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Structure and Morphology of Poly(trifluoroethylene)

Andrew J. Lovinger* and Rudolf E. Cais

AT&T Bell Laboratories, Murray Hill, New Jersey 07974. *Received August 29, 1983*

ABSTRACT: Poly(trifluoroethylene), one of the least studied fluorocarbon polymers, has become of interest as a result of its ferroelectric copolymers with vinylidene fluoride. Atactic poly(trifluoroethylene) specimens varying in molecular weight characteristics and degree of isoregicity (i.e., head-to-tail content) were crystallized isothermally from the melt and examined by thermal, diffraction, and microscopic techniques. X-ray diffraction yielded one diffuse meridional reflection on the first layer line centered at 2.29 Å; this is consistent with a disordered conformation comprising an irregular succession of TG, T$\bar{G}$, and, possibly, TT groups. This intramolecular disorder is related to the atacticity of the configuration and is also responsible for the large cross-sectional area of the chains, their arrangement in a hexagonal lattice (a = 5.61 Å), and the irregular morphological features of resulting crystals. Such crystals lack distinct crystallographic faceting but exhibit instead circular, lobed, or cellulated habits that are highly unusual in terms of the underlying single-crystal structure revealed by electron diffraction.

Introduction

Fluoro polymers have been studied and exploited widely as a result of the appealing properties of some of their members, such as poly(tetrafluoroethylene) [PTFE] (a chemically inert polymer, stable to high temperatures) and poly(vinylidene fluoride) [PVF_2] (a strong, flexible, piezoelectric and pyroelectric material). Within the family of fluoro polymers, poly(trifluoroethylene) [PF_3E] has received little attention, possibly because of its stereo- and regioirregularity. However, it has recently been found[1–4] that copolymers of trifluoroethylene and vinylidene fluoride not only are piezo- and pyroelectric over a wide range of composition but, additionally, display distinct ferroelectric transitions that, so far, have not been unequivocally demonstrated in PVF_2, itself. This has stimulated interest in the synthesis, structure, crystallization, and properties of poly(trifluoroethylene). Yagi has studied the chain microstructure of PF_3E by ^{19}F NMR[5,6] and its relaxational behavior by dynamic-mechanical and dielectric means.[5,7] On the basis of ^{19}F NMR[5,6] and ^{13}C NMR,[8] the chain structure was reported to encompass 50% or more of regioirregular defects stemming from head-to-head: tail-to-tail addition of monomeric units during free-radical polymerization, although earlier work[9] had assigned significantly lower defect contents. The more recent study of Cais and Kometani[10] showed that the percentage of inverted monomeric units varies only slightly with temperature of polymerization, ranging from 14% at 80 °C to 10% at −80 °C. In addition to these defects, PF_3E polymerization is also subject to stereoirregular addition, and PF_3E samples are in fact essentially atactic.[10]

Under these conditions, it might at first appear surprising that PF_3E does crystallize; nevertheless, as a result of the similarity in C–F and C–H bond lengths, as well as of the van der Waals radii of fluorine and hydrogen, these two elements behave isomorphically in PF_3E, allowing development of significant crystallinity. The chain conformation of PF_3E has been investigated by use of energy calculations as a function of defect content by Kolda and Lando;[11] in their detailed study, these authors calculated that atactic molecules having less than 21–22% head-to-head defects should adopt a 3/1-helical conformation, while higher defect contents should favor a trans arrangement. The actual molecular structure and chain packing are not yet known with certainty: while both Kolda and Lando[11] and Gal'perin and Strogalin[12] (using fiber diffraction techniques) found hexagonal packing of chains, the first authors[11] reported a meridional reflection at ~2.25 Å associated with a 3/1-helical conformation, whereas the second[12] proposed a repeat of 2.50 Å which they attributed to an unspecified helical conformation. A disordered all-trans conformation has also recently been proposed by Tashiro et al.[13] based on their studies of VF_2/F_3E copolymers. With regard to morphology, some fracture-surface replicas are included in Yagi's thesis,[5] but no detailed morphological investigation has yet been conducted for this polymer.

As a result of the work of Cais and Kometani[10] (preceding paper), PF_3E samples of known and controlled degrees of regioirregularity are now available over a limited defect range, including essentially isoregic material (i.e., practically free of reversed monomeric units within its macromolecules). In view of the renewed interest in PF_3E, we present in this paper the first detailed investigation of the structure and morphology of PF_3E of varying defect contents and molecular weights.

Experimental Section

Four types of sample were used in this study; their molecular characteristics are summarized in Table I. Sample A was an

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Table I
Molecular Characteristics of PF_3E Samples

sample	source	% isoregic	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
A	trifluoroethylene, emulsion polymerized at 80 °C	86.2	255 000	62 000	4.11
B	trifluoroethylene, bulk polymerized at 0 °C	88.2	123 000	57 000	2.16
C	poly(chlorotrifluoroethylene), reductively dechlorinated	98.1	368 000	166 000	2.22
D	poly(chlorotrifluoroethylene), reductively dechlorinated	98.1	43 000	15 000	2.87

experimental-grade PF_3E, emulsion polymerized by Pennwalt Corp. at 80 °C, and had the lowest isoregicity and highest polydispersity of all specimens used here. Bulk polymerization at 0 °C provided sample B, of slightly greater isoregicity and substantially lower polydispersity. Specimens of very high isoregicity (98.1%) were prepared by reductive dechlorination of a precursor polymer, poly(chlorotrifluoroethylene), using tri-*n*-butyltin hydride in the manner described previously;[10] of these, sample C was a high-molecular-weight specimen while sample D was of low molecular weight. As discussed in the preceding paper,[10] ^{19}F NMR showed all these polymers to be atactic, with a Bernoullian stereosequence distribution and a meso dyad fraction of 0.46.

