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

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

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

The model presented in Figure 4 is further supported by the fact that it provides an explanation for the observation in small-angle X-ray experiments[2] that the diffraction peak arising from clustering is observed even at very low volume fractions of clusters. This explanation is based on the proposal that the effective "Bragg" spacing associated with ionic clustering is statistically weighted to be equal to the sum of the thickness of the fluorocarbon layer plus the cluster diameter.

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

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

Andrew J. Lovinger,*[1a] G. T. Davis,[1b] T. Furukawa,[1a,c] and M. G. Broadhurst[1b]

Bell Laboratories, Murray Hill, New Jersey 07974, and National Bureau of Standards, Washington, D.C. 20234. *Received August 21, 1981*

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

Introduction

Because of its important piezoelectric and pyroelectric properties, poly(vinylidene fluoride) has attracted much scientific interest during the past few years. As has recently been summarized,[2-4] these properties are attributable to the ferroelectric nature of some of the polymorphic forms of poly(vinylidene fluoride). The most important of these polymorphs is the β phase, in which the molecules assume essentially a planar-zigzag conformation and pack in an orthorhombic unit cell whose dimensions render it pseudohexagonal.[5] The current theories[6,7] of ferroelectric polarization take advantage of this pseudohexagonal packing in considering the macroscopic alignment of dipoles resulting from electrical poling to occur through cooperative rotations of chains about their molecular axes in multiples of 60°. Ferroelectric models predict existence of a Curie temperature for this polymorph, above which polarization is lost, presumably due to a pseudohexagonal randomization of molecular packing in crystalline regions. However, other than in one report,[8] such a Curie temperature has not been found, and it is generally believed[9,10] that this temperature may lie within the region of melting of poly(vinylidene fluoride).

Attention has recently been directed toward copolymers of vinylidene fluoride with other fluorocarbons, partly in the hope that Curie transitions would be unequivocally observed. The copolymers used in this regard have been those of trifluoroethylene, since the work by Lando and Doll[11] had shown that introduction of 17 mol % of trifluoroethylene allows the resulting copolymer to adopt the all-trans conformation and unit cell of the β phase of poly(vinylidene fluoride). Yagi and co-workers have recently synthesized these copolymers over the entire range of composition,[12,13] have probed molecular conformation and crystalline form by X-ray diffraction and infrared spectroscopy,[14] and have investigated relaxational behavior by means of dielectric and dynamic mechanical measurements.[14,15] They report[12-15] that pure poly(trifluoroethylene) is stereoirregular, contains ~50% of inversely added monomeric units, and adopts a 3/1-helical conformation (as was earlier found by Kolda and Lando),[16] that copolymerization with up to ~85 mol % vinylidene fluoride yields trans- or translike conformations, and that higher concentrations of vinylidene fluoride yield a $TGT\bar{G}$ conformation.

Extensive studies have been conducted by a number of authors in the intermediate compositional spectrum (i.e., around 50 mol % of each constituent), for which a transition in the vicinity of 70 °C has been interpreted as being ferroelectric in nature. Specifically, observations of a dielectric anomaly[15,17-20] accompanied by critical slowing down of the relaxation time,[18-20] a secondary endotherm[15,19,20] associated with an anomalous peak in specific heat,[20] changes in lattice spacing,[19-21] in sample dimensions,[19] and in IR spectra,[19] and disappearance of remanent polarization[19-21] and piezoelectricity,[19] all occurring around 70 °C, have been taken[19,20] as reflecting the existence of a Curie point at this temperature.

However, the detailed structure of these copolymers above and below the transition temperature has not been determined; neither is it known whether the transition occurs *inter*molecularly (i.e., by randomization of dipole vectors of polar chains) or *intra*molecularly (i.e., by conformational changes leading to a nonpolar chain structure). We have attempted to answer these questions in this set of two companion papers: In the present article, we examine the crystalline forms in a 52/48 mol % copolymer of vinylidene fluoride and trifluoroethylene, as well as the crystalline transformations that take place as a result of drawing, poling, or annealing; the second part of this work (following paper)[22] is concerned with a detailed investigation of structural changes occurring around the transition temperature of this copolymer, as determined by dielectric, X-ray, and infrared techniques.

