Ultrathin Solid Polyelectrolyte–Surfactant Complex Films: Structure and Wetting†

3 AUTHORS:

Andreas F Thünemann

Bundesanstalt für Materialforschung und -pr…

178 PUBLICATIONS **4,968** CITATIONS

SEE PROFILE

Stephan Kubowicz

SINTEF

21 PUBLICATIONS **555** CITATIONS

SEE PROFILE

Ullrich Pietsch

Universität Siegen

412 PUBLICATIONS **3,754** CITATIONS

SEE PROFILE

Ultrathin Solid Polyelectrolyte−Surfactant Complex Films: Structure and Wetting[†]

Andreas F. Thünemann,*[,‡] Stephan Kubowicz,[§] and Ullrich Pietsch[§]

Max Planck Institute of Colloids and Interfaces, Am Mühlenberg, D-14476 Golm, Germany, and Institute of Physics, University of Potsdam, D-14415 Potsdam, Germany

A fluorinated polyelectrolyte−surfactant complex is shown to form highly ordered lamellar structures in the bulk material and in spin-cast films with a long period of 3.75 nm consisting of alternating fluorinated and polymer-rich layers. The smectic B-like structure was found to be stable up to temperatures of 185 °C. The wetting behavior of complex films with thicknesses in the range of 5.7−370 nm were investigated by using axis-symmetric drop shape analysis of contact angle measurements. Surface energies were calculated using the equation derived by Neumann and Li (ca. 11 mN/m), the Zisman critical surface tension (7 mN/m), and the Girifalco−Good−Fowkes dispersive surface energy (10 mN/m). The surface energies were found to be independent of the thickness of the films. By use of X-ray reflectivity it was found that up to 100 double layers were oriented macroscopically on silicon wafers when prepared by the spin-coat technique.

Introduction

The systematic preparation of low-energy surfaces performed via the self-assembly of polyelectrolyte−surfactant complexes has become of technological importance and is of fundamental scientific interest. Coatings, which are easy to clean and/or with low friction properties, have a great variety of applications. The outstanding feature with regard to the practical use of these materials is their easy preparation. An illustrative example of an application in daily life is the coating of polymer surfaces in order to tune their frictional properties. Here, fluorinated colloidal coatings of polymer surfaces, which can be a substitute for ski wax, were introduced initially for the use of top sportsmen in a number of ski disciplines.[1] Now these materials are on the market for leisure sportsmen as well. Their superior friction reducing properties result from the combination of fluorine moieties and the supramolecular structuring. The growing field of such solid polyelectrolyte−surfactant complexes has recently been reviewed.[2−4] Many of these complexes show the pronounced tendency of forming well-ordered liquid crystal-line-like structures with high mechanical and thermal stability. The structures of fluoro and silicone groups containing polyelectrolyte−surfactant complexes in the bulk were reported on earlier.[5−9] They include lamellar mesophase structures, perforated lamellar structures, and
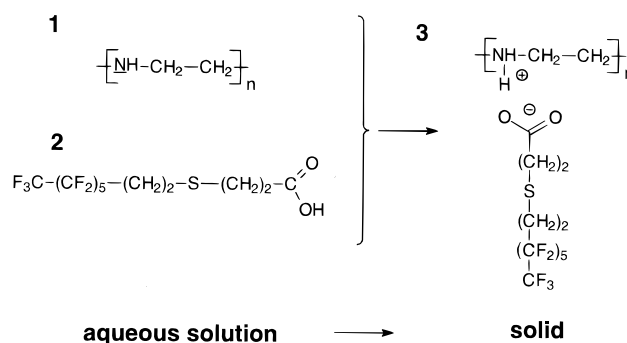

Figure 1. Sketch of complex formation: **(1)** polyethyleneimine; **(2)** 3-[(^1H,^1H,^2H,^2H-fluorooctyl)thio]propionic acid; **(3)** stoichiometric polyelectrolyte surfactant complex.

two-dimensional hexagonal and columnar mesophases. Recently we investigated the bulk structures and the surface energies of polyethyleneimine (PEI) complexes with perfluorinated carboxylic acids dependent on the lengths of the fluorinated chains.[10] It was found that even the highly branched PEI is capable of forming well-ordered mesomorphic complexes with low surface energies.

In this article we report on the complexation of PEI (**1**) with a partially fluorinated carboxylic acid **2** resulting in a polyethyleneimine carboxylate **3**, which serves as a model compound of the commercial colloidal plastic surface coating materials. We describe its structure and its physical properties in the bulk material and in thin films. The complexation is shown schematically in Figure 1. The polyethyleneimine is a branched, water-soluble polymer, which is widely used in the paper industry.[11] At low pH values, PEI has the highest known charge density of all polyelectrolytes. PEI is known to have a strong tendency to form complexes, for example, with anionic surfactants.[12] The lithium salt of **2** is used as an active spreading agent.

