Epitaxial Growth and Crystal Structure Analysis of Perfluorotetracosane

W. P. Zhang and D. L. Dorset*

Electron Diffraction Department, Medical Foundation of Buffalo, Inc., 73 High Street, Buffalo, New York 14203

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ABSTRACT: Perfluorotetracosane, $nC_{24}F_{50}$, has been epitaxially oriented on cleaved KCl and NaCl substrates in vacuo and studied by electron diffraction and microscopy. The organic film consists of lathlike crystallites perpendicular to each other, corresponding to two equivalent nucleation directions on the salt crystal surface. An orthorhombic unit cell is found, and, from systematic absences for *hkl* spots, i.e., $h + k$, $k + l$, $h + l \neq 2n$, it is face-centered. The space group can be determined as *Fmmm* if molecular chains are assumed to be cylindrically averaged, which is the only reasonable solution. The unit cell contains four molecules arranged in two molecular layers, and molecules pack in a hexagonal lattice in each layer, as revealed by *hk*0 reflections. The unit cell parameters are $a = 5.68$, $b = 9.84$, and $c = 67.4$ Å. The (00*l*) and (*hhl*) electron diffraction intensity data are fit by a cylindrical $(CF_2)_n$ rotor model ($R = 0.267$). Low-dose lattice images indicate that molecular layers run parallel to the lath elongation. The (010) plane of the fluorocarbon lies parallel to the substrate surface. When the substrates are heated at higher temperature, the fluorocarbon molecules are rearranged with their chains normal to the underlying surface.

Introduction

Oligomeric chain segments are often employed to model the structural relationships of an infinite polymer chain in the crystalline state, as evidenced, for example, by the frequent analogies made between *n*-paraffins and polyethylene.[1] Recently this laboratory has been interested in the rather severe constraints on solid-state cosolubility imposed by finite chain lengths in contrast to the rather large polydispersity accommodate by the chain-folded polymer.[2] Studies[3-6] on *n*-paraffin binary solids, where relative molecular volumes are varied within a single-crystal structure for a homologous chain-length series, have shown that interesting superlattice-like structures occur when molecular volume differences are large enough to disallow stable continuous solid solutions but are yet small enough to preclude total chain fractionation.[4,6] More recent studies[7] on oligomeric perfluoroalkanes have led to similar conclusions, although the X-ray diffraction data from these binary solids were based on bulk measurements rather than the microcrystalline electron diffraction and electron microscopic measurements used to characterize the *n*-paraffin phase separation.

It has been difficult to obtain single-crystal electron diffraction data from poly(tetrafluoroethylene) and its shorter chain oligomers because of the problem in finding suitable solvents for growth of thin microcrystals.[8] Most of the structural information we have on the perfluoromethylene chain has come from fiber X-ray diffraction data. For example, the X-ray studies of Bunn and Howells[9] on the infinite chain polymer described the existence of a low-temperature triclinic unit cell, which transforms to a more disordered state above 30 °C. Clark and Muus[10] characterized this transition in greater detail in terms of a 13_6 helical chain transforming to a 15_7 helix to produce the higher temperature hexagonal packing. Oligomers such as perfluorocetane $nC_{16}F_{34}$ resemble the higher temperature form,[9] and a homologous series is shown[7,11] to have a chain-length repeat of 1.32 Å.

Although impressive high-resolution electron microscopic "lattice images" have been obtained from the virgin polymer,[12,13] comparable data from recrystallized perfluoromethylene chain compounds are relatively scant. Transmission and reflection electron diffraction studies of *n*-perfluorodecanoic acid layers on metal surfaces by Chapman and Tabor[14] established that the chains are packed with axes normal to the layer surface and have an expanded lateral unit cell dimension similar to the value found by X-ray measurements on a perfluoroalkane.[9] A quantitative single-crystal electron diffraction structure analysis[15] of the perfluorocetane in a projection onto the hexagonal crystal plate later verified that the chain packing could be accounted for by a perfluoromethylene rotor model. However, in order to characterize binary solids of *n*-perfluoroalkanes in terms of localized microarea crystal structures, some means must be found to orient the chains parallel to a major crystal face rather than the normal projection achieved by solution growth or melt crystallization. To date, our attempts to achieve such anepitaxial crystallization from a comelt as described by Wittmann and Lotz[16] have not been successful, probably because of repulsive forces between the intended organic nucleating substrate and the fluoroalkane as they cocrystallize from a melt as a eutectic solid.[17]

