from compatible mixtures at temperatures above LCST. The spectral changes in those cases are similar to those for the different samples cast from various solvents. The molecular level of intermixing that occurs in PS/PVME blends may include dispersion forces from several chemical groups. Since the bands most sensitive to changes in compatibility are the CH out-of-plane bending of PS and the COC asymmetric stretching of PVME, among the many possibilities, interaction between the ring and the COCH$_3$ group may be influential, leading to compatibility for this pair of polymers. In this paper we gave emphasis to finding molecular spectroscopic features sensitive to compatibility. It is well-known that both thermal and mechanical properties of binary mixtures are particularly sensitive to the degree of compatibility. We have characterized the molecular response of these blends when samples are deformed macroscopically. Our results will be reported in another publication.

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Registry No. Polystyrene, 9003-53-6; poly(vinyl methyl ether), 9003-09-2.

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Ferroelectric Transition in a Copolymer of Vinylidene Fluoride and Tetrafluoroethylene

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ABSTRACT: Crystallographic changes consistent with a Curie transition have been demonstrated by X-ray diffraction in an 81/19 mol % copolymer of vinylidene fluoride (VF$_2$) and tetrafluoroethylene (F$_4$E). This allows generalization of our earlier conclusions obtained from copolymers of VF$_2$ with trifluoroethylene (F$_3$E) and circumvents any uncertainties related to the role of that comonomer; these include the similarity of the paraelectric structure to that of poly(trifluoroethylene), as well as the introduction into the PVF$_2$ chain of different chemical species, tacticity defects, and regicity defects associated with F$_3$E. In contrast, the tetrafluoroethylene copolymer investigated here is equivalent to PVF$_2$ containing a slightly higher percentage of head-to-head defects. In unpoled specimens of this F$_4$E copolymer, the ferroelectric → paraelectric transition is partly thwarted by the onset of melting, while in poled films it is almost completely aborted by melting. However, cooling from the melt causes first crystallization of the paraelectric phase and then full transformation to its ferroelectric counterpart. As in the case of F$_3$E copolymers, the all-*trans* ferroelectric phase is transformed above the Curie transition to a paraelectric state consisting of partly disordered chains that contain TG, T$\bar{\mathrm{G}}$, and TT sequences and that are packed in an expanded pseudohexagonal unit cell. In agreement with this disorder, single crystals of the F$_4$E copolymer grown at high temperatures in the paraelectric phase exhibit irregular morphological features and lack crystallographic faceting; such crystals also provide indications of an unusual phenomenon—irreversible ferroelectric → paraelectric transformation induced by electron irradiation.

Introduction

The ferroelectric behavior of poly(vinylidene fluoride) is now clearly established and has recently been reviewed.[1–4] However, a common and characteristic property of ferroelectric crystals, i.e., the existence of a Curie transition at which polarization is lost through a solid-state transformation to a paraelectric phase, is still controversial for this polymer: on the one hand, an isolated paraelectric phase has never been obtained in the ferroelectric β-phase of poly(vinylidene fluoride) [PVF$_2$], and the prior occurrence of melting at 170–185 °C has been invoked for its absence;[5,6] on the other hand, a Curie transition has been suggested around 140 °C from dielectric results,[7] while very recent X-ray data have indicated that such a transition may be commencing just below the final stages of melting in β-PVF$_2$.[8] We have obtained some insight on this topic by examining by X-ray diffraction and dielectric techniques a series of random copolymers of vinylidene fluoride (VF$_2$) and trifluoroethylene (F$_3$E);[9–11] these had previously been found to exhibit secondary DSC endotherms[12–14] that were shown to accompany solid-state transitions to a paraelectric phase.[13–16] Our results[9–11] showed that the nature of these transitions is primarily intramolecular: the ferroelectric state in copolymers containing at least 65 mol % VF$_2$ consists of molecules in an all-*trans* conformation such as that of β-PVF$_2$;[17] the paraelectric phase is very similar to that of atactic poly(trifluoroethylene),[18,19] with chains packed hexagonally and containing TG, T$\bar{\mathrm{G}}$, and

TT groups in a somewhat irregular arrangement, as evidenced by the presence of a broad and diffuse meridional X-ray reflection at 2.30 Å in oriented samples. This Curie transition was also found[9-11] to exhibit thermal hysteresis, i.e., to occur at higher temperatures during heating (ferroelectric → paraelectric) than during cooling (paraelectric → ferroelectric), and to extend in each case over a wide temperature range (30 °C or more). Further, by plotting the temperatures of maximal rate of transformation vs. composition and extrapolating to 100% VF_2, we suggested[11] that, if an equivalent transition temperature exists in β-PVF_2, it might be expected to occur around 205 °C, which is indeed ca. 20 °C above the melting point.

