

Fine Structure of ‘Crystalline’ Fluorinated Transparent Films and Fibers

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Changes in fine structure with drawing of poly[tetrafluoroethylene-*co*-(perfluoroethylvinylether)] (*abbrev.* PFA) transparent thin films and fibers were investigated by wide angle X-ray diffraction (WAXD) and small angle X-ray scattering (SAXS) methods. The PFA is random copolymer containing comonomer units of fluorinated ether derivatives as the side-chain in the repeating tetrafluoroethylene backbone. This polymer is crystallized as lamella crystal in their thin films and fibers although polytetrafluoroethylene itself usually forms extended-chain crystals because of their inflexible and rigid nature of 13/6 helices. PFA are exhibited thicker lamella thickness at least 30 nm by the SAXS measurement than general hydrogenated crystalline polymer. In these copolymers, we consider the formation of “switchboard-type” lamellae model according to P. J. Flory’s suggestion. With increase in elongation to their thin film, the four points SAXS diagrams has developed in the photograph of PFA transparent films, which means that a particular kind of layer structure is formed, alternately tilted lamella arrangements as a “Herring-bone”.

Key words: ‘Crystalline’ fluorinated transparent film, Drawing, Fluorinated comb copolymer, Small angle X-ray scattering, Wide angle X-ray diffraction

1. INTRODUCTION

Generally, polytetrafluoroethylene (PTFE; $-(CF_2-CF_2)_n-$) and its copolymers easily form rigid helices to yield extended-chain crystals. It seems difficult for PTFE to form a lamellae structure because of its rigid molecular chain.¹⁻⁵ In addition, since tetrafluoroethylene copolymers obtained by incorporation of several co-monomers exhibit extremely fast crystallization rates,⁶ their spherulites generally cannot be observed until they are sufficiently large. Therefore, PTFE exhibits a high degree of crystallinity of over 90%.⁷⁻⁹ Although there are a few reports that assume the formation of the spherulites of PTFE and their copolymers,¹⁰ it is hard to entirely believe them. These reports claim to be form folded chain of rigid fluorocarbon chain like a hydrocarbon. However, we consider that fluorocarbon chain cannot form folded chain without increase of flexibility for main-chain to incorporate several co-monomers. Accordingly, it is necessary to study the hierarchical structure of the spherulitic texture and the crystals of tetrafluoroethylene in detail.

Poly[tetrafluoroethylene-*co*-(perfluoro-alkylvinylether) (PFA)¹¹ has a unique role in the plastics industry due to its inertness, heat resistance, and low coefficient of friction in a wide temperature range. Generally, fluorinated compounds and fluoropolymers have excellent chemical resistance, oil resistance, and oil- and water-shedding resistance.¹²⁻¹⁵ They have been used as rubbers at high temperatures and as several lubricating fluorine manufactured products.

On the other hand, in the field of fundamental science, the structural studies on fluorinated polymers have progressed slowly since first reported by Bunn and Howells in 1954.¹⁶ We also found very few reports on the systematic studies on the Teflon-like fluorinated copolymer because these compounds are difficult to

synthesize due to the emission of poisonous gases.^{1, 3}

By the way, although PFA is a crystalline polymer, drawing processed PFA samples with high crystallinity are as transparent as amorphous polymers such as polymethylmethacrylate (PMMA) and poly(ethylene terephthalate) (PET), as shown Fig. 1. Generally, this experimental fact is almost ill-known. Probably, since transparency of organic materials depends on the existence of differences in density between crystal and amorphous region, high crystallinity of PFA closely relate to the occurrence of transparency. Additionally, PFA tubes break as a glass tube when applying excessive bending force on it. It is obvious that these unique property enhancements of drawing processed PFA films and fibers come from changes of crystal structure and crystalline morphology of PFA films and fibers during drawing process.

In this study, the fine structure and lamella arrangement in thin films and fibers formed by tetrafluoroethylene copolymers were investigated by using wide angle X-ray diffraction (WAXD), small angle X-ray scattering (SAXS), and

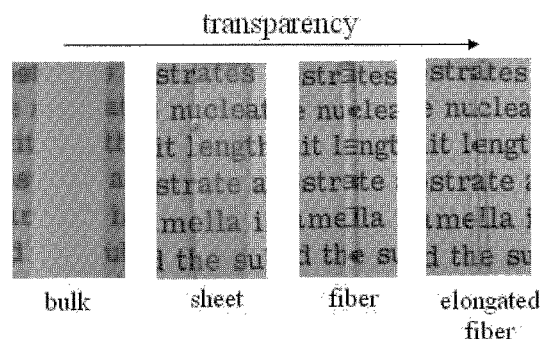


Figure 1 Changes in transparency of several materials of crystalline fluorinated copolymers.

scanning calorimetry (DSC).

