this series.[2] The exact reasons for this result are not clear. The nature of associations prevailing in the zinc and magnesium salt are significantly different from each other, as seen in Figure 8 and in other publications.[1,2,16] It is quite conceivable that owing to the rather strong ionic associations in the magnesium salt, an equilibrium network state, even in dilute solution, may not have been achieved, and consequently the rubbery plateau is somewhat lower than that of the zinc salt.

Andrianova,[11] during his extensive studies on the effect of solvent on the melt viscosities of polystyrenes and polypropylenes, found that polystyrene samples, obtained from ~40 wt % concentration, had more than 1 order of magnitude lower melt viscosities than the bulk polymer. The viscosities of the solution-recovered samples were a function of the solvent and exhibited strong time-dependent properties, even at temperatures 100 °C higher than their glass-transition temperature. In an attempt to explain this phenomenon, he postulated the formation of a structure in the solution-recovered sample. Upon annealing, the structure is destroyed, the sample's random network of fluctuating entanglements starts dominating, and its viscosity returns to the bulk melt viscosity.

Recently, Plazek[12] et al. during their creep studies on a very high molecular weight polystyrene solution ($M_w \sim 4 \times 10^7$) found a higher degree of entanglements, determined from comparisons of the width and the level of entanglement plateaus in the solutions of this polymer with those of its bulk state. They attributed this to the lack of an entanglement equilibrium state in the bulk polymer because of the slow diffusion rate of polymer chain segments resulting from its very high molecular weight.

It is not quite clear what sort of structure could be formed in the magnesium and barium sulfo-EPDM solutions other than transient ion pair aggregates. Qualitatively the phenomenon in the magnesium and other strongly associating sulfonated EPDM systems appears to be similar to those in the polystyrene studies of Plazek et al., the difference being in the type of primary interchain interactions involved and their mechanism. Certainly any type of conventional entanglement concepts[13] and reptation mechanism[14] cannot be perceived to dominate the behavior in strongly ionic associative systems.

Acknowledgment. We gratefully acknowledge various helpful discussions with Prof. W. J. MacKnight.

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Synthesis of Pure Head-to-Tail Poly(trifluoroethylenes) and Their Characterization by 470-MHz Fluorine-19 NMR

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ABSTRACT: We report the first synthesis of poly(trifluoroethylene) (PF_3E) having a pure head-to-tail (isoregic) sequence of monomer units. The procedure involves reductive debromination or dechlorination of the precursor polymers poly(bromotrifluoroethylene) (PBF_3E) or poly(chlorotrifluoroethylene) (PCF_3E). We have also prepared a model for head-to-head:tail-to-tail (syndioregic) PF_3E by the copolymerization of 1,2-difluoroethylene with tetrafluoroethylene. Regioirregular (aregic) PF_3E samples have been obtained by free-radical polymerizations over a 160 °C temperature range. The chemical microstructures of these polymers have been analyzed by high-resolution 188- and 470-MHz fluorine-19 NMR, which show that PBF_3E, PCF_3E, and PF_3E are stereoirregular (atactic) polymers. There are no head-to-head structures in PBF_3E, but PCF_3E has about 2% of these defects. Free-radical PF_3E is far more regioirregular, with defect levels increasing from 10% at −80 °C to 14% at +80 °C. The stereochemical microstructure changes little with temperature.

Introduction

There are six fluoroethylenes which differ according to the number and position of their fluorine substituents. They are vinyl fluoride, vinylidene fluoride, *cis*- and *trans*-1,2-difluoroethylene, trifluoroethylene, and tetrafluoroethylene. When the substitution patterns of the carbons in a fluoroethylene monomer are different, then that monomer is capable of forming a regioirregular polymer. Such is the case for vinyl fluoride (VF), vinylidene fluoride (VF_2), and trifluoroethylene (F_3E), which give the aregic polymers PVF, PVF_2, and PF_3E, respectively.[1,2]

We have shown in part 1 of this series that isoregic PVF can be prepared by the reductive dechlorination of appropriate precursor polymers.[3,4] This approach is now extended to the synthesis of isoregic PF_3E. We have defined the terms isoregic, syndioregic, and aregic by analogy with the terms for stereochemical structure to describe

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Table I
Conditions for the Synthesis of Aregic Poly(trifluoroethylene) (PF_3E) Samples

sample desig	polymn temp, °C	initiator	init concn, mol %	polymn time, h	polymn yield, wt %	$\bar{M}_n$	$\bar{M}_w$
PF_3E-A[a]	80					62 000	255 000
PF_3E-B	0	TCAP[b]	0.25	19	12	57 000	123 000
PF_3E-E	0	TCAP	0.10	3	2	77 000	284 000
PF_3E-F	-80	^{60}Co γ rays	*c*	24	0.3		

[a] Emulsion polymer from Pennwalt Corp. [b] Trichloroacetyl peroxide. [c] Effective dose rate 0.2 Mrd/h.

Table II
Polymerization Details for Bromotrifluoroethylene (BF_3E) and Chlorotrifluoroethylene (CF_3E)

sample desig	polymn temp, °C	initiator	init concn, mol %	polymn time, h	polymn yield, wt %
PBF_3E-G	80	AP[a]	0.5	5	38
PCF_3E-C	*b*				
PCF_3E-D	0	^{60}Co γ rays	*c*	15	32

[a] Acetyl peroxide. [b] Commercial film from 3M Co. (Kel F-81). [c] Effective dose rate 0.2 Mrd/h.

sequences in which successive monomer units have the same, opposite, and random relative directional orientations, respectively.

The pseudoasymmetric –CFH– methine carbon in PF_3E results in stereosequence isomerism. Typical samples of PF_3E prepared by free-radical polymerization are atactic as well as aregic, and we use high-resolution fluorine-19 NMR to characterize this sequence microstructure in PF_3E. The spectrum of the isoregic polymer can be analyzed to give a quantitative description of the tacticity of PF_3E, which cannot be as readily ascertained from spectra of regioirregular polymers owing to peak overlap with signals from aregic monomer sequences.

