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# Contact Angle Microscopy on a Carbosilane Dendrimer with Hydroxyl End Groups: Method for Mesoscopic Characterization of the Surface Structure

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A carbosilane dendrimer containing hydroxyl terminal groups, which showed two types of wetting in dependence of the substrate used, was studied by tapping force microscopy. Due to the preferential adsorption of the hydroxyl groups, the dendrimer displayed autophobic spreading on mica, whereas a substrate which was first coated with a semifluorinated polymer was only partially wetted. In both cases, submicrometer-sized droplets were deposited on the surface. Microscopic contact angles were measured and compared with macroscopic values obtained by a standard sessile drop technique. The comparison showed lower values for the microscopic angle which were explained by deformation of the droplets caused by the tapping tip. The oscillatory motions of the tip intermittently touching a viscoelastic sample were calculated using a simple model of the tapping mode. The indentation of the tip into the sample and the induced phase shift relative to the oscillations in air were determined from the model, showing a good agreement with experimental results. Compared to traditional methods, this approach offers advantages such as (i) three-dimensional visualization of the whole droplet, (ii) submicrometer resolution of the structure near the three-phase boundary, and (iii) accurate determination of small contact angles.

## Introduction

Scanning force microscopy (SFM) has become a unique tool with which to examine surface structures down to atomic resolution.<sup>1</sup> Nowadays SFM combines a variety of methods which besides topography explore such diverse quantities as magnetic and electrical fields, local mechanical properties, colloidal forces, biological interactions, and chemical contrast.<sup>2-4</sup>

Among the different operational principles, tapping scanning force microscopy (TSFM)<sup>5</sup> and scanning polarized force microscopy<sup>6</sup> were developed to image soft samples and weakly adsorbed species. Complimentary to the visualization of the surface topography, TSFM can be used to investigate micromechanical properties of viscoelastic solids.<sup>7</sup> Furthermore, also bulk liquids can be probed by these techniques as a result of either long range electrostatic interactions<sup>8</sup> or mechanical stiffening of the liquid as it comes in contact with the oscillating tip.<sup>9</sup>

Recently, we have demonstrated the potential use of a tapping force microscope to monitor spreading of microscopic droplets of dendrimers on a solid surface.<sup>9</sup> Due to their extraordinary high degree of branching, dendrimers represent a particular class of polymers which possess a three-dimensionally developed molecular structure.<sup>10-12</sup> The colloidal size and topologically defined surface of dendrimers justify consideration of them as *molecular particles* which carry features of both molecules and particles.<sup>9,13,14</sup> Like colloidal particles, highly branched dendrimers interact by surface forces, and their interaction, which is proportional to the size, can exceed  $kT$  significantly.<sup>15</sup> However, depending on the branching density, the molecular surface can be either rigid and smooth or spatially diffuse and dynamically rough,<sup>13,14,16</sup> and therefore interaction of dendrimers with the environment depends on overlapping and the flexibility of the branches.

It is this particulate nature, the slow molecular relaxation and peculiar cohesion of dendrimers, which allows visualization of dendrimer liquids by tapping force microscopy. In the previous work, dendrimers with a relatively rigid globular structure and a molecular surface constructed of nonpolar, inert groups were investigated with regard to their spreading on mica, glass, and

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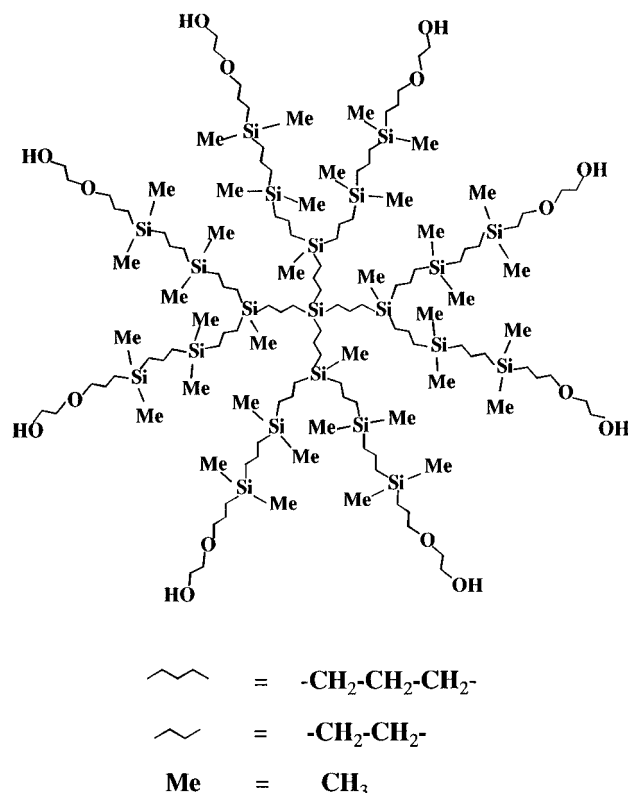
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graphite.<sup>9</sup> As these molecules did not exhibit any specific interactions but dispersion forces, the droplets slowly spread, yielding thin films independently of the type of substrate.

In this report we describe the wetting behavior of a dendrimer whose molecular surface is chemically incompatible with the interior part of the molecule. The scheme below shows the chemical structure of the dendrimer, which consists of a hydrophobic core surrounded by a shell of hydroxyl-terminated branches.



The molecules are expected to exhibit a certain amphiphilicity which is induced by rearrangements of their flexible branches upon adsorption on a solid surface. Due to the amphiphilic nature, wetting properties of the dendrimer will be determined by the chemical structure of the used substrate.

Due to the superior resolution and peculiar imaging contrast of TSFM, this technique may expand the scope of other methods used for visualization of the three-phase boundary.<sup>17–20</sup> It is attempted to measure microscopic contact angle and identify the fine structure near the contact line.

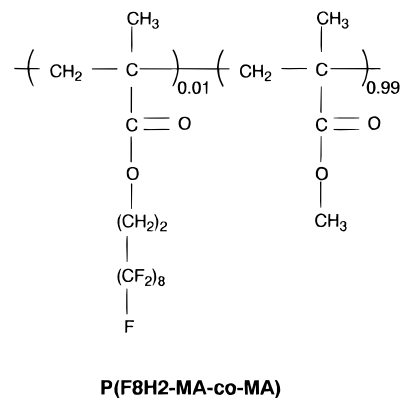
### Experimental Section

**Materials.** A carbosilane dendrimer with hydroxyl-terminated groups was prepared as described elsewhere.<sup>21</sup> First, using the divergent reaction scheme, a carbosilane core was synthesized which was subsequently clad with dimethyl(6-hydroxy-4-oxa-hexyl)silyl groups. The nominal molecular weight of the dendrimer was 2798.4 g/mol. At room temperature the material is a liquid which is characterized by a steady flow viscosity of 0.4 Pa·s.

**The dynamic shear compliance**  $J^* = J - iJ'$  was measured by a stress-controlled mechanical spectrometer.<sup>22</sup> A sample of the dendrimer was placed in a double-sandwich holder and forced to simple shear oscillation. The measurements were performed at different constant temperatures varying from  $-87$  to  $23$  °C over the frequency range from  $10^{-3}$  to  $10$  Hz. The obtained spectra were reduced to  $23$  °C to construct a master curve.

**The surface tension** of the dendrimer was measured by the Wilhelmy method using a Sigma-70 tensiometer (KSV Instruments, Helsinki). A gold plate with a perimeter of 21 mm was dipped into the pure liquid. The surface tension was derived from the force at the moment the plate was removed from the liquid.