The above findings have raised interesting questions. For example, is the great similarity of the structure of the paraelectric phase to that of 100% poly(trifluoroethylene) a result of the presence of trifluoroethylene in the copolymers? If so, the basis for generalizing our results and discussing their relevance to PVF_2 homopolymer is severely compromised. Moreover, F_3E addition is subject to tacticity defects (which are absent in PVF_2) and thus introduces a new variable to these copolymers, rendering them in fact atactic; another complication stems from the head-to-head and tail-to-tail regicity defects to which F_3E is particularly susceptible[20] (~20%) and which add to the role of similar defects already present in PVF_2 (~5%).[20] A final complicating factor arises from alteration by trifluoroethylene of the chemical structure of the PVF_2 chains through introduction of a third chemical species ($-CHF-$) to the two that are already present (i.e., $-CH_2-$ and $-CF_2-$).

These problems have been circumvented in this study by examining a copolymer of vinylidene fluoride with *tetra*fluoroethylene (F_4E), seeking evidence for the presence or absence of ferroelectric transitions and, in the former case, attempting to elucidate their nature and their relevance to homopolymeric PVF_2. The advantages of using F_4E rather than F_3E are clear and impressive: Poly(tetrafluoroethylene) is subject neither to tacticity nor to regicity defects, and its conformation (variable with temperature, but always a slightly twisted helix[21,22]) is distinctly different from those of β-PVF_2 and poly(trifluoroethylene). Importantly, F_4E monomers do not inject new chemical species into the copolymer chain since the $-CF_2-$ group is already present in PVF_2; therefore, as Lando and Doll[17] pointed out, the resulting copolymer macromolecules can be viewed essentially as PVF_2 chains with an increased content of head-to-head but not tail-to-tail defects ($-CF_2-$ being viewed as the head). Such VF_2/F_4E copolymers were first examined in 1968 by Lando and Doll,[17] who showed that copolymers containing at least 7 mol % F_4E crystallize with the all-*trans* conformation of the ferroelectric β-phase of PVF_2. In the ensuing years, infrared analysis by Latour[23] showed that electrostatic poling of one such copolymer causes alignment of dipoles parallel to the electric field direction, while piezoelectric, pyroelectric, and charge-transport studies by Davis, Broadhurst, and their co-workers[24,25] revealed significant, yet highly nonuniform polarization in films of the same copolymer. Ferroelectric hysteresis loops of electric displacement vs. field—very similar to those of PVF_2—have been obtained by Hicks et al.;[26] no evidence of a ferroelectric transition was found, and it was suggested that if such a transition exists, it would lie above the melting temperature.[26]

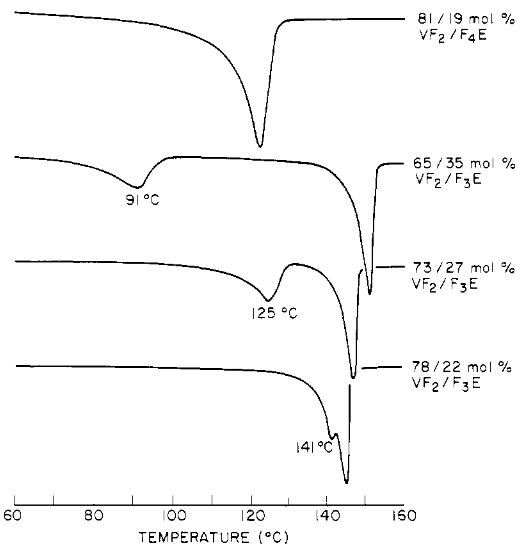

Figure 1. Differential scanning calorimetry traces of VF_2/F_4E and VF_2/F_3E copolymers originally crystallized by quenching to 0 °C and then heated to beyond their melting points at 5 °C/min.