Experimental Section

The samples used in this investigation were of a 52/48 mol % copolymer of vinylidene fluoride and trifluoroethylene, provided by Daikin Kogyo Co., Ltd, Japan.[23] They had been prepared by bulk polymerization at 22 °C using a peroxide initiator and were in random configuration.[13-15] Although the exact extent of reversed monomeric units is not known for this copolymer, poly(vinylidene fluoride) generally contains ~5% of inversely added units,[4] and poly(trifluoroethylene) ~50%.[12] For comparison purposes, an experimental sample of poly(trifluoroethylene), obtained from Pennwalt Corp., was also examined.[23] Films were made by compression molding at 180 °C and cooling to room temperature. Oriented specimens were prepared by drawing at a rate of 10%/min at the desired temperatures. Electrical poling was conducted at 25 °C and 700 kV/cm after evaporation of Au electrodes. X-ray diffraction patterns were examined at various temperatures using Cu Kα radiation detected either by a vertical goniometer or by an evacuated flat-plate camera.

Results and Discussion

A. Molecular Conformation. While earlier studies, based upon diffractometric data from the 4–5-Å region, identified copolymers in this compositional range with the β phase (all trans), examination of the *full* diffraction pattern now reveals a considerably more complicated structure. Such a diffraction pattern of melt-crystallized 52/48 copolymer, recorded at room temperature, is shown in Figure 1a: here, in addition to the strong reflection at ~4.64 Å, two weak, diffuse reflections are seen centered at ~2.56 and ~2.30 Å; the latter is particularly broad, extending from ~2.21 to ~2.38 Å. Indexing of these reflections may be made from a fiber pattern; as is discussed more fully below, this requires orientation of the specimen at temperatures above ~75 °C, lower temperatures promoting crystalline transformations. Figure 1b shows that high-temperature orientation causes the diffuse reflection at 2.56 Å to become clearly meridional, thus confirming the presence of the planar-zigzag conformation, albeit in a disordered state (as evidenced by the weakness and diffuseness of this 001 reflection). The much broader reflection centered at 2.30 Å also moves toward the meridian but remains much more arced than its counterpart at 2.56 Å.

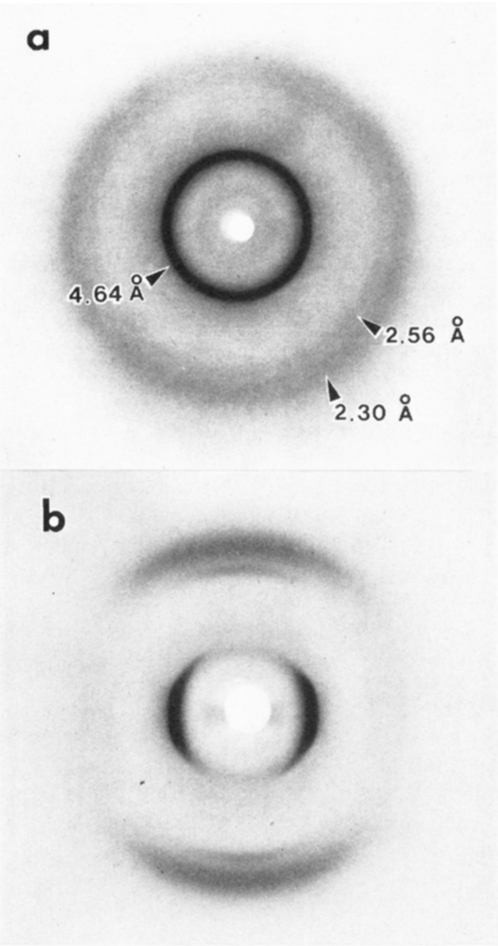

Figure 1. Room-temperature X-ray diffraction patterns of copolymer after (a) melt-solidification and (b) uniaxial orientation at 80 °C.