**Scanning force microscopy** was done on samples which were prepared by spin casting at 2000 rpm. Dilute solutions of different concentrations ranging from 0.02 to 0.03 wt % in hexane were cast under ambient conditions on a freshly cleaved piece of mica. As a result, small droplets in a submicrometer range were deposited on the substrate surface. In some experiments, a copolymer of methyl methacrylate with 1% 6-(perfluorooctyl)-1-ethyl methacrylate was cast on mica to prepare a hydrophobic substrate. The chemical structure of the P(F8H2MA-co-MMA) copolymer is shown below. A 20 nm thick film of the copolymer was prepared under ambient conditions by spin casting at 2000 rpm from a 0.1 wt % solution in toluene.



Scanning force micrographs were measured by means of a Nanoscope III (Digital Instruments, St. Barbara, CA) operated in the tapping mode at a resonance frequency of  $\sim 290$  kHz. The measurements were performed under ambient conditions using Si probes with a spring constant of  $\sim 50$  N/m. The tip sharpness was calibrated by means of the well defined stepped structure of a  $\text{SrTiO}_3$  wafer consisting of alternating (103) and (101) planes.<sup>23</sup> A simple deconvolution procedure allowed us to select tips with an apex radius below 10 nm.

**The macroscopic contact angle** between the dendrimer/air interface and the solid surface was measured by means of the sessile drop technique (Krüss G40). The reported angles are the average values of 10 measurements from different droplets.

**Microscopic contact angles** were derived from a cross-sectional profile of the droplets measured by the scanning force microscope. The angle was measured directly between the substrate plane and the tangent to the droplet or by assuming a spherical shape of the droplet, for which the contact angle can be calculated as

$$\tan \frac{\theta}{2} = \frac{h}{R} \quad (1)$$

where  $h$  and  $R$  are the height and radius (Figure 1) of the droplet, respectively.

### Results and Discussion

**SFM Observations.** The system which will be considered here is a microscopic droplet of the hydroxyl

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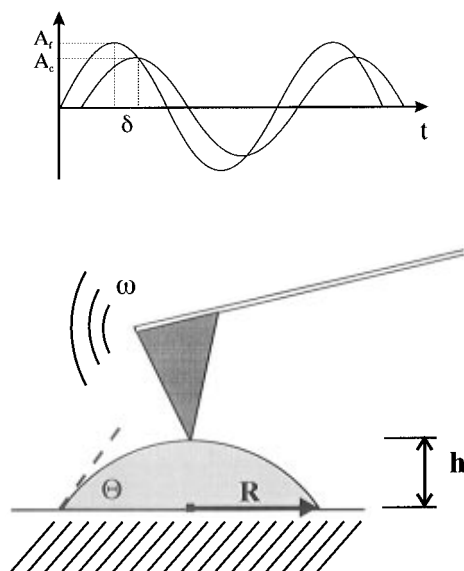
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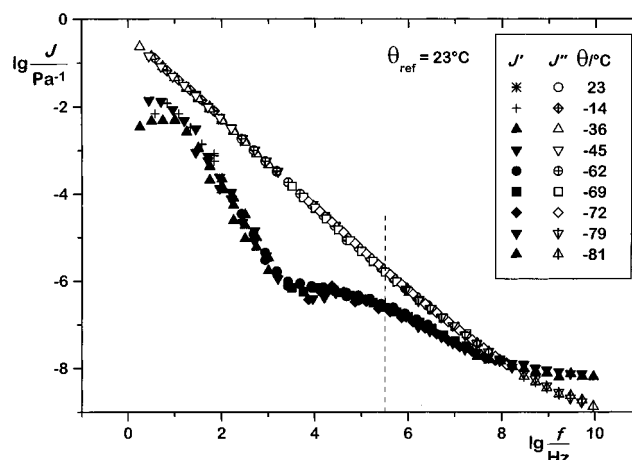


**Figure 1.** Schematic drawing of a tapping force microscope monitoring the microscopic contact angle  $\theta$  of a dendrimer droplet on a solid surface. The cantilever oscillates with a frequency  $\omega$  and intermittently touches the spherical droplet, which is given by the radius  $R$  and height  $h$ . The microscope registers two values as the tip touches the sample: the difference between the free amplitude  $A_f$  and the amplitude  $A_c$  in contact with the sample, and the phase shift  $\delta$  relatively to the oscillation in air.

dendrimer on a flat solid surface. We attempted to use a tapping force microscope to record the full shape of the droplet as it is schematically illustrated in Figure 1. The tapping mode imaging is implemented by oscillating the cantilever–tip assembly near its resonance frequency.<sup>5</sup> As the tip begins to touch the surface intermittently, the cantilever oscillation is perturbed. Two quantities, the reduction in amplitude and the phase shift, are used to visualize surface structure. If the interaction time, during which the tip is in contact with the droplet, is shorter than the characteristic relaxation times of the material, the droplet is expected to sustain the applied stress and preserve the equilibrium structure.

Although TSFM probes the micromechanical behavior of the droplet, which depends on the size and structure of the droplet, macroscopic properties can give valuable information on the expected response of the material. Therefore, the dynamic viscoelasticity of the dendrimer was investigated prior to the SFM experiments. Figure 2 shows two master curves which depict the dependence of the storage  $J'(\omega)$  and loss  $J''(\omega)$  shear compliances on the oscillation frequency  $\omega$  at 23 °C. In a low-frequency region, below  $10^3$  Hz, the dendrimer exhibited flow behavior, which was characterized by a  $-1$  slope of the loss compliance in the double-logarithmic plot. When the frequency was increased further, the compliance decreased and the flow zone was followed by a distinct plateau in  $J'$  between  $2 \times 10^3$  and  $4 \times 10^5$  Hz. Above the frequency  $2 \times 10^6$  Hz the sample underwent a diffused transition into a glassy state.

The plateau covers the frequency of the tip oscillation (290 kHz) which is marked by the dashed line in Figure 2. By making model calculations of the tapping mode, it will be shown further in this report that the stiffness of the dendrimer at the tapping frequency is sufficiently high to cause measurable changes in the amplitude of the oscillating cantilever. The latter represents a condition for scanning over the droplet surface without damaging the droplet with the tip.



**Figure 2.** Master curve of the shear compliance  $J^* = J' - iJ''$  reduced to 23 °C. The terminal compliance at low frequencies resulted partly from the surface tension of the carbosilane dendrimer. The dashed line gives the tapping frequency of the SFM tip.

Samples for SFM measurements were prepared by spin casting. After the solvent evaporated, optically invisible droplets remained on the surface. The droplets were uniformly distributed over the substrate, and their size was controlled by the concentration of the solution. By lowering the concentration, droplets could be obtained with sizes from hundreds down to tens of nanometers in diameter.

The preparation procedure represented actually a combination of adsorption from solution and casting the solute as the solvent evaporated. The drying process was followed by dewetting of the substrate as the solution layer became thinner below a certain equilibrium thickness.<sup>24</sup> After the solvent evaporated, the spreading of the nonvolatile dendrimer was determined by the spreading parameter  $S = \gamma_s - \gamma_{sl} - \gamma_l$  and the difference of two Hamaker constants  $A = A_{sl} - A_{ll}$ ,<sup>25</sup> where  $\gamma_s$  is the surface energy of the dry substrate,  $\gamma_{sl}$  is the solid/liquid interfacial energy, and  $\gamma_l$  is the surface tension of the dendrimer.