Experimental Section

The VF_2/F_4E copolymer studied here was an experimental-grade sample of Kynar 7200 manufactured by Pennwalt Corp.; its composition is 81/19 mol% VF_2/F_4E (equivalent to 73/27 wt % VF_2/F_4E) and the comonomer sequences are random. Thin films (~25–50 μm) of this material were prepared by melt-pressing and subsequent quenching to 0 °C, a procedure yielding a crystallinity of the order of 35%.[24,25] Some of these were then poled at 500 kV/cm and 25 °C for 1 h; these conditions are well above the minimum ones required to yield saturation of the steady-state pyroelectric coefficient (200 kV for 5 min at this temperature).[25] The copolymer films were examined by differential scanning calorimetry at a heating rate of 5 °C/min or by wide-angle X-ray diffraction using Ni-filtered Cu Kα radiation; in the latter case, both diffractometric and flat-film vacuum-camera photographic techniques were employed at various temperatures. Ultrathin films (~10–20 nm) were prepared for electron microscopy by casting above the melting point from a 0.05 wt % solution in dimethylformamide; these were then recrystallized isothermally at 115 °C for 3 days, carbon-backed and shadowed in the usual manner, and examined at room temperature and 100 keV by transmission electron microscopy and electron diffraction.

Results and Discussion

The earliest indications of a ferroelectric transition in copolymers of vinylidene fluoride with *tri*fluoroethylene arose from the presence of secondary endotherms below the melting points in DSC scans of these copolymers.[12] The quenched copolymer with *tetra*fluoroethylene investigated here does not exhibit such a secondary endotherm according to the DSC heating data of Figure 1: these show only a melting peak at 123 °C, in contradistinction with the two peaks (Curie and melting transitions) seen for similarly crystallized samples of three different VF_2/F_3E copolymers. The melting point of PVF_2 is known[27] to decrease with increasing head-to-head and tail-to-tail defect content, in view of which the very low melting point of the F_4E copolymer is understandable; the higher melting points of F_3E copolymers are probably associated with the additional chemical species present ($-CHF-$), which no longer allows the macromolecules to be considered simply PVF_2 chains with increased head-to-head defect content. Based on the absence of a secondary endotherm in the F_4E copolymer, it is not surprising that, despite the behavior of its F_3E counterparts, no ferroelectric transition had been found earlier,[26] or was expected in this case. However, there is a clear trend in the F_3E copolymers toward a merging of Curie and melting transitions with increasing VF_2 content (see again Figure 1); in fact, we have previously shown[11] that melting interferes with and eventually aborts an incipient ferroelectric → paraelectric transition

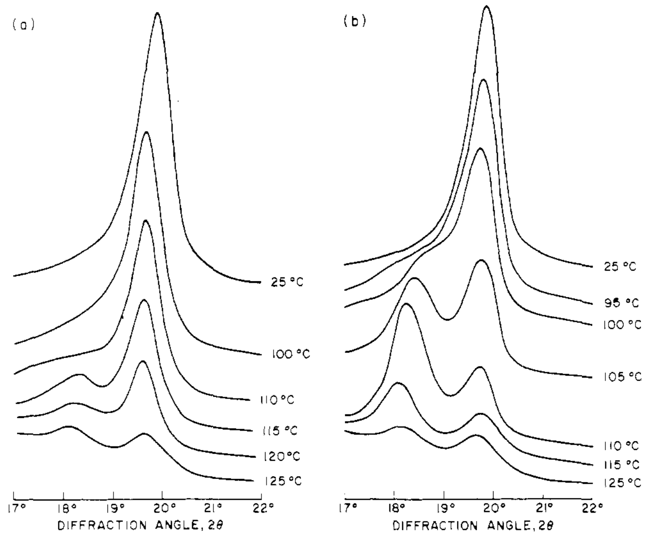

Figure 2. X-ray diffractograms of unpoled specimens of the VF_2/F_4E copolymer at different temperatures, reflecting intermolecular changes during (a) heating from 25 to 125 °C and (b) subsequent cooling from 125 to 25 °C.

in the 78/22 mol % VF_2/F_3E copolymer. Hence, absence of a secondary endotherm in the VF_2/F_4E copolymer might be due to a similar effect of melting and does not necessarily preclude existence of a Curie transition.