As will be shown in this paper, an alternative approach, suggested by analogous vapor deposition experiments of Wittmann and Lotz,[18] has succeeded in achieving the desired perfluoroalkane chain orientation and enables us to determine its crystal structure in a projection onto the chain axes from single-crystal electron diffraction intensity data.

Materials and Methods

Perfluorotetracosane, $nC_{24}F_{50}$, with a melting point of 188–190 °C was purchased from Aldrich Chemical Co. The material was deposited onto KCl and NaCl substrates under a vacuum of 10^{-5} Torr. The alkali halides were cleaved along their (001) face in air and outgassed in vacuo by heating and then returned to room temperature for the sublimation experiment. This involved placing the fluoroalkane into a perforated molybdenum boat and subliming it onto the cleaved salt surface by mild resistive heating of the metal container. Some samples were annealed later on the substrate at different temperatures on a Mettler FP82 hot stage. Finally, the organic films were backed with a thin layer of carbon, floated onto pure water surface to dissolve away the salt substrates, and picked up on 400-mesh copper grids for electron microscopy.

Samples were examined by means of a JEOL JEM-100CX II electron microscope equipped with a minimum-exposure device,

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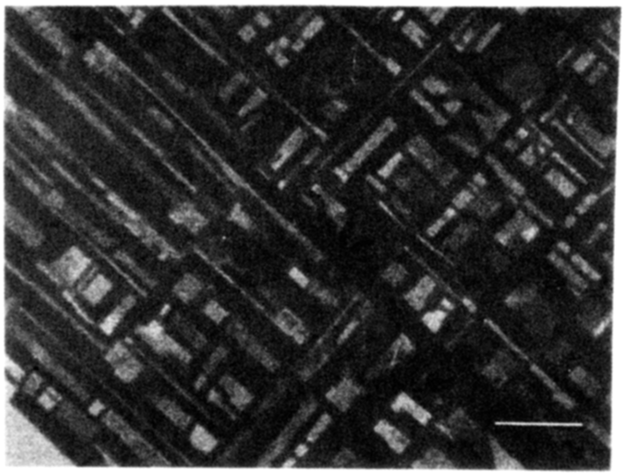

Figure 1. Electron micrograph of perfluorotetracosane thin film epitaxially grown on KCl substrate at room temperature. The bar indicates 1 μm.

with the precaution of using a low electron beam current to avoid serious radiation damage. Electron diffraction patterns and micrographs were recorded on Kodak DEF-5 X-ray film. The diffraction camera length was calibrated with gold Debye–Scherrer diagrams. Measurements of lattice spacings on diffraction patterns were made with a film-reading device manufactured by Charles Supper, Inc. Intensities were measured by integrating under peaks traced by scans of the diffraction films with a Joyce Lobel MkIIIC flatbed microdensitometer.