To identify the broad reflection at 2.30 Å, we first take account of the contribution of planar-zigzag segments: as is known from the structure of β-PVF$_2$,[5] the 001 reflection is accompanied by a strong, composite {201, 111} reflection. Assuming hexagonal packing of all-trans segments on a lattice consistent with the strong reflection at 4.64 Å (this assumption is discussed in detail below), the {201, 111} composite is expected to be off-meridional at a spacing of 2.24 Å. This would explain the arcing of the reflection centered at 2.30 Å but not its *d* spacing or breadth. A full

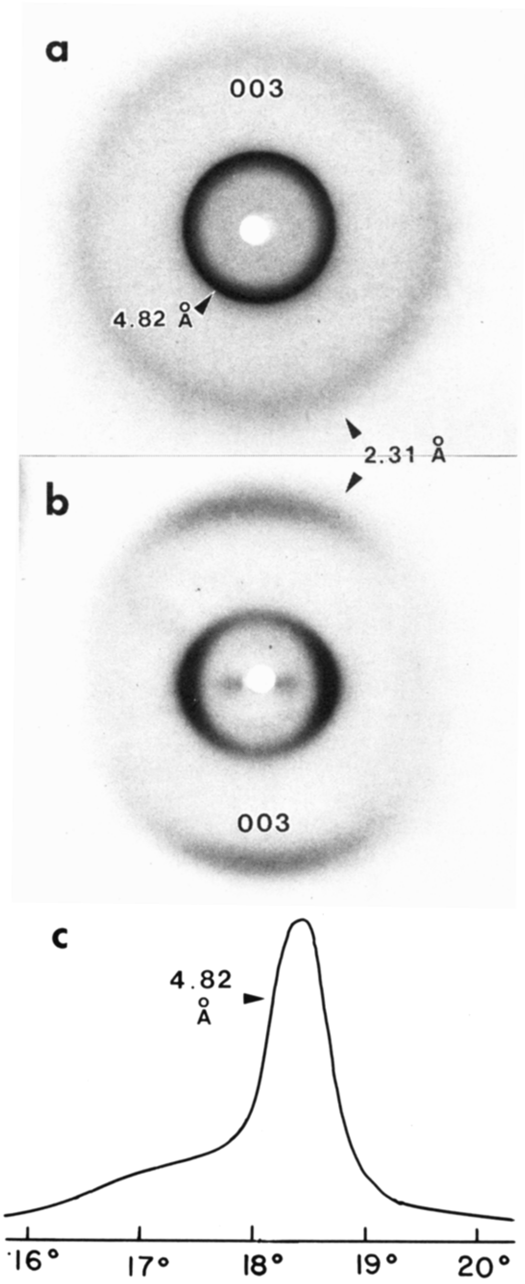

Figure 2. Room-temperature X-ray diffraction patterns of melt-crystallized trifluoroethylene homopolymer (a) before and (b) after uniaxial orientation at 25 °C. A diffractometric scan of the strongest reflection is given in (c).

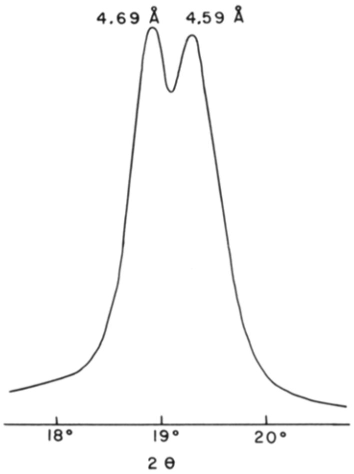

Figure 3. Equatorial diffractometric scan at 25 °C, showing resolution of the strongest reflection of melt-crystallized copolymer into two peaks.

