

polymer papers

Crystallographic changes characterizing the Curie transition in three ferroelectric copolymers of vinylidene fluoride and trifluoroethylene: 1. As-crystallized samples

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Copolymers of vinylidene fluoride/trifluoroethylene of molar composition 65/35, 73/27 and 78/22% respectively, are ferroelectric and undergo a Curie transition to the paraelectric state at high temperatures. In contrast to the irregular structure found earlier for the 52/48 mol% copolymer, the structures of these three compositions in the low-temperature state are all well ordered and analogous to that of β -poly(vinylidene fluoride): they consist of molecular chains in a polar *trans* conformation whose order is improved with increasing vinylidene fluoride content, packed pseudo-hexagonally in unit cells whose dimensions decrease with increasing vinylidene fluoride content. In their paraelectric phase, the chains assume a partly disordered conformation consisting of irregular *TG*, $\overline{T\overline{G}}$ and *TT* sequences and are packed on an expanded pseudo-hexagonal lattice. The Curie transitions were found to occur over a broad temperature range, encompassing $\sim 30^\circ\text{C}$, and in the case of the 78/22 mol% copolymer to extend into the melting region; they were also found to exhibit hysteresis by occurring at much lower temperatures upon cooling than upon heating.

Keywords Poly(vinylidene fluoride); ferroelectricity; piezoelectric polymers; pyroelectric polymers; crystal structure; X-ray diffraction

INTRODUCTION

It is by now well accepted that poly(vinylidene fluoride) (PVF₂) is the first clearly demonstrated example of a ferroelectric polymer; the underlying evidence from hysteresis loops, X-ray, i.r. and other techniques has been summarized in recent extensive reviews¹⁻³. A major characteristic of most ferroelectric crystals is the Curie temperature, at which polarization is lost through an order-disorder or a displacive-type transition, so that the material becomes paraelectric. In PVF₂, the existence of such a ferroelectric-to-paraelectric transition is still uncertain, and, in fact, it is generally believed that melting may intervene before the onset of such a transition^{4,5}. To circumvent this problem, a number of investigators⁶⁻¹⁰ have examined various copolymers of vinylidene fluoride with trifluoroethylene; these have a structure similar to that of the piezoelectric β -phase of PVF₂^{11,12}, and have, indeed, yielded Curie temperatures that vary with composition⁶⁻¹⁰. In an effort to analyse the precise nature of this ferroelectric transition, we have examined the crystalline structure of one such copolymer¹³ (containing 52 mol% vinylidene fluoride and 48 mol% trifluoro-

ethylene), as well as the structural and dielectric changes it undergoes in the vicinity of the transition¹⁴. We found that, when crystallized from the melt, molecules of this particular copolymer do not adopt the all-*trans* conformation typical of β -PVF₂, but assume a disordered, essentially two-phase structure: this consists of discrete sequences of *trans* bonds, interspersed by random lengths and combinations of *TG* and $\overline{T\overline{G}}$ groups; these irregular *TG* and $\overline{T\overline{G}}$ sequences yield a broad meridional reflection at 2.30 Å and were described as a disordered 3/1 helix, a conformation that had in fact been used earlier to refer to the molecular structure of trifluoroethylene homopolymer¹⁵. Nevertheless, this disordered and irregular conformation could be transformed to a regular *trans* conformation (analogous to that of β -PVF₂) by uniaxial drawing or electrical poling¹³. At the region of the ferroelectric transition (around 70°C), all samples were found¹⁴ to undergo drastic *intramolecular* changes through introduction of *G* and \overline{G} bonds, leading to an irregular succession of *TG* and $\overline{T\overline{G}}$ groups similar to the disordered 3/1 helical conformation of polytrifluoroethylene¹⁵; no X-ray reflections characteristic of the *trans*-planar repeat were observed, indicating that if any

trans sequences survive above the Curie temperature, they must be very short (e.g. T_3G , $T_3\bar{G}$, T_5G , $T_5\bar{G}$). At the same time, the *intermolecular* packing was also found to change to a slightly larger lattice, the increase occurring gradually in the as-crystallized samples and discretely in the drawn or poled films¹⁴. From the above, we concluded that while this 52/48 mol% copolymer does indeed undergo a ferroelectric-to-paraelectric transition, this deviates from the usual Curie-point phenomenon by involving major *intramolecular* changes in addition to the *intermolecular* ones.

