

difference in the corresponding slope values.

Conclusion

The present investigation confirms the fact that it is not possible to describe the shape of the globular protein by means of a well-defined geometry. Construction of best-fitting ellipsoids and the calculation of solvent contact areas for the residues in a set of globular proteins demonstrate a definite relationship between the contact areas of residues and their spatial positions from the centroids of the ellipsoids. The presence of clefts and crevices in the protein globule is due to the peculiar placement of certain residues against their intrinsic spatial preferences. The varying exposure behavior of residues determines the prevailing surface shape. We note, more or less, a uniform atomic level surface roughness and a differential macroscopic shape in the proteins, which means that the local short-range interactions influence the surface roughness whereas the long-range interactions influence the shape.

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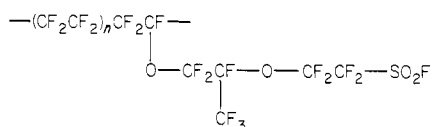
Crystallinity in Perfluorosulfonic Acid Ionomers and Related Polymers

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ABSTRACT: In spite of a large number of bulky side groups, perfluorosulfonic acid ionomers and their precursors have significant levels of crystallinity. The crystal structure appears to be similar to that of poly(tetrafluoroethylene) at elevated temperatures. The size of the crystallites is greater than the average separation between side groups. A model is suggested which is consistent with these observations. The polymer is thought to be arranged in bilayers with ionizable side groups extending on either side. An optical diffraction pattern based on this model is similar to the X-ray diffraction patterns. In earlier work it was concluded that ionic domains are separated by walls 10 Å thick, the correct magnitude for two layers of fluorocarbon. The model is also consistent with the results of recently published small-angle X-ray experiments.

Perfluorosulfonic acid ionomers are derived from copolymers of tetrafluoroethylene (TFE) and a perfluorovinyl ether terminating in a sulfonyl fluoride group and having the structure



Since the molecular weights of TFE and the comonomer are 100 and 446, respectively, the equivalent weight (EW) per sulfonyl fluoride group is

$$\text{EW} = 100n + 446$$

The copolymers of greatest interest have about 6-13 TFE units per comonomer unit.

The sulfonyl fluoride groups can be hydrolyzed to give sulfonic acid groups or various metal sulfonates. The acid and salt forms are hydrophilic. Gierke¹ concluded that the ionic domains are about 40 Å in diameter and are separated by walls of fluorocarbon about 10 Å thick.

The samples discussed here were prepared in the same manner as those in earlier work by Gierke and co-workers.^{1,2}

Table I
DSC Data

EW	T_m , °C peak/end	ΔH_f , cal/g
	SO ₂ F Form	
1050	236/254	1.16
1100	231/257	1.48
1350	251/278	3.34
1500	256/283	4.13
1790	266/286	6.92
	SO ₃ H Form	
1100	207/235	1.06
1350	231/253	1.68
1500	249/265	4.98

Degree of Crystallinity

Data from DSC scans at 20 °C/min on a series of copolymers in the sulfonyl fluoride form are summarized in Table I. As shown in Figure 1, the heat of fusion (ΔH_f) is a linear function of equivalent weight and extrapolates to zero at EW = 910 or a TFE/comonomer mole ratio of about 5. Thus, some crystallinity remains at a very high concentration of bulky side groups. The melting point also increases with increasing equivalent weight. The data are

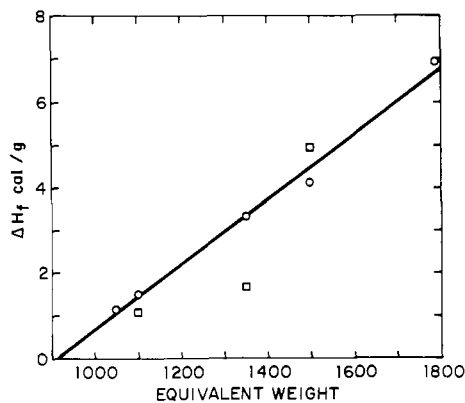


Figure 1. Heat of fusion vs. equivalent weight: (O) SO₂F form; (□) SO₃H form.

