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# Complexes of Polyethyleneimine with Perfluorinated Carboxylic Acids: Wettability of Lamellar Structured Mesophases

Andreas F. Thünemann

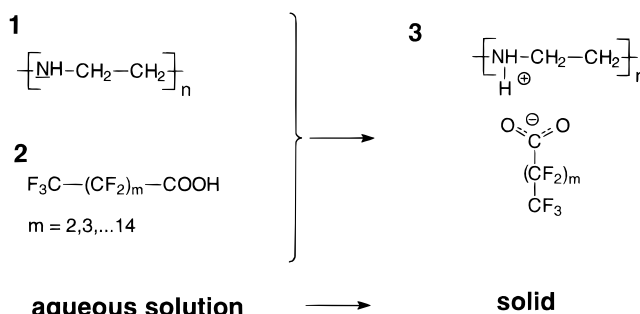
Max Planck Institute of Colloids and Interfaces, Am Mühlenberg, D-14476 Golm, Germany

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Structures of water-insoluble complexes of polyethyleneimine (PEI) and fluorinated acids, varying in chain length from 4 to 16, were examined via contact angle measurements, X-ray diffraction, and infrared spectroscopy. The wettability of complex surfaces was shown to decrease with increasing chain length. The surface energy of the complexes can be adjusted in the range from about 19 to 9 mN/m. Complexes of PEI with perfluorobutanoic acid and perfluoropentanoic acid are amorphous. Complexes with perfluoroheptanoic acid, perfluorodecanoic acid, and perfluorododecanoic acid are mesomorphous, while the complex with perfluorohexadecanoic acid is partially crystalline.

## Introduction

The systematic preparation of low-energy surfaces performed via the self-assembly of polyelectrolyte–surfactant complexes is potentially of high technological importance as well as of fundamental scientific interest. Coatings, especially in this case, seem to have a great variety of applications for these new materials because they are easy to prepare. Such coatings are very promising for self-cleaning surfaces or as very thin protective coatings for walls which are prone to contamination (graffiti<sup>1</sup>). The growing field of solid polyelectrolyte–surfactant complexes has recently been reviewed.<sup>2,3</sup> Many of these complexes show the pronounced tendency of forming well-ordered liquid crystalline-like structures with high mechanical and thermal stability. Little is known in the field of fluorosurfactants and silicone surfactants containing polyelectrolyte–surfactant complexes. Up to now systems with lamellar mesophase structures, perforated lamellar structures, and two-dimensional hexagonal and columnar mesophases have been found.<sup>4–9</sup> Here we report on lamellar mesophases formed by the complexation of polyethyleneimine (PEI) **1** with perfluorinated carboxylic acids **2** resulting in polyethyleneimine perfluorocarboxylates **3**. The complexation is shown schematically in Figure 1. Polyethyleneimine is a branched, water-soluble polymer that is widely used in the paper industry.<sup>10</sup> 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.<sup>11</sup> To investigate the influence of fluorine on the structure and surface properties of PEI complexes, seven polymer



**Figure 1.** Sketch of complex formation: (1) polyethyleneimine; (2) perfluorinated acid; (3) stoichiometric polyelectrolyte–surfactant complex.

complexes, varying in the length of the fluorinated chains, were prepared (PEI–C4, ..., PEI–C16).

## 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  $M_w = 25\,000$  g/mol.<sup>10</sup> The perfluorinated acids (butanoic (C4), pentanoic (C5), heptanoic (C7), octanoic (C8), decanoic (C10), dodecanoic (C12), hexadecanoic acid (C16)) and the solvent 1,1,1,3,3,3-hexafluoropropanol were supplied by Aldrich and used as received.

**B. Preparation.** One millimole of perfluorinated acid (chain length 4–16) was dissolved in 100 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 white precipitate, separated, and dried for 12 h at reduced pressure of 0.1 mbar. The yield was in the range of 90–95%.