Partial wetting occurs when the liquid forms droplets with a finite contact angle on a dry solid. Neglecting long range interactions, the spreading parameter should be negative ( $S < 0$ ) to obtain droplets with a nonzero contact angle  $\theta$  defined by the Young equation  $\gamma_s = \gamma_{sl} + \gamma_l \cos \theta$ . Because  $S$  and  $A$  are independent variables and can be of either sign, contributions from short and long range interactions can cause so-called pseudo-partial-wetting for  $S > 0$  but  $A < 0$ .<sup>25</sup> In this case, the final state is a droplet surrounded by a thin film of a certain equilibrium thickness.

Spreading can also be prevented if the substrate surface is modified by adsorption of an oriented monolayer of the solute molecules, creating a new interface to the liquid with an unfavorable interaction energy. In this particular case, the liquid is unable to spread on its own adsorbed film, demonstrating so-called autophobic behavior.<sup>26,27</sup> Two cases, i.e. partial and autophobic wetting, will be considered in this paper.

**Autophobic Wetting of Mica.** Freshly cleaved mica is one of the most suitable substrates for wetting experiments because the resulting surface is hard, homogeneous, impermeable, and atomically flat. As the surface energy

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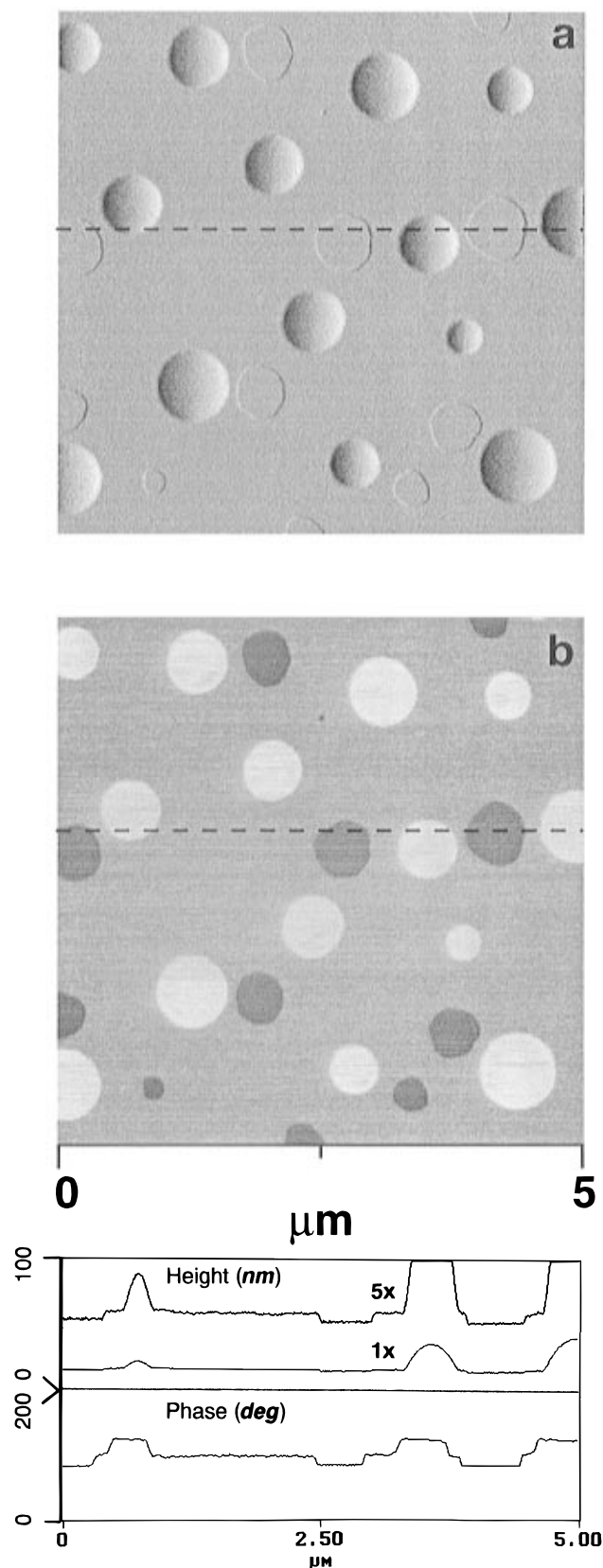
of mica of about  $300 \text{ mJ/m}^2$  (in air)<sup>28</sup> is much higher than the surface tensions of hexane ( $18.6 \text{ mN/m}$ ) and the dendrimer ( $29.3 \text{ mN/m}$ ), it satisfies the macroscopic condition for spreading ( $S > 0$ ). However, this did not occur, as is shown in Figure 3a, where one can see droplets on top of a thin layer adsorbed directly on the substrate. Besides the droplets, the image shows that the substrate is covered by a monolayer of adsorbed molecules which contains holes exposing the uncovered mica.

The thickness of the layer was measured to be about  $14 \text{ \AA}$  (Figure 3c), which was approximately half a hypothetical "hard core" diameter  $d_p = 25 \text{ \AA}$  of a single dendrimer with the bulk density  $0.9 \text{ g/cm}^3$  of a carbosilane. Apparently, the molecules lying on the surface are deformed. This and the formation of the droplets on the layer surface indicate that the adsorption of the dendrimer leads to a peculiar reorganization of the branched structure when the hydroxyl terminal groups are preferentially adsorbed on the mica, exposing a hydrocarbon core to the surface.<sup>29</sup> Such a rearrangement of the branches lowered the surface energy of the film relative to that of the bulk liquid and may be suggested as an explanation for the autophobic property of the dendrimer on mica.

The incomplete coverage of the mica surface might be due to the fact that actually both components of the solution adsorbed on the surface, one of which (hexane) evaporates and the other of which (dendrimer) dewets the surface of mica. The topographic interpretation was consistent with simultaneous measurements of the phase shift. The micrograph in Figure 3b clearly reveals three distinct regions which strongly differ in phase, i.e. (i) fluid droplets, (ii) a solid-like monolayer, and (iii) hard mica. A cross-sectional phase profile in Figure 3d shows a stepwise variation of the phase measuring  $39^\circ$  between the droplets and mica and  $26^\circ$  between the droplets and the monolayer. The relatively large phase shift of  $26^\circ$  gives another piece of evidence that the film represents a monolayer of the dendrimer on the mica surface. The experimentally measured phase shifts and their relation to the mechanical properties will be analyzed quantitatively in the second part of the paper.

The interpretation of the autophobicity was checked by adsorption of the dendrimer on the surface of pyrolytic graphite. As the latter is indifferent to the hydroxyl groups on the molecular surface, any preferential orientation of the terminal groups hardly takes place. The structure formed by the adsorbed dendrimers is shown in Figure 4a. In contrast to the droplet formation on mica, dendrimer molecules aggregated into flat lamellae parallel to the substrate plane. The cross-sectional profile in Figure 4c shows that each lamella consists of two layers with a uniform thickness of  $16 \text{ \AA}$ . Also in this case, the layer thickness is smaller than the hard core diameter of a single dendrimer. The flattening can be partly explained by the interaction with the substrate and the deformation induced by the tapping tip, and partly it may be regarded as an indication of the inherent softness of the molecules whose branching density was lower compared to that of the dendrimer in ref 9.