Melt-pressed samples of these polymers were crystallized at various temperatures in a Mettler FP-52 microscope oven and then examined by DSC in a Du Pont 900 thermal analyzer at a heating rate of 10 °C/min or by flat-film X-ray diffraction in a vacuum camera using Ni-filtered Cu Kα radiation. For electron-microscopic examination of their morphology and diffraction pattern, the specimens were first deposited on freshly cleaved mica from boiling dilute solution in dimethylformamide. After evaporation of the solvent, the resulting thin films were melted and recrystallized at the desired temperatures, shadowed with Pt/C, coated with carbon, floated off their substrates in water and onto copper grids, and examined in a JEOL 100-CX transmission electron microscope at 100 keV.

Results and Discussion

(a) Melting Behavior. Melting endotherms of the various samples crystallized at a number of temperatures are seen in Figure 1. Sample A, having the highest polydispersity, displays a series of broad endotherms; for the specimen crystallized at 165 °C, the lowest endotherm reflects melting of crystals formed as the sample was being cooled to room temperature. Sample B, of slightly higher isoregicity and substantially lower polydispersity, yields a sharper, single endotherm, with only a shoulder associated with crystals grown during quenching of the specimen from 160 and 170 °C. The almost totally isoregic sample D displays only one broad endotherm at low temperatures as a result of its very low molecular weight, while its high-molecular-weight counterpart (sample C) exhibits melting behavior similar to that of sample B but displaced to lower temperatures by 12–13 °C. This may reflect a tendency of melting point to increase with increasing extent of syndioregicity, although the restricted range of sample regioregularities available and the effects of molecular weight and tacticity do not allow verification of such a trend. However, we should note that such a trend is consistent with the fact that for PVF_2 a 97% syndioregic sample melts at a much higher temperature (305 °C)[14] than its common, ca. 95% isoregic counterpart (T_m typically around 180 °C).

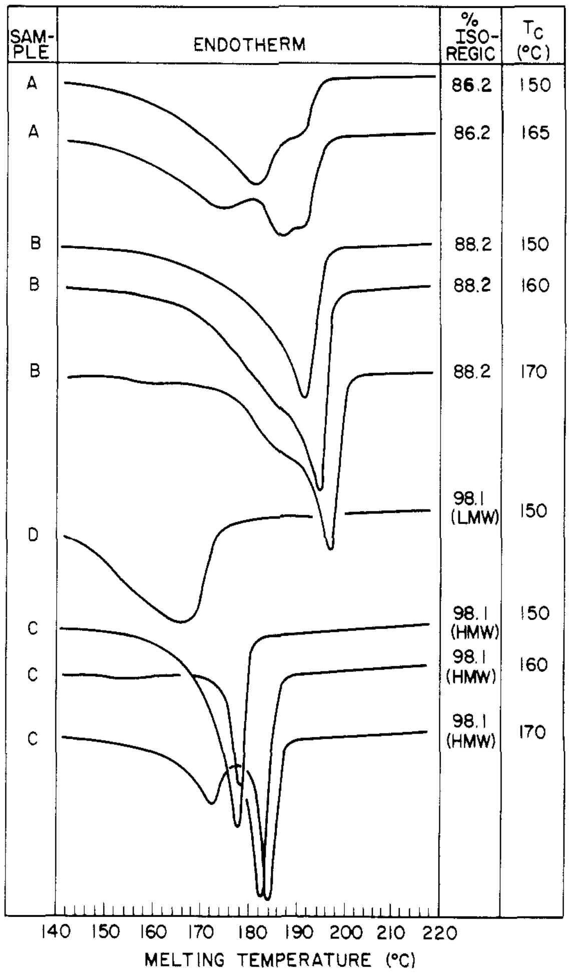

Figure 1. Melting endotherms of different PF_3E samples after crystallization at various temperatures.

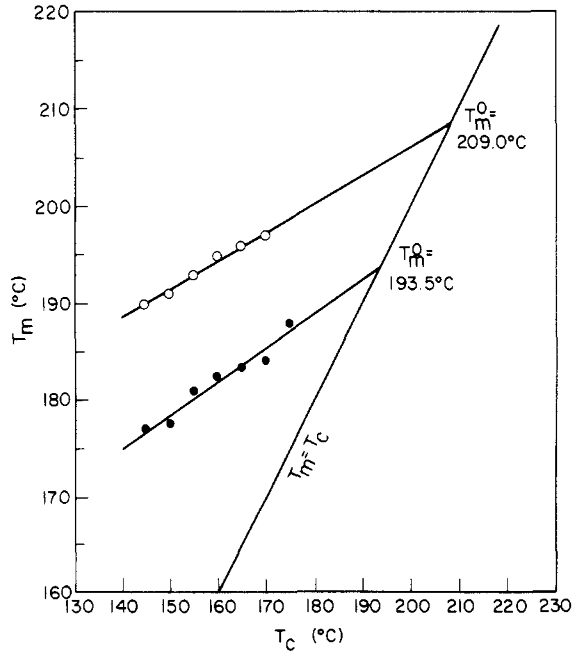

Figure 2. Dependence of melting temperature on temperature of crystallization for various PF_3E specimens: (●) sample C (98.1% isoregic); (○) sample B (88.2% isoregic).