Structure factors F_{hkl} of $(00l)$ and (hhl) reflections were calculated by using kinematical diffraction theory,[19] i.e.

$$F_{hkl} = \sum f_j'(\mathbf{s}_{hkl}) \exp(2\pi i \mathbf{r}_j \cdot \mathbf{s}_{hkl})$$

where f_j' is the Doyer–Turner[20] electron form factor for atom j corrected for isotropic thermal motion, $\mathbf{r}_j$ is the atomic position in the unit cell, and $\mathbf{s}_{hkl}$ is the reciprocal vector for reflection (hkl). The following parameters[21] were used in the computation: C–C bond length = 1.54 Å, C–F bond length = 1.41 Å, C–C–C spacing = 2.64 Å, and $\angle$F–C–F = 109.5°. Isotropic thermal parameters used were $B_c = 6.0$ Å^2 and $B_F = 6.0$ Å^2. The usual crystallographic R factor

$$R = \left(\sum ||F_{\mathrm{obs}}| - k|F_{\mathrm{cal}}||\right) / \sum |F_{\mathrm{obs}}|$$

was used to judge the fit of structure model to observed data, where k is a scale factor such that $\sum|F_{\mathrm{obs}}| = k\sum|F_{\mathrm{cal}}|$.

Results and Discussion

Determination of Unit Cell and Space Group. Perfluorotetracosane thin films epitaxially grown on KCl are composed of lathlike crystallites perpendicular to each other, as shown in Figure 1. Two equivalent nucleation directions on the salt (100) surface result in the two orthogonal orientations of the fluoroalkane crystals. The corresponding electron diffraction pattern (Figure 2a) shows a superposition of two identical diagrams crossing each other. One pattern is labeled by the arrows, with the c^* direction indicated. The inner, closely spaced $00l$ spots are from the lamellar repeat of the molecules, corresponding to a lattice distance of 33.7 Å, in close agreement with Starkweather's measurement.[11] The diffuse line at wide angle has a real space distance of about 1.32 Å, which is the projected distance between two adjacent carbon atoms along the chain direction. This is also close to the value found earlier.[7,11]

To determine the unit cell parameters and symmetry, a diffraction pattern from another reciprocal plane (Figure 2b) has been obtained by tilting samples around c^* by 30°. Combining with Figure 2a, an orthorhombic unit cell, with lattice parameters $a = 5.68$, $b = 9.84$, and $c = 67.4$ Å, is established. Thus, parts a and b of Figure 2 depict $h0l$ and hhl reflections, respectively. In Figure 2a, 200 spots are perpendicular to the $00l$ row and give a real space distance of 2.84 Å. In Figure 2, hkl spots appear only when $h + k = 2n$, $h + l = 2n$, and $k + l = 2n$. This extinction corresponds to a face-centered lattice. In orthorhombic systems, there are five space groups with face-centered symmetry: $F222$, $Fmm2$, $Fdd2$, $Fmmm$, and $Fddd$. To determine the space group, the average molecular shape must be taken into account.