**C. Methods.** The FTIR spectra were recorded on a Nicolet Impact 400 spectrometer using KBr pellets. 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 mL liquid drop, and the static contact angle was obtained from a drop (ca. 5 mL) on the surface. Within the experimental error of 1°, the static contact angles are 1–2° below the advancing contact angles. The linear alkanes decane, dodecane, and hexadecane were used as test liquids. Wide-angle X-ray scattering (WAXS) measurements were carried out with a Nonius PDS120 powder diffractometer in transmission ge-

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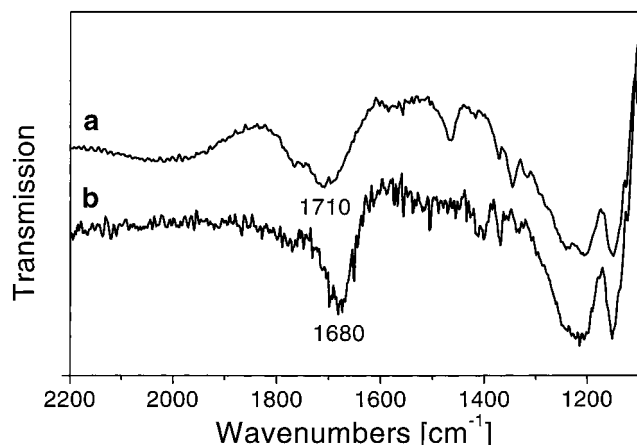
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**Figure 2.** FTIR spectrum of perfluorodecanoic acid (C10, curve a) and that of its complex with polyethyleneimine (PEI-C10, curve b). In the spectrum of C10 an intense carboxylic acid band at a wavenumber of 1710  $\text{cm}^{-1}$  is found, which results from the C=O stretch vibration. This band is absent in the spectrum of PEI-C10. The acid carbonyl adsorption band is replaced by a band at 1680  $\text{cm}^{-1}$  which indicates a stoichiometric 1:1 complexation.

ometry. A FR590 generator was used as the source of Cu  $K\alpha$  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 better than 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).

### Results and Discussion

Comparison of the IR spectra of **2** and **3** shows that the carboxylic acid vibration found for **2** at 1710  $\text{cm}^{-1}$  is absent for **3** (see Figure 2). Instead of the carboxylic acid band in the spectrum of **2**, an intense band at 1680  $\text{cm}^{-1}$  is present in **3** resulting from carboxylate structures. From this it can be concluded that the complex is stoichiometric as was found earlier for a nonfluorinated polyethyleneimine complex.<sup>12</sup>

**Surface Energies.** Complex surfaces were prepared by spin-casting a 0.1% (w/w) complex solution onto silicon wafers. After the evaporation of the solvent (1,1,1,3,3,3-hexafluoropropanol), the wafers were stored overnight at 30 °C and then for 60 min at 100 °C. From the weight uptake, the thicknesses of the resultant complex coatings were calculated to be in the range of 100–400 nm. The wettability of the complex surfaces with *n*-decane, *n*-hexadecane, diiodomethane, and water was then determined by dynamic contact angle measurements (see Tables 1–4). It was found that the contact angles of the test liquids increase with increasing chain length. By comparison, the static contact angles of PEI-C10 ( $\theta_{\text{st}}$ , *n*-hexadecane = 77°) and PEI-C12 ( $\theta_{\text{st}}$ , *n*-hexadecane = 82°) complex surfaces are at least as high as those found for adsorbed monolayers of C10 ( $\theta_{\text{st}}$ , *n*-hexadecane = 72°) and C12 ( $\theta_{\text{st}}$ , *n*-hexadecane = 78°) on platinum surfaces.<sup>13,14</sup> The latter are known to be the surfaces showing the lowest critical surface tension observed to date (6 mN/m). Similar high contact angles have been reported for side-chain crystalline polymers