* To whom correspondence may be addressed. E-mail: andreas.thuenemann@mpikg-golm.mpg.de.

[†] Part of the Special Issue "Colloid Science Matured, Four Colloid Scientists Turn 60 at the Millennium".

[‡] Max Planck Institute of Colloids and Interfaces.

[§] Institute of Physics, University of Potsdam.

(1) Information was supplied by the manufacturer, Colloid Surface Technologies GmbH, Wiesbaden, Germany, official suppliers of the Swiss National Ski Teams and a number of other world class athletes in skiing and biathlon (www.cerax.de).

(2) Ober, C. K.; Wegner, G. *Adv. Mater.* **1997**, *9*, 17.

(3) Antonietti, M.; Burger, C.; Thünemann, A. F. *TRIP* **1997**, *5*, 262.

(4) Thünemann, A. F. Submitted for publication in *Polym. Int.*

(5) Antonietti, M.; Henke, S.; Thünemann, A. F. *Adv. Mater.* **1996**, *6*, 41.

(6) Thünemann, A. F.; Lochhaas, K. H. *Langmuir* **1998**, *14*, 4898.

(7) Thünemann, A. F.; Lochhaas, K. H. *Langmuir* **1998**, *14*, 6220.

(8) Thünemann, A. F.; Lieske, A.; Paulke, B. R. *Adv. Mater.* **1999**, *11*, 321.

(9) Thünemann, A. F.; Lochhaas, K. H. *Langmuir* **1999**, *15*, 6724.

(10) Thünemann, A. F. *Langmuir* **2000**, *16*, 824.

(11) Information was supplied by the manufacturer, BASF, Specialty Chemicals, Ludwigshafen, Germany.

(12) Bronich, T. K.; Cherry, T.; Vinogradov, S. V.; Eisenberg, A.; Kabanov, V. A.; Kabanov, A. V. *Langmuir* **1998**, *14*, 6101.

Experimental Section

A. Materials. Polyethyleneimine (PEI, Lupasol WF) was supplied by BASF and used as received. The polymer is highly branched with a molar ratio of primary to secondary to tertiary amino groups of 34:40:26 and a molecular weight of $M_w = 25000$ g/mol.[11] The lithium 3-[(^1H,^1H,^2H,^2H-fluorooctyl)thio] propionate (Zonyl FSA) was supplied by DuPont. This compound, which contains 2-propanol and water, was purified by crystallization in hydrochloric acid producing a white to yellow powder. The purified product shows a sharp melting transition at 45 °C. The solvent 1,1,1,3,3,3-hexafluoropropanol was supplied by Aldrich and used as received.

B. Preparation. A 1 mmol quantity of the surfactant was dissolved in 200 mL of water (Millipore). At 90 °C the solution was stirred and a solution of 1.0 equiv of polyelectrolyte in 50 mL of water was added in droplets. The stoichiometry was calculated with respect to the charges. A solid complex was obtained as a precipitate, separated, and dried for 12 h at a reduced pressure of 0.1 mbar. The yield was in the range of 90–95%. Complex solutions of 0.1% (w/w) in 1,1,1,3,3,3-hexafluoropropanol were used for the preparation of thin films. Naturally oxidized silicon wafers served as substrates. The complex was deposited on the wafers using the spin-coat technique at a speed of 2000 rpm.

C. Methods. The FTIR spectra were recorded on a Nicolet Impact 400 spectrometer using KBr pellets. Differential scanning calorimetry (DSC) measurements were made with a Netzsch DSC 200 (Germany). The samples were examined at a scanning rate of 10 K/min by applying one cooling and two heating scans. Thermogravimetric analysis (TGA) was performed in an oxygen atmosphere and with a heating rate of 10 K/min using a Netzsch TG 209 instrument. The contact angle measurements were performed on a G10 contact angle goniometer (Krüss, Germany); the angles reported here are the average of five measurements. The advancing contact angle was measured by injecting a 5 μL liquid drop, and the static contact angle was obtained from a drop (ca. 5 μL) on the surface. Within the experimental error of 1°, the static contact angles are 1–2° below the advancing contact angles. The linear alkanes, hexane, octane, decane, dodecane, and hexadecane, and further PDMS, a commercial product of poly(dimethylsiloxane) oligomers (trimethylsiloxy terminated) from Geltest, Inc., α-bromonaphthalene, and diiodomethane were used as test liquids. Wide-angle X-ray scattering (WAXS) measurements were carried out with a Nonius PDS120 powder diffractometer in transmission geometry. A FR590 generator was used as the source of Cu Kα radiation. Monochromatization of the primary beam was achieved by means of a curved Ge crystal, and the scattered radiation was measured with a Nonius CPS120 position-sensitive detector with a resolution in 2θ of 0.018°. The small-angle X-ray scattering measurements were recorded with an X-ray vacuum camera with pinhole collimation (Anton Paar, Austria; model A-8054) equipped with image plates (type BAS III, Fuji, Japan). The image plates were read by a MACScience dip-scanner IPR-420 and IP reader DIPR-420 (Japan). X-ray reflectivity was performed with a $\theta/2\theta$ instrument (Sot/Superman DF4, $U = 40$ kV, $I = 30$ mA, $\lambda = 0.154$ nm). The beam divergence of the incoming beam was 0.1°, the resolution in 2θ was 0.05°. A secondary monochromator selected the Cu Kα lines; a scintillation counter served as detector.