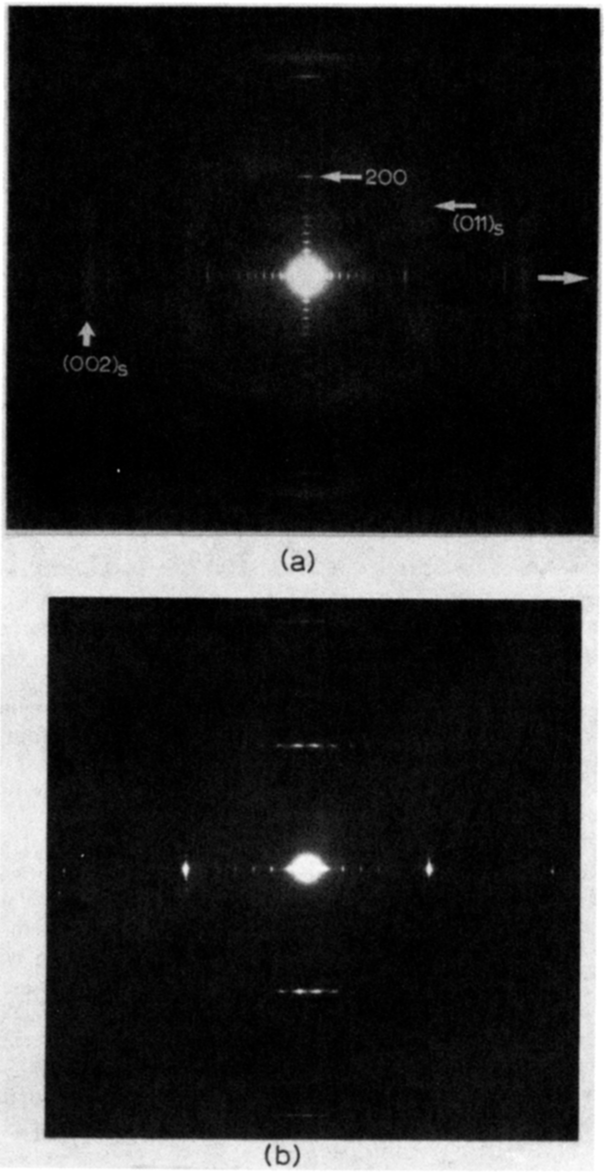

Figure 2. (a) $h0l$ diffraction pattern from untilted crystals of perfluorotetracosane grown on KCl. The diffuse spots are indexed as a polyethylene-like subcell. (b) hhl electron diffraction pattern of perfluorotetracosane obtained by tilting the samples about 30° around the $00l$ row with extinctions for the hkl spots: $h + k = 2n + 1$ and $k + l = 2n + 1$.

After the aggregate is annealed at 80 °C for 1 h, crystallites are produced with molecules that have lost their epitaxial relationship with the substrate, as revealed by the electron diffraction pattern along the molecular axis (Figure 3). The diffraction pattern has hexagonal symmetry, but if it is indexed as an orthorhombic lattice, it has two of the same lattice parameters given above. For a face-centered lattice, {110} reflections should not appear, as they do in Figure 3. The appearance of these extinct reflections from multilayered crystals can be well understood in terms of the diffraction incoherence caused

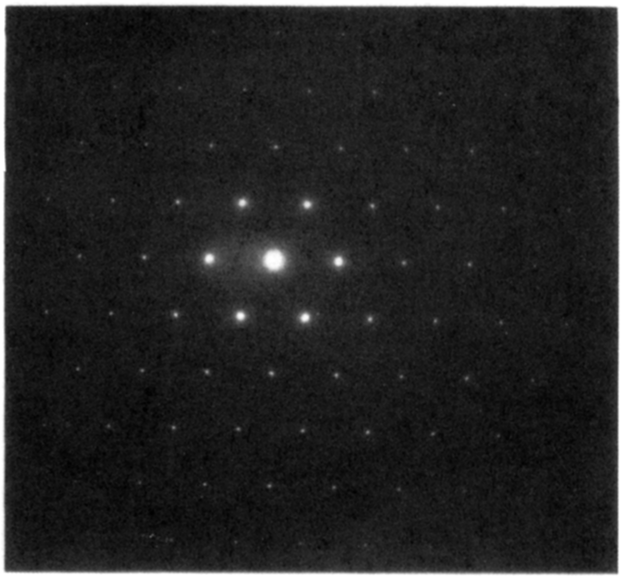

Figure 3. Electron diffraction pattern of perfluorotetracosane film annealed at 80 °C for 1 h producing an orthogonal orientation to Figure 2.

by elastic crystal bending,[22] which is most apparent when the electron beam parallels a long unit cell axis. As found with the paraffins, the diffraction intensities will correspond only to single molecular layers. This effect was also seen earlier with perfluorocetane.[15]

It is important to explain this effect in some detail in order to appreciate how the intensity data may be used for structure analysis. Since the films studied here are very thin (about 100–200 Å), they are certainly slightly deformed by elastic bends. The effect of such bending in the diffraction intensities was successfully modeled by Cowley[23] in his early work on electron diffraction from silicates. For kinematical diffraction, the diffracted intensity, $I(\mathbf{s})$, is the Fourier transform of the Patterson function, which is modulated by a Gaussian term incorporating the bend; i.e.