2. EXPERIMENTAL

2.1 Materials

2.1.1 Materials and sample preparation

The fluorinated copolymers used in this study were provided by DuPont-Mitsui Fluorochemicals Co. Ltd. PFA is a random copolymer obtained from the co-polymerization of tetrafluoroethylene $(-\text{CF}_2-\text{CF}_2)_n$ and perfluoroethylvinylether $(-\text{CF}_2-\text{CF}(\text{OCF}_2\text{CF}_3)-)_n$. The amounts of co-monomer amounts of these materials are about 5–8 wt%. The molecular weights of these copolymers are examined by a computer simulation based on viscoelasticity in the molten state because these polymers are difficult to dissolve any organic solvents.

2.1.2 Drawing of PFA films and fibers

The PFA thin films and fibers were drawn by use of a hand-drawing apparatus in an air oven at 280 °C. The surface of film specimen was marked at intervals of 2 mm to measure the draw ratios. The drawing speed was fixed at 20 mm/min, and the film was annealed at 280 °C for 3 min before drawing. From these methods, we obtain thin films with an extreme transparency (Fig.2).

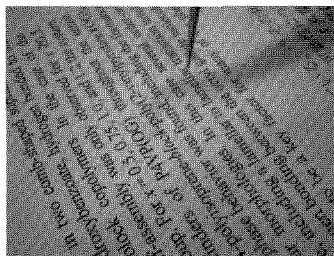


Figure 2 PFA 'crystalline' thin film having high transparency.

2.2 Experimental methods

2.2.1 Small-angle X-ray scattering (SAXS)

The crystalline morphology of the Teflon copolymers was characterized with a SAXS instrument (M18XHF, MAC Science Co.) consisting of an 18 kW rotating-anode X-ray generator with a Cu target (wavelength, $\lambda = 0.154$ nm) operated at 50 kV and 300 mA.¹⁷ This instrument comprised a pyrographite monochromator, pinhole collimation system ($\phi \sim 0.3, 0.3, 1.1$ mm), vacuum chamber for the scattered beam path, and a two-dimensional imaging plate detector (DIP-220). The sample-to-detector distance was adjusted to 710 mm. The exposure time for each sample was 30 min. For the SAXS measurements, the sample of approximately 0.5 mm thickness was placed in the sample holder so that its position remained unchanged. Theoretical detective limit of SAXS measurement in this study is almost corresponded to value of $q=0.128 \text{ nm}^{-1}$ estimated by camera distance (from sample to the imaging plate) in the apparatus. However, actual detective limit examined by counting pixel numbers of enlarged

SAXS patterns on monitor of analytical computer, is $q=0.170 \text{ nm}^{-1}$. Hence, the observable maximum value of long period between the center of gravity of lamellas in this study is 36.9 Å.

2.2.2 Wide-angle X-ray diffraction (WAXD)

To obtain WAXD data for the drawn films, a R-Axis diffractometer (Rigaku Co.) was operated at 45 kV and 200 mA to generate $\text{CuK}\alpha$ radiation ($\lambda = 0.1542$ nm). By use of a graphite monochromator and a 0.3 mm pinhole collimator, WAXD photographs of the samples were taken at room temperature. Diffraction data were recorded on a cylindrical imaging plate detector equipped with interface to a computer system. The camera length was 127.4 mm, and the exposure time was 600 sec.

2.2.3 Differential scanning calorimetry (DSC)

To examine the thermal properties of the drawing films, a DSC apparatus (Perkin-Elmer DSC Pyris1) was utilized in the range of 25 - 300 °C at a heating rate of 10 °C/min under a helium purge. The temperature and heat of transition obtained by the instrument were calibrated with indium and zinc standards before the measurements.

3. RESULTS AND DISCUSSION

Figure 3 show the SAXS patterns for DR1 (draw ratio 1), DR2, and DR3 thin film samples, respectively. A ring-shaped SAXS pattern was observed for the undrawn DR1 sample, while two- or four-point patterns were observed for the DR2 or DR3 samples. The former indicates random lamellar texture, and the latter some oriented lamellar structures with respect to the draw direction. Similar results were obtained for the case of the drawn PFA fibers.

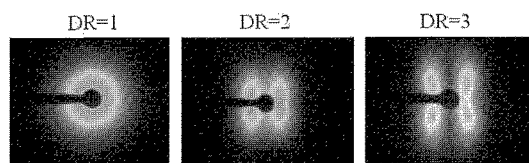


Figure 3 SAXS patterns of 'crystalline' transparent films of fluorinated copolymers at several draw ratios.