**Table 1. Dynamic Contact Angles of the Polyethyleneimine Perfluorocarboxylate Complexes, Perfluorinated Acids Monolayers, and Fluorinated Polymers against *n*-Decane ( $\gamma_1 = 23.9 \text{ mN/m}$ )<sup>a</sup>**

samples	$\theta_{\text{adv}}$ (deg)	$\theta_{\text{st}}$ (deg)	$\theta_{\text{rec}}$ (deg)	$\gamma_{\text{s,adv}}$ (mN/m)	$\gamma_{\text{s,st}}$ (mN/m)
PEI-C4	37	37	36	19.4	19.4
PEI-C5	51	50	44	16.1	16.4
PEI-C7	61	59	47	13.3	14.0
PEI-C8	68	67	61	11.7	12.0
PEI-C10	78	76	71	9.2	9.7
PEI-C12	80	79	76	8.7	9.0
PEI-C16	80	78	75	8.7	9.2
C10 <sup>b</sup>		62			13.3
C12 <sup>c</sup>		70			11.0
I-6,6-F8H4 <sup>d</sup>	71	66	62	10.9	12.2
F8-St <sup>e</sup>	71		56	10.9	

<sup>a</sup>  $\theta_{\text{adv}}$ ,  $\theta_{\text{st}}$ , and  $\theta_{\text{rec}}$  are advancing, static, and receding angles.  $\gamma_{\text{s,adv}}$  and  $\gamma_{\text{s,st}}$  are surface energies calculated using eq 1, first with static and then with receding angles, respectively. <sup>b</sup> Reference 13. <sup>c</sup> Reference 14. <sup>d</sup> Reference 17. <sup>e</sup> Reference 15.

**Table 2. Dynamic Contact Angles of the Polyethyleneimine Perfluorocarboxylate Complexes, Perfluorinated Acid Monolayers, and Fluorinated Polymers against *n*-Hexadecane ( $\gamma_1 = 27.6 \text{ mN/m}$ )<sup>a</sup>**

samples	$\theta_{\text{adv}}$ (deg)	$\theta_{\text{st}}$ (deg)	$\theta_{\text{rec}}$ (deg)	$\gamma_{\text{s,adv}}$ (mN/m)	$\gamma_{\text{s,st}}$ (mN/m)
PEI-C4	50	49	46	19.0	19.3
PEI-C5	64	62	57	14.9	15.5
PEI-C7	70	68	66	13.1	13.7
PEI-C8	71	71	66	12.8	12.8
PEI-C10	79	77	64	10.5	11.0
PEI-C12	82	82	75	9.7	9.7
PEI-C16	83	80	69	9.4	10.8
C10 <sup>b</sup>		72			12.5
C12 <sup>c</sup>		78			10.8
I-6,6-F8H4 <sup>d</sup>	81	75	69	10.0	11.7
F8-St <sup>e</sup>	82		60	9.7	
F8-MA <sup>f</sup>	81		71	10.0	
PTFE <sup>g</sup>	51		40	18.7	

<sup>a</sup>  $\theta_{\text{adv}}$ ,  $\theta_{\text{st}}$ , and  $\theta_{\text{rec}}$  are advancing, static, and receding angles.  $\gamma_{\text{s,adv}}$  and  $\gamma_{\text{s,st}}$  are surface energies calculated using eq 1, first with static and then with receding angles, respectively. <sup>b</sup> Reference 13. <sup>c</sup> Reference 14. <sup>d</sup> Reference 17. <sup>e</sup> Reference 15. <sup>f</sup> Reference 16. <sup>g</sup> Reference 23.

**Table 3. Dynamic Contact Angles of the Polyethyleneimine Perfluorocarboxylate Complexes, Perfluorinated Acid Monolayers, and Fluorinated Polymers against Diiodomethane ( $\gamma_1 = 50.0 \text{ mN/m}$ )<sup>a</sup>**

samples	$\theta_{\text{adv}}$ (deg)	$\theta_{\text{st}}$ (deg)	$\theta_{\text{rec}}$ (deg)	$\gamma_{\text{s,adv}}$ (mN/m)	$\gamma_{\text{s,st}}$ (mN/m)
PEI-C4	83	81	75	19.8	20.7
PEI-C5	92	92	88	15.6	15.6
PEI-C7	96	96	92	13.8	13.8
PEI-C8	99	98	90	12.6	13.0
PEI-C10	104	104	91	10.5	10.5
PEI-C12	106	103	90	9.8	11.0
PEI-C16	108	107	89	9.1	9.4
C10 <sup>b</sup>		90			16.5
C12 <sup>c</sup>		103			11.0