$$I(\mathbf{s}) = \sum W_i(\mathbf{s}) \exp(2\pi i \mathbf{r}_i\cdot\mathbf{s}) \exp(-\pi^2\gamma^2 s^2 z_i^2)$$

Here $W_i(\mathbf{s})$ is the electron scattering factor corresponding to the ith Patterson peak at position $\mathbf{r}_i$, γ is the crystal bending in radians, and z_i is the component of $\mathbf{r}_i$ in the incident beam direction. The bend is assumed to be uniform so γ is a constant. It is clearly shown that structural details due to long Patterson vectors, especially those with a large z_i value, are most readily suppressed by bending because the last term in the above equation falls off quickly with the increase of z_i, while features due to shorter vectors are retained. For the reflections from crystallites with molecular chains parallel to the substrate surface (parts a and b of Figure 2), the unit cell dimension along the incident beam direction is small; coherent diffraction includes several molecular layers, so that the actual crystal symmetry is now represented by the reflection intensities. For those reflections from crystals with molecular chains normal to the substrate surface, on the other hand, the unit cell dimension is large (e.g., molecular layer thickness is 33.7 Å in this case). Diffraction intensities are produced almost solely by perfluoromethylene repeats so that only the crystal symmetry of one molecular layer appears in the diffraction pattern (Figure 3). Since this incoherence isolates the scattering from individual layers, we find that the fluorocarbon molecules pack in a hexagonal lattice in each layer.

An orthohexagonal molecular arrangement has been used to model the so-called "rotator" phase of alkanes,[24] as shown in Figure 4. Such a structure can also be used in our case if the molecules are assumed to have a cylindrically averaged packing. This results in a space group of *Fmmm*, in agreement with an earlier model for the high-temperature paraffin packing.[25] This space group is obtained from a statistical averaging of molecular orientations corresponding to a rotational freedom in the crystal packing explained by the cylindrical surface of the molecular helix.[9]

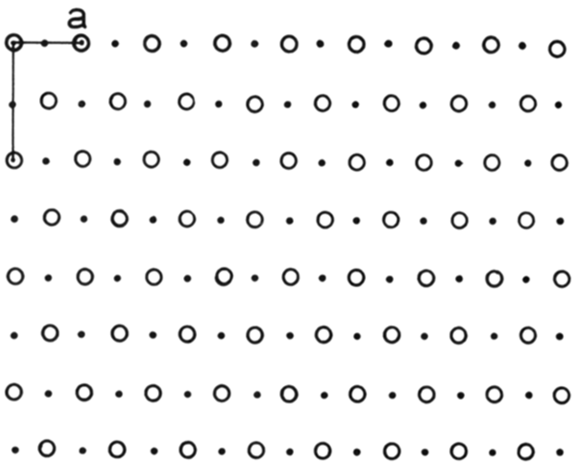

Figure 4. [001] projection of molecular packing of perfluorotetracosane in an orthorhombic lattice (molecules are considered to be cylinder-like). The lattice points denoted by circles are located $c/2$ above (or below) those denoted by dots.

Table I
Calculated and Observed Structure Factors for $n\mathrm{C}_{24}\mathrm{F}_{50}$

hkl	$\lvert F_{\mathrm{obs}}\rvert$	$\lvert F_{\mathrm{cal}}\rvert$	*hkl*	$\lvert F_{\mathrm{obs}}\rvert$	$\lvert F_{\mathrm{cal}}\rvert$
002	0.89	0.64	0,0,20	0.30	0.32
004	0.87	0.63	0,0,22	0.27	0.26
006	0.83	0.60	0,0,24	0.25	0.22
008	0.71	0.59	111	2.59	4.29
0,0,10	0.62	0.55	113	1.63	1.42
0,0,12	0.51	0.50	115	1.05	0.84
0,0,14	0.46	0.46	117	0.91	0.59
0,0,16	0.37	0.41	119	0.48	0.44
0,0,18	0.35	0.35			