The syndioregic structure is an alternative pure regioregular form with a head-to-head:tail-to-tail sequence of monomer linkages. We show that the equivalent structure for PF_3E results from the 1:1 alternating copolymerization of tetrafluoroethylene (TFE) with 1,2-difluoroethylene (DFE). Examination of both isoregic and syndioregic PF_3E by NMR assists in the interpretation of spectra from the usual aregic polymers.

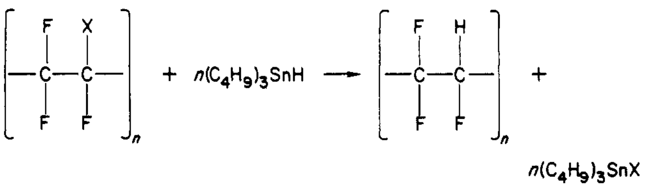
We describe here the syntheses of aregic PF_3E with variable regioirregular defect content, as well as isoregic and syndioregic PF_3E. The microstructures of the isoregic precursor polymers poly(bromotrifluoroethylene) (PBF_3E) and poly(chlorotrifluoroethylene) (PCF_3E) are also examined by NMR. The accompanying paper by Lovinger and Cais examines the structure and morphology of these isomers of PF_3E.

Experimental Section

The monomers DFE (mixed cis and trans), F_3E, BF_3E, CF_3E, and TFE were obtained from PCR Research Chemicals Inc. They were purified by the same general procedure, which involved drying and removal of inhibitor (where present) by passage through columns of silica gel and molecular sieves and then degassing and distillation under high vacuum. Most polymerizations involved bulk monomer sealed in heavy-wall glass ampules.

Details of F_3E polymerizations are shown in Table I. Trichloroacetyl peroxide (TCAP) was prepared from trichloroacetyl chloride and sodium peroxide according to a standard procedure[5] and added as a solution in 1,2-dichlorotetrafluoroethane. Polymer was recovered by stripping off residual monomer under high vacuum. Molecular weights were determined by gel permeation chromatography on a Waters liquid chromatograph fitted with μ-Styragel columns and calibrated with monodisperse polystyrene standards. The solvent was tetrahydrofuran.

Scheme I[a]



[a] X = Br or Cl.

Table III
Molecular Weights of the Isoregic PF_3E Samples Obtained by Reductive Debromination of PBF_3E and Dechlorination of PCF_3E

sample desig	precursor polym	$\bar{M}_n$	$\bar{M}_w$
PF_3E-G	PBF_3E-G	3 800	7 600
PF_3E-C	PCF_3E-C	166 000	368 000
PF_3E-D	PCF_3E-D	15 000	43 000

The halotrifluoroethylenes BF_3E and CF_3E were polymerized under the conditions given in Table II. Acetyl peroxide was obtained as a 25% solution in dimethyl phthalate from Pfaltz and Bauer. The commercial Kel-F film was dissolved in mesitylene at 160 °C and reprecipitated by cooling the solution to room temperature. The copolymer of DFE and TFE was prepared at -80 °C by exposing an equimolar monomer mixture to 4 Mrd of cobalt-60 γ radiation. A poor yield of an oily wax was obtained.

Reductive debromination or dechlorination of the precursor polymers was done at 60 °C for 24 h in tetrahydrofuran containing a molar excess of tri-*n*-butyltin hydride and ca. 10 mol % azobis(isobutyronitrile), according to Scheme I. Although PBF_3E dissolved completely in tetrahydrofuran, PCF_3E was not as soluble and gave a hazy suspension which cleared as the reduction progressed.

The product PF_3E remained in solution and was recovered by precipitation in hexane. It was necessary to extract the PF_3E with refluxing hexane to remove traces of tin residues to below the level of one part per thousand. Analysis by X-ray fluorescence spectroscopy showed that removal of bromine or chlorine was quantitative. The molecular weights of PF_3E samples obtained from PBF_3E and PCF_3E are listed in Table III.

A Varian XL-200 spectrometer was used to acquire fluorine-19 NMR data at 188.22 MHz. Typically 1000 transients were recorded from an 8% by weight polymer solution placed in a 5-mm sample tube. A sweep width of 24 kHz was used with 32K computer locations (acquisition time 0.667 s) and a 5.0-s delay between 90° pulses (9.0-μs duration). Protons were decoupled as required by broad-band irradiation centered at 200 MHz. Solvent and observation temperature depended on the polymer and are given in the figure captions. Chemical shifts are referenced to internal hexafluorobenzene, which is assigned a value of -163 ppm with respect to $CFCl_3$.

High-field 470.55-MHz fluorine-19 NMR spectra were obtained on a JEOL GX-500 spectrometer with a 100-kHz sweep width and 132K data points. The acquisition time was 0.66 s and the pulse width was 12.0 μs (90° flip = 14.5 μs). A pulse delay of 4.0 s was used. Broad-band proton decoupling was not possible with our present fluorine probe configuration on the GX-500.

Results

1. Chemical Microstructure of the Isoregic Precursor Polymers. (a) PBF_3E.

Figure 1 shows the fluorine-19 NMR spectrum of PBF_3E-G at 188 MHz. The $-CF_2-$ fluorines resonate from -95 to -105 ppm (low field), and the –CFBr– fluorine resonates from -125 to -130 ppm

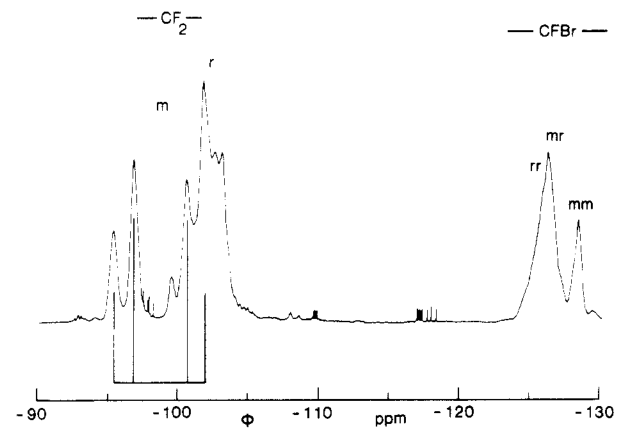


Figure 1. 188.22-MHz fluorine-19 NMR spectrum of poly(bromotrifluoroethylene) sample PBF$_3$E-G observed at 130 °C in 1,3,5-trimethylbenzene. The stick spectrum indicates the AB quartet from the geminal $-CF_2-$ fluorines in a meso dyad with $J = 270$ Hz and $J/\Delta\nu = 0.28$.