<sup>a</sup>  $\theta_{\text{adv}}$ ,  $\theta_{\text{st}}$ , and  $\theta_{\text{rec}}$  are advancing, static, and receding angles.  $\gamma_{\text{s,adv}}$  and  $\gamma_{\text{s,st}}$  are surface energies calculated using eq 1, first with static and then with receding angles, respectively. <sup>b</sup> Reference 13. <sup>c</sup> Reference 14.

with C<sub>8</sub>F<sub>17</sub> fluorocarbon substituents with a polystyrene ( $\theta_{\text{adv}}$ , *n*-hexadecane = 82°),<sup>15</sup> a methacrylate ( $\theta_{\text{adv}}$ , *n*-hexadecane = 81–82°)<sup>16</sup> and an ionene-6,6 backbone ( $\theta_{\text{adv}}$ , *n*-hexadecane = 81°,  $\theta_{\text{st}}$ , *n*-hexadecane = 75°),<sup>17</sup> which were all shown to yield

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**Table 4. Dynamic Contact Angles of the Polyethyleneimine Perfluorocarboxylate Complexes, Perfluorinated Acid Monolayers, and Fluorinated Polymers against Water ( $\gamma_1 = 72.3$  mN/m)<sup>a</sup>**

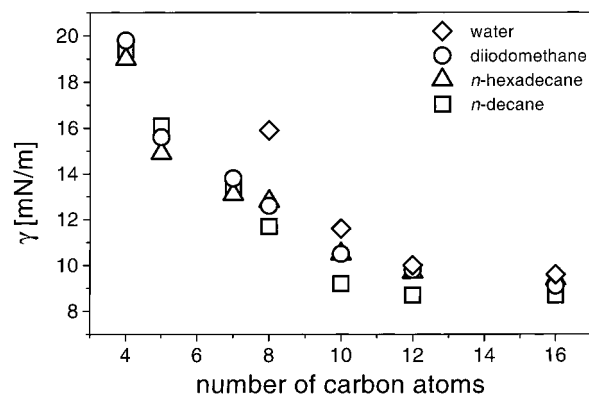
samples	$\theta_{adv}$ (deg)	$\theta_{st}$ (deg)	$\theta_{rec}$ (deg)	$\gamma_{s,adv}$ (mN/m)	$\gamma_{s,st}$ (mN/m)
PEI-C8	112	110	103	15.9	17.1
PEI-C10	120	117	105	11.6	13.1
PEI-C12	123	120	109	10.0	11.6
PEI-C16	124	120	100	9.6	11.5
C10 <sup>b</sup>		102		21.8	
C12 <sup>c</sup>		103		21.2	
I-6,6-F8H4 <sup>d</sup>	121		111	11.1	

<sup>a</sup>  $\theta_{adv}$ ,  $\theta_{st}$ ,  $\theta_{rec}$  are advancing, static and receding angles.  $\gamma_{s,adv}$  and  $\gamma_{s,st}$  are surface energies calculated using eq 1, first with static and then with receding angles, respectively. <sup>b</sup> Reference 13. <sup>c</sup> Reference 14. <sup>d</sup> Reference 17.

double layers of the hydrocarbon backbone and their fluorocarbon chains. The use of contact angles to calculate surface energies is only reliable in the case of homogeneous and smooth surfaces. On some rough surfaces abnormally high contact angles can be found. Two examples are the Lotus effect, which is observed for a number biological surfaces such as plant leaves,<sup>18–20</sup> and super water- and oil-repellent surfaces, which result from fractal surfaces.<sup>21</sup> To be sure that the high contact angles found for the PEI carboxylate complex surfaces were not due to roughness, the surfaces were investigated by scanning electron microscopy. It was found that all complex surfaces are smooth on length scales in the range from several millimeters down to values lower than 1  $\mu$ m. Therefore roughness as being responsible for the high contact angles of the complex surfaces can be excluded. Thus dynamic contact angles can be used as a measure of the surface energy. To compare the contact angle data, the solid surface energies were calculated using the equation derived by Neumann and Li:<sup>22</sup>