By isothermally crystallizing at different temperatures the two polymers, B and C, that show sharp melting points, we obtain the Hoffman–Weeks plot[15] of Figure 2, from which thermodynamic melting points may be estimated.

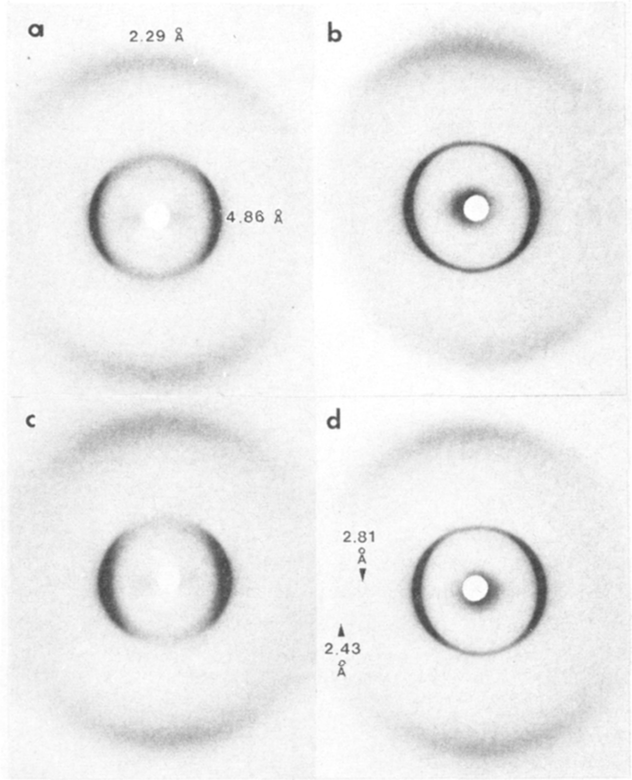

Figure 3. X-ray diffraction patterns of uniaxially oriented specimens of PF_3E: (a) sample A; (b) sample B; (c) sample C; (d) sample D.

The very highly isoregic (98.1%) specimen has an extrapolated $T_m°$ of 193.5 °C, while its less isoregic (88.2%) counterpart has a substantially higher value of 209.0 °C. These values are to be compared with the corresponding results of Yagi[5] (213 °C) and Welch and Miller[16] (222 °C). Our results, summarized in Figure 2, are consistent with such high thermodynamic melting points provided that the latter arise from specimens of lower isoregicity than our own; the extent of isoregicity of one of these specimens is not known,[16] while that of the other is reported at 50% or less[5] (although such low isoregicities are questionable[10]).

(b) X-ray Diffraction. Typical diffraction patterns from oriented PF_3E samples of various extents of isoregicity and molecular weights are shown in Figure 3. In general, the specimens (particularly those of low molecular weight or high polydispersity) did not sustain high degrees of orientation, which may explain the arcing of all reflections. It is seen in Figure 3 that all four patterns reflect the same crystalline structure, which is therefore inferred to be independent of defect content at degrees of isoregicity greater than at least 86%. Further, diffraction patterns from unoriented specimens were consistent with those seen in Figure 3, implying that in homopolymeric poly(trifluoroethylene) there are no mechanically induced solid-state phase transformations such as had been found earlier in some of its copolymers with vinylidene fluoride.[4] Despite their large breadth, the strong equatorial reflections at 4.86 Å are singlets, as was shown by high-resolution diffractometric tracing, so that their broadening probably reflects small crystallite sizes. The three equatorial reflections at 4.86, 2.81, and 2.43 Å are indexed respectively as 100, 110, and 200 of a hexagonally based lattice having $a = 5.61$ Å and are therefore in agreement with earlier reports.[11,12] There is also seen in Figure 3 a very broad and diffuse meridional reflection centered at 2.29 Å. This spacing differs from the 2.50 Å reported by Gal'perin and Strogalin;[12] their larger c-axis repeat is more consistent with a distorted trans conformation than with an unspecified helical one proposed by them.[12] It is exactly such a disordered all-trans arrangement that Tashiro et al.[13] have recently proposed for PF_3E based on their study of its copolymers with vinylidene fluoride. However, in all our diffraction patterns (both X-ray and electron) no reflection was ever seen in the 2.50–2.60-Å range that would have suggested the 001 of an all-trans conformation. In the vicinity of 1.20–1.30 Å, where the 002 would lie, only a very weak and highly arced reflection was observed in our electron-diffraction patterns (but not in the X-ray) at 1.26 Å (see Figure 4a). However, not only is this much weaker and more arced than the one attributed to the trans-planar conformation in ref 12, it also implies a contraction of the normal trans repeat when an expansion is expected by the presence of the three fluorine atoms. Moreover, while all trans conformations should be favored for sample isoregicities less than ~78%,[11] it is not clear how such samples may be produced, for even high-temperature polymerization (80 °C) yields isoregicities greater than 86%.[10] (Specimen characterization or origin is not given in ref 12.)

