical absorption is neglected).

For dry films, a homogeneous layer provides a good description. The ambient was air, i.e. in the model a refractive index n=1 was taken. For the thicker films (HD, and MD) we used as fitting parameters the film thickness d, and the two Cauchy parameters A and B. The resulting fit parameters are summarized in Table I.

For the thinnest film (LD), it proved difficult to separate the refractive index contribution from that of the thickness. For these low film thickness values, optical reflection measurements are only sensitive to the product $n \cdot d$ of the refractive index and the thickness. Considering these as fit parameters results in undefined fits with a high correlation between A and d. As such, for the low grafting density brush we used an average of the Cauchy parameters of the thicker films and only fitted the thickness. The resulting value is included in Table 1.

The PNIPAM brushes in water at room temperature (25°C) exhibit considerable swelling. Correspondingly, their optical properties become very much diluted. To obtain acceptable fits, it was necessary to use a more complicated model in the analysis, taking into account a density gradient over the film thickness. The ambient is water in the model, represented by a wavelength-dependent refractive index as tabulated in literature.

For the high and medium grafting density films, a two-layer model was used to describe the optical response of the brush film. In this two-layer model, a dense film at the substrate side of the film was modelled with a thickness d_1 and Cauchy parameters A_1 and B_1. The outer part of the film (for the low grafting density the entire film) was modelled using a graded Cauchy film, with parameters d_2, A_2 and B_2 and an exponential grading of the A_2 parameter. The total film thickness d is the sum of d_1 and d_2.

The exponential grading of the parameter $A_2(z)$ as used in the analysis can represented by

$$A_2(z) = A_2\left(1 - \frac{\delta A}{2} + \delta A \cdot z^t\right)$$

where z is the relative position within the film (the substrate is at z=0, while z=1 corresponds to the outer interface of the film) and t and δA are fitting parameters. A negative value of the grading parameter δA corresponds to a decreasing density, i.e. lower refractive index for larger distances from the substrate.

The fit parameters summarized in Table 2 show that approximately 8-10% of the film is described by a homogeneous Cauchy dispersion. The rest of the film (referred to as the second layer) shows a decline of the refractive index to values very close to that of water with decreasing distance from the substrate. As already described above, the outer parts of the layer are diluted to such an extent that only a few PNIPAM brush-ends are surrounded by a large amount of water.

Similar to the difficulties with the dry samples, here there is also a problem with obtaining reliable fit results on the LD sample. The additional dense layer at the substrate is not required. The value of the exponent was also fixed. Using these values a relatively large gradient is observed, which may be related to the omission of a dense layer at the substrate side of the film.

Finally, the PNIPAM brush films immersed in water at 37°C were modelled by a Cauchy layer with a very limited grading over the film thickness. A linearly decaying gradient of less than 2% is needed to slightly improve the fit results as compared to a homogeneous Cauchy film. The resulting fit parameters are summarized in Table 3. Again, the optical properties of the thinnest LD film are fixed to obtain acceptable fits; only the thickness is varied.

Comparing the results of the collapsed PNIPAM brushes with the swollen films at lower temperatures reveals that indeed the thickness is much smaller, while the (optical) density is considerably higher. The thickness of the films collapsed at elevated temperatures is identical to those of the dry films. The optical density, i.e. the refractive index, is slightly lower than those of the dry films. We ascribe this to a slight impregnation of the collapsed films with water molecules.

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Table 1. Fit parameters for the optical modelling of dry PNIPAM films using a single homogeneous Cauchy layer. The values between brackets () were inserted into the model, but have not been varied in the fitting procedure.

	HD	MD	LD
d (nm)	245.5	103.1	8.73
A (μm^2)	1.453	1.467	(1.46)
B (μm^2)	0.00495	0.00621	(0.0055)

Table 2. Fit parameters for the optical modelling of PNIPAM films immersed in pure water at 25°C, using a two-layer model as described in the text. The values between brackets () were inserted into the model, but have not been varied in the fitting procedure.

	HD	MD	LD
d (nm)	901.5	567.4	35.5
d_1 (nm)	90.0	52.4	0.0
A_1 (μm^2)	1.416	1.389	-
B_1 (μm^2)	0.00529	0.00322	-
d_2 (nm)	811.5	515.0	35.5
A_2 (μm^2)	1.396	1.360	1.429
B_2 (μm^2)	0.00414	0.00467	(0.0)
δA (%)	-10.3	-5.79	-14.6
t	0.171	0.327	(0.3)

Table 3. Fit parameters for the optical modelling of PNIPAM films immersed in pure water at 37°C, using a graded Cauchy model as described in the text. The values between brackets () were inserted into the model, but have not been varied in the fitting procedure.

	HD	MD	LD
d (nm)	246.9	128.3	11.5
A_2 (μm^2)	1.436	1.440	(1.440)
B_2 (μm^2)	0.00555	0.00573	(0.00565)
δA (%)	-1.16	-1.38	(-1.25)