Results and Discussion

Comparison of the IR spectra of **2** and **3** shows that the carboxylic acid vibrations found for **2** at 1690 cm^{-1} (C=O stretch, dimer) and at 1300 cm^{-1} (C–O stretch, dimer) are absent in the spectrum of **3** (see Figure 2). From this it can be concluded that the complex has a 1:1 stoichiometry as was found earlier for a nonfluorinated polyethyleneimine complex.[13]

Thermal Properties. The thermal properties of **2** and **3** were investigated by using DSC and TGA. The second heating DSC traces are shown in Figure 3. A sharp

(13) Thünemann, A. F.; Ruppelt, D.; Ito, S.; Müllen, K. *J. Mater. Chem.* **1999**, *9*, 1055.
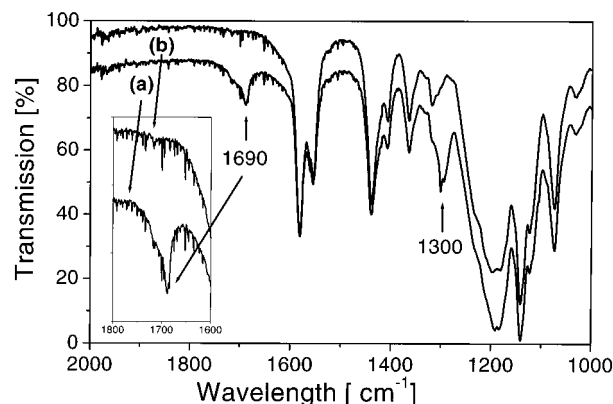

Figure 2. FTIR spectrum of the surfactant **2** (curve a) and that of its complex **3** with polyethyleneimine **1** (curve b). In the spectrum of **3** an intense carboxylic acid band at a wavenumber of 1690 cm^{-1} is found. This results from the C=O stretch vibration. This band is absent in the spectrum of **3** and is an indication of a stoichiometric 1:1 complex. The insert shows an enlargement of this region of the wavelength.
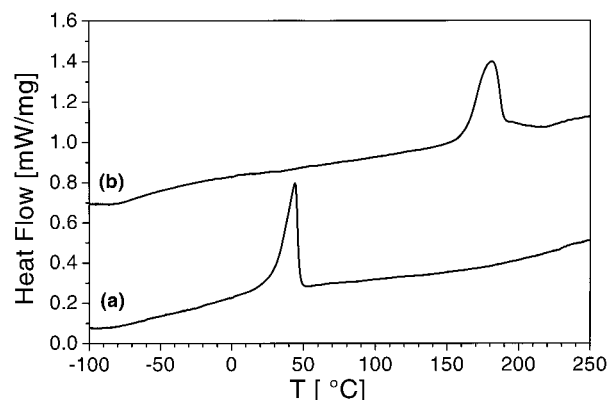

Figure 3. DSC heating traces of the surfactant **2** (curve a) and the complex **3** (curve b). Melting points are at 45 and 180 °C for **2** and **3**, respectively.

endothermic peak at 45 °C is present for **2** and a peak at 180 °C for **3**. We attribute these peaks to the melting transitions of the compounds. Below these temperatures the morphology of the compounds can be assumed to be constant. The considerable rise of 135 °C in the melting point of the complexed surfactant **3** compared to that of the noncomplexed compound **2** is surprising and must be considered as a consequence of the stabilizing effect of the complexation. It is known that polyethyleneimine possess good thermal stability compared to other polyelectrolytes and that substantial decomposition in air does not occur below 300 °C.[14] Therefore we suggested that its complexes with fluorinated surfactants are also thermally stable. This was proved by TGA. It can be seen in Figure 4 that decomposition of the complex starts at temperatures above 280 °C, followed by a rapid degrease of about 80% mass up to 350 °C. Therefore we conclude that the thermal stability of the complex is not much lower than that of PEI.

Surface Energies. Complex surfaces were prepared by spin-casting a 0.1% (w/w) complex solution onto silicon wafers. Dynamic contact angles θ of the test liquids with different surface tensions were measured by means of the sessile drop method[15] after the evaporation of the solvent (1,1,1,3,3,3-hexafluoropropanol). It was found, in par-

(14) Overberger, C. G.; Menges, G.; Kroschwitz, J. I. *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Wiley: New York; 1985; Vol. 1, p 689.