$$\cos \theta = -1 + 2 \sqrt{\frac{\gamma_s}{\gamma_1}} \exp[-\beta(\gamma_1 - \gamma_s)^2] \quad (1)$$

where  $\beta$  is a constant (0.000 124 7 m mJ<sup>-1</sup>),  $\gamma_s$  is the surface energy of the solid, and  $\gamma_1$  is the surface tension of the test liquid. Thus, the surface energy of the solid can be determined from the experimental contact angles and the liquid surface tension. For carboxylic chain lengths larger than four, the surface energies calculated using eq 1 result in surface energies significantly lower than 18.5–20 mN/m, which is the value for the standard low surface energy of poly(tetrafluoroethylene),<sup>23,24</sup> which shows an advancing contact angle against hexadecane of 51°. In Tables 1–4 it can be seen that the surface energies calculated on the basis of advancing angles ( $\gamma_{s,adv}$ ) differ only slightly from the values which were calculated using stationary angles ( $\gamma_{s,st}$ ). In addition, the difference between the advancing and the receding contact angles is low (about 10°), which is further indicative of the low degree of roughness of the complex surfaces. In the case of PEI-C16 this hysteresis is significantly larger (11–20°); this is possibly due to the



**Figure 3.** Surface energies for polyethyleneimine carboxylate complexes are dependent on the chain length of the fluorinated carboxylate moieties. The surface energies were calculated using eq 1 for water (diamonds), diiodomethane (cycles), *n*-hexadecane (triangles), and *n*-decane (squares) as test liquids.

long fluorinated chain length. The surface energies decrease with an increasing chain length from values of about 19–20 mN/m (PEI-C4) down to about 8–9 mN/m (PEI-C12 and PEI-C16). It can be seen from Figure 3 that constantly low values are reached at a chain length of about 12. The calculated values using *n*-decane, *n*-hexadecane, and diiodomethane match very well. Their surface tensions cover a relatively large range (23.9 mN/m, *n*-decane, to 50.0 mN/m, diiodomethane), but their interactions with the complex surfaces are exclusively dispersive. By contrast, the surface energy values calculated using water as a test liquid are more complicated because of the high dipole moment of water. The complex surfaces of PEI-C4, PEI-C5, and PEI-C7 were attacked by water, and therefore no contact angles could be measured. In the cases of PEI-C8 and PEI-C10 the surface energies are significantly higher possibly due to a surface reconstruction, as observed earlier for polyelectrolyte-surfactant complexes<sup>8</sup> as well as for fluorinated side chain ionenes.<sup>17</sup> The surface reconstruction seems to be absent or very much lower for PEI-C12 and PEI-C16. Probably in these cases the ionic polymer backbone is far enough below the surface to allow the attack of water, at least, within the time of the experiments (30 min). Contact angle hysteresis between advancing angle and receding angle are typically in the order of 10°. This can be caused by small imperfections, e.g., heterogeneity, swelling, and penetration by the wetting liquid.

**Molecular Order.** The molecular order of fluorinated side chain polymers is determined largely by the length of the fluorinated moieties which act in addition as mesogenic groups.<sup>17,25</sup> Recently we showed that the ordering of fluorinated chains in solid polyelectrolyte-fluorosurfactant complexes are liquidlike<sup>4,7</sup> for short-chain surfactants, and this ordering can be tuned between liquidlike and crystalline by the charge density of the polyelectrolyte.<sup>5</sup> In the case of long-chain surfactants it is semicrystalline.<sup>26</sup> In the wide-angle diagram of the PEI complexes (Figure 4) it can be seen that the reflection pattern, and therefore the molecular ordering, changes with the chain length of the perfluorinated acid. For the shorter chain length complexes (PEI-C4 to PEI-C10) only one broad reflection was found (curve a and b in Figure 4). Its maximum corresponds to a Bragg spacing of 0.51 nm. The presence of only very broad wide-angle reflections