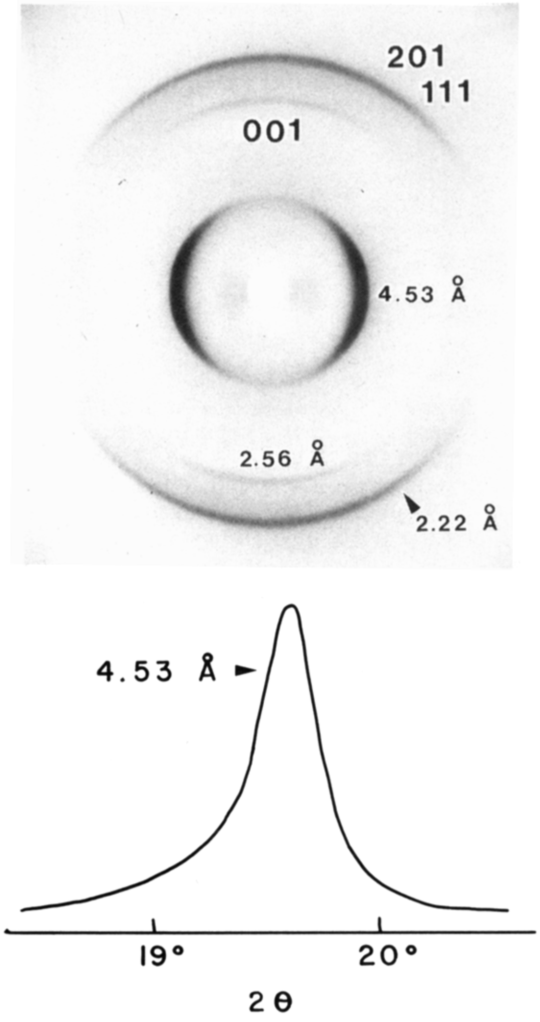

Figure 4. Flat-plate X-ray diffraction pattern and equatorial diffractogram recorded at room temperature from a specimen drawn 4:1 at 50 °C.

explanation requires knowledge of the diffraction pattern of trifluoroethylene homopolymer: as seen in Figure 2 —and in agreement with the earlier results of Kolda and Lando[16]—this polymer is characterized by a broad, arced, and diffuse meridional reflection at 2.31 Å that is identified as 003 of a disordered 3/1-helical conformation. An exact 3/1 helix (i.e., a carbon chain of normal bond distances and angles) would have a 003 repeat of 2.1 Å; the higher value obtained here is common among fluoro polymers[16] and is primarily due to the large van der Waals radius of fluorine as compared to hydrogen and to the disorder resulting from stereoirregularly and inversely added monomeric units. This disorder causes random deviations from the $(TG)_3$ and $(T\bar{G})_3$ conformations of regular 3/1 helices, leading to the observed difuseness of the meridional reflection. The great similarity in spacing, breadth, and arcing between the two corresponding reflections in poly(trifluoroethylene) and its 52/48 copolymer with vinylidene fluoride is obvious from Figures 1b and 2b.

As a result, we conclude from the above that the molecules in this particular copolymer take on two disordered conformations upon crystalization from the melt: some chain segments adopt a planar-zigzag conformation, while others crystallize in a 3/1 helix; presumably, molecular regions rich in vinylidene fluoride would favor the former, while those containing mostly trifluoroethylene would favor

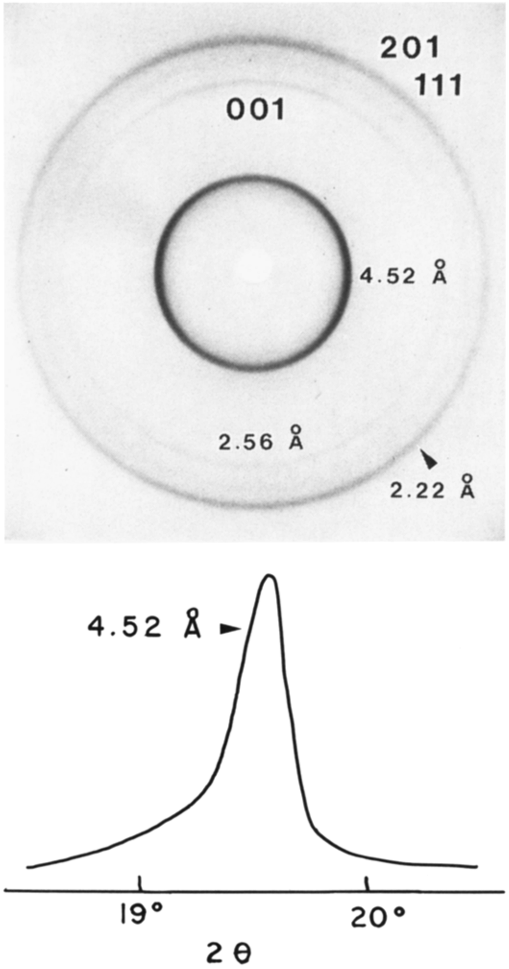

Figure 5. Flat-plate X-ray diffraction pattern and equatorial diffractogram recorded at room temperature from a specimen poled at 700 kV/cm at 25 °C.