Table 1. List of Contact Angles of Different Test Liquids on Materials Coated with Complex 3 at 20 °C[a]

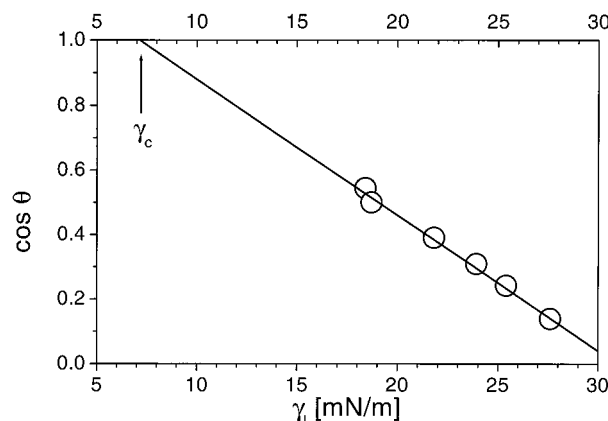| solvent	γ_l (mN/m)	advancing angle (deg)[b]	stationary angle (deg)[b]	receding angle (deg)[b]	γ_s (mN/m)
glass slide					
hexane	18.4	57	55	39	11.1
PDMS[c]	18.7	60	59	40	10.7
octane	21.8	67	65	60	10.9
decane	23.9	72	72	65	10.7
dodecane	25.4	76	74	69	10.3
hexadecane	27.6	82	80	73	9.7
α-bromonaphthalene	44.0	93	93	87	12.6
methylene iodide	50.0	102	100	90	11.4
water	72.7	80	75	20	35.5

[a] The surface tensions of the test liquids, γ_l, and advancing, stationary, and receding contact angles are measured by a Krüss contact angle goniometer and are listed. γ_s is the surface energy calculated by using eq 1 and advancing contact angles. [b] Error of measurement ca. 1°. [b] Commercial product of poly(dimethylsiloxane) oligomers (trimethylsiloxy terminated) from Geltest, Inc.
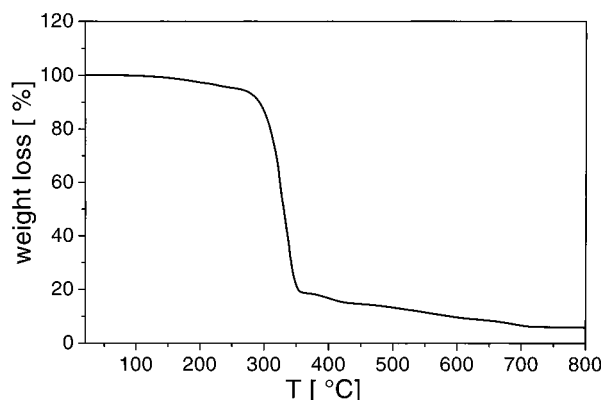
Figure 4. Thermogram of complex **3** at a heating rate of 10 K/min in air. Decomposition of the complex starts at temperatures above 280 °C.

Figure 5. Zisman plots for complex-coated silicon wafers. Points are obtained with (1) hexane, γ_l = 18.4 mN/m; (2) PDMS, γ_l = 18.7 mN/m; (3) octane, γ_l = 21.8 mN/m; (4) decane, γ_l = 23.9 mN/m; (5) dodecane, γ_l = 25.4 mN/m; and (6) hexadecane, γ_l = 27.6 mN/m. The critical surface tension of a complex on a silicon wafer was calculated to be 7.1 ± 1.2 mN/m by extrapolating a linear fit (solid line) of the cos θ (cycles) to cos θ = 1. Advancing contact angles were used for cos θ.

ticular, that all nonpolar liquids, which spread readily on uncoated surfaces, showed high contact angles on complex-coated surfaces (Table 1). In addition the values of the contact angles are independent of the film thickness in the experimental range of 5.7–370 nm (see section, thin films). However, direct measurement of the surface energies of nonelastomeric solid materials is complicated. For practical reasons, procedures based on contact angle measurements are regularly used.[16–22] Neumann and Li have derived an equation by which it is possible to calculate the surface free energy[23]

$$\cos\theta = -1 + 2(\gamma_s/\gamma_l)^{1/2}\exp(-\beta(\gamma_l - \gamma_s)^2) \quad (1)$$

where β is a constant (1.247×10^{-4} m^2 mJ^{-1}). Thus, the surface energy γ_s of the solid can be determined from experimental contact angles and the liquid surface tension γ_l. The surface energies calculated using eq 1, range from 9.7 to 12.6 mN/m for all test liquids with surface tensions in the range of 18.4–50.0 mN/m (Table 1). These values are close to the surface energies found for the fluorinated polymer (FC-725)-coated wafers,[22] which range from 11.8 to 13.2 mN/m. The critical surface tension γ_c of a surface can often be determined from the contact angles of a