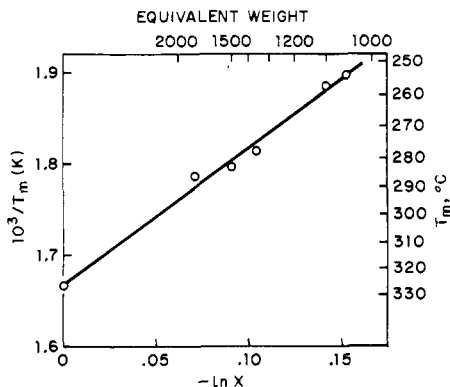


Figure 2. Melting point vs. equivalent weight for the SO₂F form. plotted in Figure 2 according to Flory's equation for the melting points of copolymers³

$$\Delta H_m = \frac{-R \ln X}{1/T_m - 1/T_m^0}$$

where ΔH_m is the heat of fusion per mole of monomer units, X is the mole fraction for the crystallizable comonomer, and T_m^0 and T_m are the absolute melting points for the homopolymer and copolymer, respectively. The appropriate melting point is the temperature at which the last crystal is in equilibrium with the melt, i.e., the upper end of the melting range, not the DSC peak. This treatment gives a heat of fusion of 1.33 kcal/mol of TFE units, in good agreement with the value of 1.37 kcal/mol given by Lupton.⁴ This agreement is probably fortuitous. The equation is based on the assumption that the second monomer is completely excluded from the crystals. The effects of differences in crystal size are not included. A recent determination of the heat of fusion of poly(tetrafluoroethylene) using the Clausius-Clapeyron equation gave a value of 2.22 kcal/mol.⁵ The depression of the melting point is greater than would have been expected from the revised heat of fusion and the Flory equation. That equation would not be applicable to the model of the crystalline structure presented in this paper.

Unit Cell

Most of the X-ray data were taken with a diffractometer, which facilitates locating relatively broad crystalline peaks which may be on top of an amorphous background. Fiber samples were mounted on a four-circle orienter. In this way, one can study meridional reflections which would not appear on a film pattern from an untilted fiber.

The X-ray diffraction pattern obtained from an oriented fiber of an ionomer precursor (sulfonyl fluoride form) of EW 1176 using copper K α radiation is shown schematically in the units of an undistorted reciprocal lattice rotated

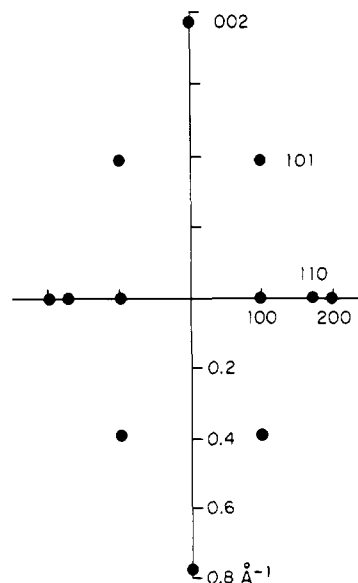


Figure 3. X-ray diffraction fiber pattern shown schematically in terms of an undistorted reciprocal lattice.

Table II
Crystallographic Data on the Sulfonyl Fluoride Form

EW	100		101		<i>a</i> , Å	<i>c</i> , Å
	2 θ , deg	<i>d</i> , Å	2 θ , deg	<i>d</i> , Å		
1050	17.5	5.07	38.8	2.32	5.85	2.62
1100	17.5	5.07	39.0	2.31	5.85	2.59
1176 ^{a,b} (fiber)	17.55	5.05	38.7	2.32	5.83	2.58
1350	17.9	4.96	39.5	2.28	5.73	2.57
1500	17.9	4.96	38.5	2.34	5.73	2.65
1790 ^a	18.04	4.92	39.2	2.30	5.68	2.60

^a 110 and 200 reflections also observed. ^b 002 reflection observed in meridional scan at $2\theta = 73.5^\circ$, $d = 1.288$ Å.

about the c axis in Figure 3. Quantitative data for samples of various equivalent weights are given in Table II.