Film formation of the dendrimer on mica has been studied systematically by experiment and computer simulation of the adsorption process.<sup>29</sup> The obtained results are consistent with the interpretation of the autophobic spreading which is schematically illustrated in Figure 5. During the casting procedure, first an oriented

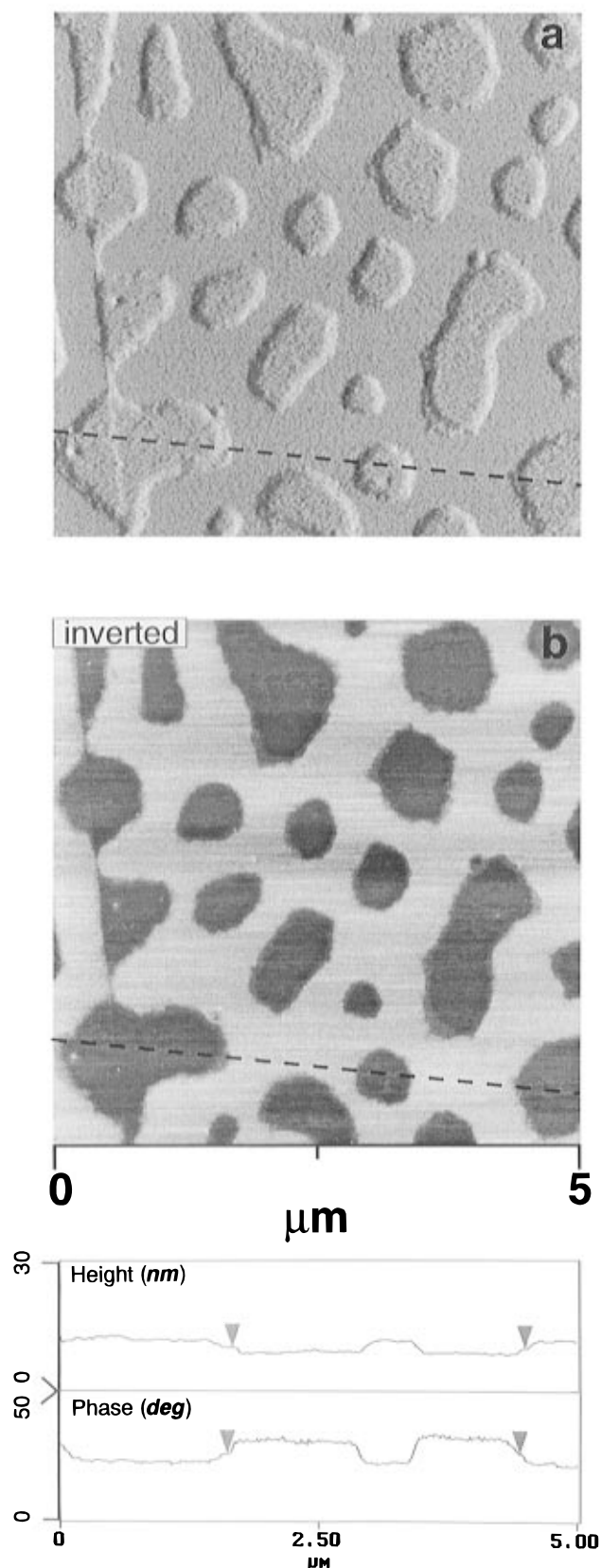


**Figure 3.** Amplitude (a) and phase (b) SFM micrographs demonstrating autophobic wetting of the mica surface by the carbosilane dendrimer with hydroxyl end groups. Fluid droplets with a contact angle of about  $8.7^\circ$  were observed. The cross-sectional profiles of the height and phase shift were recorded along the reference lines indicated in parts a and b, respectively.

monolayer of dendrimers was adsorbed on the mica surface and then droplets with a finite contact angle were formed on top of its own monolayer. The angles were determined

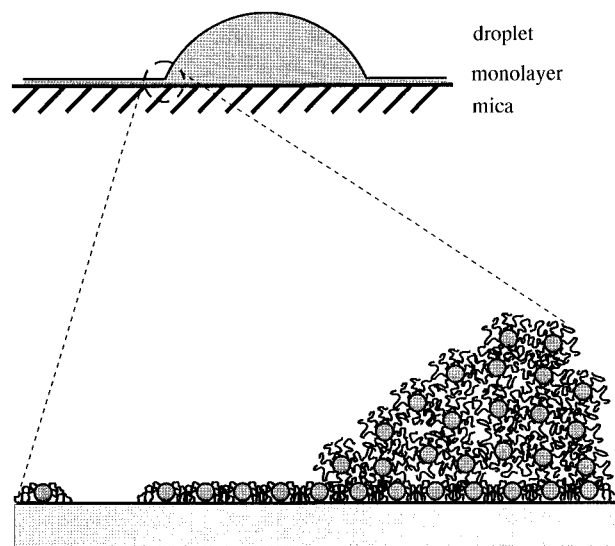
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**Figure 4.** Amplitude (a) and phase (b) SFM micrographs demonstrating spreading of the dendrimer on the surface of pyrolytic graphite. Instead of forming droplets as was shown in Figure 3, the dendrimers built lamellae with a uniform thickness of about 3.4 nm. Two steps in the cross-sectional profile (▼) correspond to the bilayer structure of the lamellae.

from cross-sectional profiles of the droplets (Figure 3) and by assuming a spherical shape of the droplet when evaluating the height and the radius (eq 1). Results are



**Figure 5.** Two-dimensional sketch of the autophobic spreading of the carbosilane dendrimer on mica shown in Figure 3. Due to the preferential adsorption of the end OH-groups on the surface of mica, the hydrocarbon core gets exposed to air. The picture is consistent with scanning force microscopy studies and molecular dynamic simulation of the dendrimer on mica.<sup>29</sup>

**Table 1. Contact Angles Measured by the Scanning Force Microscope ( $\theta_1$ ,  $\theta_2$ ,  $\theta_3$ ) and the Sessile Drop Technique ( $\theta_4$ )**

system	$\theta_1^a$	$\theta_2^b$	$\theta_3^c$	$\theta_4^d$
(A) autophobic spreading on mica	8.4	8.9	14	13
(B) wetting of the copolymer film	18	19	27	26

<sup>a</sup> Angle between the substrate plane and the tangent to the droplet. <sup>b</sup> Determined from eq 2. <sup>c</sup> Recalculated from eq 2 assuming deformation  $Z_{\text{def}}$  of the droplets by the SFM tip. <sup>d</sup> Macroscopic angle determined by the sessile drop technique.

summarized in Table 1 and are in good agreement, i.e. 8.4° and 8.9°, respectively. This similarity is consistent with the fact that the droplets have the shape of a spherical cap. Moreover, one should notice the perfect contour of the droplets free of any defects near the contact line. This observation demonstrates a rather uniform and homogeneous structure of the monolayer.

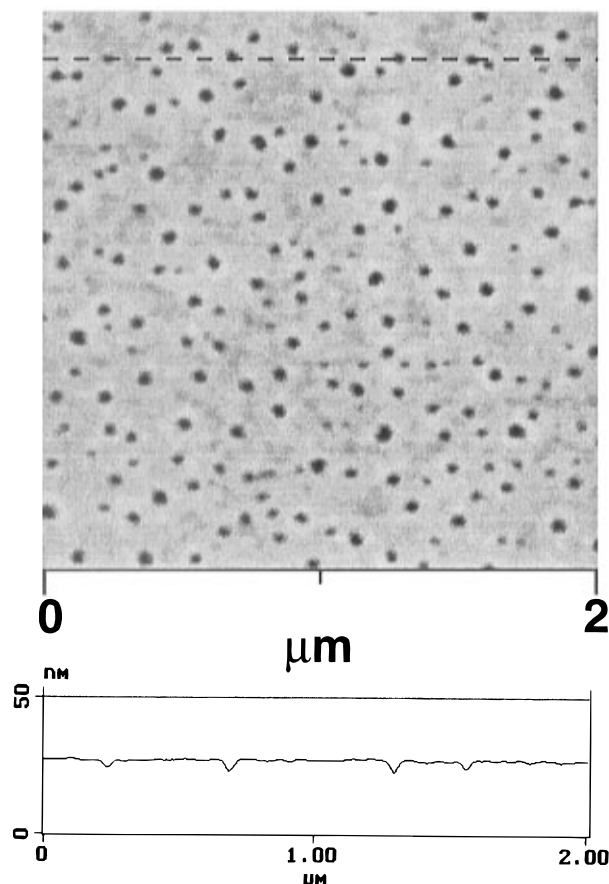
**Partial Wetting of a Semifluorinated Film.** To obtain droplets which are thermodynamically stable and uniformly distributed over the substrate by the spin-casting technique, the substrate we used was selected to have the following properties: (i) the interaction with the solvent (hexane) and the solute (dendrimer) molecules is mainly determined by dispersion forces and not affected by specific interactions, e.g. hydrogen bonding; (ii) the surface energy of the substrate is intermediate between the surface tensions of hexane and the dendrimer to attract molecules of both components;<sup>15</sup> (iii) the surface structure is chemically and physically stable during its contact with hexane, dendrimer, and air.