These results have now led us to an examination of other copolymer compositions containing larger fractions of vinylidene fluoride. We have endeavoured to find how general (or unique) the behaviour of the 52/48 mol% copolymer is, and how the structure and the ferroelectric transitions of as-crystallized, drawn, or poled specimens of different compositions vary with temperature. More importantly, by concentrating on compositions of high VF_2 content, we may be able to speculate on an informed basis about expectations of a Curie transition in homopolymeric PVF_2 . Our results are presented in two companion papers for three compositions of vinylidene fluoride/trifluoroethylene copolymers, i.e. 65/35, 73/27 and 78/22 mol%. This first article deals with the structure (and its variation with temperature) of as-crystallized samples, i.e. those not subjected to any subsequent mechanical or electrical treatment. The second article¹⁶ examines the same questions for samples that had been uniaxially oriented or macroscopically polarized in a high electric field, and draws general conclusions from both investigations.

EXPERIMENTAL

The copolymers used in this study were experimental samples, kindly donated by Daikin Kogyo Co., Ltd, Japan, and having nominal compositions 65/35, 73/27 and 78/22 mol% vinylidene fluoride/trifluoroethylene. These copolymers had been synthesized by polymerization at 22°C using a peroxide initiator and had a random configuration¹⁷⁻¹⁹. The extent of reversed monomeric units ('head-to-head, tail-to-tail') in these copolymers is not known exactly, but is probably significant, being ~5% in PVF_2 ³ and ~20% in polytrifluoroethylene²⁰. Melting points for quenched specimens of these copolymers, determined by disappearance of birefringence at a heating rate of 2°C min⁻¹, were: 153.2°C for 65/35, 149.8°C for 73/27, and 148.9°C for 78/22 (these values are in close agreement with the d.s.c. results of Yagi *et al.*¹⁹). These copolymers were moulded into thin films (~0.1 mm) in a hot press, cooled rapidly to room temperature, and then examined by X-ray diffraction as a function of temperature using Ni-filtered $\text{Cu K}\alpha$ radiation that was detected either by a diffractometer (reflection geometry) or by a flat-plate camera. In the first case, films on the diffractometer stage were electrically heated from the bottom, the temperature being measured by a thermocouple embedded near the sample and calibrated by melting-point standards used in the same configuration. For photographic X-ray recording, an evacuated camera was used to minimize air scattering; the films were placed into a heating holder equipped with a thermocouple and attached to a controller, with the temperature at the irradiated region of the sample having been calibrated by use of melting-point standards.

RESULTS AND DISCUSSION

Our results are presented separately for the three copolymers and compared to each other and to the 52/48 mol% composition studied earlier^{13,14}.

65/35 mol% copolymer

Diffractograms of the as-crystallized 65/35 mol% samples are seen in *Figure 1* as functions of temperature: the initial heating and cooling cycles are displayed in *Figures 1a* and *b*, respectively, while the second heating programme is depicted in *Figure 1c*. The angular range covered in these figures (and in all others except *Figure 2*) corresponds to the region of the strongest reflections; these are equatorial in oriented specimens (see following paper¹⁶) and therefore reveal the *intermolecular* packing of copolymer chains. The single peak at 19.52° 2 θ at room temperature (*Figure 1a*) corresponds to an interplanar spacing of 4.54 Å and shows that the chains are packed on a hexagonal (or pseudo-hexagonal) lattice of axial length 5.24 Å. This packing scheme is very similar to that exhibited by the common piezoelectric β -phase of PVF_2 , in which molecules of an all-*trans* conformation are arranged in a polar orthorhombic unit cell whose dimensions render it only 1% different from an equivalent hexagonal one²¹. To determine whether copolymer chains adopt conformations similar to the all-*trans* of β - PVF_2 , we have scanned the angular regions of the meridional reflections, around 30–45° 2 θ (see *Figure 2*). The 001 reflection in β - PVF_2 has a *d*-spacing of 2.56 Å and is accompanied by a strong, composite (201, 111) reflection at 2.20 Å²¹. Similar peaks are also observed in *Figure 2* not only for the 65/35 copolymer but also for the 73/27 and 78/22; as seen in this figure, these peaks increase in strength and resolution with VF_2 content, indicating progressive improvement of the all-*trans* order.