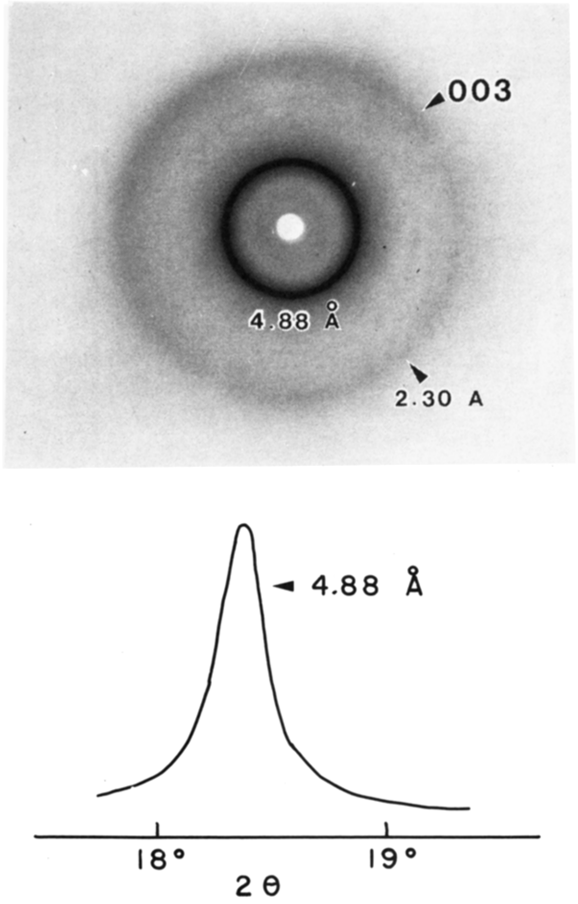

Figure 6. Flat-plate X-ray diffraction pattern and equatorial diffractogram recorded at 90 °C from an unoriented specimen.

the latter. It should again be emphasized that both of these conformations are adopted in a *disordered* manner, so that the overall chain structure may approximate an irregular succession of TT, TG, and T$\bar{G}$ sequences.

B. Molecular Packing. After determining that copolymer chains crystallize from the melt in a mixture of disordered trans and 3/1-helical conformations, we examine the manner in which these chains pack. The equatorial reflection at 4.64 Å (see Figure 1b), considered a singlet by most authors,[15,20,21] has recently been described by Yamada et al.[19] as a closely spaced doublet at room temperature. A detailed study of this reflection as a function of temperature is given in the second part of our work (following paper);[22] here, we discuss only an equatorial scan at 25 °C (Figure 3) showing that the strong reflection at 4.64 Å in Figure 1 is indeed caused by the superposition of two independent peaks at 4.59 and 4.69 Å. Keeping in mind the two-phase nature of this copolymer determined above from meridional X-ray data, this equatorial doublet leads to the following inferences on chain packing: Either (a) each phase gives rise to only *one* peak, thus implying hexagonal (or pseudohexagonal) packing of molecules in both phases, or (b) at least one phase contributes to *both* peaks and its therefore of orthorhombic or lower symmetry. Yamada and co-workers,[19] not having the meridional evidence for a two-phase structure described above, accepted the second interpretation by associating the two equatorial peaks with the 200 and 110 reflections of a single phase; we show presently that the first interpretation is correct by obtaining each phase separately and demonstrating hexagonal (or, at least, pseudohexagonal) packing of molecular chains.