homologue series of nonpolar liquids.[16] γ_c defines the wettability of a solid by noting the lowest surface tension a liquid can have and still exhibit a contact angle greater than 0°. The γ_c value of a surface is usually obtained from a Zisman plot of the contact angles,[16] such that a plot of cos θ against the surface tensions of liquids γ_l is a straight line with the slope m:

$$\cos\theta = 1 + m(\gamma_l - \gamma_c) \quad (2)$$

The extrapolation of γ_l to cos θ = 1 gives γ_c. Zisman plots result in a critical surface tension of 7.1 ± 1.2 mN/m for complex-coated silicon wafers (see Figure 5). Within the experimental range of error, which was measured for an oriented close-packed monolayer of perfluorododecanoic acid, the value is equal to the lowest critical surface tension observed to date (6 mN/m).[24] It is widely accepted that such low critical surface tensions characterize the resulting properties of a surface of closed-packed perfluoromethyl −CF$_3$ groups.[25,24] Therefore, we conclude that the complex-coated surfaces presented are strongly enriched with CF$_3$ groups. It must be stressed here that although γ_c values are widely used for surface characterization, there is no theoretical justification for equating the critical surface tension with the surface energy of a material. The

(15) Augsburg, A.; Grundke, K.; Pöschel, K.; Jacobasch, H.-J.; Neumann, A. W. *Acta Polym.* **1998**, *49*, 417.

(16) Zisman, W. A. *Ind. Eng. Chem.* **1963**, *55*, 18.

(17) Fowkes, F. M. *J. Phys. Chem.* **1962**, *66*, 382.

(18) Girifalco, L. A.; Good, R. J. *J. Phys. Chem.* **1957**, *61*, 904.

(19) Drummond, C. J.; Georgaklis, G.; Chan, D. Y. C. *Langmuir* **1996**, *11*, 2617.

(20) J. Höpken, M. Möller, *Macromolecules* **1992**, *25*, 1461.

(21) Wang, J.; Ober, C. K. *Macromolecules* **1997**, *30*, 7560.

(22) Kwok, D. Y.; Lam, C. N. C.; Li, A.; Leung, A.; Wu, R.; Mok, E.; Neumann, A. W. *Colloids Surf.* **1998**, *142*, 219.

(23) Li, D.; Neumann, A. W. *J. Colloid. Interface Sci.* **1992**, *148*, 190.

(24) Hare, E. F.; Shafrin, E. G.; Zisman, W. A. *J. Colloid Sci.* **1954**, *58*, 236.

(25) Wang, J.; Mao, G.; Ober, C. K.; Kramer, E. J. *Macromolecules* **1997**, *30*, 1906.
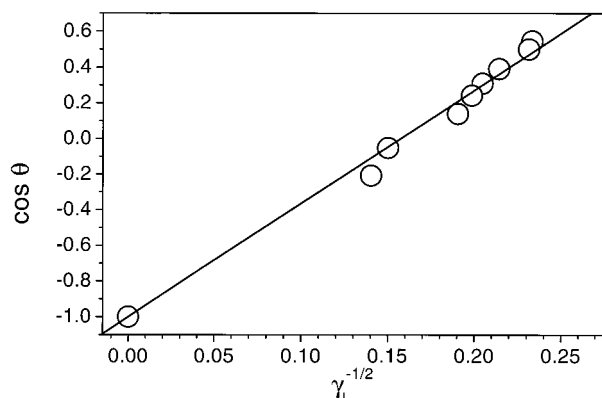
Figure 6. Girifalco−Good−Fowkes−Young plots for the determination of the dispersive surface energy of a complex-coated silicon wafer surface. From left to right the points are values obtained with (1) methylene iodide, $\gamma_l = 50.0$ mN/m; (2) α-bromonaphthalene, $\gamma_l = 44.0$ mN/m; (3) hexadecane, $\gamma_l = 27.6$ mN/m; (4) dodecane, $\gamma_l = 25.4$ mN/m; (5) decane, $\gamma_l = 23.9$ mN/m; (6) octane, $\gamma_l = 21.8$ mN/m; (7) PDMS $\gamma_l = 18.7$ mN/m; and (8) hexane $\gamma_l = 18.4$ mN/m. γ_s^d was calculated to be 10.1 $\pm$ 0.3 mN/m from the slope (circles are measured angles, solid line is least-squares fit).