Fluorocarbon polymers are widely used to prepare chemically inert coatings imparting water- and oil-repellent properties. Depending on the chemical composition of copolymers of *n*-(perfluoroalkyl)-1-alkyl methacrylate and methyl methacrylate, the surface energy of a copolymer coating can be varied within a broad range from 9 to 40 mJ/m<sup>2</sup>.<sup>30–32</sup> The lower border corresponds to the surface composed solely of CF<sub>3</sub> groups,<sup>31</sup> whereas the

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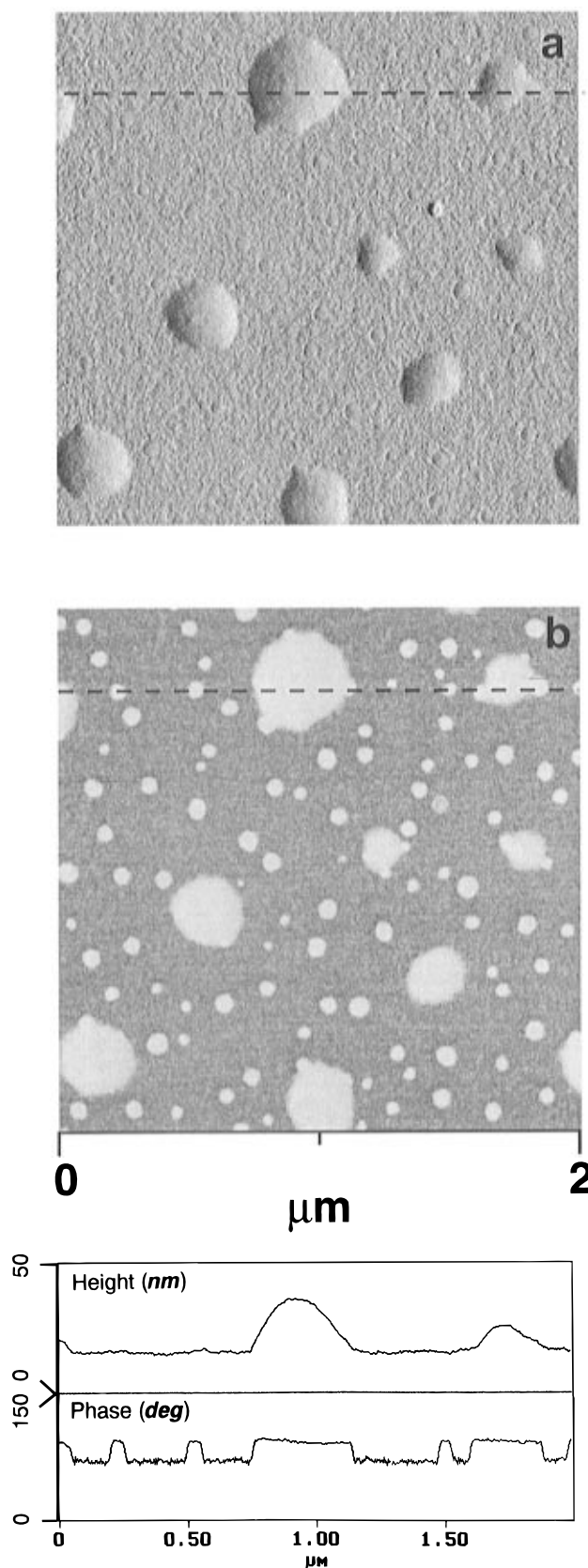


**Figure 6.** SFM micrograph of a 20 nm thick film of the P(F10H6-MA-co-MMA) 1:99 copolymer on a glass substrate as prepared by spin casting from a 0.1 wt % solution in toluene. The cross-sectional profile along the dashed line in the micrograph depicts small holes with a depth of about 3.7 nm.

upper value is limited by the surface energy of pure PMMA. The surface properties of the P(F8H2MA-co-MMA) copolymer which contained only 1 mol % 6-(perfluorooctyl)-1-ethyl methacrylate were characterized by a critical surface tension of 23 mN/m. Because this value is in between the surface tensions of hexane and the dendrimer, the substrate attracts both liquids, resulting in partial wetting of the copolymer surface by the dendrimer.

In contrast to the bare mica, the surface of the copolymer coating appeared to be heterogeneous or uneven on the nanometer scale. This is demonstrated by the topography image in Figure 6. The surface contains small holes with a diameter from 20 to 50 nm (black spots) and a depth of about 3.7 nm (Figure 6b). The depth was measured only for the large holes and corresponds to the bilayer spacing resulting from the alternating arrangement of the fluorocarbon side chains and the PMA backbone.<sup>32</sup> It was shown before that these holes formed upon lateral shrinkage of the surface layer as the solvent evaporated.

As was expected from the surface energy relation, dendrimer droplets with a finite contact angle of about  $18.5^\circ$  were formed on the copolymer surface (Figure 7). The angles determined from cross-sectional profiles in Figure 7c are summarized in Table 1. In contrast to the case of autophobic wetting, the shape of the droplets was not perfectly spherical and the contact line exhibited deviations from the circular contour. Apparently, the observed pinning of the contact line is caused by a heterogeneous structure of the film.<sup>33,34</sup>

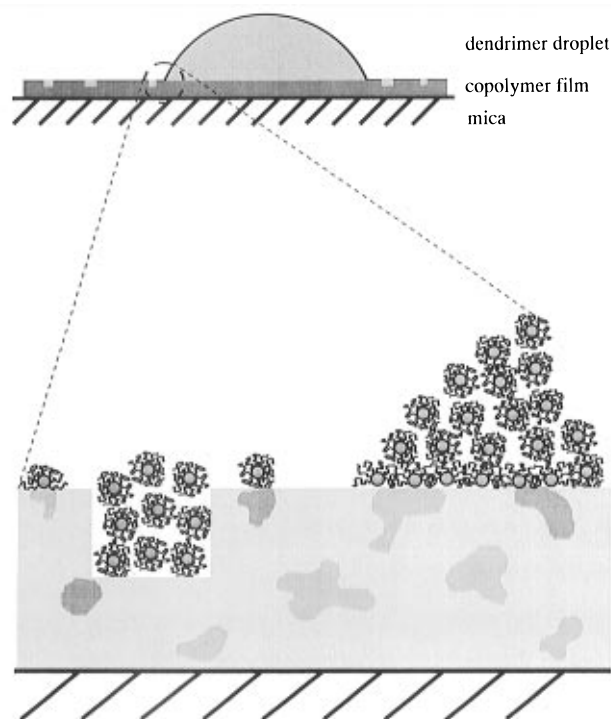


**Figure 7.** Amplitude (a) and phase (b) SFM micrographs demonstrating partial wetting of the copolymer film by the carbosilane dendrimer. Fluid droplets with a contact angle of about  $18.5^\circ$  were observed on the film surface. Moreover, the holes in the film (Figure 5) were filled with the dendrimer and could only be detected by measuring the phase shift. The cross-sectional profiles of the height and phase shift were recorded along the reference lines indicated in parts a and b, respectively. The phase profile shows the same phase shift for the droplets and filled holes.