In the case of PTFE, the SAXS pattern is obscure and the corresponding profile exhibits an extremely low intensity because this polymer almost forms an extended chain and not a lamellae structure. On the contrary, it is found that the tetrafluoroethylene copolymer form lamellae structures since undrawn PFA used in this study exhibit isotropic SAXS patterns. The long period of DR1 is estimated to be 23.9 nm. High crystallinity PFA sample forms relatively thicker lamellae than general hydrogenated crystalline polymers.

From the results of SAXS measurements in DR1, we suggest the lamellar model of tetrafluoroethylene copolymers, as follows. According to A. Keller's suggestion,¹⁸ it is assumed that general crystalline polymers form regular sharp hold in Fig. 4(a),

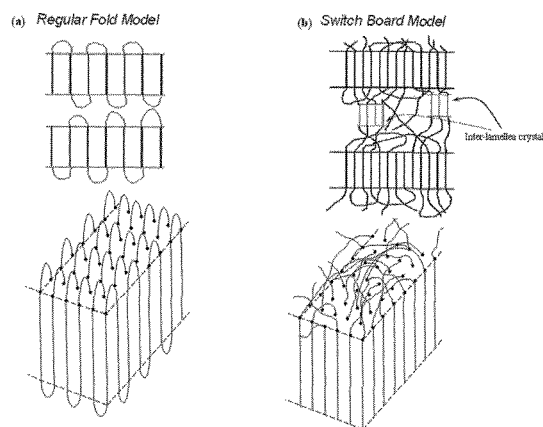


Figure 4 Schematic illustration of lamellae models of general crystalline polymers ((a) regular sharp fold model), and our proposed that of tetrafluoroethylene copolymers ((b) switch board model).

tetrafluoroethylene copolymers in this study are hard to form arrangement of this “adjacent re-entry” because of existence of rigid molecular chain and lack of flexible part. Probably, it seems that folded parts are formed in ether bond rich region within fluorinated main-chain. However, so many perfluoroalkylvinylether units cannot contribute formation of folded parts because absolute amounts of co-monomer ratio are extremely low. Hence, we proposed switch-board type lamellae model of these tetrafluoroethylene copolymers according to P. J. Flory’s suggestion in Fig. 4(b).^{19, 20} In this case, it is supposed that there is relatively large amorphous region with subtle inter-lamellae crystal because of existence of large long-period structure estimated by SAXS.

For the sake of convenience, a diagrammatic representation of the four-point pattern is shown in Fig. 5, where φ is the angle between the lamellar normal and the vertical axis (or draw direction) and α is the distance between maxima and origin. The higher the value of the drawing ratio was, the higher the φ angle was. In addition, the α values increased with increasing the draw ratio. The long periods or inter-planar spacings were calculated to be 21.0 and 17.5 nm for DR2 and DR3, respectively. These values were smaller than that (23.9 nm) of undrawn sample. This feature of long periods is quite different from that of polyethylene (PE) or polypropylene (PP) fibers. Those fibers usually show an increase in long period with drawing process.

In order to explain those SAXS results and structural changes of PFA thin films or fibers during drawing process, we tried to apply a model, which is widely developed for the PE fibers in practice.^{21, 22} A schematic diagram for this model is shown in Fig. 6. As the thin films or fiber is drawn, the interlamellar and/or intralamellar slips probably occurred, forming the

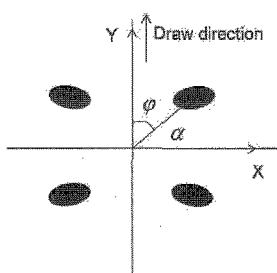


Figure 5 Diagrammatic representation of four-point scattering patterns.

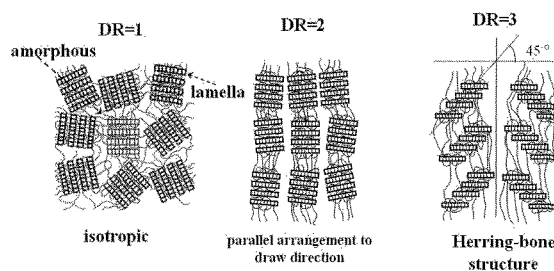


Figure 6 Schematic models of changes in lamella arrangement of crystalline fluorinated copolymers.

small kink bands in the lamellae. In parallel with the changes in lamellae, the grain boundaries or amorphous parts between two neighboring lamellae are also distributed regularly towards the draw direction, and they thus give a periodic change in density in the direction normal to them, which will account for the four-point diffraction pattern. That is to say, with an increase in elongation of the PFA sample, a particular kind of layer structure is formed in the thin films, alternately tilted as a Herring-bone.