For this reason, changes in the X-ray diffractogram of the F_4E copolymer were investigated as functions of temperature: heating curves of unpoled specimens from room temperature to the melting region are seen in Figure 2a, and the subsequent cooling curves in Figure 2b. The angular region depicted encompasses the intermolecular-packing reflections and shows a single reflection at 19.8° (d = 4.48 Å) at room temperature, indicating that the molecules are packed in a pseudohexagonal lattice with a = 5.17 Å. This is the ferroelectric phase (analogous to the β-phase of PVF_2[17]), which is seen in Figure 2a to remain stable to ca. 110 °C with only a moderate decrease in peak intensity and with a shift of this peak to lower angles due to lattice expansion. With further heating to 115 °C, a new peak at 18.3° (d = 4.85 Å) is seen for the first time, while the ferroelectric peak is decreased in intensity; appearance of this new peak and its interplanar spacing are exactly analogous to the early stages of the ferroelectric → paraelectric transition in F_3E copolymers[11] and may be associated with a paraelectric phase in this VF_2/F_4E copolymer. However, there are two reasons for caution: (1) the new peak does not increase in intensity as its ferroelectric counterpart is decreased at higher temperatures and (2) it appears somewhat broad and amorphous-like. Both of these effects may be due to competition from melting, as was found in the 78/22 mol % VF_2/F_3E copolymer.[11]

To elucidate this uncertainty, we may study the cooling curves of Figure 2b. These show that the diffractometric changes observed in the heating part of the cycle are in fact not reversible: the new, low-angle peak is increased markedly at 115 °C, and by 110 °C it has become by far the dominant reflection in the diffractogram; its nature is undoubtedly crystalline and its d spacing is consistent with that of the paraelectric phase found in VF_2/F_3E copolymers. Further cooling shows clearly the paraelectric → ferroelectric transformation, as evidenced by the relative heights of the two peaks. This transition continues with decreasing temperature, only traces of the paraelectric phase surviving at 95 °C. The above pattern of crystallographic changes is entirely in agreement with what was observed in F_3E copolymers, not only in regard to the previously mentioned aspects but also to (1) the thermal hysteresis shown through occurrence of the ferroelectric → paraelectric transition at slightly higher temperatures than the reverse, (2) the broad temperature range of the transition, in which both phases coexist, (3) the partial thwarting of the ferroelectric → paraelectric transition by incipient melting, and (4) the subsequent direct crystallization of the paraelectric phase from the melt during cooling.

The relationship of these *inter*molecular changes to corresponding *intra*molecular processes accompanying the transition is seen with the aid of flat-plate diffraction patterns in Figure 3. The all-*trans* conformation of the ferroelectric phase of this F_4E copolymer is evidenced by the 001 and (201, 111) reflections at 2.56 and 2.21 Å, respectively, in Figure 3a. The drastic diminution of the intensities of these two reflections (as well as of the intermolecular-packing reflection at 4.48 Å) upon heating to 125 °C is seen in patterns b and c of Figure 3. A strong but diffuse reflection appearing just inside the 4.48-Å ring in these figures arises from contributions of the emerging paraelectric phase and the amorphous melt. Cooling to 110 °C (Figure 3d) shows clearly the paraelectric phase, making its crystalline nature evident through the sharp ring at 4.88 Å. The accompanying paraelectric → ferroelectric transition, already under way at 110 °C, is seen to be almost complete by 100 °C (Figure 3e).

The paraelectric phase of Figure 3c,d is characterized not only by the 4.88-Å reflection but also by a very broad and diffuse reflection centered at 2.31 Å. This latter reflection becomes meridional in oriented specimens and is therefore associated with the molecular conformation; its spacing, breadth, and diffuseness appear identical with the corresponding attributes of the meridional reflection in VF_2/F_3E copolymers.[9-11] The 2.31-Å spacing is indicative of the repeat of TG, T$\bar{G}$, or TT groups having their G, $\bar{G}$, or one of the T bonds, respectively, parallel to the molecular axis (or close thereto); this may occur in such arrangements as (TG)(T$\bar{G}$), $(TG)_3$, $(T\bar{G})_3$, (TT)(TG)(TT)(T$\bar{G}$), $(TG)_2$ $(T\bar{G})_2$, $(TT)_2$(TG)(T$\bar{G}$), etc. Exact conformational assignment requires examination of additional reflections; however, it is clear from Figure 3 that their number, intensity, and definition are totally insufficient for this task. Nevertheless, it is also apparent from the breadth and diffuseness of the 2.31-Å reflection that the conformation cannot be highly regular but is probably some partly disordered arrangement of TG, T$\bar{G}$, and TT sequences. The important conclusion from the above is that the structure of the paraelectric phase in this VF_2/F_4E copolymer appears to be analogous to that of the previously investigated VF_2/F_3E copolymers: consequently, despite its great similarity to the structure of poly(trifluoroethylene), the structure of the paraelectric phase is not attributable to comonomer influences but should be an inherent characteristic of PVF_2.