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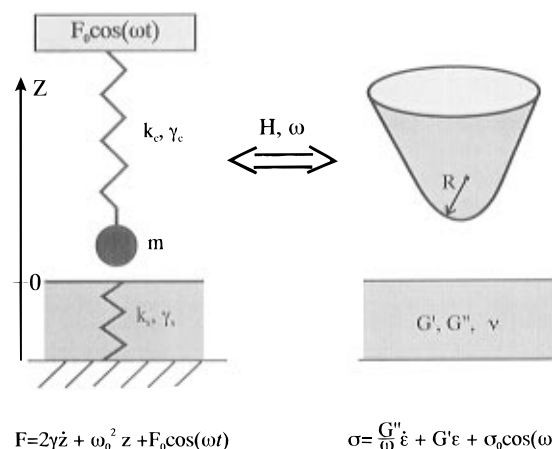


**Figure 8.** Two-dimensional sketch of Figure 7 illustrating drops (partial wetting) of the carbosilane dendrimer on the copolymer film. Small holes in the film formed "dendrimer wells". Variation of the gray color depicts the microheterogeneous structure of the copolymer, which might be considered as an explanation for the pinning of the contact line observed in Figure 7.

The small holes in the substrate were filled with the dendrimer after hexane evaporated. They became hardly discernible in the topographic images, and only by measuring phase variations could we identify locations of the "dendrimer wells". In the phase image in Figure 7b the droplets and filled holes are depicted as white domains which correspond to a phase shift of about  $25^\circ$  relative to the gray areas of the uncovered substrate (Figure 7d). Although the location of the filled holes could be identified, the wetting profile inside the holes remained unknown because of the small size of the holes relative to the radius of the tip.

Figure 8 illustrates the structure resulting from the spreading of the dendrimer on the surface of the copolymer film. The structure corresponds to the experimentally observed situation when all holes are filled with dendrimer molecules and the excess of the compound is segregated into the droplets. Variation of the gray color depicts the heterogeneous structure of the film caused by the hydrocarbon-fluorocarbon composition of the copolymer. Although statistical copolymerization yields a fine mixture of the methacrylate and fluorocarbon species, it is quite feasible that the copolymer undergoes phase separation on a mesoscopic scale. In either case, the distorted shape of the droplets and the observed pinning of the contact line strongly suggest a nonhomogeneous structure of the copolymer surface.

Sessile drop measurements were used to determine macroscopic contact angles of the systems studied by SFM. Relatively large droplets of about 1 mm in diameter were placed on the surface of mica and on the surface of the copolymer coating. After 1 h of equilibration, these two systems were characterized by contact angles of  $13^\circ$  and  $26^\circ$ , respectively. The contact angles were invariant during 1 week after the sample preparation. The obtained values were markedly larger than the contact angles determined by SFM.



**Figure 9.** Model of the forced cantilever oscillation (a) and its relation with the mechanical properties of the interacting bodies (b). The latter are represented by the spherical ( $R$ ) hard tip and flat viscoelastic ( $G'$ ,  $G''$ ) sample. The cantilever is approximated by a spring with a spring constant  $k_c$  and a damping constant  $\gamma_c$ . The inertial part of the cantilever is described as a mass point with mass  $m$ . When the tip is in contact with the sample, the latter is introduced by the spring constant  $k_s$  and the damping constant  $\gamma_s$ .

**Table 2. Properties of the Tip/Cantilever Assembly Used in Experiment and for the Model Calculations**

spring constant ( $k_c$ )	50 N/m
quality factor ( $Q_c$ )	300
resonance frequency ( $f_c = \omega_c/2\pi$ )	288.71 kHz
tapping frequency ( $f = \omega/2\pi$ )	288.47 kHz
piezoamplitude ( $a_p$ )	0.4 nm
resonance amplitude ( $a_{\max}$ )	120 nm
set-point amplitude ( $a_{\text{set}}$ )	72–48 nm
radius of the tip ( $R$ )	$10 \pm 1$ nm

Underestimated contact angles were expected because of the inherent softness of the droplets relative to the Si tip. The indenting tip detects the less protruding shape of the droplets and therefore results in lower values for the contact angle. Our next task was to estimate the deformation of the dendrimer induced by the tapping tip.

**Quantitative Evaluation.** Recently, a simple model was proposed to describe forced oscillation of the tip which intermittently contacts with the sample surface.<sup>35,36</sup> Figure 9 illustrates the model and the relation between the model parameters and the material properties. The detailed structure of the model is described in the Appendix.

In the following we are going to adopt our model to experiment by simulating experimental conditions which were used to image the dendrimer droplets. The properties of the used cantilever are summarized in Table 2. In detail, the cantilever was characterized by the spring constant 50 N/m and the resonance frequency 288.71 kHz. The amplitude of the piezo-oscillation  $a_p = 0.4$  nm and the quality  $Q_c = 300$  of the cantilever were determined from the shape of the resonance curve in air. The tapping frequency  $\omega$  was set at the lower frequency side of the curve at the amplitude 72 nm, which was 75% of the maximum amplitude  $a_{\text{set}} = 120$  nm. The tip radius was measured to be  $10 \pm 1$  nm.<sup>23</sup>

Table 3 describes the viscoelastic properties of three different materials, i.e. dendrimer, polystyrene (PS), and

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**Table 3. Viscoelastic Properties and Spring Constant  $k_s$  Determined for Three Different Samples, i.e. Dendrimer, Polystyrene, and Mica, for the tapping frequency  $f = 288$  kHz and room temperature,  $T = 23$  °C**

samples	material properties at $f = 288$ kHz, $T = 23$ °C				spring constant, $k_s$ (N/m)
	$G^a$ (Pa)	$G'^a$ (Pa)	$\nu^b$	$tg\delta = G''/G'$	
dendrimer	$10^5$	$6 \times 10^5$	0.5	6	$10^{-3}$ to $10^{-2}$
polystyrene	$10^9$	$8 \times 10^6$	0.3	$0.8 \times 10^{-2}$	7–70
mica <sup>38</sup>	$2 \times 10^{10}$	$< 2 \times 10^5$	0.25	$< 10^{-4}$	130–1300

<sup>a</sup> Measured by a stress-controlled mechanical spectrometer.