After drawing process, the PFA thin films or fibers showed higher transparency and much lower gas permeability as compared with undrawn ones as mentioned above. Such peculiar features of drawn PFA are probably attributed to smaller size of crystallites and/or lower content or size, of voids in their bulk, respectively. Bring about the unique molecular characteristics of fluorinated copolymers including their helical confirmation, weak-intermolecular interaction and rod-like configuration, PFA chains might slip, each other easily and form a quite close packing structure of polymer chains during drawing process. From the strong improvements in the optical and gas permeation properties through drawing process, perfluoropolymers such as, PFA may be more favorable for this kind of drawn thin film and fiber applications than hydrocarbon crystalline polymers such as PE and PP.

Figure 7 shows the WAXD patterns for DR1, DR2, and, DR3 samples, respectively. For the undrawn POF0 sample, uniform Debye rings in WAXD pattern was observed, indicating the random crystalline structure. On the other hand, we see quite different WAXD patterns with some line streaks in equatorial reflections appeared for the drawn samples. These results imply orientation of polymer chains to the draw direction. In addition, the diffuse streaks in the layer lines indicate the disorder in the packing of the molecules in the lattice. Similar WAXD results were also obtained for the fiber samples.

With increasing the draw ratios for PFA thin film, those streaks of equatorial reflections became sharp spots with stronger intensity, suggesting the higher oriented PFA chains or the larger amount of oriented parts with drawing process.

In assumption that the PFA crystals are in quasi-hexagonal form like PTFE crystals with lattice constant: $a' = b' = 5.59 \text{ \AA}$, $c = 16.88 \text{ \AA}$, and $\gamma' = 119.3^\circ$, the d -spacing were calculated (so-called d_{cal}). Alternatively, from the diffraction peak in the two dimensional horizontal profiles of the equatorial reflections the d_{obs} (d -spacing observed) values were calculated by

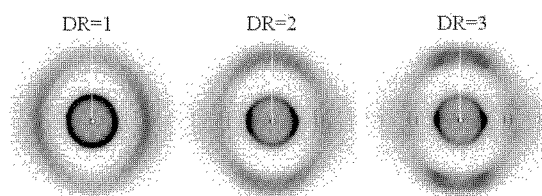


Figure 7 WAXD patterns of 'crystalline' transparent films of fluorinated copolymers at several draw ratios.

use of Bragg's law and were compared with those d_{cal} values. Table 1 shows results of X-ray analysis for undrawn and drawn PFA fibers. The d_{obs} values were consistent with d_{cal} values for (110), (200), (120), and (300) reflection planes. The PFA samples showed slightly higher d_{obs} values for (100) reflection than that (d_{cal}) of PTFE due to existence of fluorinated ether units as side-chain in PTFE chains. The WAXD results suggest that PFA crystals were in quasi-hexagonal form, and the parameters of their unit cell were constant during drawing process. In other words, the distance between adjacent helices seems to be unaffected by drawing the PFA thin films and fibers.

Table 1 Observed d -spacings by X-ray diffraction of undrawn and drawn PFA thin films.

$2\theta/\text{degree}$	d -spacings		hkl	Intensity/count.sec ⁻¹
	$d_{\text{obs}}/\text{\AA}$	$d_{\text{cal}}/\text{\AA}$		
DR1				
8.7		10.17		247
17.8	4.84	4.99	100	369
38.2				146
Halo (amorphous part)				
DR2				
8.8		10.05		378
17.8	4.84	4.99	100	5660
31.3	2.80	2.86	110	290
36.4	2.42	2.47	200	317
48.4	1.83	1.88	120	205
56.0	1.61	1.64	300	180
DR3				
8.9		9.94		576
18.0	4.84	4.93	100	17535
31.5	2.80	2.84	110	686
36.5	2.42	2.46	200	633
49.2	1.83	1.85	120	349
56.0	1.61	1.64	300	294

4. CONCLUSION

From the small angle X-ray scattering and wide angle X-ray diffraction measurements for the drawn PFA thin films and fibers, some preliminary results were obtained as follows;

1. The orientations of PFA polymer molecules and their lamellar texture strongly took place by drawing the thin films or fibers.
2. Similar WAXD and SAXS patterns were obtained for thin film and fiber samples.
3. After the drawing process, the PFA crystals were in quasi-hexagonal form, and the lateral dimension of their unit cell did not change significantly.
4. The short periods (inter-planar spacings of adjacent polymer chains) were unaffected by drawing process, while the long periods (distances between central points of two neighboring lamellae) decreased.

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(Received December 5, 2007; Accepted February 15, 2008)