The effect of poling on the ferroelectric transition may be seen in Figure 4. Comparison of the 115 and 125 °C curves with the corresponding curves from unpoled specimens (Figure 2a) shows that the ferroelectric phase in macroscopically polarized films survives to slightly higher temperatures. This is again analogous to the behavior of VF_2/F_3E copolymers. As was shown earlier,[10,11,28] the transition temperature is raised upon poling (e.g., from ~68 to ~80 °C for 52/48 mol % VF_2/F_3E specimens), presumably as a result of macroscopic stabilization of the polar lattice. For higher VF_2 contents (e.g., 78 mol %), for which the Curie temperature of unpoled samples is very

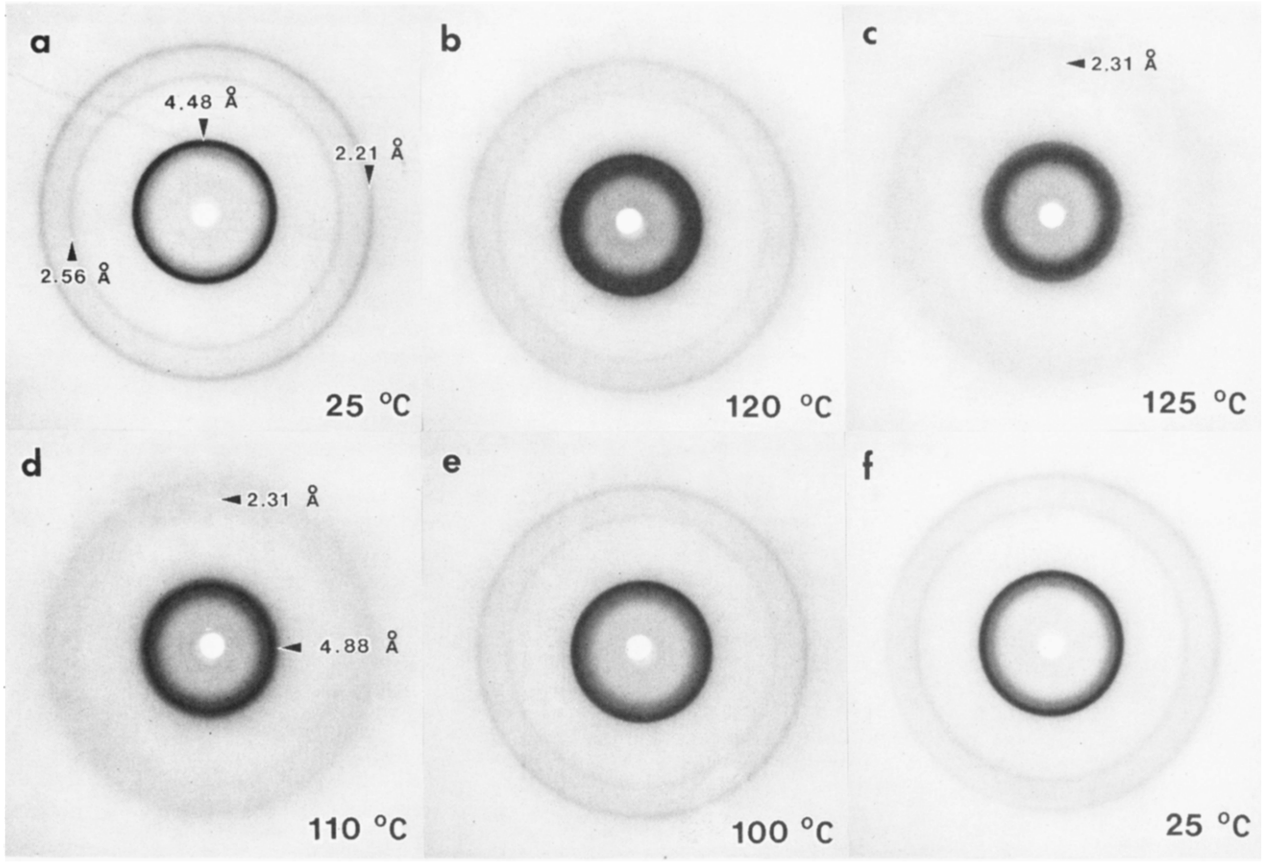

Figure 3. Flat-film X-ray diffraction patterns during a heating-and-cooling cycle for an unpoled VF_2/F_4E sample, reflecting inter- and intramolecular changes associated with the Curie transition.