<sup>b</sup> Poisson ratio. <sup>c</sup> Calculated from eq 3 for the tip radius 10 nm and the tip indentation 0.1–50 nm.

mica. While the dendrimer and mica were introduced before, a PS sample was measured separately to obtain the best fit for the unknown damping coefficient ( $\gamma_s$ ). Shear moduli ( $G$ ,  $G'$ ) of the dendrimer at the tapping frequency  $\omega$  were determined from the master curve in Figure 2 using the following relations between the modules and compliance.<sup>39</sup>

$$G'(\omega) = \frac{J(\omega)}{J(\omega)^2 + J''(\omega)^2}$$

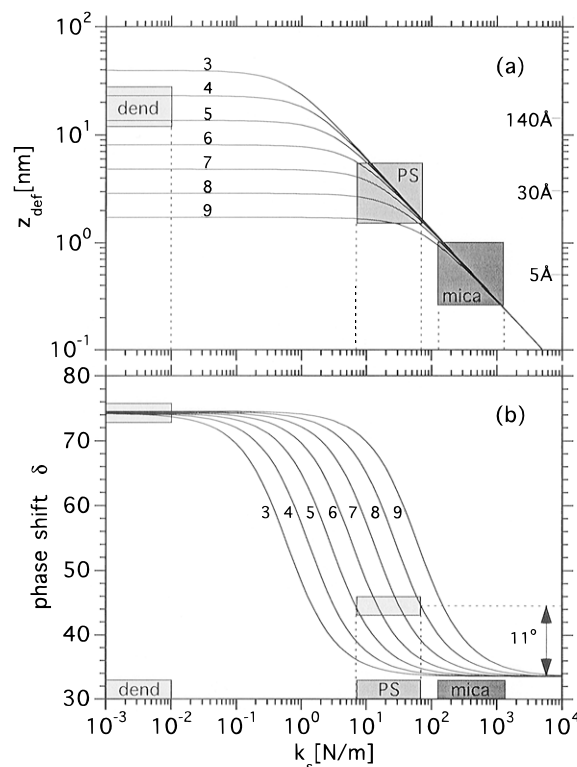
$$G''(\omega) = \frac{J''(\omega)}{J(\omega)^2 + J''(\omega)^2}$$

Two quantities were determined from the model calculations: (i) the indentation of the tip into the sample  $Z_{\text{def}}$  (negative  $z(t)$ ) and (ii) the phase shift of the forced oscillation with respect to the driving force. The deformation of the dendrimers was of primary interest, as it will be used for correction of the measured contact angles.

Figure 10a depicts the dependence of the sample deformation on its stiffness  $k_s$  and damping property  $\gamma_s$ , introduced in the model as  $2\gamma_s = 10^{-3+n/3}\omega_c$ , with  $n = 3, 4, \dots, 9$ . The analyzed range of the spring constants covered three intervals corresponding to the elastic properties of the dendrimer, polystyrene, and mica (Table 3). Besides the obvious fact that the deformation decreases with increasing stiffness and damping of the sample, the dependence  $Z_{\text{def}}(k_s)$  revealed two asymptotic regimes for very compliant and very stiff samples. For a given  $\gamma_s$  one can find a remarkably large range of  $k_s$ , where the deformation does not depend on sample stiffness. On the other hand, for all damping constants the curves of the sample deformation approach a limiting curve which decreases with increasing sample stiffness like  $Z_{\text{def}} \sim k_s^{-2/3}$ .

Whereas the deformation of stiff samples (e.g. mica) shows a weak dependence on  $\gamma_s$ , for compliant materials, like polystyrene and dendrimer, the damping properties strongly affect the tip oscillation and therefore define the deformation of the sample. Especially the deformation of the dendrimer (Figure 10a) is solely determined by its viscosity and might vary in a very broad range up to 40 nm if the damping constant  $\gamma_s$  changes from  $10^{-2}\omega_s$  to  $\omega_s$ . Therefore, the damping property of the dendrimer requires more precise evaluation.

For this purpose, the phase shift was calculated and compared with experiment to estimate  $\gamma_s$  of the dendrimer. Figure 10b shows the dependence of the phase shift on sample stiffness for various  $\gamma_s$ . For all damping constants the phase shift decreases with increasing sample stiffness, approaching two limiting values, i.e. the curve for the infinite sample damping (top line) and the curve for zero



**Figure 10.** Deformation  $Z_{\text{def}}$  (a) and phase shift  $\delta$  (b) versus the sample stiffness  $k_s$  for various damping constants  $\gamma_s$ . The phase shift is measured between the piezo-oscillation and the oscillation of the cantilever touching the sample during one period. The damping constant is  $2\gamma_s = 10^{-3+n/3}\omega_c$ , where  $n = 3, 4, \dots, 9$  and  $\omega_c$  is the resonance frequency of the cantilever. The damping constant increases from top to the bottom in part a and from left to right in part b. The colored squares depict intervals of  $k_s$  and  $\gamma_s$  which were empirically determined for the dendrimer, polystyrene, and mica.

**Table 4. Phase Shifts Calculated from the Model and Measured Experimentally for Different Set-Point Amplitudes**

$a_{\text{set}}^a$ (nm)	72	66	60	54	48
$\Delta\varphi_{\text{mod}}^b$ (deg)	36	41	46	50	55
$\Delta\varphi_{\text{exp}}^c$ (deg)	32	41	50	51	53

<sup>a</sup> Set point amplitudes used for the model calculations and SFM measurements. <sup>b</sup> Phase difference between two limiting values  $\varphi_0$  and  $\varphi_\infty$  corresponding to the limits  $k_s \rightarrow 0$  and  $k_s \rightarrow \infty$ , respectively.

<sup>c</sup> Phase difference induced by contact of the tip with the dendrimer droplets relative to the mica substrate.

sample damping (bottom line) in the limits  $k_s \rightarrow 0$  and  $k_s \rightarrow \infty$  respectively.

Therefore, the compliant dendrimer ( $k_s = 10^{-3}$  to  $10^{-2}$  N/m) and stiff mica ( $k_s = 10^2$  to  $10^3$  N/m) may be considered as two boundary points corresponding to the lower and upper values of the phase shift, respectively. Table 4 compares the shifts in phase for the dendrimer droplets relative to mica which were calculated and measured experimentally for a series of set-point amplitudes from 72 to 48 nm. The table presents only relative values to ensure more accurate comparison with experiment. It was a remarkable fact that the obtained data on the phase shift revealed only little discrepancy between theory and experiment. In both cases the phase shift increased upon decreasing the set-point, and the relative values measured experimentally and computed theoretically differed by less than 10% of the absolute value.

Thus, the model correctly describes the phase difference between the two extreme cases of mica and the dendrimer. However, because of the strong asymptotic behavior of

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**Table 5. Indentation  $Z_{\text{def}}$  of the SFM Tip into the Dendrimer, Polystyrene, and Mica Samples Determined from the Model Calculations Assuming the Defined Intervals of Spring ( $k_s$ ) and Damping ( $\gamma_s$ ) Constants**

sample	$k_s$ (N/m)	$\gamma_s$ (n) <sup>a</sup>	$Z_{\text{def}}$ <sup>b</sup> (Å)
dendrimer	$10^{-3}$ to $10^{-2}$	4–5	140
polystyrene	7–70	6–7	30
mica	130–1300	3–4	5

<sup>a</sup> The damping constant is  $2\gamma_s = 10^{-3+n/3}\omega_c$ , where  $n$  is an arbitrary integer and  $\omega_c$  is the resonance frequency of the cantilever.

<sup>b</sup> The averaged values are determined for the set-point amplitude 72 nm with an error of 50%.

the samples, an accurate evaluation of the dendrimer damping constant is not possible yet. Polystyrene (PS) was chosen as a reference material whose elastic properties were intermediate between those of mica and the dendrimer.

A thin PS film on mica was prepared and scanned with the same tip which was used for the dendrimer. The phase shift for the PS film relative to that for the mica substrate was measured to be  $11 \pm 2^\circ$ , which falls in between the two limits in Figure 10b. Accordingly, the PS sample, whose spring constant ranges from 7 to 70 N/m, has a damping constant within the range  $n = 6-7$ . As the loss modulus  $G''$  of the dendrimer is about 1 order of magnitude lower than that of polystyrene, the damping constant of the dendrimer is assumed to have lower values within the range  $n = 4-5$ .

Finally, the sample deformation was evaluated based on the determined damping constants. Three differently colored squares in Figure 10a correspond to the intervals of  $k_s$  and  $\gamma_s$ , which were empirically evaluated for the dendrimer, polystyrene, and mica, respectively. As was expected, the hard mica was found on the limiting curve  $Z_{\text{def}} \sim k_s^{-2/3}$ , which showed weak dependence of the deformation on the damping properties. Contrary to that, deformation of the soft polystyrene and even more of the fluid dendrimer was a function of the damping constant  $\gamma_s$ .