(high field). This assignment follows from the twofold area of the low-field signals compared to the high-field signals. There are weak multiplets, which may be due to traces of the cyclic dimer (mixed *cis*- and *trans*-1,2-dibromohexafluorocyclobutane)[6] and end groups, which ought to be prominent owing to the low degree of polymerization (ca. 50, Table III).

The main $-CF_2-$ and $-CFBr-$ resonances are split owing to homonuclear spin coupling and different stereochemical environments. Vicinal and longer range couplings are not resolved and are negligible in comparison with the $-CF_2-$ geminal coupling.[7]

The fluorine nuclei of the $-CF_2-$ group in a meso stereochemical dyad are nonequivalent and give rise to an AB quartet,[7] with $J_{gem} = 270$ Hz and $J/\Delta\nu = 0.28$, as indicated by the stick spectrum in Figure 1 (lines at −95.46, −96.91, −100.72, and −102.16 ppm). To a first approximation the geminal fluorines are equivalent in the racemic stereochemical dyad. Nontheless they must be sensitive to tetrad stereosequences since three distinct lines are resolved at −99.61, −102.76, and −103.37 ppm. Thus, two singlets arise from the homosteric fluorines in the mrm and rrr tetrads, and a quartet from the heterosteric fluorines in the mrr tetrad.[8] In fact only three of these six lines are resolved as noted above, but the resolution is improved at 470 MHz (below), and the underlying structure is revealed by 2D J-resolved spectroscopy.[9]

The unconditional probability of meso dyad placement in the polymer, $p(\mathrm{m})$, can be deduced as follows. Since the doublet components at −95.46 and −96.91 ppm are well resolved, their area, which is exactly half of that from the AB quartet associated with meso stereochemical dyads, can be compared accurately with the total $-CF_2-$ resonance area. Accordingly $p(\mathrm{m})$ is 0.47, and PBF$_3$E, like other typical free-radical vinyl polymers, has a slight bias in favor of racemic dyads.[8]

The $-CFBr-$ resonance region consists of a major peak at −126.48 ppm and a minor peak at −128.66 ppm. The probability associated with the minor peak is 0.22, which corresponds exactly to that expected for the mm triad, given $p(\mathrm{m}) = 0.47$ with a Bernoullian stereosequence distribution. The triad stereosequence assignments in Figure 1 are made on this basis. Five shoulders can be detected on the major peak (rr + mr), which indicates partial long-range sensitivity to pentad stereosequences. Spectra were recorded in different solvents such as chloroform, acetone, and dioxane in an attempt to split the fine structure, without success.

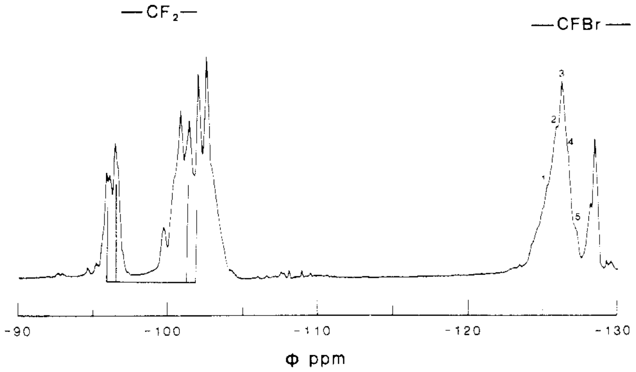


Figure 2. 470.55-MHz fluorine-19 NMR spectrum of poly(bromotrifluoroethylene) sample PBF$_3$E-G observed at 130 °C in 1,3,5-trimethylbenzene. The stick spectrum indicates the AB quartet from the geminal $-CF_2-$ fluorines in a meso dyad with $J/\Delta\nu = 0.11$. This sample has been washed to remove the impurities that gave the weak multiplets around −110 and −117 ppm in Figure 1.

Resolution is improved in the high-field 470-MHz fluorine-19 NMR spectrum of PBF$_3$E as shown in Figure 2. The most significant changes are in the $-CF_2-$ region owing to a spreading out of the AB quartets from nonequivalent geminal fluorines. Thus the main AB quartet from the $-CF_2-$ fluorines in a meso dyad now approaches an AX pattern at the higher field with $J/\Delta\nu = 0.11$. The four components are indicated by the stick spectrum in Figure 2. The variation in this pattern with field strength confirms our assignment of the peak multiplicity to geminal coupling. There is at least one closely spaced AB quartet with $J/\Delta\nu \sim 0.5$ from heterosteric fluorines within the racemic-centered resonances, as mentioned above. This structure has been observed by an elegant experiment involving 2D J-resolved fluorine-19 spectroscopy, which will be the subject of a separate publication.[9] There is not as much change in the $-CFBr-$ resonance in the higher field spectrum of Figure 2, though the shoulders from pentad fine structure are more evident.

(b) PCF$_3$E. The 50.3-MHz fluorine-coupled carbon-13 NMR spectrum of PCF$_3$E-D shows multiplet structure, but only due to the heteronuclear coupling ($^1J_{^{13}C-^{19}F} = 280$ Hz; $-CF_2-$, triplet, $\delta = 115.7$; $-CFCl-$, doublet, $\delta = 106.9$). Fluorine-19 NMR is more sensitive to the microstructure of PCF$_3$E, as shown by the 188-MHz spectra in Figure 3.