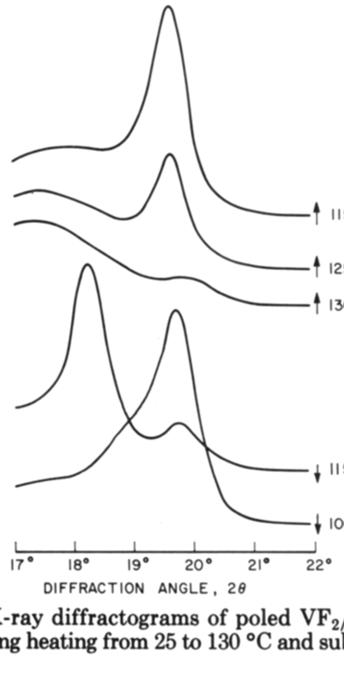

Figure 4. X-ray diffractograms of poled VF_2/F_4E specimens obtained during heating from 25 to 130 °C and subsequent cooling to 100 °C.

close to their melting points, poling thus eliminates almost totally any crystallographic evidence of a ferroelectric → paraelectric transition, essentially raising it to or above the melting point. This appears to be the case also for this VF_2/F_4E copolymer, since Figure 4 exhibits no discernible paraelectric peak when the temperature is raised to 130 °C. As before, cooling from the melt causes crystallization predominantly of the paraelectric phase (115 °C curve), followed immediately by solid-state transformation to its ferroelectric counterpart. The paraelectric peak at 115 °C in Figure 4 is higher than in Figure 2b, probably because of the more complete melting achieved by heating the specimen to 130 °C. It should be noted that this effect of poling in raising the Curie transition of the VF_2/F_4E copolymer is somewhat surprising in view of the findings by Broadhurst et al.[25] that, in films of this copolymer poled at room temperature, polarization is concentrated in a thin layer adjacent to the positive electrode.

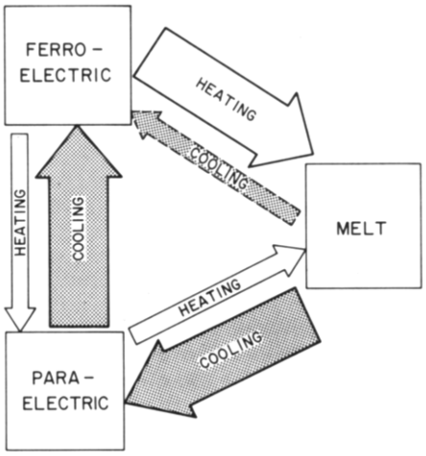

Figure 5. Schematic representation of the interrelationships among ferroelectric, paraelectric, and molten phases of the VF_2/F_4E copolymer observed during heating and cooling treatments.

The overall phase-transition properties of this VF_2/F_4E copolymer can now be summarized with the aid of Figure 5. Heating of the ferroelectric phase of unpoled specimens shows only a limited transformation to the paraelectric state, with the bulk of the sample melting instead. Poling of samples stabilizes their ferroelectric phase to higher

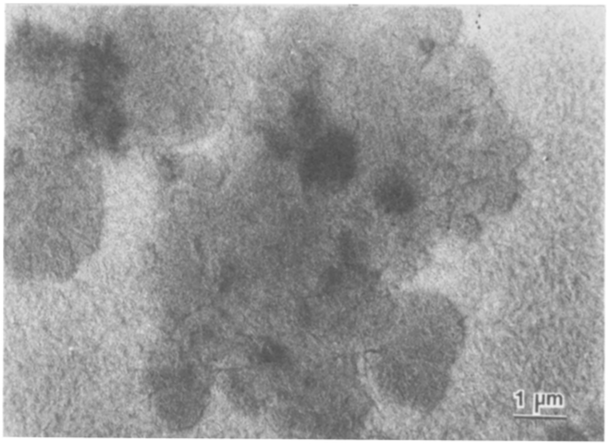

Figure 6. Transmission electron micrograph of a single crystal of VF_2/F_4E copolymer grown from the melt at 118 °C for 4 days followed by quenching to 25 °C.

temperatures, resulting eventually in melting with no crystallographic evidence for a viable intermediate paraelectric phase. Cooling of both poled and unpoled samples from the melt causes crystallization to occur almost totally in the paraelectric phase, although there is some evidence from Figures 2b and 4 that a small amount of its ferroelectric counterpart is formed as well. Further cooling provides clear evidence of a solid-state paraelectric → ferroelectric transformation in this VF_2/F_4E copolymer.

