Do Perfluorinated Chains always have to be Twisted?

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Short perfluorinated carbon chains do not take on a helical structure when they are closely packed.

The general accepted structure of a perfluorinated n-alkane involves a helical conformation of the backbone.[1] A perfluorinated fatty acid should be an ideal substance to form a Langmuir–Blodgett film because the helical structure of the perfluorinated hydrophobic tail has a very similar diameter to the hydrophilic head group. The molecules should therefore stand upright and untilted on the substrate surface. There is some experimental evidence[2,3] and a molecular dynamics simulation[4] that conflicts with this picture.

Perfluorododecanoic acid is too short a molecule to be deposited properly by the LB technique. We used instead a thermal evaporation technique to form regular multilayers.[5] Evaporation and deposition was performed in an Edwards 306 coating unit at about 10^{-5} Torr, an evaporation rate of 20 nm per minute and a substrate temperature of −10 °C. The substrates were glass, cleaned by standard procedures to produce a hydrophilic surface.

The structure of the deposited layers was investigated by low angle X-ray diffraction to determine the layer spacing and by X-ray grazing incidence diffraction (GID)[6] to study the in-plane structure. The experimental set-up used for the low angle diffraction measurements has been described before.[7] The results are given in Table 1. They show all the features of a multilayered assembly and can be interpreted as two phases, **I** and **II**, co-existing at the substrate. The tilt angles are 10 and 29°, respectively.

For the GID experiment the three-axis diffractometer at the D4-beam line of the HASYLAB, DESY in Hamburg, Germany, was used. The wavelength of the monochromatic radiation was 0.159 nm. The reflected radiation was detected by a position sensitive detector at the angle 2θ from the direction of incidence. A typical diffraction pattern is given in Fig. 1(*d*).

To understand the results of both types of X-ray experiments, molecular modelling was performed using the CERIUS and POLYGRAF program obtained from Molecular Simulations Inc. The force field parameters and atomic charges used in this simulation were found by modelling the four modifications of poly(vinyldenefluoride) (PVF2) and comparing the model crystal data with experimentally found ones. PVF2 was used for this purpose because of its diverse structures and their precise description in the literature.[8] The general behaviour of the model made it possible to use the unchanged DREIDING II force field.[9] The model reacted very sensitively to the charges assumed. The Gasteiger procedure[10] gave the best agreement between measured and simulated crystal data for all four modifications of PVF2.

With the experimental X-ray data in mind we studied only models of multiple bilayers with varying in-plane structures. Two different stable structures could be found by minimisation of the potential energy and dynamic simulation at 25 °C. Model X-ray data that correspond to the two used experiments which we carried out are given for both structures in Table 1 and Fig. 1. The superposition of the simulated X-ray patterns for both the (001) and the in-plane peaks reproduce the experimental data. This supports the model structures and the postulated coexistence of the two modifications on the substrate. Structure **I**, with four molecules in the unit cell, is much like the orthorhombic structure found in Langmuir–Blodgett films of ordinary fatty acids. Structure **II**, with two molecules in the unit cell, corresponds to a tilted hexagonal one. Surprisingly, the molecules are untwisted in both simulated structures. Perfluorinated n-alkanes usually exhibit a helical structure which leads to the torsion angles of the backbone being shifted from 0° for the plane zigzag layout of n-alkanes to either +15 or −15° for the lowest-energy conformation. The parameters which we employ in our model reproduce this feature for isolated molecules. The molecules untwist only when packed in a periodic structure.