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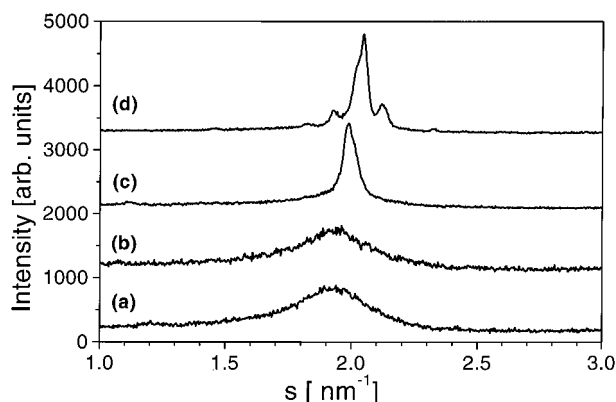
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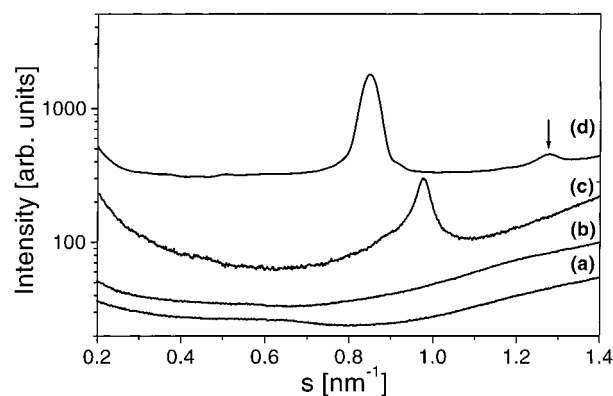




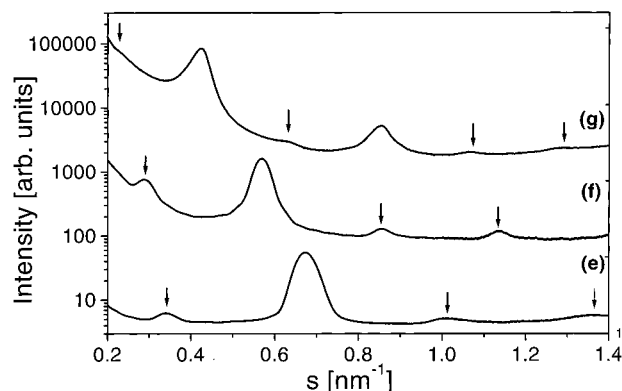
**Figure 4.** Wide-angle X-ray scattering diagrams of complex powder of PEI-C8 (a), PEI-C10 (b), PEI-C12 (c), and PEI-C16 (d). The scattering vector is defined as  $s = 2/\lambda \sin \theta$ .

confirms that the complexes PEI-C4, PEI-C5, PEI-C7, PEI-C8, and PEI-C10 are noncrystalline materials. In the wide-angle diagram of PEI-C12 a reflection with a slightly lower Bragg spacing of 0.50 nm, but with a significantly smaller width, was found (Figure 4c). This is indicative for a better lateral ordering of the adjacent fluorinated chains than those present in PEI-C4 to PEI-C10. The simplest molecular arrangement that conforms to the sharper wide-angle reflection of PEI-C12 is that of a parallel alignment of the rodlike perfluoroalkyl chains arranged in a two-dimensional lattice with rotational disorder and an average distance of 5.7 nm between the chains. A similar molecular ordering has been reported for a fluorinated poly( $\alpha$ -L-glutamate) with a C12 semifluorinated side chain.<sup>25</sup> As can be seen in Figure 4d, in addition to an intensive reflection (Bragg distance of 4.88 nm), further weak reflections were found (Bragg distances of 0.430, 0.472, 0.518, 0.548 nm) in the wide-angle X-ray scattering curve of PEI-C16. This finding is consistent with a further increase in the molecular order. Probably the order is three-dimensional with a chain-to-chain distance of 0.56 nm. This is similar to the close packing of fluorinated chains in poly(tetrafluoroethylene) crystals of the hexagonal IV phase with chain-to-chain distance of 0.57 nm.<sup>27</sup> The presence of side-chain crystallinity of PEI-C16 was confirmed by a first-order transition in the DSC thermogram with a maximum at 163 °C (not shown). This transition was ascribed to the melting of crystalline C16 side chains. By contrast, no thermal transitions were observed in DSC for the other complexes.