C. Effect of Drawing or Poling. The all-trans phase may be obtained separately by a transformation accompanying drawing or poling at temperatures below ~65 °C. Photographic and diffractometric evidence for this effect of drawing is seen in Figure 4. Here, the 001 and {201, 111} reflections of the all-trans phase are clearly resolved; their intensity is significantly greater than in the unoriented specimen (Figure 1a) or that drawn at high temperature (Figure 1b). At the same time, these meridional reflections become sharp, and practicaly all traces of the broad reflection at 2.30 Å, attributable to the disordered 3/1-helical conformation, disappear. The equatorial diffractogram in Figure 4 shows that these meridional changes are accompanied by transformation of the doublet at 4.69 and 4.59 Å to a single peak at 4.53 Å. All this X-ray evidence may be interpreted as follows: Drawing at low temperatures causes not only molecular orientation but also a transformation of a mixture of disordered 3/1-helical and planar-zigzag chain segments to a *well-ordered* all-trans phase; it is this much more ordered structure that we consider responsible for the more efficient hexagonal packing of chains at 4.53 Å, and we therefore identify the 4.59-Å peak with the disordered trans phase.

Poling proceeds easily at room temperature and low fields and causes the same transformation as drawing; Figure 5 shows the changes in the diffraction pattern and equatorial diffractogram (the poled specimen was an extruded thin film and is therefore very slightly oriented; the very weak ring located between the 001 and {201, 111} reflections stems from the evaporated gold used in poling). Thus, it is seen that, at low temperatures, poling has the