The unit cell is hexagonal as in PTFE, but for the lower equivalent weights, only the 100 reflection is observed on the equator. This suggests that there are variations of at least 25–35% in the interchain separation.⁶ The 110 and 200 reflections were present in a film pattern from an oriented fiber of EW 1176 and a diffractometer scan from an unoriented film of EW 1790. The interchain separation, a , decreases with increasing equivalent weight, gradually approaching the value of 5.66 Å for PTFE at room temperature.⁷

A meridional scan from the fiber contained a peak at $2\theta = 73.5^\circ$, corresponding to a spacing of 1.29 Å. This is equivalent to the 0015 reflection in PTFE and is due to diffraction from the projection of the carbon atoms on the c axis acting as a one-dimensional lattice.

All samples gave a peak at $2\theta \sim 39^\circ$. The fiber pattern showed that it is an off-meridional reflection equivalent to a combination of the 107 and 108 reflections in PTFE. Projecting its position on the meridian indicated a spacing of 2.60 ± 0.03 Å, corresponding to two carbon atoms in the chain.

Matsushige et al.⁸ have reported that as PTFE is heated, the number of helix reversals increases until at 120 °C and above, the time-averaged chain conformation is a planar zigzag and the 107 and 108 reflections are merged. It appears that the crystal structure of these copolymers at room temperature is equivalent to that of PTFE at much higher temperatures. We have assigned them a hexagonal

Table III
Comparative X-ray Data from an Oriented Fiber
before and after Hydrolysis

	unhydro- lyzed	hydrolyzed	
		50% RH	100% RH
Equatorial Peak			
2θ , deg	17.55	17.6	17.55
d , Å	5.05	5.04	5.05
a , Å	5.84	5.82	5.84
min crystal width, ^a Å	39	32	32
no. of chains	8	6	6
orientation angle, deg	16	23	22.5
Meridional Peak			
2θ , deg	73.5	73.5	73.5
d , Å	1.29	1.29	1.29
c , Å	2.58	2.58	2.58
min crystal length, ^a Å	44	37	39
no. of carbon atoms	34	29	30

^a These calculations assume that all of the peak broadening is due to the small crystal size and neglect broadening due to crystal imperfections or instrumental factors.

unit cell with $c = 2.6$ Å. Thus, the meridional reflection is indexed as 002 and the off-meridional reflection as 101. While there is much positional disorder, it is clear that the crystal structure has true three-dimensional character.

X-ray diffraction data from the oriented fiber of EW 1176 before and after hydrolysis with KOH are compared in Table III. The positions of the 100, 101, and 002 reflections are essentially unchanged as the sulfonyl fluoride groups are converted to sulfonates. There is some broadening of the peaks, which will be discussed below. Saturating the hydrolyzed form with water produces little additional change in the X-ray pattern. This pattern is clearly associated with the hydrophobic fluorocarbon parts of the polymer and is little affected by the ionic domains.

Crystal Size

In the fiber pattern, from the sulfonyl fluoride form, the equatorial peak at $2\theta = 17.55^\circ$ had a width at half-maximal of 2.3° and the meridional peak at $2\theta = 73.5^\circ$ had a width of 2.5° . This broadening probably includes effects of both lattice distortions and small crystallite size, but we lack sufficient data to separate them. Assuming that the size effect is dominant, the Scherrer equation⁶ was used to compute minimum values for the crystallite size. The width of the 100 reflection corresponds to a lateral crystallite size of 39 Å or about eight polymer chains. The width of the 002 reflection indicates a crystallite size along the c axis of 44 Å or 34 carbon atoms. This is surprising because the average number of CF_2 groups between comonomer units is only 15. It may be that the 002 reflection is due to longer sequences of TFE crystallizing preferentially or the chain may maintain an extended conformation through a sequence which contains several comonomer units. It is important to note in this connection that Gierke, Munn, and Wilson have observed a meridional peak for this fiber at $2\theta \sim 0.6^\circ$, corresponding to a spacing of about 150 Å.²