The generally accepted explanation for the helix is the greater van der Waals radius of the fluorine as compared with hydrogen. A simulation using van der Waals forces alone shows that, assuming reasonable values for the radius of fluorine, the

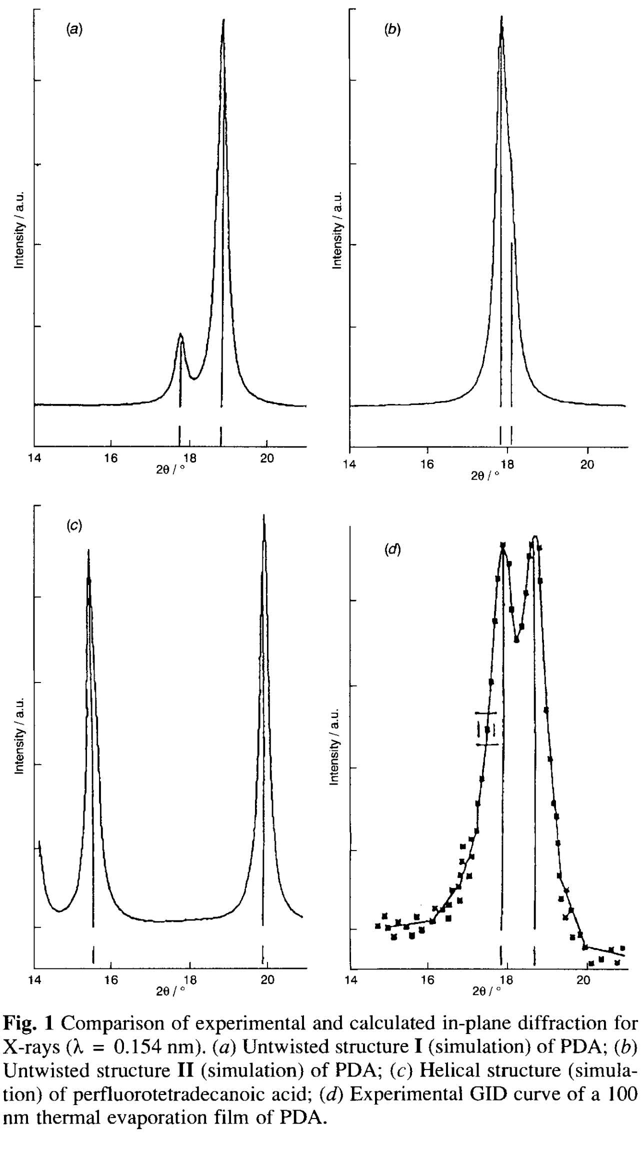

Fig. 1 Comparison of experimental and calculated in-plane diffraction for X-rays (λ = 0.154 nm). (*a*) Untwisted structure **I** (simulation) of PDA; (*b*) Untwisted structure **II** (simulation) of PDA; (*c*) Helical structure (simulation) of perfluorotetradecanoic acid; (*d*) Experimental GID curve of a 100 nm thermal evaporation film of PDA.

Table 1 X-Ray specular reflection data of PDA multilayers

Experiment		Model **II**		Model **I**	
d-Spacing/Å	Intensity	*d*-Spacing/Å	Rel. intensity	*d*-Spacing/Å	Rel. intensity
34.69	194.7	—	—	34.35	38.5
31.66	235.0	30.11	21.9	—	—
17.19	589.8	—	—	17.18	88.4
15.91	1890.3	15.05	66.6	—	—
11.57	57.0	—	—	11.45	2.5
10.78	48.5	10.03	3.4	—	—
8.69	99.1	—	—	8.58	16.9
8.02	274.9	7.53	15.3	—	—
6.98	47.6	—	—	6.87	0.3
6.27	45.8	6.02	2.7	—	—

largest obtainable shift of the *trans* state is 3°. Only after activating the model charges is the helical state obtained. This result leads us to the conclusion that the molecular packing of perfluorinated fatty acids and perfluorinated n-alkanes in general is determined mainly by Coulomb interactions in contrast to the van der Waals dominated structures of ordinary n-alkanes. Since the Coulomb potential generates long range interactions, intermolecular forces have a much larger influence on the intramolecular geometry of perfluorinated chains than they do with ordinary n-alkanes or alkyl chains.

It should be mentioned that this untwisting of the helices when they are packed in a periodic structure vanishes for chains longer than 12 carbon atoms in the backbone. For perfluoro-n-eicosane our model reproduces the experimental results of Strobl *et al.*[11] that prove the existence of a helical conformation for this model.

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