The final data on the sample deformation for the determined spring and damping constants are summarized in Table 5. The average values of the tip are 140, 30, and 5 Å for the dendrimer, polystyrene, and mica, respectively. These values were determined with an error of 50% and represent the rough estimation of the deformations which might be expected in the tapping mode experiments. The model calculations were performed for the set-point amplitude of 72 nm, i.e. for the least deformed samples. Experimentally, the height of the droplets reduced by 10% upon decreasing the set-point amplitude from 72 to 48 nm, whereas the monolayer thickness does not show any measurable changes.

The determined deformation of the dendrimer was added to the experimentally measured height of the droplets. Assuming the corrected height  $h_{\text{cor}} = h + Z_{\text{def}}$ , the contact angle  $\theta_3$  was recalculated (eq 1) and showed very good agreement with the macroscopic sessile drop measurements ( $\theta_4$ ) in Table 1. Because adhesion and capillary forces between the tip and the sample were neglected, the calculations gave only lower limits of the induced deformation. Therefore, larger values for the corrected contact angle have to be assumed.

The effect of adhesion was analyzed in detail by numerical simulations of the JKRS model in comparison with the Hertz model.<sup>40</sup> Consistent with our calculations it was shown that the damping properties of the sample

might determine an upper limit of the tip indentation and that effects of the elastic properties, i.e. stiffness and adhesion, can be neglected. Since the viscosity of the dendrimer is relatively high, we believe that the error caused by omitting the adhesion between the tip and the sample is negligible. This is clearly demonstrated by Figure 10a.

Certainly, the bulk properties of the dendrimer are not applicable for the monolayer. Short and long range interactions with the substrate and constraining effects induced by the hard wall should be taken into account. The proximity of the solid surface can shift the relaxation spectrum to lower frequencies<sup>41</sup> and affect wetting behavior considerably.<sup>42–46</sup>

## Conclusion

When carbosilane dendrimers containing hydroxyl-terminated groups were adsorbed from hexane on the solid surface of either mica or fluorinated copolymer, the molecules segregated into microscopic droplets with a finite contact angle. Although droplets were observed on both substrates, the origin of the incomplete wetting was different. In the first case, the drops formed due to the autophobic spreading of the dendrimer on the  $\text{SiO}_2$  surface of mica. In contrast, the copolymer surface, characterized by the critical surface tension 23 mN/m, could only be partially wetted by the dendrimer, whose surface tension was as high as 29 mN/m.

Furthermore, the shape of the droplets provided a suitable tool to identify the nonuniformity of the surface on a mesoscopic scale. Compared to the perfectly spherical shape of the droplets on the flat and homogeneous surface of mica, the copolymer coating induced pinning of the contact line and distortions of the spherical shape. The latter resulted from the fluorocarbon–hydrocarbon composition of the coating and might point to the microphase separation of the strongly incompatible constituents.

The dendrimer droplets were visualized by means of a tapping force microscope using the amplitude and phase detection systems. Although the samples were fluid at room temperature, the dendrimer underwent a transition to a viscoelastic state below the tapping frequency of about 290 kHz. Due to the peculiar mechanical properties and partly because of the interaction and constraining effects induced by the solid wall, the droplets could be probed by the oscillating tip and retained their mechanical integrity.

The microscopic contact angles of the droplets were measured and compared with macroscopic values obtained by a standard sessile drop technique. The lower values for the microscopic angles were explained by deformation of the droplets caused by the tapping tip. A simple model of the tapping mode was used to estimate upper limits for the indentation of the tip into the sample and the induced phase shift relative to the oscillations in air. The best correlation of the model with experimental results was achieved when the viscoelastic response of the dendrimer was calculated and compared with that of polystyrene and mica. The lower limit of the tip indentation was estimated with an error of 50% to be 140, 30, and 5 Å for the dendrimer, polystyrene, and mica, respectively.

In conclusion, the following advantages of the described method for the investigation of dendrimer drops on a solid surface may be considered: (i) the scanning probe

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determines a full shape of the droplet in three dimensions, which is important for characterization of spreading drops whose contact angles vary along the contact line; (ii) due to the superior resolution of SFM, one can discern mesoscopic features of the system with an emphasis on the submicrometer heterogeneity of the surface and the liquid profile at the contact line; (iii) the mass of the system is conserved, and the microscopic scale of the measurements is not affected by gravitation; (iv) the method allows accurate determination of small ( $<5^\circ$ ) contact angles.

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### Appendix

The tip/cantilever assembly was approximated by a point mass  $m$ , which experiences a harmonic potential  $V(z, t)$ :

$$V(z, t) = \frac{k_c}{2}(z - z_e(t))^2 + \frac{k_s}{2}z^2(1 - \theta(z))^2 \quad (2)$$

where  $z$  is the distance between the mass and the surface and  $\theta(z)$  is the step function

$$\theta = 1, \quad z > 0 \text{ (in air)}$$

$$\theta = 0, \quad z \leq 0 \text{ (in contact)}$$

The cantilever was described as a harmonic oscillator with a spring constant  $k_c$ , a damping coefficient  $\gamma_c$ , and the time dependent equilibrium position  $z_e(t)$ :

$$z_e(t) = z_0 + a \cos(\omega t)$$

The viscoelastic sample was introduced as a harmonic spring with a constant  $k_s$  and a damping coefficient  $\gamma_s$ . The equation of motion of the mass  $m$  in the potential  $V(z, t)$  (eq 2) is given by

$$\ddot{z}(t) + 2(\gamma_c + \gamma_s(1 - \theta(z)))\dot{z}(t) + \omega_c^2(z(t) - z_0) + \omega_s^2 z(t)(1 - \theta(z)) = a\omega_c^2 \cos(\omega t)$$

where  $\omega_c$  and  $\omega_s$  are the resonance frequencies of the cantilever and the sample, respectively.

Upon touching the sample surface, the oscillation of the tip is perturbed. The solution  $z(t)$  is then periodic but not necessarily harmonic. The induced changes of the amplitude and phase shift relative to the oscillation in air are two quantities which were measured by the tapping force microscope. In our measurements as well as in the model calculations the microscope was operated in a constant amplitude mode. Via a feedback loop the position of the cantilever  $z_0$  is adjusted to keep the amplitude of the oscillations equal to a set value (set-point)  $a_{\text{set}}$ .

The relations between model parameters ( $k_s$ ,  $\gamma_s$ ) and material properties ( $G$ ,  $G'$ ,  $\nu$ ) depend on the size and shape of the interacting bodies and the type of deformation experienced by the system. The spring constant of the sample was related to material properties by using the Hertz model, which describes deformation of two elastic bodies in the absence of adhesion.<sup>37</sup> For the case of a rigid sphere of radius  $R$  (tip) and a flat surface (sample), the deformation of the sample  $d$  is related to the applied force  $F$  by

$$F = \frac{8GR^{1/2}d^{3/2}}{3(1 - \nu)}$$

where  $G$  is the equilibrium shear modulus of the sample assuming that the tip is much stiffer. The spring constant of the sample is obtained as a first derivative of the force with respect to  $h$

$$k_s = \frac{4GR^{1/2}d^{1/2}}{1 - \nu} \quad (3)$$

Thus, using the Hertz theory and assuming a rather perfect geometry of the two bodies, we could estimate the spring constant  $k_s$  (eq 3), whereas  $\gamma_s$  remained unknown and will be used as an adjusting parameter of the model.

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