As indicated in Table III, the positions of the 100, 101, and 002 reflections in the fiber pattern are unchanged by hydrolysis. There are, however, several subtle changes. The orientation angle is increased from 16 to 23° , and the intensity of the crystal diffraction pattern is reduced. These changes suggest some relaxation of the oriented crystalline structure. The peaks are broadened, indicating that the crystals are smaller or less perfect. Saturating the

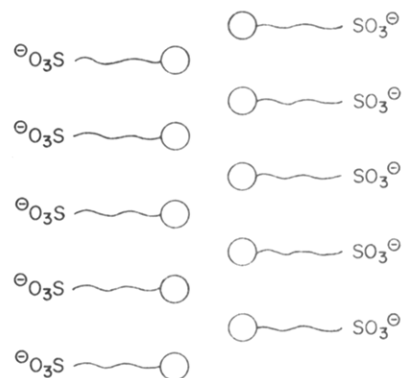


Figure 4. Model for the structure in the plane normal to the chain axes.

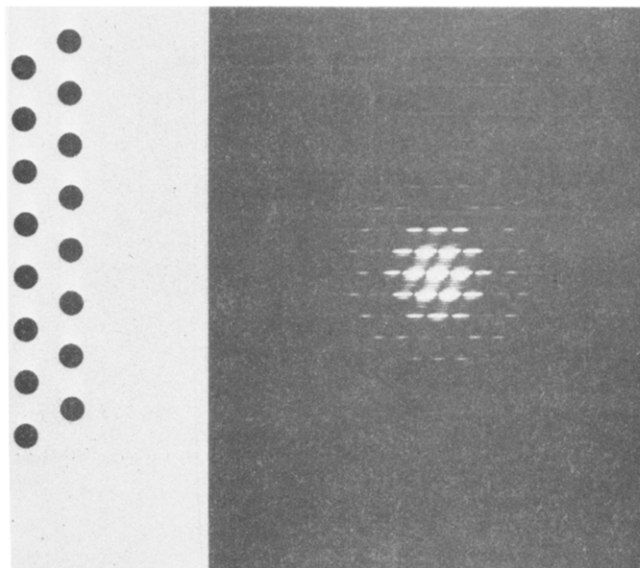


Figure 5. Optical diffraction pattern for the model in Figure 4.

hydrolyzed fiber with water produces little additional change in the diffraction pattern.

Model for the Crystalline Structure of Perfluorosulfonic Ionomer Polymers

The degree of three-dimensional crystalline order revealed by X-ray diffraction is surprising in a polymer consisting of a nonpolar backbone and rather large polar side groups. A possible explanation was suggested by the work of Gierke.¹ He found that the average diameter of the ionic domains is 40 Å and the separation between their centers is 50 Å. Thus, the wall thickness is about 10 Å, the width of two fluorocarbon chains.

A possible structure for the walls is shown schematically in Figure 4. The circles, drawn as two rows of a hexagonal lattice, represent polymer chains seen end-on. The sulfonate-bearing side groups extend on either side into the ionic domains. Of course, the side groups on these chains would not all be on the same level. If the comonomer units add to the chains head-to-tail and the average conformation is planar zig-zag, all the side groups will be on the same side of a chain.

A test of the diffraction pattern of this model in two dimensions, i.e., the equatorial diffraction, is shown in Figure 5. The pattern on the left side of the figure, consisting of two rows of eight dots on a hexagonal lattice, was made into a 35-mm slide. From it the optical diffraction pattern on the right was obtained. It consists of a full two-dimensional hexagonal pattern. The inner ring of six spots around the central spot consists of 100 re-

flections. In a fiber diagram from a sample having cylindrical symmetry, one could imagine this pattern being spun about the central spot.