**Supramolecular Structure.** Earlier investigations of fluorinated polyelectrolyte-surfactant complexes revealed that they have highly ordered mesomorphous structures.<sup>4-7</sup> Therefore an ordering on a length scale in the range of 1–10 nm was assumed for the PEI perfluorocarboxylate complexes. Small-angle X-ray measurements were performed in order to prove this assumption. The scattering curves of complex powders are shown in Figures 5 and 6. It can be seen that no reflections are present for PEI-C4 and PEI-C5 (Figure 5 a,b), and consequently a regular supramolecular order can be ruled out for these complexes. By contrast, a single reflection at 0.977 nm<sup>-1</sup> was found for PEI-C7 (Figure 5c) and two for PEI-C8 (Figure 5d) to six for PEI-C16 (Figure 6g) reflections are present in the diagrams of the complexes with the longer chains. These reflections are indicative of the presence of a supramolecular order in the complexes PEI-C7 to PEI-C16. The increasing number of reflections is indicative of



**Figure 5.** Small-angle X-ray scattering diagrams of complex powder of PEI-C4 (a), PEI-C5 (b), PEI-C7 (c), and PEI-C8 (d).



**Figure 6.** Small-angle X-ray scattering diagrams of complex powder of PEI-C10 (e), PEI-C12 (f), and PEI-C16 (g).

**Table 5. Small-Angle X-ray Diffraction Maxima in Units of the Scattering Vector  $s$  (nm<sup>-1</sup>) ( $s = 2/\lambda \sin \theta$ ) and Estimates of the Observed Relative Intensities ( $s = \text{strong}, w = \text{weak}$ )**

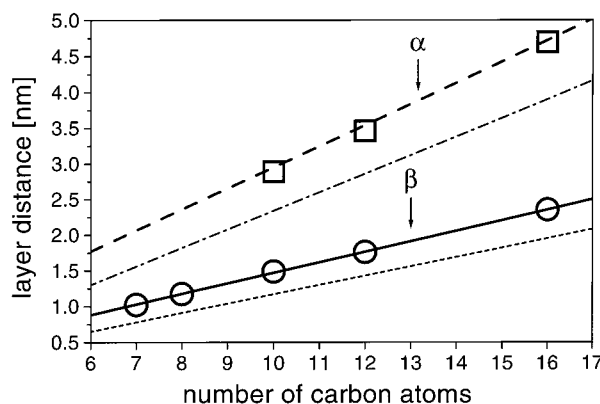
PEI-C7	PEI-C8	PEI-C10	PEI-C12	PEI-C16
0.977 s	0.852 s	0.342 w	0.289 w	0.220 w
	1.275 w	0.672 s	0.568 s	0.425 s
		1.011 w	0.860 w	0.640 w
			1.134 w	0.853 s
				1.062 w
				1.294 w

an increasing supramolecular ordering with an increasing chain length of the fluorinated moieties. The reflex maxima positions are summarized in Table 5. From these the relative reflex positions were determined to be 2.0:3.0 (PEI-C8), 1.0:2.0:3.0 (PEI-C10), 1.0:2.0:3.0:3.9 (PEI-C12), and 1.0:2.0:3.0:4.0:5.0:6.1 (PEI-C16). Such integral ratios are highly indicative of lamellar structures of the complexes PEI-C7 to PEI-C16. In the same sequence from PEI-C7 to PEI-C16 the long period increases with increasing chain length of the fluorinated chains. The appearance of supramolecular ordered structures may be explained as follows: Fluorinated carboxylate molecules in a complex act as mesogens in a way similar to that of the mesogens of side-chain polymer liquid crystals. Generally lamellar mesophase structures dominate the phase diagram of single-chain fluorinated carboxylates.<sup>28</sup> The frequent occurrence of lamellar mesophases is due to the bulky perfluorinated chains which behave similarly to bilayer-forming nonfluorinated double-chain alkyl surfactants. Therefore both the small-angle data and the