Crystal Structure Analysis. Since the layer packing producing the electron diffraction pattern in Figure 3 has been determined earlier for a shorter chain homologue,[15] we proceed directly to a quantitative determination with intensities obtained from epitaxially oriented samples. A list of observed structure factors for 17 (00*l*) and (*hhl*) reflections from perfluorotetracosane is given in Table I. Kinematical structure factors were calculated by using the cylindrically averaged molecular packing model, as required by the unit cell symmetry. For computation, the model was simulated as follows. The long molecular center line was chosen as the rotator axis, and each carbon or pair of fluorine atoms at the same z level were represented, respectively, by 16 identical atoms with fractional occupancy oriented at intervals around the circular annulus with constant radii from the rotator center. We therefore did not infer any features of the chain helix in this model. A pure rotor model would result in only slightly different CF_2 z/c coordinates than, say, an open 15_7 helix.[10] It seems that a rather loose helical structure may be indicated by the diffuse $h0l$ spots in Figure 2 at $c_s{}^*$ and $c_s{}^*/2$ so that it approximates an untwisted zigzag.

A reasonably good fit of calculated structure factors to the observed data has been obtained with $R = 0.267$ when the temperature factors are defined $B_c = B_F = 6.0$ Å^2. One observed intensity that is somewhat small with respect to

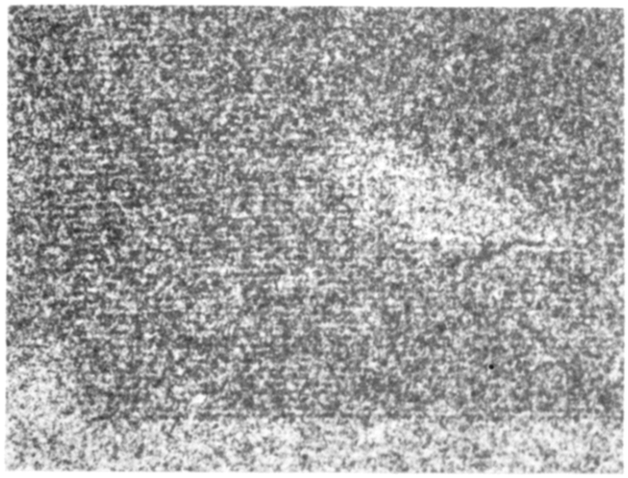

Figure 5. Low-dose electron microscope lattice image of epitaxially oriented $nC_{24}F_{50}$ showing the orientation of molecular layers along the lath direction.

the calculated value is I_{111}. The (hhl) data were obtained by tilting the crystals about 30° around the $00l$ reciprocal row; a few degrees away from the exact reciprocal plane may result in a sizable deviation for the intensity data, even though the R value is still in the range acceptable for an electron diffraction structure analysis.

High-Resolution Electron Microscopy. Because of the small size of the lathlike crystallites, it is somewhat difficult to ascertain the molecular orientation with respect to the crystal habit, since the epitaxial nucleation produces two orthogonal orientations. In their high-resolution work on rods of virgin poly(tetrafluoroethylene), Chanzy et al.[13] noted that the chain axes parallel the lath direction. Analogy to the n-paraffins,[26] however, would place the molecular axes normal to the lath elongation.

A typical low-dose electron image from an epitaxially crystallized crystal of $nC_{24}F_{50}$ obtained at a direct magnification of 19 000× is shown in Figure 5. The lamellar lines, which correspond to molecular layers, are shown to parallel the crystallite lengths as found with n-paraffin crystals. Optical transforms of these micrographs indicate that these images are obtained at a typical resolution of 11 Å, or 3 orders of the 33.7 Å layer repeat.