This conclusion immediately presents the first difference in behaviour between these three copolymers and the 52/48 mol% studied earlier^{13,14}. In the latter, the *trans* segments exhibited disorder through X-ray line broadening, and were accompanied by substantially irregular *TG* and $T\bar{G}$ sequences whose presence was manifested in the form of a very broad second meridional reflection centred at 2.30 Å¹³. This is also observed in *Figure 2*, where we have included the trace from the 52/48 sample: the very broad reflection at ~2.30 Å is actually the strongest, while those associated with the *trans* segments are weak and broad. It is interesting to notice the broad shoulder around 2.30–2.35 Å in the 65/35 copolymer, indicating that despite the regularity of its extensive *trans* segments, a small percentage of *TG* and $T\bar{G}$ groups must also be present (such appear to be increasingly absent at the higher VF_2 compositions).

The above differences between 65/35 and 52/48 copolymers are also exhibited in their *intermolecular* packing. It will be recalled that the equatorial diffractogram of the 52/48 samples exhibited two closely spaced peaks (4.59 and 4.69 Å) at room temperature, contrary to the situation in *Figure 1a*; these were correlated with the packing of *trans* and disordered *TG* and $T\bar{G}$ segments, respectively, so that the appearance of the single peak for the 65/35 sample at 25°C points to its fairly regular, single-phase, hexagonal (or pseudo-hexagonal) molecular lattice.

When such copolymers are first heated, the all-*trans* structure persists through 70°C (see, again, *Figure 1a*); the

earliest indications of a transformation are seen in the 80°C curve, which is where the ferroelectric-to-paraelectric transition is expected on the basis of d.s.c. and piezoelectric data^{8,19} (other authors¹⁰ report slightly higher values). At this temperature, a new peak is seen in the vicinity of 18.2° 2θ that appears at the expense of the all-*trans* peak around 19.5°. By associating this new peak with a concurrently observed broad and diffuse meridional reflection at ~2.3 Å (see also X-ray fibre patterns in the following paper¹⁶), we attribute it to the previously described paraelectric phase resulting from introduction of conformational changes from *T* to *G* and \bar{G} . As the

temperature of the samples is increased, we see a continued decrease in the intensity of the ferroelectric peak in favour of its paraelectric counterpart (Figure 1a). By 100°C—the Curie temperature based on dielectric^{8,10} and some¹⁰ d.s.c. data—practically all of the regular *trans* peak has disappeared. We thus see immediately that the underlying structural changes causing the ferroelectric-to-paraelectric phase transition do not occur at a sharp temperature, but rather over a *broad* range extending from below 80°C to above 100°C. This may explain the aforementioned differences in reported transition temperatures, since particular techniques may be sensitive to different stages of the transformational range. We should also notice that the two peaks in Figure 1a remain separate and do not merge into each other at intermediate values of 2θ. This is contrary to the behaviour found in as-crystallized specimens of the 52/48 copolymer (where the changes in 2θ were continuous), but analogous to that of drawn or poled films of this 52/48 composition (where the changes were discrete). This was interpreted¹⁴ as being due to the disordered nature of the as-crystallized 52/48 copolymer which allowed intermediate packings, whereas its drawn or poled specimens were in an ordered all-*trans* phase that consequently underwent the discrete changes found here for *unpoled* and *undrawn* films of the 65/35 composition. We should also notice that in this figure (and, in fact, in all similar ones for any of the compositions studied) the all-*trans* peak is always significantly broader than its paraelectric counterpart. This is probably due to the bulky trifluoroethylene units which at low temperatures must be accommodated into the smaller all-*trans* lattice, and therefore cause more disorder and possibly also smaller crystallite sizes than in the less compact high-temperature phase.