The 2.29-Å reflection found in our specimens is more consistent with a corresponding meridional reflection at 2.25 Å that Kolda and Lando[11] attribute to the 3/1-helical conformation which they showed to be energetically the most favored at degrees of isoregicity greater than ~78%.

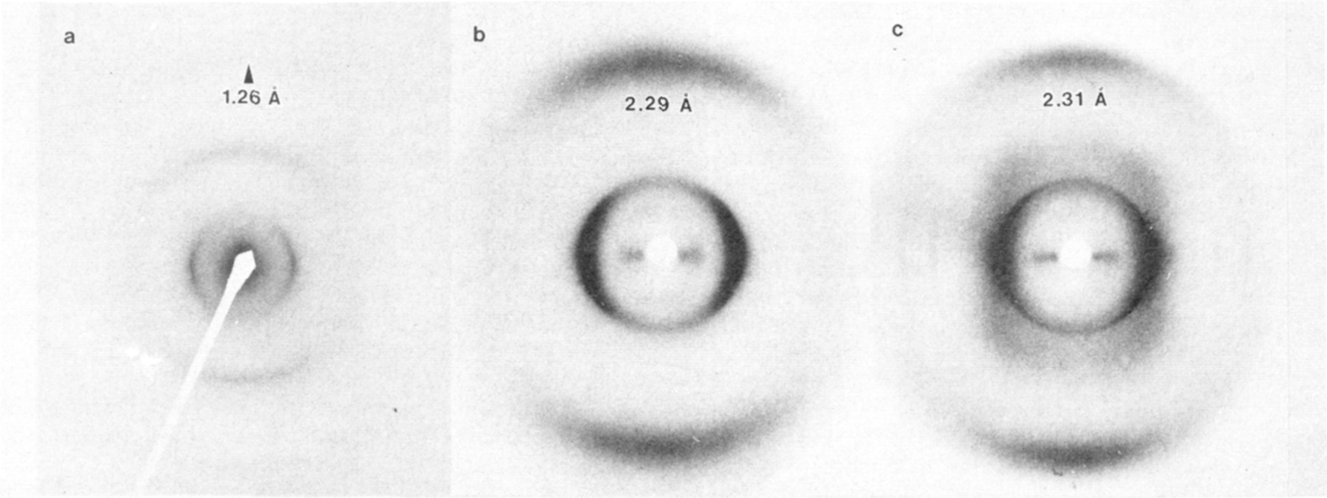

Figure 4. Comparison of (a) electron-diffraction fiber pattern of PF_3E with X-ray fiber patterns of (b) PF_3E and (c) the paraelectric phase of a 65/35 mol % VF_2/F_3E copolymer.

A regular undistorted 3/1 helix would consist of $(TG)_3$ or $(T\bar{G})_3$ sequences, for which the monomeric subrepeat (TG or T$\bar{G}$) has a period of 2.1 Å parallel to the chain axis. Expansion of the chain parallel to this axis, resulting from the bulkiness of the fluorine substitutents, could explain the larger repeat observed here; such expansion is seen in other fluoro polymers (e.g., poly(vinylidene fluoride)),[17] as well as in other macromolecules adopting 3/1-helical conformations (e.g., isotactic polystyrene).[18] At the same time, however, presence of intramolecular disorder is also required to explain the broad and diffuse appearance of the 2.29-Å reflection, as is clearly anticipated from the atacticity of all molecules. For such disorder to be consistent with the observed repeat period, conformational deviations from the regular $(TG)_3$ or $(T\bar{G})_3$ sequences are expected through substitution of some G or $\bar{G}$ bonds with each other or with T. In one extreme (hypothetical) case, this would result in a regular alternation of TG and T$\bar{G}$ groups, for which the undistorted axial repeat is 2.2 Å; however, a TGT$\bar{G}$ conformation was found energetically unfavorable.[11] Another possibility consistent with a 2.29-Å subperiod is a $T_3GT_3\bar{G}$ conformation, as adopted by the γ-phase of PVF_2.[19-21] The potential energy of this conformation relative to the others has not been calculated for PF_3E.[11]

However, the broad and diffuse appearance of the meridional reflection, as well as the lack of any intermediate layer lines, argues strongly against any of the above regular conformations. Specifically, for a 3/1-helical conformation the 2.29-Å meridional reflection should have lain on the third layer line, while for a TGT$\bar{G}$ or $T_3GT_3\bar{G}$ it should have been on the second or fourth layer lines, respectively. Yet, this reflection is in fact on the *first* layer line, as is made particularly clear by comparison of the PF_3E fiber diffraction pattern (Figure 4b) with that from one of its copolymers with vinylidene fluoride (Figure 4c). Those among the latter that contain ~50–80 mol % VF_2 have been found[4] to possess a paraelectric phase whose structure is similar to that of PF_3E. The intermediate-layer-line reflections seen in Figure 4c imply that molecules of this copolymer possess some coherent structural organization at multiples of 2.29 Å, although this is significantly defective, as evidenced by the high breadth and streak-like appearance (parallel to c^*) of these intermediate reflections. Since even this defective extended organization is apparently absent in the PF_3E samples studied here, we conclude that their molecular conformation consists of an *irregular* succession of TG, T$\bar{G}$, and possibly also TT sequences; the latter, while energetically not favored at high levels of isoregicity,[11] could be accommodated with a ~2.29-Å repeat if one of the T bonds is parallel (or nearly so) to the chain axis.