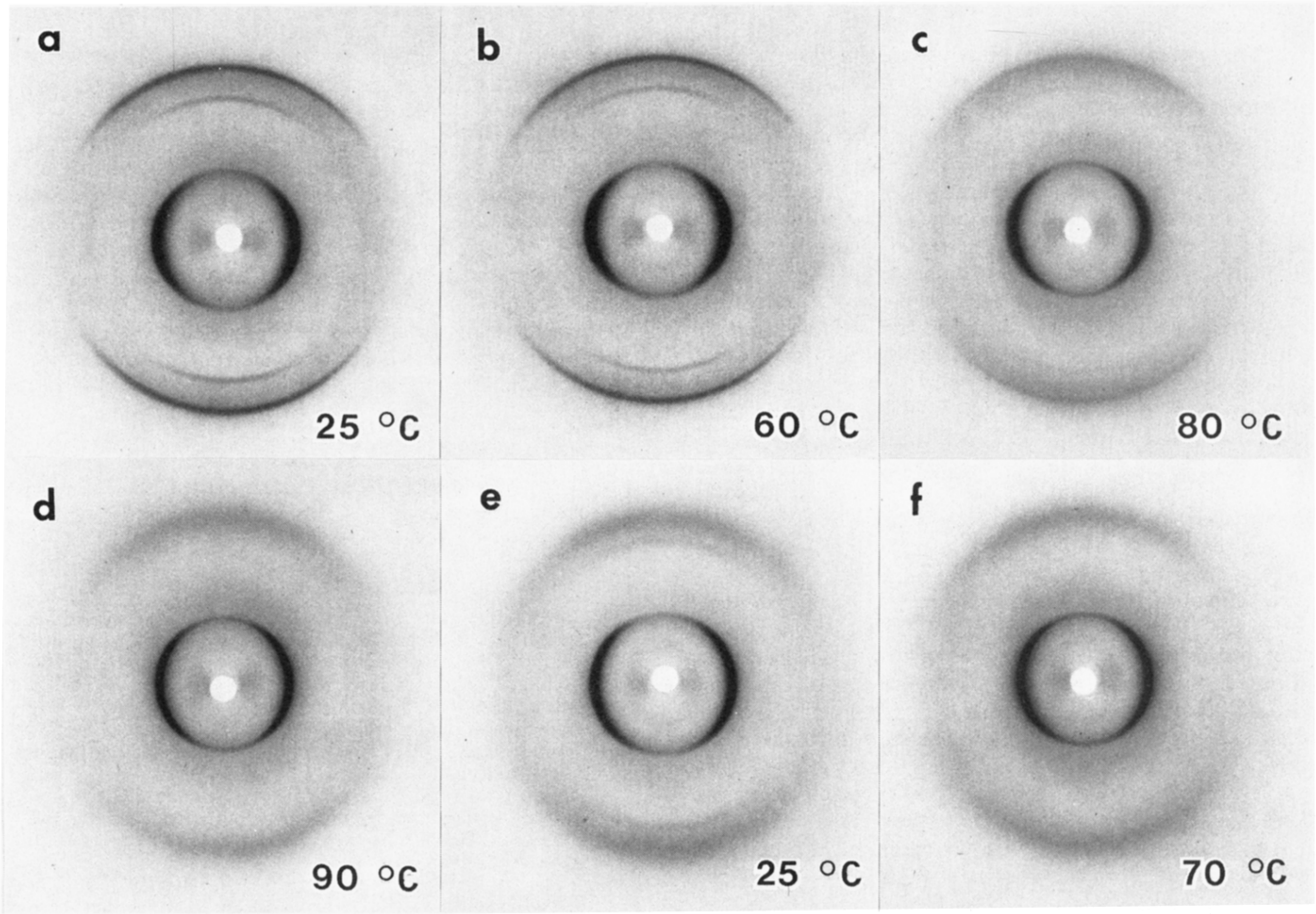

Figure 7. Transformations in the structure of oriented copolymer as reflected in its diffraction pattern recorded at the following temperatures: (a) 25 °C, (b) 60 °C, (c) 80 °C, (d) 90 °C, (e) after cooling to 25 °C, and (f) after subsequent reheating to 70 °C.

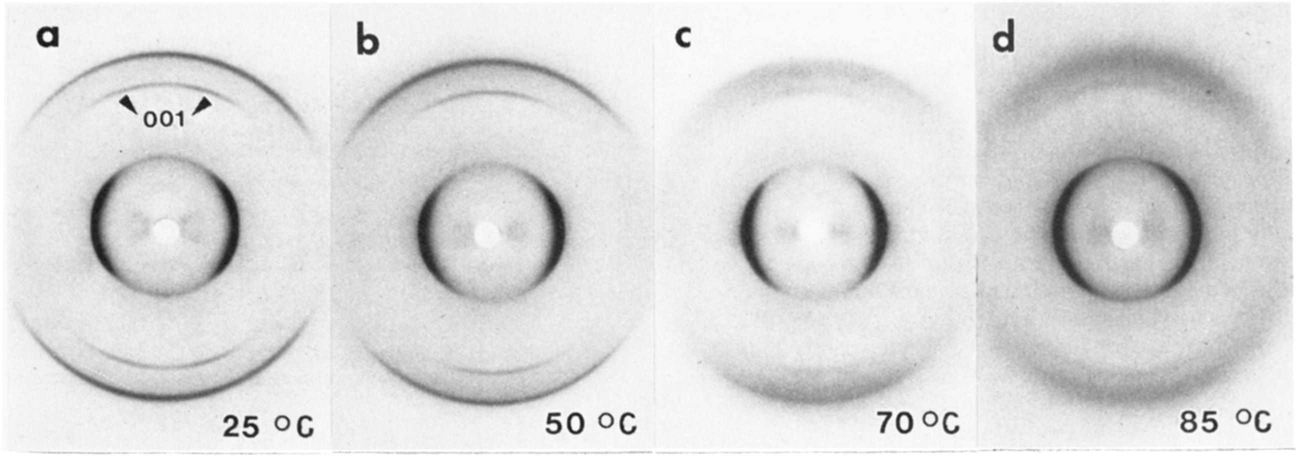

Figure 8. Effect of draw temperature on the structure of copolymers uniaxially oriented 4:1. Diffraction patterns recorded at room temperature after drawing at (a) 25, (b) 50, (c) 70, and (d) 85 °C.

same effect as mechanical drawing in causing a transformation to a well-ordered, hexagonally packed, all-trans phase. On the other hand, poling above ~60 °C becomes progressively less effective, and no permanent polarization is imparted to specimens poled above 70 °C; reasons for this lie in the nonpolar structure of the samples at these temperatures, as discussed immediately below.