If we now examine the cooling curves of Figure 1b, we

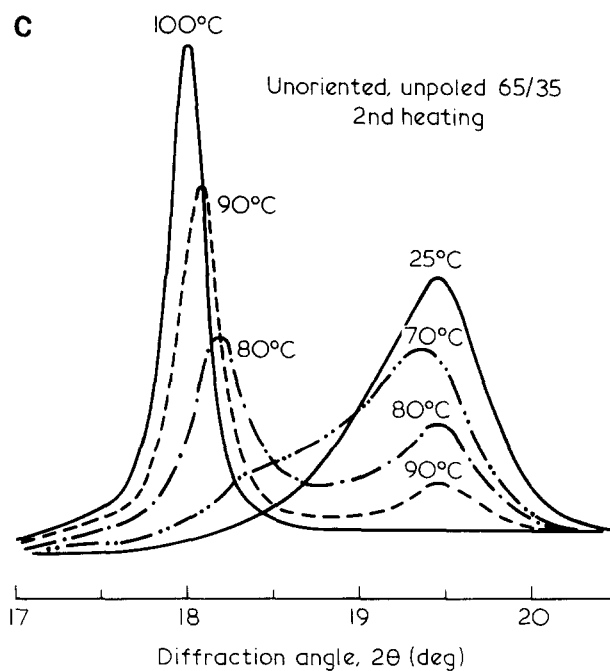
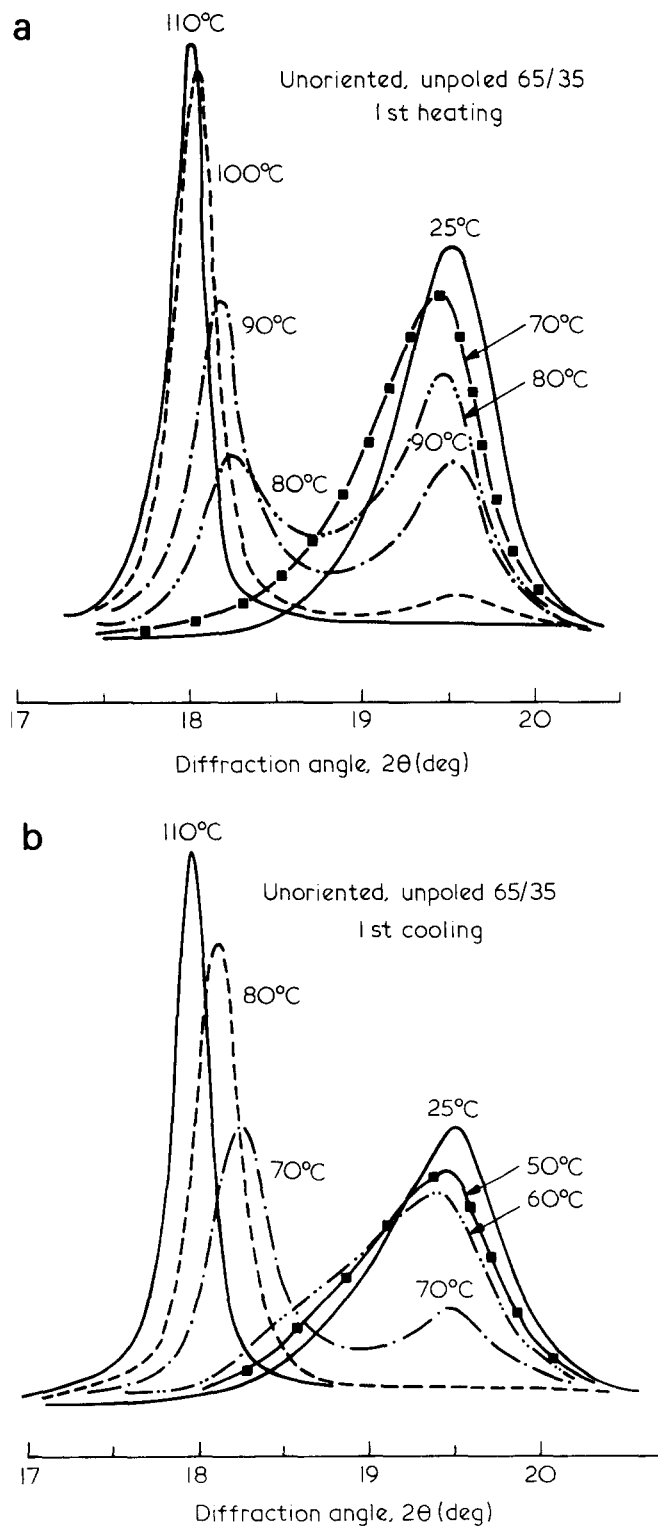