One aspect of this disorder is that the chains will contain slight kinks, because G and $\bar{G}$ bonds in sequences of one hand (i.e., $(TG)_n$ or $(T\bar{G})_n$) will be parallel to the chain axis, whereas in alternating sequences (i.e., TGT$\bar{G}$ or $T_3GT_3\bar{G}$) they will be slightly inclined to it. As a result of their disordered conformation, the chains will also have an irregular cross-sectional profile and will therefore tend to pack like cylinders in a hexagonal lattice. This regular order perpendicular to *c* and the attendant disorder along *c* are evidenced by the relative sharpness of the equatorial reflections compared to the meridional one and by the overall dearth of reflections; these diffraction features of PF_3E are thus reminiscent of the disordered phase of PTFE above 30 °C.[22] For the same reasons, the unit-cell base of PF_3E will tend to be large, as may be seen with the aid of Figure 5. Although from the point of view of chemical structure PF_3E is intermediate between PVF_2 and PTFE, its molecular cross-sectional area is in fact commensurate with that of PTFE. In a similar manner, the ferroelectric and paraelectric phases of a 52/48 mol % copolymer of VF_2/F_3E, which are structurally similar to β-PVF_2 and PF_3E, respectively, also exhibit molecular cross-sectional areas that approach those of the corresponding homopolymers (see Figure 5). A final expectation arising from the disordered crystal structure of PF_3E is small mosaic domain sizes of its crystallites, as inferred from the considerable breadth of reflections in Figures 3 and 4. On the basis of these results, we now examine the influence of molecular disorder and of other factors on the morphology of melt-crystallized PF_3E.

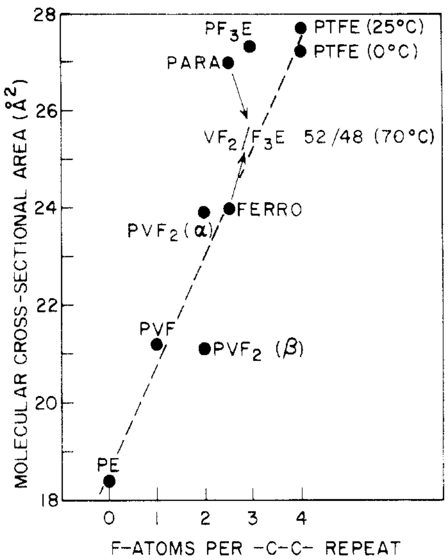

Figure 5. Molecular cross-sectional areas of various polyfluorocarbons as functions of fluorine content.

(c) Morphology. We first investigate and discuss results from the two polymers that show sharp melting points (samples B and C). The morphology of the highly isoregic, high-molecular-weight specimen C is seen in Figure 6 for three different crystallization temperatures. At very high temperatures of crystallization, e.g., 175 °C, only irregularly shaped crystals having diffuse boundaries are grown (these are the dark entities in Figure 6a, the very thin lamellae covering the field having grown only during quenching of the sample to room temperature). Despite their irregular and diffuse appearance, these entities are single crystals whose molecules are hexagonally packed and normal to their broad surfaces, as evidenced by the electron-diffraction pattern inset in Figure 6a (the weak extra spots in this pattern arise because the intermediate-lens aperture included a small contribution from the lower crystal seen in this figure). The spacing of reflections in this and all other electron diffraction patterns from our samples was always 4.95–4.97 Å, i.e., somewhat larger than the 4.86 Å that was obtained by X-ray diffraction; this is not uncommon in electron diffraction and is attributable to a slight expansion of the lattice as a result of radiation damage from the high-energy electrons.

Although these crystals were allowed to grow very slowly (they were held at 175 °C for 4 days), no evidence of any regular habit or crystallographic faceting is seen; yet, despite their generally circular and diffuse boundaries, they possess a unique crystallographic orientation characteristic of single crystals. Reasons for this irregular habit are associated with the disordered nature of PF_3E macromolecules which, on the basis of our X-ray results, is expected to allow only very limited morphological and fold-