The fluorine-19 NMR spectrum from PCF$_3$E is remarkably similar to that from PBF$_3$E and shows $-CF_2-$ fluorine resonances from −101 to −108 ppm and $-CFCl-$ fluorine resonances from −124 to −128 ppm. These chemical shifts vary somewhat with solvent and temperature. As expected the low-field resonance region has twice the area of the high-field resonance region.

The AB quartet from the $-CF_2-$ fluorines in a meso stereochemical dyad has components at −102.05, −103.54, −105.41, and −106.90 ppm ($J_{gem} = 280$ Hz, $J/\Delta\nu = 0.44$), as indicated by the stick spectrum in Figure 3a. The low-field half of this quartet is well resolved in 1,3,5-trimethylbenzene at 160 °C, and a $p(\mathrm{m})$ value of 0.48 is obtained from its area relative to the entire $-CF_2-$ resonance area. The AB quartet is not so well resolved in tetrahydrofuran at 60 °C (Figure 3b), although it is clear that the J_{gem} and $\Delta\nu$ values change with solvent and temperature, probably due to a change in relative populations of the different rotational isomeric states. For example, the low-field outer line of the AB quartet at −102 ppm in Figure 3b decreases in relative intensity as the $J/\Delta\nu$ value increases. We have confirmed this AB pattern by a 2D J-resolved experiment.[9]

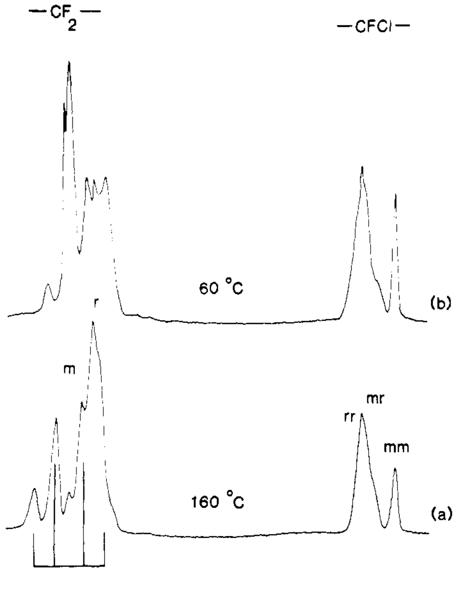


Figure 3. 188.22-MHz fluorine-19 NMR spectra of poly(chlorotrifluoroethylene) sample PCF$_3$E-D observed at (a) 160 °C in 1,3,5-trimethylbenzene and (b) 60 °C in tetrahydrofuran. The stick spectrum indicates the AB quartet from the geminal –CF$_2$– fluorines in a meso dyad with J = 280 Hz and $J/\Delta\nu = 0.44$.

The –CF$_2$– fluorines in a racemic stereochemical dyad are more shielded than those in a meso dyad, as deduced by Tiers and Bovey from model compounds.[10] However, they underestimated the p(m) value of PCF$_3$E at about 0.33, since it was not obvious from their 40-MHz spectra that half of the resonance pattern from meso –CF$_2$– groups was combined with resonances from racemic –CF$_2$– groups. At least four racemic resonances can be observed in Figure 3, indicating partial sensitivity to tetrad stereosequences. They are not resolved well enough at 188.22 MHz for assignment, but our 2D experiments reveal several AB quartets in this region from heterosteric fluorines.[9]

The –CFCl– resonance pattern is virtually identical with that for the –CFBr– fluorine in PBF$_3$E, and it is assigned similarly. The minor peak at −127.57 ppm in Figure 3a has a probability of 0.22, which is very close to the value of 0.23 predicted for the mm triad with p(m) = 0.48 and a Bernoullian stereosequence distribution. Thus the major peak at −125.22 ppm in Figure 3a is assigned to the syndiotactic and heterotactic triads.

The 470-MHz fluorine-19 NMR spectrum of PCF$_3$E is shown in Figure 4. The large AB quartet from the meso geminal fluorines now has a $J/\Delta\nu$ value of 0.18, with the components indicated. The line intensities for this AB pattern are consistent with its spacing. There is more new detail in the –CFCl– resonance, where all seven stereochemical pentads from the syndiotactic and heterotactic triads are resolved. Their overlap is too severe to make assignments in this 1D spectrum.

2. Isoregic Poly(trifluoroethylenes) from the Precursor Polymers. The precursor polymers are reductively debrominated or dechlorinated according to Scheme I to give isoregic PF$_3$E. The 188-MHz fluorine-19 NMR spectra of PF$_3$E derived from PCF$_3$E in this manner are shown in Figure 5, where the appearance of the spectrum changes slightly with solvent and temperature. The fine structure indicates that the polymer is atactic. The reduction of PBF$_3$E gives a material with an identical spectrum, except for very minor defect peaks which will be discussed below.

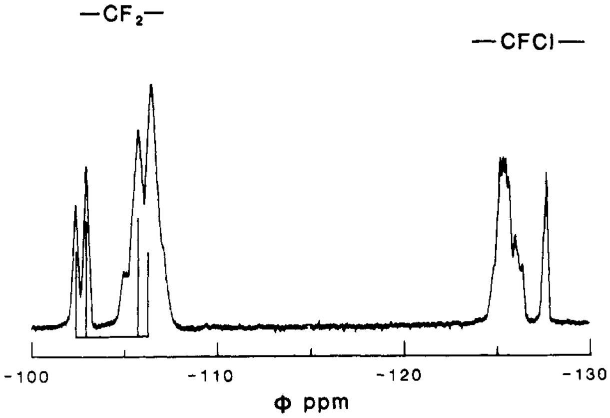


Figure 4. 470.55-MHz fluorine-19 NMR spectrum of poly(chlorotrifluoroethylene) sample PCF$_3$E-D observed at 160 °C in 1,3,5-trimethylbenzene. The stick spectrum indicates the AB quartet from the geminal –CF$_2$– fluorines in a meso dyad with $J/\Delta\nu = 0.18$. The seven possible pentads from the syndiotactic and heterotactic –CFCl– resonances are just resolved.