Figure 1 X-ray diffractograms of 65/35 mol% copolymer as functions of temperature, reflecting changes in intermolecular packing associated with the ferroelectric-to-paraelectric transition: (a) first heating, (b) first cooling, and (c) second heating cycles

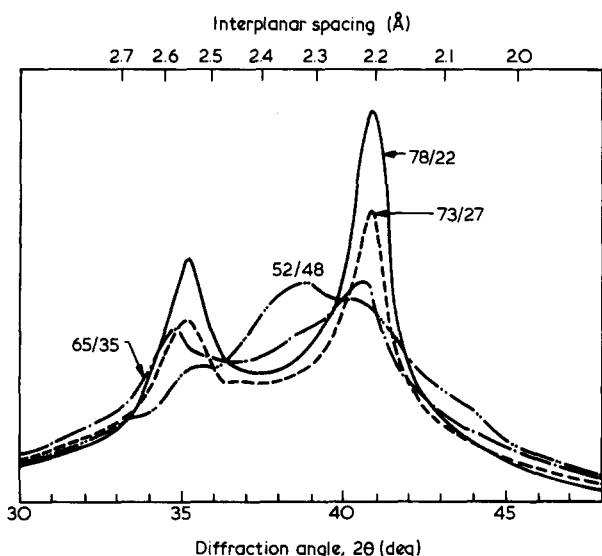


Figure 2 X-ray diffractograms of various copolymers, reflecting the variation of molecular conformation with composition

observe that the paraelectric phase persists to lower temperatures than found during heating; specifically, no trace of the disordered phase was seen at 70°C in the heating portion of the cycle, yet, at the same temperature upon cooling most of the sample is in that phase. The ferroelectric-to-paraelectric transition is therefore seen to exhibit *hysteresis-like behaviour*. In the case of the 65/35 copolymer, Figure 1b shows that the films must be cooled to 60°C to return to the regular all-*trans* structure. Moreover, this structure is now somewhat more imperfect than the starting one, as evidenced by the lower and broader peaks at 19.5° (compared to those of Figure 1a). This is possibly due to some residual disorder from the paraelectric phase.

This more poorly ordered *trans* structure enables the ferroelectric-to-paraelectric transition to occur at lower temperatures in subsequent heating cycles. If we compare the second heating cycle (Figure 1c) to the first (Figure 1a), we see that now the early signs of transformation are already evident at 70°C. Further, at each successively higher temperature more of the sample has transformed than during the initial heating, and the phase change is in fact complete at 100°C (instead of the original 110°C). Subsequent thermal cycles are then stable from this stage on, i.e. cooling behaviour is as that of the first cooling cycle and heating behaviour as that of the second heating cycle.