wettability data were also used to determine the dispersion force component of the surface energy γ_s^d by using the Girifalco−Good-Fowkes-Young equation,[17,18] which has the form

$$\cos\theta = -1 + 2(\gamma_s^d/\gamma_l)^{1/2} \qquad (3)$$

This equation is utilized by plotting $\cos\theta$ against $(1/\gamma_l)^{1/2}$ for a family of dispersive liquids with the ordinate of the best linear fit located at -1 and the gradient being $2(\gamma_s^d)^{1/2}$. The Girifalco−Good−Fowkes−Young plots are used to show the dynamic advancing contact angle data obtained for complex surfaces on silicon wafers (see Figure 6). Linear fits result in a dispersive surface energy of $\gamma_s^d = 10.1 \pm 0.3$ mN/m. This value is close to those found for a highly fluorinated side-chain homopolymer p-[(perfluorooctyl-ethylene)oxy]methyl]styrene (9.3 mN/m).[20] Both γ_c and γ_s^d values indicate a fairly ordered packing of the perfluorinated segments exposing CF_3 groups on the surface. It is particularly interesting that the contact angles of water (the most polar test liquid with $\gamma_l = 72.7$ mN/m) are smaller than those of methylene iodide ($\gamma_l = 50.0$ mN/m). The calculated surface energy using the eq 1 was determined to be 35.5 mN/m. The low surface energies determined for nonpolar liquids were reproduced, even when the complex-coated surfaces were dried after re-immersion in water. This indicates a reversible reconstruction of the complex surface after it has been in contact with water. By contrast, the low-energy surfaces of perfluorinated acids adsorbed on platinum were removed quickly when they came in contact with water.[24] Surface reconstruction phenomena are widespread in polymer coatings, such as self-organizing semifluorinated side-chain ionenes[21] and surprisingly polymers containing only a few polar groups, such as Teflon-PFA.[26] It is worth noting that surface reconstructions seem to be very fast when in contact with water, as shown by the constant contact angle of water which adjusts to an equilibrium within a few seconds. We suggest that the reason for this could be found on a nanometer scale such as the leopard's fur pattern, which we found for a polymeric complex of a fluorinated
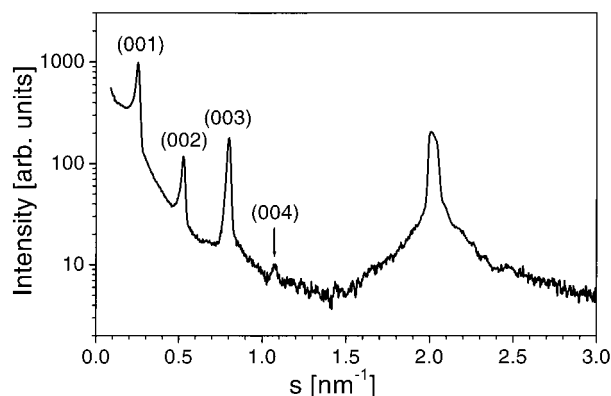
(26) Yasuda, H.; Okuno, T.; Sawa, Y.; Yasuda, T. *Langmuir* **1995**, *11*, 3255.

Figure 7. X-ray diffraction pattern of a complex **3** powder measured in transmission geometry. The length of the scattering vector is defined as $s = 2/\lambda \sin\theta$.

double-chain surfactant.[27] This nanoscale structured surface was proved to perform fast and reversible surface reconstruction when in contact with water.

   Structure in Bulk Material. The molecular order of fluorinated side chain polymers is determined primarily by the length of the fluorinated moieties which act in addition as mesogenic groups.[28,29] Recently we have shown that the ordering of fluorinated chains in solid polyelectrolyte−fluorosurfactant complexes are liquidlike[5,8] for short chain surfactants, and that the ordering can be tuned between liquidlike and crystalline by the charge density of the polyelectrolyte.[6] In the case of long-chain surfactants this is semicrystalline.[30] It can be seen in the wide-angle diagram of a powder of **3** (Figure 7) that an intense reflection is present in the wide-angle region at 2.0 nm^{-1}. This indicates a two-dimensional hexagonal lattice which we interpret as arising from the close packing of the fluorinated segments which have a chain-to-chain distance of 0.577 nm. A similar molecular ordering has been reported for a fluorinated poly(α,L-glutamate) with a C12 semifluorinated side chain.[29] Furthermore, this is similar to the close packing of fluorinated chains in poly-(tetrafluoroethylene) crystals of the hexagonal IV phase with a chain-to-chain distance of 0.57 nm.[31] The finding of a side chain crystallinity is consistent with the DSC measurements, from which it was concluded that the crystalline side chains melt at 180 °C. This result is similar to the side-chain crystallinity of a complex of PEI with perfluorinated acids, where a melting transition was observed at 163 °C for a fluorinated chain length of C16. In contrast to complexes of PEI with perfluorinated acids, the fluorinated chains of **3** are significantly shorter (C8) but show a higher melting point. This may be attributed to the better packing of the latter. It can be seen in the small-angle region of Figure 7 that four equidistant reflections are present, this is characteristic of a layered structure in the bulk material. A layer distance of $d = 3.75$ nm was determined from the peak positions. This is consistent with earlier investigations of fluorinated polyelectrolyte−surfactant complexes and revealed that they have highly ordered mesomorphous structures.[5−8] By analogy with strongly separated mesophase structures, we interpret the lamellar structure as consisting of sheets