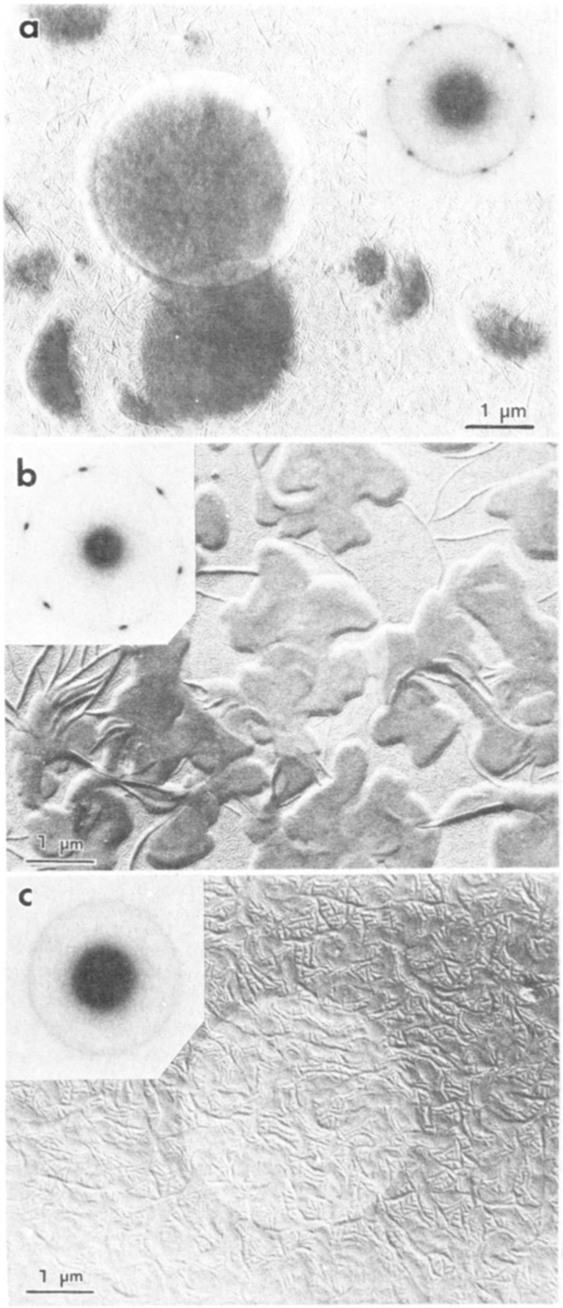

Figure 6. Electron-microscopic appearance and electron-diffraction patterns from high-molecular-weight 98.1% isoregic PF$_3$E (sample C) crystallized isothermally at (a) 175 °C for 4 days, (b) 155 °C for 1 day, and (c) 140 °C for 1 h.

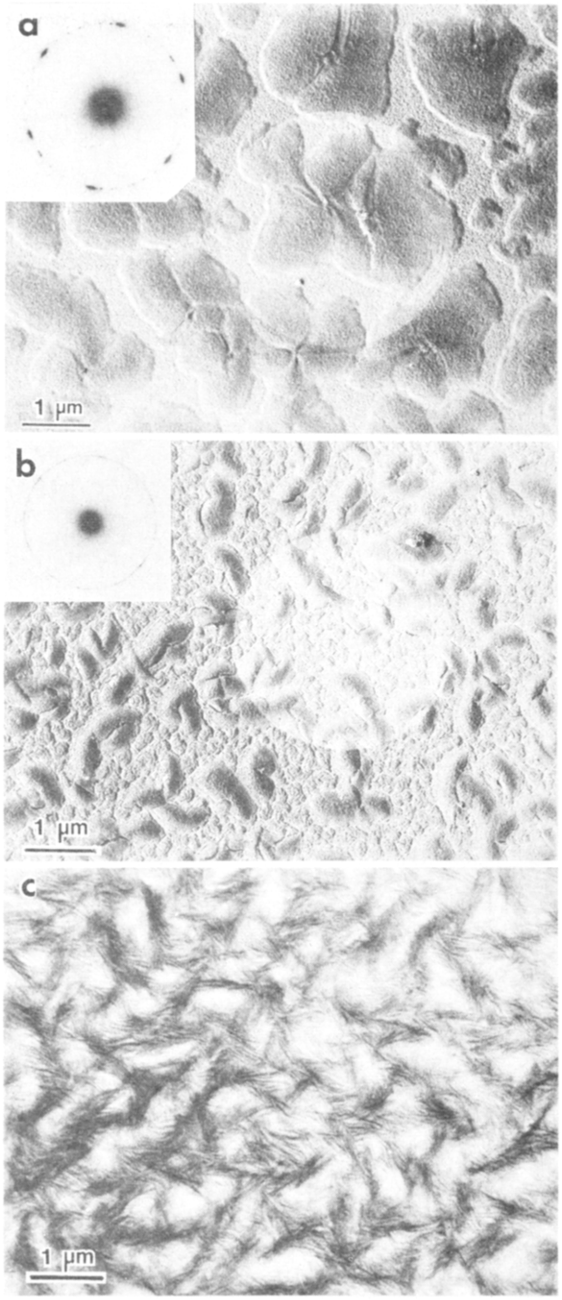

Figure 7. Electron-microscopic appearance and electron-diffraction patterns from 88.2% isoregic PF$_3$E (sample B) crystallized isothermally at (a) 175 °C for 4 days, (b) 155 °C for 1 day, and (c) 140 °C for 1 h.

domain coherence, leading to development of mosaicity on a very fine scale. Very similar circular growth habits have been observed earlier by Barnes and Khoury[23] in a related polymer, poly(chlorotrifluoroethylene), crystallized from solution. In that polymer, growth rate and solvent were found not to play a significant role in inducing the irregular growth habit, so that configurational irregularity[24] was mentioned as a possible cause.[23] Our X-ray and electron-microscopic results from a different polymer, crystallized very slowly and in the absence of solvent, also point to the same cause and therefore render it most probable as the origin of the similar morphology in poly(chlorotrifluoroethylene) as well.