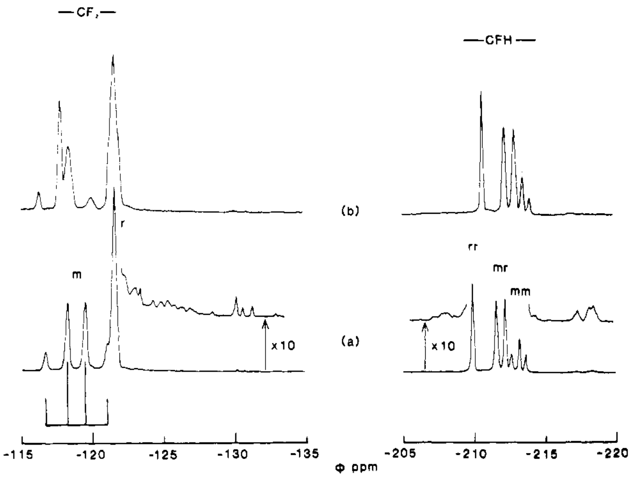


Figure 5. 188.22-MHz fluorine-19 NMR spectra of isoregic poly(trifluoroethylene) sample PF$_3$E-D observed at (a) 18 °C in acetone-d_6 and (b) 50 °C in dioxane-d_8. The stick spectrum indicates the AB quartet from the geminal –CF$_2$– fluorines in a meso stereochemical dyad. Weak peaks can be seen with 10-fold vertical expansion which confirm the presence of trace amounts of head-to-head and tail-to-tail structural defects.

The –CF$_2$– resonance is sensitive to stereosequence dyads, so that the geminal fluorines are magnetically equivalent in the racemic dyad, resulting in a singlet, but magnetically nonequivalent in the meso dyad, resulting in an AB quartet at lower field. The AB quartet has J_{gem} = 290 Hz and $J/\Delta\nu = 0.55$, with components at −116.69, −118.23, −119.47, and −121.01 ppm, when the solvent is acetone (Figure 5a). This quarter is very clear in the 2D J-resolved experiment.[9] When the solvent is dioxane (Figure 5b), the unresolved vicinal coupling of the methine fluorine increases for one of the geminal fluorines, so the quartet no longer appears symmetrical. This fact is more obvious in the 470-MHz spectrum in dioxane (not shown). By comparing peak areas in the manner described in section 1a, we obtain a p(m) value of 0.46 for the isoregic polymer, which then allows us to assign the stereochemical splitting in the upfield –CFH– resonance region by assuming that the peak probabilities conform to Bernoullian statistics.

The major splitting of the –CFH– resonance is due to stereochemical triads, with pentad fine structure on the heterotactic and isotactic peaks, as shown in Figure 5a. Racemization takes place during the reduction procedure outlined in Scheme I,[11] so that the tacticity of the precursor

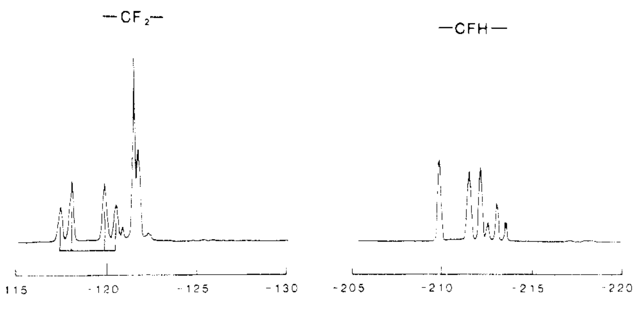


Figure 6. 470.55-MHz fluorine-19 NMR spectrum of isoregic poly(trifluoroethylene) sample PF_3E-D observed at 20 °C in acetone-d_6. This spectrum is proton coupled, which causes the slight broadening of the -CFH- resonances.

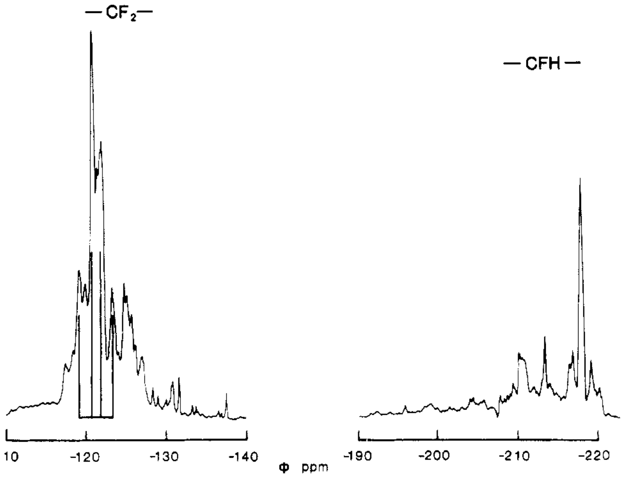


Figure 7. 188.22-MHz fluorine-19 NMR spectrum of the DFE–TFE copolymer, which models syndioregic PF_3E, observed at 20 °C in acetone-d_6. The stick spectrum indicates the major AB quartet from the nonequivalent geminal $-CF_2-$ fluorines with J = 280 Hz.

PCF_3E is not preserved in the derived PF_3E. As we have seen, the probability of meso dyads decreases slightly from 0.48 to 0.46. The observed values for the triad fractions are mm = 0.209, mr = 0.505, and rr = 0.286.

Weak peaks can be observed in Figure 5a with 10-fold vertical amplification of the spectrum. These are due to head-to-head and tail-to-tail defects, and their area can be used to measure the deviation from a pure isoregic structure (next section). This is the first evidence reported for head-to-head structures in PCF_3E. These defects cannot be detected readily in the fluorine-19 NMR spectra of the precursor polymer (Figures 3 and 4), where the peaks are broader and not as well resolved. No such defects could be observed when the precursor polymer was PBF_3E.

Figure 6 shows the 470-MHz fluorine-19 NMR spectrum of isoregic PF_3E. The AB quartet from $-CF_2-$ fluorines in a meso dyad is now fully resolved and has a $J/\Delta\nu$ value of 0.22. The racemic-centered resonance is starting to split due to sensitivity to tetrad stereosequences. The -CFH- resonances are no better resolved than at the lower field, mainly due to our inability to decouple protons with the fluorine probe on the GX-500.