73/27 mol% copolymer

There is confusion in the literature about the location of the Curie transition in this copolymer. Endothermic d.s.c. peaks by Yagi and coworkers¹⁹ suggest values around 92°C, those of Higashihata *et al.*⁸ around 103°C, while those of Yamada and Kitayama¹⁰ about 115°C. Dielectric results based on the peak of the relative dielectric constant ϵ/ϵ_0 yield a transition temperature in the vicinity of 130°C⁸, while those based on its maximum slope¹⁰ are around 115°C. Maximal values of piezoelectric constants for this copolymer have been reported around 100°C¹⁰ or 80–90°C⁸, with piezoelectricity falling off rapidly in the region of 110°C^{8,10}. We shall reconcile these widely divergent data on the basis of structural changes observed by X-ray diffraction.

X-ray diffractograms of the equatorial region (17–20° 2 θ), obtained during initial heating of as-crystallized copolymer from 25° to 140°C, are seen in Figure 3a. Again, a single peak is obtained at room temperature, which, together with the meridional results of Figure 2, shows that the 73/27 copolymer also crystallized directly into a phase analogous to β -PVF₂, with a hexagonal or pseudo-hexagonal lattice of unit length $a = 5.16$ Å. Diffractograms taken up to 90°C (not shown in Figure 3a for the sake of clarity) indicate no sign of transformation. The first such sign is seen in Figure 3a at 100°C with the appearance of a new, small peak around 18° 2 θ . It is interesting to observe that, up to 120°C, this new peak does not arise at the expense of the ferroelectric peak around 19.7° 2 θ , which—if anything—increases slightly. This implies that there is also a very slight improvement in the molecular packing of the sample up to ~120°C, possibly associated with expansion of the lattice. These phenomena are analogous to annealing with the added feature that at these temperatures there now coexist (in competition) two crystalline phases. It is only above ~120°C that the intensity of the all-*trans* peak falls off, and particularly beyond 130°C it does so cataclysmically, leaving no trace of this peak by 140°C. As before, examination of the meridional region (not shown here for the sake of brevity) reveals the new, high-temperature phase to have the same disordered conformation found for the paraelectric phase of 52/48 and 65/35 copolymers.

When this specimen is cooled back to room temperature (see Figure 3b), it undergoes a similar hysteresis-like behaviour as that exhibited by the 65/35 composition. The paraelectric peak remains equally strong and sharp between 140° and 90°C, its only change being a shift to higher angles concomitant with the contraction of the lattice upon cooling. Between 90° and 80°C there is a dramatic decrease in the intensity of this peak, most of the specimen now being back in the ferroelectric *trans* phase; this trend continues at a reduced rate down to room temperature. Finally, if the specimen is reheated (Figure 3c), it now adopts the paraelectric structure somewhat earlier and at a much more rapid rate: this is particularly clear at 130°C, where almost all of the sample has now transformed, contrary to its behaviour during the initial heating cycle (Figure 3a).

From all of the above, we conclude that the major phase changes associated with the ferroelectric transition in the 73/27 copolymer are initiated slightly below 100°C and are not completed before 140°C, thus showing that the previously reported dielectric, thermal and piezoelectric data^{8,10} are sensitive only to isolated (and, apparently, different) stages within this very broad transformational range. The d.s.c. technique and the loss in polarization appear to be sensitive to earlier manifestations of the transition than are dielectric measurements (piezoelectric data will be discussed in relation to our poled samples in the following paper¹⁶). Our results do not substantiate thermal manifestation of transformation at temperatures as low as 92°C¹⁹, unless the earlier data had been taken from reheated specimens, or there is a prodromal stage of the transition that preserves the all-*trans* conformation and lattice (e.g. a rotator phase); this possibility is currently under investigation, particularly since our earlier dielectric results on the 52/48 copolymer¹⁴ indicate coexistence of dipolar rotational motions with the overall conformational changes.