At lower crystallization temperatures (e.g., 155 °C as in Figure 6b), the same general features prevail. Lamellar single crystals are again observed, with the macromolecules in a hexagonal arrangement perpendicular to the broad lamellar surfaces. The crystals still have a totally irregular habit, but now they are generally broken up into lobes and protrusions; at the higher growth rate prevailing here, these are probably a result of preferred crystallization at asperities facing the melt. The fibrous entities in Figure 6b are simply lamellae on edge; at the left side of this figure, a flat crystal is seen broken up into protrusions, some of which have twisted to an edge-on orientation. Finally, at even lower crystallization temperatures, nucleation and growth rates increase rapidly, so that by 140 °C the entire sample is crystallized within a few minutes; as seen in Figure 6c, it consists of aggregates of small lamellae in random orientation.

The morphology of sample B at the same three crystallization temperatures is seen in Figure 7. At 175 °C, this specimen yields irregularly shaped, multilobed single crystals (Figure 7a) whose appearance is remarkably reminiscent of that of very highly isoregic samples crystallized

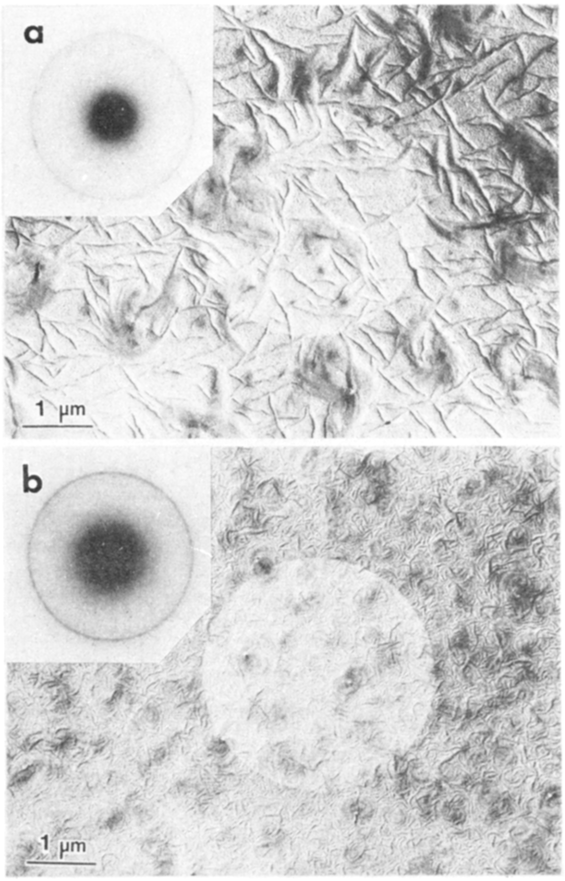

Figure 8. Electron-microscopic appearance and electron-diffraction patterns from 86.2% isoregic PF_3E (sample A) crystallized isothermally at (a) 155 °C for 1 day and (b) 140 °C for 1 h.

at temperatures 20 °C lower (Figure 6b). A similar conclusion is also reached when comparing the morphology of sample B crystallized at 155 °C to that of the isoregic sample C grown at 140 °C (Figure 6c), both specimens exhibiting small, irregularly shaped lamellar crystals. The same trend continues to lower temperatures, with sample B showing immature spherulites at 140 °C (Figure 7c), i.e., ~15–20 °C higher than specimen C. This consistent morphological shift with temperature for these two polymers parallels closely their difference in both actual and thermodynamic melting points (see again Figure 2); thus, the samples exhibit analogous morphologies at *equivalent undercoolings*. We therefore conclude that differences in degree of isoregicity from 98.1% to 88.2% for specimens of similar polydispersity have no significant additional influence on morphology other than through their effects on the melting point.

Sample A has a similar regioregularity as sample B, intermediate molecular-weight averages between those of specimens B and C, and a much higher polydispersity than either of these polymers. Consistently with these molecular characteristics, its thermal behavior is more complicated than that of its counterparts, exhibiting a multitude of melting endotherms that almost span the temperature range where these transitions are observed in the other polymers (see again Figure 1). Also consistent with these characteristics is the morphology of sample A, which may be described as combining features similar to those seen in specimens B and C at each temperature. For example, in Figure 8a, irregularly shaped crystals, intermediate in size and shape to those of Figures 6b and Figure 7b, are seen at a crystallization temperature of 155 °C. A similar morphological effect is seen for T_c of 140 °C (Figure 8b), although high nucleation densities and small crystal sizes render comparison more tenuous.