Although thermal treatment renders the ferroelectric → paraelectric transition virtually inaccessible (due to incipient melting), it has been found here—in the course of a morphological investigation using electron microscopy—that such a crystalline transformation can be made to occur irreversibly by electron irradiation. A detailed study of such electron-beam-induced transformations in this and other copolymers of PVF_2 is in progress. However, the basic phenomenon will be briefly described below as it relates to the morphology of this VF_2/F_4E copolymer.

Electron-microscopic appearance of a thin film crystallized at 118 °C for 4 days and then quenched to room temperature is seen in Figure 6. The irregularly shaped entity in the center of this figure is a single crystal with the molecules packed hexagonally normal to its base plane, as evidenced by its diffraction patern in Figure 7a; the speckled appearance of this VF_2/F_4E crystal and of the backgorund is due to small lamellae grown during quenching to room temperature, whose presence is also manifested by the ring superimposed on the single-crystal reflections in Figure 7a. At its crystallization temperature the crystal was grown with the paraelectric structure, which was subsequently transformed to the ferroelectric during cooling; indeed, the diffraction pattern of Figure 7a is consistent with the ferroelectric unit cell (albeit slightly larger than was found by X-ray diffraction, such expansion being a common effect of the early stages of electron-beam damage in polymers). While the crystal of Figure 6 is undoubtedly somewhat distorted by the unit-cell shrinkage that accompanies the paraelectric → ferroelectric transition, its irregular boundaries make it clear that it never possessed the long-range crystallographic faceting common in polymeric single crystals.[29] This irregular morphology is strikingly reminiscent of the appearance of other structurally disordered polymeric single crystals such as those of poly(trifluoroethylene)[19] or poly(chlorotrifluoroethylene)[30] and thus offers further support in favor of a similarly disordered paraelectric structure for this copolymer. In contrast, regular conformations such as the (TG)(T$\bar{G}$) or (TT)(TG)(TT)(T$\bar{G}$) of 100% PVF_2 (α- and γ-phases, respectively) allow growth of single crystals characterized by sharp crystallographic faceting.[31,32]

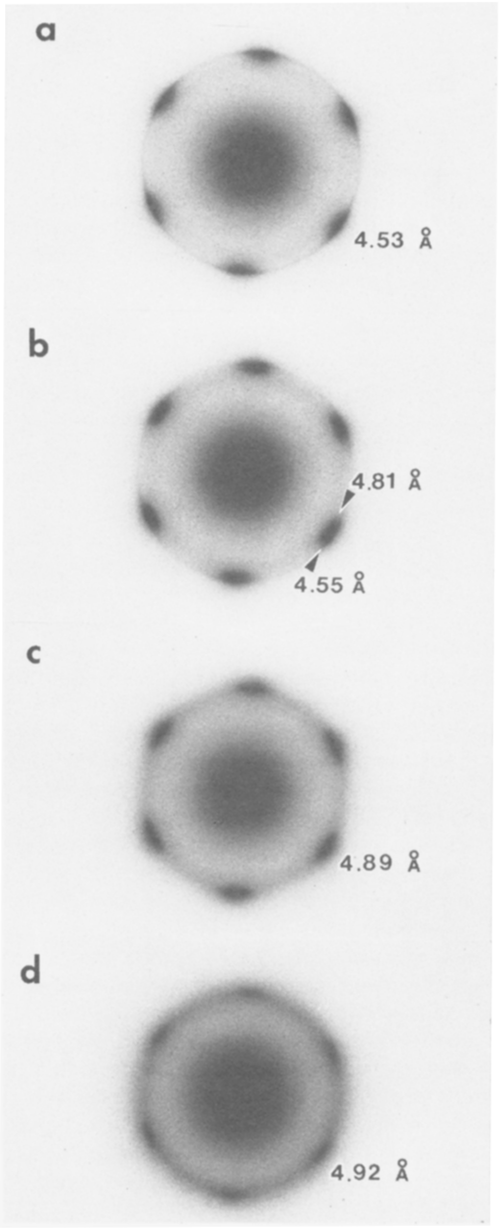

Figure 7. Consecutive changes in the electron-diffraction pattern of the crystal of Figure 6 with increasing radiation dose during observation in the electron microscope at room temperature.