Discussion

From the above considerations it is clear that a chain rotor model in a centered orthorhombic unit cell, similar to the packing proposed by some co-workers for the "rotator" premelt form of n-alkanes, fits the observed electron diffraction intensity data from an oligomeric n-perfluoroalkane. Although in our earlier study of the hexagonal layer packing of a fluorocarbon[15] the chain packing was considered as a possible model for this alkane pretransition, it is now clear that a close analogy cannot be made. In a single-crystal study of the n-paraffin premelt transition using epitaxially oriented samples,[27] it was noted that the salient change in the observed diffraction data at high temperatures was a reduction in resolution of $00l$ reflections, as if modulated by a Gaussian function. Such a resolution restriction is not noted here for the diffraction patterns in parts a and b of Figure 2. Since the resolution loss in the paraffin crystals was attributed to Gaussian disorder at the lamellar interfaces, it is clear that the corresponding structure in the fluoroalkanes must be well-ordered. Further, it was found[27] that a slight helical arrangement would not disturb this chain ordering since the alignment of carbon atoms along the c axis is not affected by a slight molecular twist.

It is not possible from this determination to ascertain just what the helical twist of the perfluoroalkane chain is. Bunn and Howells[9] stated that the fluoroalkane structures are similar to higher temperature forms of the polymer. The $h0l$ diffraction data in Figure 2a suggest that the helical twist is very gradual. That is to say, the appearance of diffuse diffraction lines midway between the origin and the $d_{00l}^* = (1.32\ \text{Å})^{-1}$ line, as well as this latter line (Figure 2a), i.e., where the two reflections would correspond to (011) and (002) in polyethylene, indicates that the $-CF_2-$ segments retain a nearly common orientation for long periods of the chain length that is near that of a planar zigzag structure.

It remains to be shown how the epitaxy between the salt substrate and fluorocarbon is achieved. Presumably, this should involve a tight lattice register between the two at an interface so that the mismatch $\Delta = 100(d_c - d_s)/d_s$, where d_c and d_s are the respective interacting lattice distances of crystal and substrate, is within ±15%.[28] Ueda and Ashida[29] have shown that n-hexatriacontane epitaxially oriented on NaCl or KCl has its c axis parallel to the substrate [110] direction, resulting in respective mismatches of $100(2d_c - d_s)/d_s = 26.1\%$ and 14.8%. The lateral chain packing (110) plane with $d_{110} = 4.15$ Å gives a better match in the orthogonal direction where $100(d_c - d_s)/d_s = 4.7\%$ for NaCl and 6.5% for KCl.

The orientation of n-perfluorotetracontane on these salt substrates places the (010) face parallel to the substrate (100). If the fluorocarbon were to grow with chains parallel to [100] of NaCl or KCl, then the lateral lattice mismatch would be very small, i.e., 0.89% for NaCl and 9.55% for KCl. The fit along the chain direction would also be favorable in both cases; i.e., $100(2d_c - d_s)/d_s = 6.22\%$ for NaCl and 15.9% for KCl. Were the (110) planes of the alkali halides used to orient the fluoroalkane, then reasonable nucleations would only occur with more complicated relationships where $\Delta = 100(nd_c - md_s)/md_s$. Given the differences in ionic radii,[30] however, (i.e., Na^+, 0.95 Å; K^+, 1.33 Å; Cl^-, 1.81 Å) this diagonal nucleation many also be an important consideration since this is the only way that rows of smaller ions can intersperse between larger ion rows. Thus, the lattice match of the perfluoroalkane lateral packing with the (110) planes of NaCl or KCl would amount to $\Delta = 100(4d_c - 5d_s)/5d_s = 14.2\%$ or 2.3%, respectively. Observation of the crystallite orientation on KCl substrates by light microscopy favors the latter epitaxial interaction since the laths are parallel to the (110) planes of KCl.

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Registry No. *n*-$C_{24}F_{50}$, 1766-41-2; poly(tetrafluoroethylene) (homopolymer), 9002-84-0.