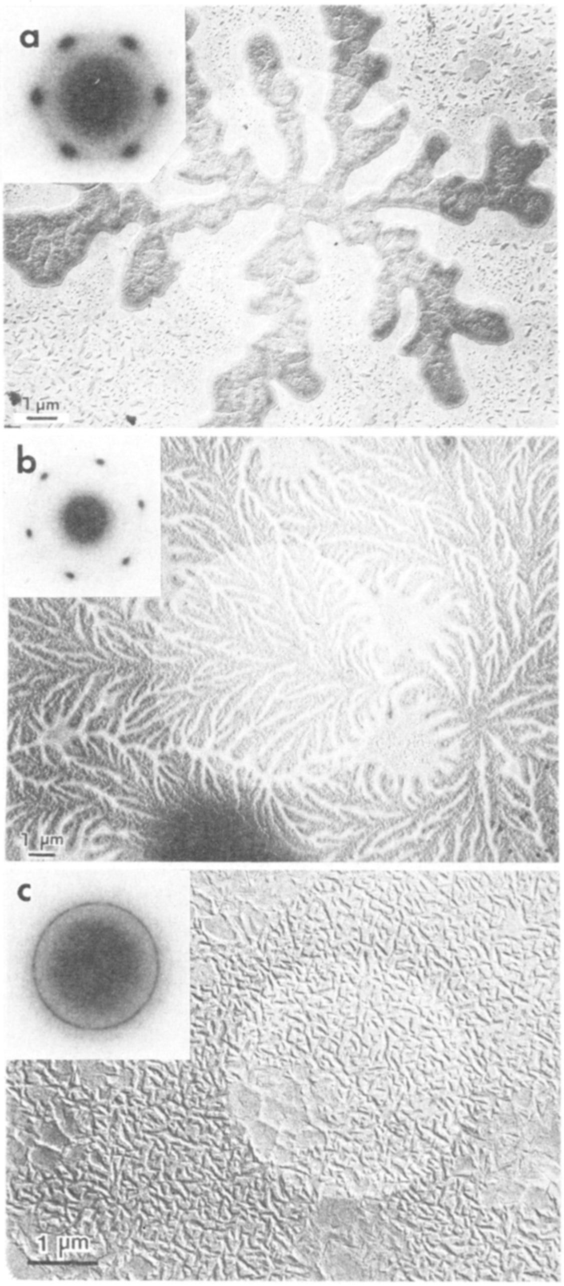

Figure 9. Electron-microscopic appearance and electron-diffraction patterns from low-molecular-weight 98.1% isoregic PF_3E crystallized isothermally at (a) 160 °C for 3 h, (b) 140 °C for 1 h, and (c) 100 °C for 10 min.

Finally, we investigate the morhology of the highly isoregic sample D of very low molecular weight; since its degree of isoregicity is the same as of sample C, we can thus compare the effects of molecular weight on crystallization and morphology of PF_3E. Because of the lower melting point of this sample, crystallization must be conducted at somewhat lower temperatures than had been employed for the other specimens. The resulting morphologies are very different from what has been obtained from PF_3E samples of higher molecular weight, and are in fact quite unusual among all polymers. At high temperatures, e.g., 160 °C (Figure 9a), very large structures consisting of irregularly shaped and branched arms are obtained; their electron-diffraction patterns once again clearly establish their single-crystal identity and hexagonal molecular packing. The irregular habit is attributable as before to disorder in molecular conformation and packing. The fact that the crystal shapes are no longer circular or lobed but branched is the result of much lower molecular weight, higher polydispersity, and faster growth: growth protrusions that might develop will be bathed in fresh melt, while the channels between them will become concentrated in rejected molecules.[25,26] Such diffusion-controlled cluster formation has recently been simulated by Monte Carlo techniques by Witten and Sander[27] and Meakin:[28] The similarity between and simulated morphologies (as seen, e.g., between Figure 9a of this article and Figures 2, 7, 8, and 10 of ref 28) is remarkable. The eventual depletion of crystallizable molecules from these channels is also strikingly illustrated in Figure 9a upon quenching the film to room temperature after 3 h of crystallization at 160 °C: minute crystallites then appear within the fresh melt, but always outside an "impurity"-rich layer surrounding the growth outline of the original crystal and not at all within its narrower channels. Another feature of importance concerns the many fissures and discontinuities seen inside the isothermally grown crystal of Figure 9a: these may be domain boundaries where the cumulative effects of lattice distortions have introduced discontinuities. It should be noticed that these cracks are directed mostly normal to their local growth front, so that they may alternatively be postcrystallization features arising from lattice contraction during quenching of the specimen to room temperature.

Figure 9b depicts the morphology of sample D crystallized at a lower temperature (140 °C). This morphology is extraordinary insofar as what appears to be a most typical spherulite, nucleated at the lower right side of this figure and exhibiting a profusion of apparent noncrystallographic branching, is in fact seen by electron diffraction to be a very large single crystal. There is no detectable branching–crystallographic or noncrystallographic. The origin of the apparent branches lies again in channel formation, as discussed above; the similarity to spherulitic branching arises from the high growth rate which causes a reduction in thickness of the "impurity"-rich layer surrounding growth tips (and, therefore, also of the widths of channels and crystals in this two-dimensional case).[25,26] Formation of even finer channels has been observed in the related polymer poly(chlortrifluoroethylene) and interpreted similarly.[23] Further lowering of crystallization temperature for our sample D (e.g., to 100 °C) yields small, randomly oriented lamellae resulting from dense nucleation, as seen in Figure 9c.

Conclusions

Variations in degree of isoregicity from 86.2% to 98.1% were seen to have no significant effect on the crystalline structure of PF_3E: in all cases, atacticity is the major determining factor leading to a disordered conformation and hexagonal packing of macromolecules. The disorder is reflected in the morphology of melt-solidified PF_3E specimens, all of which exhibit irregular growth habits even in the form of single crystals. The degree of regioregularity influences the temperature dependence of morphology mainly by decreasing the melting temperature for specimens of almost perfect isoregicity.

Acknowledgment. We thank Mrs. J. M. Kometani for technical assistance with polymer syntheses and Mrs. M. Y. Hellman for molecular-weight determinations.

Registry No. PF_3E (homopolymer), 24980-67-4.

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