3. Syndioregic Poly(trifluoroethylene) by Copolymerization. Figure 7 shows the 188-MHz fluorine-19 NMR spectrum of the DFE–TFE copolymer formed at -80 °C, which models syndioregic PF_3E. The ratio of the $-CF_2-$ resonance area (-117 to -132 ppm) to the -CFH- resonance area (-207 to -221 ppm) is 2.0:1, which means that this copolymer has an equimolar composition. Furthermore, the monomer sequence structure must be close to 1:1 alternating, since the rate of homopolymerization of DFE at -80 °C is negligible.[12] Moreover, long blocks of TFE units would give a prominent single peak at 122 ppm.[13]

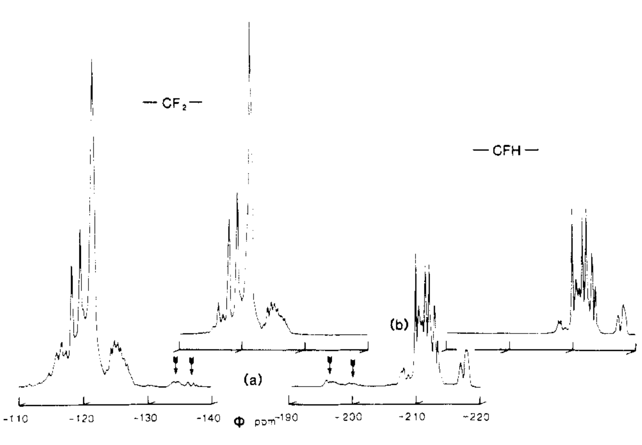


Figure 8. 188.22-MHz fluorine-19 NMR spectra of aregic poly(trifluoroethylene): (a) sample A and (b) sample E observed at 20 °C in acetone-d_6. The peaks indicated by arrows in spectrum (a) were not observed in the other PF_3E samples.

To a first approximation the spectrum of syndioregic PF_3E should show a single AB quartet for the nonequivalent geminal $-CF_2-$ fluorines and a doublet for the -CFH- fluorines from M and R stereochemical dyads in the 11 regiosequence (upper case M and R are used to distinguish these dyads from the m and r dyads in the 101 sequence, where 0 = CF_2 and 1 = CFH). The spectrum from the DFE–TFE copolymer is more complicated than this. The complication is not due simply to fine structure from higher order stereosequence dyads in the 1001 sequence and most likely arises from end groups, as the copolymer has a very low molecular weight. However, since most peak intensity is concentrated in the $-CF_2-$ quarter centered at -121 ppm and the -CFH- doublet centered at -217 ppm, these positions are assigned to the syndioregic sequences in aregic PF_3E (next section).

4. Aregic Poly(trifluoroethylene) by Addition Polymerization. The monomer F_3E was polymerized over a temperature range of 160 °C as shown in Table I. The fluorine-19 NMR spectra of representative polymers PF_3E-A and PF_3E-E are shown in Figure 8. The emulsion polymer from Pennwalt gave anomalous peaks from -133 to -138 and -195 to -202 ppm (indicated by the arrows in Figure 8a) which were not observed for any of the PF_3E samples prepared in our laboratory.

The fluorine-19 NMR spectra from similar PF_3E samples prepared by free-radical polymerization have been reported by Zotikov et al.[14] and Yagi.[15] However, an unambiguous analysis of the polymer microstructure is not at all straightforward and cannot be made without examination of the isoregic and syndioregic polymers, as described in the present work, owing to the severe overlap of signals from atactic and aregic sequences. Empirical chemical shift predictions based on a conformational analysis of the PF_3E chain[16] are required as well to help deconvolute the $-CF_2-$ and -CFH- resonance patterns into their component regiosequence n-ads S_n.[17] There are four distinct triads (n = 3) and eight pentads (n = 5), which are listed in Table IV using simple binary notation (0 = CF_2, 1 = CFH).

Figure 9 shows the 188-MHz fluorine-19 NMR spectrum of aregic PF_3E in detail, with bars indicating the chemical shift range predicted[16] for the various regiosequence pentads in Table IV. The shaded peaks show only the isoregic components. The multiplicity of peaks from aregic PF_3E

Table IV
Set of Observationally Distinct 1- and 0-Centered Regiosequence Triads (S_3) and Pentads (S_5) for Poly(trifluoroethylene) (0 = CF_2, 1 = CFH)[a]

A_3	010	α_3	101
B_3	011	β_3	100
A_5	10101	α_5	01010
B_5	00101	β_5	11010
C_5	10110	γ_5	01001
D_5	00110	δ_5	11001

[a] A regiosequence n-ad has n elements (0's and 1's) and is defined in more detail in ref 17.

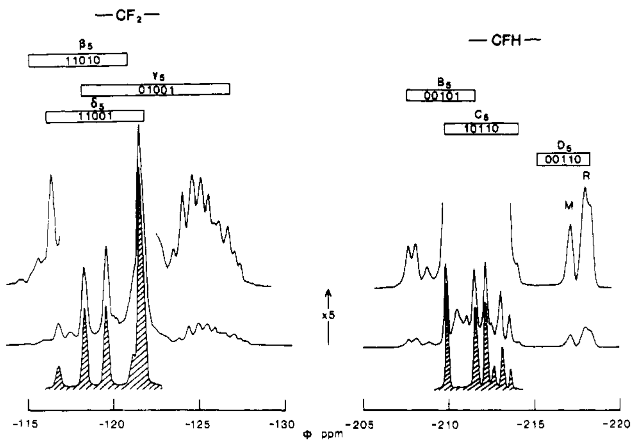


Figure 9. 188.22-MHz fluorine-19 NMR spectrum of aregic poly(trifluoroethylene) sample B observed at 20 °C in acetone-d_6, with the predicted chemical shift dispersion for the different regiosequence pentads.[16] This dispersion includes the effects of stereochemical nonequivalence and $-CF_2-$ geminal coupling. The shaded peaks are due to the isoregic sequences α_5 ($-CF_2-$) and A_5 (-CFH-).