(27) Thünemann, A. F.; Lochhaas, K. H. *Langmuir* **1999**, *15*, 4867−4874.
   (28) Wang, J.; Ober, C. K. *Macromolecules* **1997**, *30*, 7560.
   (29) Dessipri, E.; Tirrell D. A.; Atkins, E. D. T. *Macromolecules* **1996**, *29*, 3545.
   (30) Thünemann, A.; Lochhaas, K. H. *Langmuir*, in press.
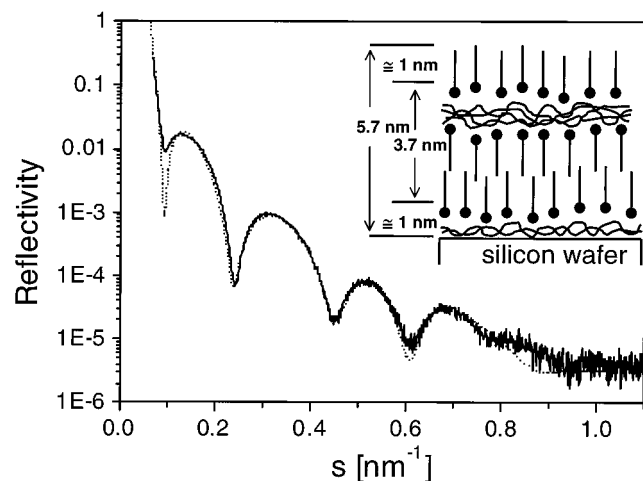   (31) Seperati, C. A. *Physical Constants of Fluorpolymers*, 3rd ed.; Wiley: New York, 1996.

Figure 8. X-ray reflectivity curve of an ultrathin complex film (5.7 nm) on a silicon wafer (solid line, experimental curve; dotted line, fitted curve). The insert shows a sketch of the film structure in the direction vertical to the wafer surface.
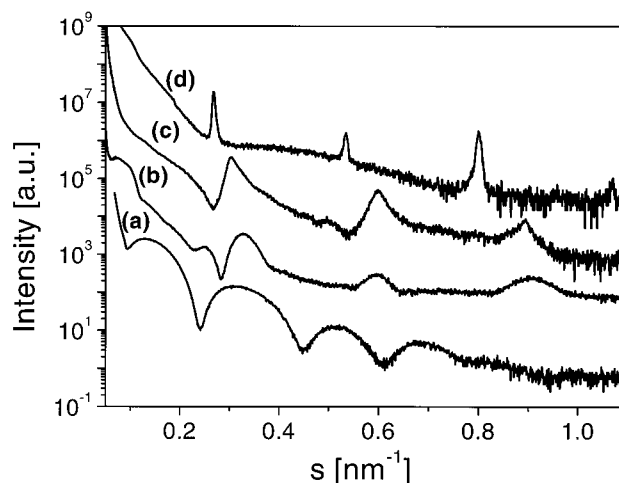

Figure 9. X-ray reflectivity curves of complex films on silicon wafers with vertically ordering of alternating fluorinated and ionic layers. The film thicknesses are 5.7 nm (curve a), 16 nm (curve b), 39 nm (curve c), and 370 nm (curve d).

of a thickness d_1, which are enriched in their fluorinated groups, and sheets of a thickness d_2, which are enriched in their ionic groups and their polymer backbones. The long period is given by $d = d_1 + d_2$. From the relative intensities of the lamellar (001) to (004) reflections, we calculated the thicknesses of d_1 and d_2. They were calculated to be 1.70 ± 0.05 and 2.05 ± 0.05 nm by using the stacking model.[32] Using the terminology of the description of liquid crystals, we designate the structure of complex **3** as bulk material which has a smectic B structure and is stable, at least from 20 to 185 °C. The remarkably high thermal stability of the smectic B structure is comparable to that observed for a complex of a rodlike polyelectrolyte, which was investigated by temperature-dependent X-ray scattering.[33] The next question is, are ordered supramolecular structures possible in view of the branching of the PEI? This commercial product, which is used widely in the paper industry, has a molecular weight of $M_w = 25\,000$ g/mol and ratios of primary to secondary to tertiary amino groups of 34:40:26. Chen and Hsiao have reported on lamellar complexes with dodecylbenzenesulfonic acid for the same PEI.[34] They showed that considerable branching does not hinder the formation of an ordered supramolecular complex structure. Further, Hwang and Kim have shown that PEI of the same molecular weight and degree of branching could be very effective in assembling rigid Langmuir–Blodgett monolayers of fatty acids.[35] Therefore, the occurrence of self-assembled structures with a high degree of order is not inconsistent with the irregular structure of the polymer backbone of PEI.