D. Effect of Heat Treatment. The 3/1-helical phase may be obtained separately by heating of samples to temperatures above 70 °C (see Figure 6). For unoriented specimens, the diffuse reflection at 2.56 Å is no longer visible above 70 °C. As is discussed in greater detail in the second part of this report (following paper),[22] the equatorial peak at 4.69 Å rapidly increases in d spacing and by 70 °C has attained the value characteristic of poly(trifluoroethylene); it is therefore attributed to the packing of the original 3/1-helical phase of the copolymer. At higher temperatures (i.e., ~90 °C), the all-trans equatorial peak also reaches the spacing of trifluoroethylene homopolymer. These results show that heating beyond the 70 °C transition temperature to ~90 °C causes transformation of the original disordered mixture of phases to a single, disordered 3/1-helical phase analogous to that of poly(trifluoroethylene) and that such helices are hexagonally (or pseudohexagonally) packed. Moreover, the ineffectiveness of poling at high temperatures is now clearly attributable to the nonpolar nature of the disordered helical conformation.

In the case of oriented or poled films, the more orderly packed structure allows survival of the meridional all-trans reflection to temperatures slightly higher (i.e., 80–85 °C) than the 70 °C transition. This is illustrated in Figure 7, where little change in the diffraction pattern is seen between 25 and 60 °C and where reflections attributable to the well-ordered trans-planar phase have substantially disappeared by about 80 °C. At 90 °C the pattern is uniquely characteristic of the disordered 3/1-helical phase, whereas subsequent cooling to room temperature causes a return to a mixture of disordered trans-planar and 3/1-helical phases. Interestingly, while this heating and cooling cycle erases the high trans order induced by drawing, it conserves the simultaneously imparted uniaxial orientation (see Figure 7e). From that point on, the copolymer, although molecularly oriented, undergoes transformations as if unoriented; for example, Figure 7f shows that the 2.56-Å reflection disappears at ~70 °C during the second heating cycle rather than ~85 °C, as observed during the first.

E. Effect of Draw Temperature. It is clear from the above that low temperatures favor the all-trans conformation and high temperatures the disordered helical one. This trend also applies to the temperature of drawing, which controls the polymorphism, order, and molecular orientation of the final structure. As seen in Figure 8, all reflections are generally highly arced despite the considerable extension (4:1), presumably as a result of an imperfect realignment of chains that stems from the profusion of molecular defects. This misalignment is especially pronounced at room temperature (Figure 8a), where restricted flow allows the molecules only to *approach*, rather than to *attain*, full parallelism with the draw direction; the splitting of arcs seen in Figure 8a in fact indicates a double orientation, equivalent to a quasi-twinned structure. Drawing at higher temperatures up to ~65 °C causes transformation to the well-ordered all-trans phase, as discussed above, the molecular chains now becoming more fully parallel to the draw direction (see Figure 8b). With increasing temperature, more of the original blend of disordered phases is preserved and less is oriented to the well-ordered planar-zigzag structure (Figure 8c). Above the transition temperature (i.e., 75 °C or higher), drawing results in orientation of the original disordered mixture without any ordering or transformation (see Figure 8d). At the same time, the specimens become increasingly weak and flow easily; orientation at 85 °C (Figure 8d) could be achieved only at very low rates (0.5%/min) and to limited draw ratios (2:1).

Conclusions

From the above results, we conclude that the melt-crystallized 52/48 mol % copolymer of vinylidene fluoride and trifluoroethylene contains a mixture of disordered trans-planar and 3/1-helical phases, each packed in a hexagonal (or pseudohexagonal) manner. Drawing or poling at temperatures up to ~65 °C causes both a transformation to a single all-trans phase and a substantial improvement in conformational and packing order; at higher temperatures, poling is ineffective, while drawing results only in orientation of the originally disordered structure. Heating of specimens to these high temperatures causes a progressive transformation to a hexagonally (or pseudohexagonally) packed, nonpolar, disordered 3/1-helical phase, analogous to that of trifluoroethylene homopolymer. These conclusions are further substantiated in the following article,[22] in which we discuss the structural and dielectric changes occurring as the copolymer is heated through the transition region.

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(1) (a) Bell Laboratories. (b) National Bureau of Standards. (c) Permanent address: Institute of Physical and Chemical Research, 2-1 Hirosawa, Wako-shi, Saitame 351, Japan.

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