cannot be accounted for by a simple linear combination of spectra from the model isoregic and syndioregic polymers (i.e., a regiosequence triad analysis), so that the pentads S_5 must be considered as indicated. This order of regiosequence sensitivity is consistent with the triad and pentad stereosequence sensitivity of the -CFH- resonances in isoregic PF_3E, and the empirical chemical shift calculations.[16]

As mentioned previously the overlap of fluorine-19 resonances from stereosequence and regiosequence nonequivalence in PF_3E is particularly severe. In fact the $-CF_2-$ region is almost useless for sequence analysis at 188.22 MHz, because the large geminal homonuclear coupling further disperses resonances which are already spread into virtually a continuum from -115 to -128 ppm by structural isomerism. The improvement in the 470-MHz spectrum (not shown) is not that substantial. At best the components from the isoregic sequence α_5 can be subtracted from the rest ($\beta_5 + \gamma_5 + \delta_5$) given the assignments from the model polymer (Figure 5). The -CFH- region is more amenable to analysis because the syndioregic sequence D_5 is well separated from the others, as indicated by the model polymer spectrum (Figure 7) and the calculated chemical shifts. Similarly, the components from the isoregic sequences A_5 can be subtracted, using the spectrum in Figure 5 as a guide, from the remaining -CFH- resonance area to give the area corresponding to $B_5 + C_5$.

In this way values of $P_{obsd}(S_5)$, where $P_{obsd}(S_n)$ is the unconditional probability of observing the regiosequence n-ad S_n,[17] can be derived for the resolved sequences. The $-CF_2-$ resonance area is halved and then all S_5 areas are normalized to sum to unity, as shown in Table V for the various PF_3E samples.

Table V
Unconditional Probabilities of Those Regiosequence Pentads in Poly(trifluoroethylene) Which Can Be Resolved by Fluorine-19 NMR[a]

	P_{obsd}				
	$-CF_2-$		-CFH-		
sample desig	α_5	A_5	$B_5 + C_5$	D_5	% defect
PF_3E-A	0.288[b]	0.289[b]	0.146	0.065	13.8
PF_3E-B	0.314	0.324	0.115	0.061	11.8
PF_3E-F	0.318	0.347	0.107	0.046	10.0
PF_3E-D	0.480	0.471	0.019	0.010	1.9
PF_3E-G	0.500	0.500	0.00	0.00	0.0

[a] The corresponding values for the defect level are calculated with eq 3-6. [b] It is necessary that $P_{obsd}(\alpha_5) = P_{obsd}(A_5)$, so their differences here reflect an uncertainty of 10% in the P_{obsd} values.

Table VI
Unconditional Probabilities of Stereosequences in A_5 (10101) and D_5 (00110) Regiosequences of Poly(trifluoroethylene) Samples

	unconditional probabilities					
	A_5				D_5	
sample desig	m[a]	mm	mr + rm	rr	M	R
PF_3E-A	0.51	0.27	0.48	0.25	0.29	0.71
PF_3E-B	0.53	0.29	0.49	0.22	0.29	0.71
PF_3E-F	0.54	0.30	0.47	0.23	0.28	0.72
PF_3E-D	0.46	0.21	0.50	0.29	0.30	0.70
PF_3E-G	0.46	0.20	0.51	0.29		

[a] Obtained according to $p(m) = p(mm) + p(mr)$.

5. Tacticity of Poly(trifluoroethylenes). None of the polymers examined here are stereoregular. Table VI gives the unconditional probabilities of various stereosequences resolved in the fluorine-19 NMR spectra of PF_3E. The isoregic sequence A_5 (10101) is split into syndiotactic (rr), heterotactic (mr + rm), and isotactic (mm) triad peaks centered at -209.9, -211.9, and -213.1 ppm, respectively, whereas the syndioregic sequence D_5 (00110) is split into meso (M) and racemic (R) dyad peaks at -217.2 and -218.2 ppm.

Samples PF_3E-D and PF_3E-G have undergone racemization during reductive dechlorination (section 2) and have therefore identical stereochemical distributions, unlike their precursor polymers, which have slightly different $p(m)$ values. The $p(m)$ values for the samples prepared from F_3E change slightly with polymerization temperature, and the triad probabilities may be approximated by Bernoullian statistics:[8]

$$p(mm) = p(m)^2$$

$$p(mr) + p(rm) = 2p(m)p(r)$$

$$p(rr) = (1 - p(m))^2$$

where $p(m)$ is calculated according to

$$p(m) = p(mm) + p(mr)$$

Discussion

1. Regiosequence Probabilities and Defect Content. We now consider the results from quantitative analyses of the fluorine-19 NMR spectra as described above, where peak areas corresponding to given microstructural features have been converted into unconditional probabilities. These allow us to measure regiosequences and the level of structural defects associated with head-to-head and tail-to-tail monomer linkages.

First it is necessary to consider precisely how the defect level in a regioirregular polymer is defined. The definition can be based on monomer units, bonds linking monomer units, or regiosequence dyads. For example, polymers like PVF_2, which are predominantly isoregic with a low ($\sim$5%) defect content, have been characterized according to the monomer-based definition (1):[17]

$$\% \text{ defect} = 100m_r \tag{1}$$

where m_r is the mole fraction of "reversed" monomer units. Alternatively, definition (2), which considers the type of bond between monomer units, has been used:[18]

$$\% \text{ defect} = 100f_{hh} = 100f_{tt} \tag{2}$$

where f_{hh} is the fraction of the bonds formed between monomer units which are head-to-head and f_{tt} is the fraction which are tail-to-tail.

However, NMR cannot tell the directional sense of a monomer unit, so the designation of a "reverse" monomer unit is arbitrary. Moreover, NMR cannot always tells if any given carbon–carbon bond in the polymer backbone (e.g., 01) exists within a single monomer unit or between a pair of units. For these reasons we have introduced definition (3), which is based on regiosequence dyads that may be measured unambiguously by NMR:[17]

$$\% \text{ defect} = 100(p(11) + p(00)) \tag{3}$$

where $p(11)$ and $p(00)$ are the unconditional probabilities of 11 and 00 dyads.