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general phase behavior of perfluorinated acids lead to the conclusion that lamellar mesophases are present in PEI–C7 to PEI–C16 complexes. The absence of such a structuring in PEI–C4 and PEI–C5 can be explained as being due the chain lengths of perfluorobutanoic and perfluoropentanoic acid, which are not long enough to induce a periodic microphase separation. 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 paper industry, has a molecular weight of  $M_w = 25\,000$  g/mol and a ratio 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.<sup>29</sup> They proved that high branching does not hinder 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.<sup>30</sup> 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. It is striking that in the scattering curves of PEI–C10, PEI–C12, and PEI–C16 the first reflection is much weaker in intensity than the second. To our knowledge there is no chemically meaningful model which explains a small-angle scattering that is in agreement with the experimentally established intensity ratios. The simplest way to explain the observed ratios is the presence of two lamellar structures, an  $\alpha$  phase and a  $\beta$  phase. Assuming this, the long period of  $\alpha$  is about twice as large as the long period of  $\beta$ . The reflections with the indices  $l = 2, 4, 6$  of the  $\alpha$  modification are found at the same  $s$ -values as the reflections with  $l = 1, 2, 3$  of the  $\beta$  modification. From the high intensity of the reflection (001) of the  $\beta$  phase (overlapped by reflection (002) of the  $\alpha$  phase) compared to the reflection (001) of the  $\alpha$  phase, we conclude that the  $\beta$  modification is dominant. The increases of the long periods of the  $\alpha$  and  $\beta$  phases as functions of the number of carbon atoms of the carboxylate chains are linear (see Figure 7). The increase of the long period per  $\text{CF}_2$  group was determined to be  $0.295 \pm 0.010$  nm and  $0.147 \pm 0.002$  nm ( $\alpha$  and  $\beta$  phase, respectively) from the straight lines in Figure 7. The length of an axial projection of a  $\text{CF}_2$  group in a fluorinated chain is 0.13 nm,<sup>31</sup> which gives a thickness of  $(n - 1)(0.13)$  nm of fluorinated sheets in a monolayer arrangement and  $2(n - 2)(0.13)$  nm of fluorinated sheets in a bilayer arrangement of the perfluorinated acids.  $n$  is the number of carbon atoms of the acids. It can be seen in Figure 7 that the theoretical and experimental slopes are in good agreement with a bilayer arrangement of the fluorinated chains in the  $\alpha$  phase and a monolayer arrangement in the  $\beta$  phase. Within this model the layer distances of the  $\alpha$  phase are 2.92 nm (PEI–C10), 3.46 nm



**Figure 7.** Layer distances of PEI complexes are dependent on the number of carbon atoms of the fluorinated acid used for complexation. In the lamellar  $\alpha$  phase, the fluorinated chains are arranged in bilayers (squares are measured values, the dashed line is a linear fit, and the dash-dotted line represents the theoretical values of fluorinated bilayer sheets, only). In the lamellar  $\beta$  phase the fluorinated chains are arranged in monolayers (cycles are measured values, solid line is a linear fit, and the dotted line represents the theoretical values for fluorinated monolayer sheets).

(PEI–C12), and 4.55 nm (PEI–C16). For the shorter chain length the  $\alpha$  phase was not observed. The layer distances of the  $\beta$  phase are 1.02 nm (PEI–C7), 1.17 nm (PEI–C8), 1.49 nm (PEI–C10), 1.76 nm (PEI–C12), and 2.35 nm (PEI–C16). It must be said that more complicated structures than those proposed are possible. The error of the layer distances is about  $\pm 0.05$  nm. A clear structure proof is nearly impossible by scattering on unoriented samples. Therefore additional experimental evidence, such as electron microscopy or structure-sensitive solid-state NMR, is needed. These experiments are currently in progress.

### Summary and Conclusions

It has been shown that the complexation of perfluorinated acids with polyethyleneimine produces a series of low surface energy forming materials with lamellar mesomorphous structures. The surface energy of these complexes decreases with increasing chain length and reaches constantly low values at a chain length of about 12. The simplicity of their synthesis, which simplifies the “fine-tuning” of the resulting structures and of the wetting properties, makes them attractive for the study of self-assembled fluorinated structures as well as for new coating materials.

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