Structure of Thin Films. Thin complex films on silicon wafers were prepared by the spin-coat technique from complex solutions. The film structure was then investigated by X-ray reflectivity. Reflectivity curves of ultrathin and thin complex films are shown in Figures 8 and 9. To our surprise well-defined double-layer stacks developed within a few seconds simply as the result of the deposition of droplets of the complex solution. In Figure 8 the presence of Kiessig fringes indicates a smooth complex film. A thickness of 5.7 ± 0.5 nm was calculated from the angular positions of the fringes.[36] The reflectivity curve can be explained as resulting from 1.5 double layers. Here the double layer is defined as a structure building block with an ionic sheet surrounded by fluorinated sheets. The latter are formed by the tails of the amphiphiles. With this definition the structure is given as follows: half an ionic layer (ca. 1.0 nm) lies at the complex/wafer interface, a double layer is in the middle (3.75 nm), and finally a fluorinated layer (ca. 1.0 nm) is located at the complex/air interface (see Figure 8, insert). This assumption was confirmed using a box model based on the Parrat formalism.[37] The resultant fit was shown in Figure 8 (dotted line). The lowest thickness of films we were able to prepare was 5.7 nm. For films of larger thicknesses, which were in the range of about 20–400 nm, as determined by a surface profiler, three Bragg peaks appear. The differences between the peak positions are equidistant. Examples are shown in Figure 9 (curves b, c, and d). A lamellar spacing of 3.70 ± 0.05 nm was calculated from the reflex positions. Within the experimental error this value is identical to that determined for the complex material in bulk form (3.75 nm). Because of the same mesomorphous structure was developed in a slow film forming process (solvent casting) and in a fast film forming process (spin coating), we conclude that the time which is necessary for the formation of the mesophase is shorter than the time necessary for the formation of films. The latter is in the order of a second. Furthermore, as expected for a stack of multilayers, the sharpness of the Bragg peaks increases with increasing film thickness in the line from curve b to d (Figure 9). Vertical correlation lengths of 16 ± 1 nm (b), 39 ± 2 nm (c) and 370 ± 10 nm (d) were determined from the integral widths of the reflections. The structure of the films can be explained as consisting of multilayers aligned parallel to the wafer surface. In addition, from the result of the contact angle measurements and from the good adhesion of the films on the wafers, we conclude that a fluorinated layer lies on the complex/air interface and an ionic layer lies on the wafer/complex interface. Therefore the film resulting in curve b (Figure 9) contains 4.5 double layers, that resulting in curve c contains 10.5 double layers, and curve d contains about 100 double layers. The observed macroscopic orientation of the complex to multilayers with

(32) Wolf, T.; Burger, C.; Ruland, W. *Macromolecules* **1994**, *27*, 3001–3309.
(33) Thünemann A. F.; Ruppelt, D.; Schnablegger, H.; Blaul, J. *Macromolecules* **2000**, *33*, 2124.
(34) Chen, H.-L.; Hsiao, M.-S. *Macromolecules* **1999**, *32*, 2967.
(35) Hwang, M.-J.; Kim K. *Langmuir* **1999**, *15*, 3563.
(36) Holy, V.; Pietsch U.; Baumbach, T. In *Springer Tracts in Modern Physics, Vol. 149: High-Resolution X-ray Scattering from Thin Films and Multilayers*; Springer: Berlin, 1999.
(37) Parrat, L. *Phys. Rev.* **1954**, *95*, 359.

a variability of about 2 decades in their thicknesses which were produced in a single-step procedure is, in our opinion, significant progress in using self-assembly for the preparation of thin organic films. Mechanical fields, present at the spin-coating procedure, are probably the reason for the macroscopic orientation of the lamellar stacks parallel to the underlying substrate surface.

Summary and Conclusions

The complex formation of two commercially available compounds, polyethyleneimine and 3-[($^1H,^1H,^2H,^2H$-fluorooctyl)thio] propionic acid, serves as a model system for new colloidal coating materials, which show low surface energies and low friction properties. In contrast to classical fluorinated polymers these materials are characterized by highly ordered lamellar mesophases. Further, in contrast to the preparation of other lamellar structured thin films prepared by the established Langmuir−Blodgett and layer-by-layer deposition techniques, multilayer films of the complex can be prepared in a time-saving single-step procedure. The high degree of self-assembly is attributed to the strong incompatibility of fluorinated and ionic moieties. Furthermore the structure formation is very fast, which makes such fluorinated complexes attractive as new materials for thin organic film coatings with low adhesion and low friction properties.