It can be shown that definitions (2) and (3) are always equivalent numerically but that definition (1) is the same only in the special case where reversals of monomer units are isolated. Thus all three definitions give the same % defect for polymers like PVF_2 where this number is low so that pairs or longer runs of "reversed" monomer units are extremely unlikely.

On the other hand, consider the hypothetical polymer formed by the head-to-head combination of two growing isoregic chains of identical length. Here precisely half of the monomer units are reversed, but there is only one head-to-head linkage for a very large number of head-to-tail linkages. The defect level is 50% according to definition (1) but almost 0% according to definitions (2) and (3). Clearly, the latter number better represents this polymer, which would be virtually indistinguishable from the pure isoregic polymer on the basis of its physical properties. Therefore definition (3) will be used for the following, where we note that[17]

$$p(11) + p(00) = P_{\text{obsd}}(B_3) = P_{\text{obsd}}(\beta_3) \tag{4}$$

Since regiosequence pentads have to be considered for PF_3E, the following additional equations will prove useful:[17]

$$P_{\text{obsd}}(B_3) = P_{\text{obsd}}(C_5) + P_{\text{obsd}}(D_5) \tag{5}$$

and

$$P_{\text{obsd}}(B_5) = P_{\text{obsd}}(C_5) \tag{6}$$

Thus the defect levels shown in Table V are calculated with eq 3–6.

It is crucial in obtaining the correct defect levels that the order of regiosequence splitting be assigned properly. For example, if the spectra were deconvoluted erroneously as a simple linear combination of just isoregic and syndioregic triads α_3, β_3 ($-CF_2-$) and A_3, B_3 ($-CFH-$), then the calculated defect levels would nearly double to 20, 18, and 16% for PF_3E samples A, B, and F, respectively.

2. Effect of Temperature on Poly(trifluoroethylene) Microstructure. Temperature does not have a large effect on the microstructure of PF_3E prepared by the free-radical polymerization of F_3E monomer. The defect level is lowered slightly from 14% to 10% for a 160 °C fall in polymerization temperature (Table V), so it is not feasible to eliminate defects entirely by simply lowering temperature to make isoregic PF_3E.

Likewise the tacticity changes little with temperature (Table VI). The isoregic sequences in all polymers are nearly perfectly atactic (Bernoullian with $p(m) = 0.5$). It appears that isotactic sequences become more favored at lower temperatures, in contrast to most vinyl polymers, which become more syndiotactic (enhanced $p(r)$ values).[8] However, it is difficult to verify this apparent trend for PF_3E owing to the overlap problem for aregic polymers, which sets an accuracy of about ±5% on $p(m)$ values.

3. Comparison with the Literature. In an early chemical study of the reactivity of F_3E, Haszeldine and Steele[19] found that radical attack was directed 80% on the CHF group and 20% on the CF_2 group. Zotikov et al.[14] found 10% defects from their NMR study, which is in close agreement with the present work, but they reported that PF_3E is predominantly syndiotactic, which we cannot substantiate (Table VI).

Yagi[15] deduced that PF_3E had 50% of regioirregular defects from 56.4-MHz fluorine-19 NMR spectra, but this number is clearly in error. The analysis was based solely on the $-CF_2-$ resonance region, where the nonequivalence of the geminal fluorines was not recognized so that their coupling was misinterpreted in part as splitting from different regiosequence pentads. As we have seen, the $-CF_2-$ resonances are very difficult to analyze for aregic PF_3E even at an observing frequency of 470 MHz.

4. Comparison with Other Aregic Poly(fluoroethylenes). Of all the poly(fluoroethylenes) that have directional isomerism, PF_3E contains the most defects at 14%. There are slightly fewer defects in PVF at 11%,[4] and substantially less in PVF_2 at 5%.[17] This order correlates with the regiospecificity of attack of difluoromethyl and trifluoromethyl radicals on fluoroethylenes, which increases in the sequence $F_3E < VF < VF_2$.[20] Both PF_3E and PVF are atactic, but the latter has a slight bias in favor of syndiotactic sequences, as indicated by the respective $p(m)$ values of 0.51 and 0.46.

5. Comparison with Poly(vinyl halides). Head-to-head addition was not observed in PBF_3E, but nearly 2% of these defects were detected in PCF_3E after reductive dechlorination (Table V). Clearly, bromine is a more effective blocking group than chlorine in hindering this mode of addition. The analogous trihydro polymers, poly(vinyl bromide) and poly(vinyl chloride), have regiosequence defect levels of 0 and 0.2–0.3%, respectively.[21,22] However, these defects can rearrange in poly(vinyl chloride) to chloromethyl branches,[22] which is an option not available to its more stable perfluoro analogue PCF_3E.

Acknowledgment. We thank M. Y. Hellman for molecular weight determinations and S. M. Vincent for X-ray fluorescence spectroscopy. The emulsion polymer from Pennwalt Corp. was donated by G. Leader and made available to us by F. C. Schilling.

Registry No. PBF_3E (homopolymer), 55157-25-0; PCF_3E (homopolymer), 9002-83-9; DFE–TFE (copolymer), 67291-14-9; PF_3E-A (homopolymer), 92008-04-3; PF_3E-A (SRU), 91900-23-1.

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Structure and Morphology of Poly(trifluoroethylene)

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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$\bar{\text{G}}$, 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$_3$E] 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$_3$E 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$_3$E polymerization is also subject to stereoirregular addition, and PF$_3$E samples are in fact essentially atactic.[10]

Under these conditions, it might at first appear surprising that PF$_3$E 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$_3$E, allowing development of significant crystallinity. The chain conformation of PF$_3$E 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$_3$E 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$_3$E 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$_3$E, we present in this paper the first detailed investigation of the structure and morphology of PF$_3$E 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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