This pattern does not prove that the model in Figure 4 is correct, but it does indicate that it is possible. It is difficult to think of any other way in which crystalline order could occur in a polymer having the known concentration of bulky branches. The model reflects a very efficient use of the polymer's components. The walls contain a minimal amount of structural material. The lower equivalent weights discussed here are close to the limit for the formation of crystalline order as indicated in Table I and Figure 1. This may also constitute a limit for forming separate nonpolar and aqueous phases. The crystal dimensions of 30-40 Å indicated in Table III are reasonable values for the width of the facets of a polyhedron having an overall diameter of 50 Å.

In considering this model, it is necessary to return to the earlier discussion of the 100 reflection and the size of the crystals in directions normal to the chain axes. If the crystals are only two chains wide in one dimension, much of the peak broadening will be due to that factor, and the crystal widths given in Table III are presumably less than the true values in the other dimension. This point is reflected in the shapes of the spots in the optical diffraction pattern in Figure 5. It is worth noting, however, that the 100 spots are more nearly round than those lying further from the origin.

The model presented in Figure 4 is further supported by the fact that it provides an explanation for the obser-

vation in small-angle X-ray experiments² that the diffraction peak arising from clustering is observed even at very low volume fractions of clusters. This explanation is based on the proposal that the effective "Bragg" spacing associated with ionic clustering is statistically weighted to be equal to the sum of the thickness of the fluorocarbon layer plus the cluster diameter.

The model is similar to the familiar bilayers formed by soap molecules. The incorporation of this arrangement in a polymeric system permits it to serve structural and surface-active functions simultaneously.

Acknowledgment. X-ray experiments on the fiber samples were done by F. C. Wilson, and the optical diffraction experiment was performed by Peter Avakian.

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Crystalline Forms in a Copolymer of Vinylidene Fluoride and Trifluoroethylene (52/48 mol %)

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ABSTRACT: The structure of a 52/48 mol % copolymer of vinylidene fluoride and trifluoroethylene has been investigated at various temperatures by X-ray diffraction. Melt-solidified samples consist of a mixture of two disordered crystalline phases, one trans planar, the other 3/1 helical. Samples may be transformed to either phase by appropriate means to reveal a hexagonal (or pseudohexagonal) molecular packing. The all-trans phase may be obtained by drawing or poling at low temperatures; both treatments cause a transformation of the disordered mixture of phases into a well-ordered planar-zigzag phase. Isolation of the disordered 3/1-helical phase is achieved by heating to high temperatures, whereupon all samples, irrespective of orientation or polarization, undergo transformation to a poorly ordered helical structure analogous to that of trifluoroethylene homopolymer; upon cooling, the original, disordered mixture of phases is recovered.

Introduction

Because of its important piezoelectric and pyroelectric properties, poly(vinylidene fluoride) has attracted much scientific interest during the past few years. As has recently been summarized,²⁻⁴ these properties are attributable to the ferroelectric nature of some of the polymorphic forms of poly(vinylidene fluoride). The most important of these polymorphs is the β phase, in which the molecules assume essentially a planar-zigzag conformation and pack in an orthorhombic unit cell whose dimensions render it pseudohexagonal.⁵ The current theories^{6,7} of ferroelectric polarization take advantage of this pseudohexagonal packing in considering the macroscopic alignment of di-

poles resulting from electrical poling to occur through cooperative rotations of chains about their molecular axes in multiples of 60°. Ferroelectric models predict existence of a Curie temperature for this polymorph, above which polarization is lost, presumably due to a pseudohexagonal randomization of molecular packing in crystalline regions. However, other than in one report,⁸ such a Curie temperature has not been found, and it is generally believed^{9,10} that this temperature may lie within the region of melting of poly(vinylidene fluoride).

Attention has recently been directed toward copolymers of vinylidene fluoride with other fluorocarbons, partly in the hope that Curie transitions would be unequivocally