During observation, the electron-diffraction pattern of VF_2/F_4E single crystals was found to change in the manner seen in Figure 7 a–d. The reflections of the ferroelectric structure (Figure 7a) diminish in intensity and eventually disappear. At the same time new reflections appear at a higher spacing (similar to that of the paraelectric phase) but at the same geometrical disposition (Figure 7b); since the two sets of reflections are spaced very closely to each other, they may not be clearly discernible in the photograph of Figure 7b, which was chosen to show them at approximately equal intensities. Upon further irradiation, the inner reflections first increase in brightness until they attain the appearance of Figure 7c and then become progressively weaker (Figure 7d) and degrade to an amorphous ring. The latter sequence (Figure 7c → 7d) is most common in polymers and is associated with the formation of free radicals and subsequent cross-linking resulting from the high electron doses received;[33] the former (Figure 7a

→ 7c) reveals a beam-induced solid-state transformation to a lattice characteristic of the paraelectric phase and is an unusual phenomenon. This should not be confused with such cases as the electron-induced orthorhombic → hexagonal transformation in polyethylene,[34,35] where beam damage causes the orthorhombic reflections to move *continuously* toward higher spacings while being broadened and thus leads to a damaged hexagonal phase en route to amorphicity. In the case of the VF_2/F_4E copolymer, the ferroelectric-phase reflections disappear in favor of discrete new reflections that are as sharp as (or even sharper than) their predecessors; at intermediate radiation doses, *both* sets of diffraction spots coexist (Figure 7b). Details and possible origins of this phenomenon, as well as its exact dependence on radiation dose, will be described in a separate publication.

Conclusions

Detection of Curie transitions in this VF_2/F_4E copolymer allows generalization of earlier results from VF_2/F_3E copolymers. It confirms that such transitions were not exclusive to that comonomer, despite the similarity of the structure of the paraelectric phase to that of poly(trifluoroethylene); it also removes the complications arising from the presence of –CHF– groups in VF_2/F_3E copolymers, as well as from tacticity and regicity defects associated with addition of trifluoroethylene. In both F_3E and F_4E copolymers, the transition involves intramolecular changes and leads to a partly disordered conformation containing TG, T$\bar{G}$, and TT sequences. This disordered structure is consistent with the lack of crystallographic faceting found in single crystals of the F_4E copolymer.

Because the molecular structure of this VF_2/F_4E copolymer is equivalent to that of PVF_2 having a somewhat higher concentration of head-to-head (but not tail-to-tail) sequences, the observation of Curie transitions in this copolymer allows us to anticipate with confidence that such transitions should be possible in PVF_2 homopolymer as well. Moreover, the demonstration that melting thwarts the ferroelectric → paraelectric transformation in this VF_2/F_4E copolymer (partly so for its unpoled specimens and almost completely for the poled) reinforces our earlier suggestion[11] that this transition might lie above the melting point for β-PVF_2 (such an assumed transition might then be centered around 205 °C,[11] as described in the Introduction). At the same time, our results for F_3E and F_4E copolymers show that the crystallographic changes involved in the ferroelectric → paraelectric transformation encompass a broad temperature range (typically ca. 30 °C), so that the earliest manifestations of such a transition in β-PVF_2 may actually become perceptible before complete melting. This conclusion is in agreement with the results of a recent preprint of Tashiro et al.,[8] who report a brief appearance of a new X-ray reflection in the latter stages of melting of β-PVF_2; this is a very weak reflection that appears only after ~90% of the intensity of the ferroelectric peak is lost, but its presence is consistent with our findings in F_3E and F_4E copolymers of limited appearance of a paraelectric phase that is in the process of being aborted by melting.

In addition to X-ray diffraction, dielectric, dynamic mechanical, and DSC techniques are now being applied to the investigation of isothermally crystallized specimens of the VF_2/F_4E copolymer studied here. Crystallization at 120 °C shifts the melting point to ~134 °C, thus rendering the Curie region less susceptible to competition from melting.

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