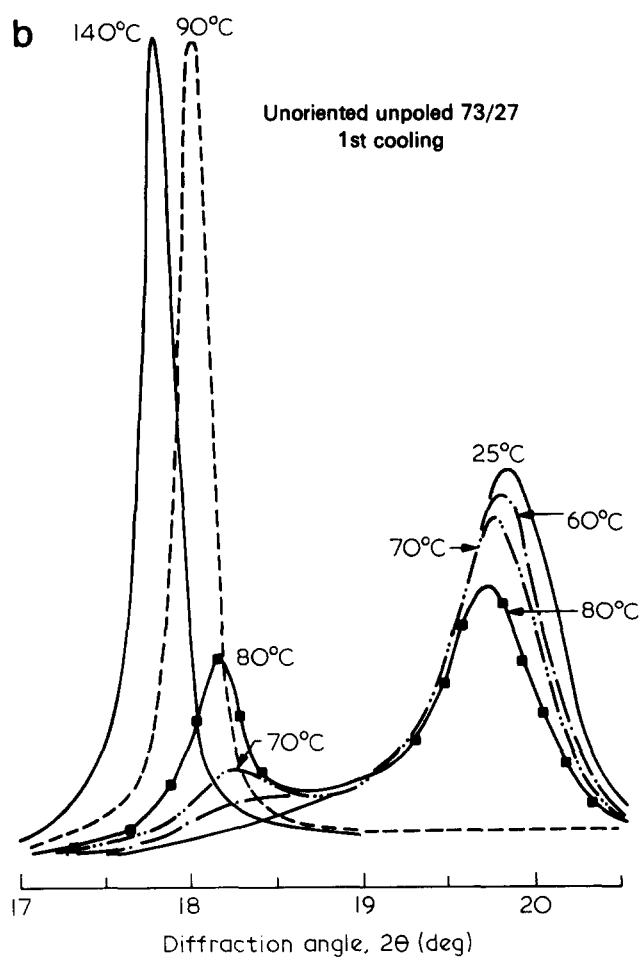
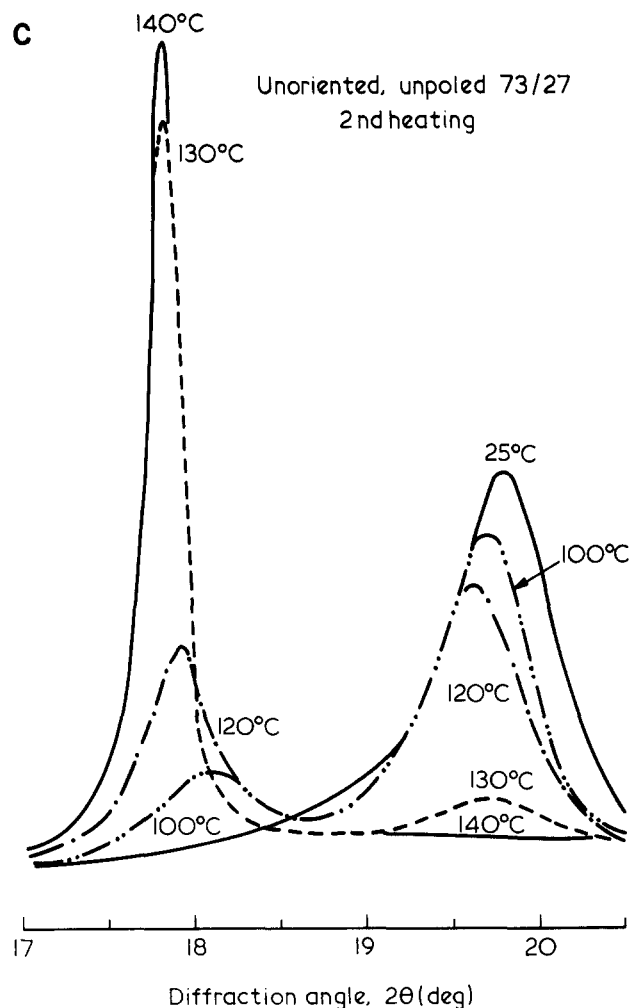
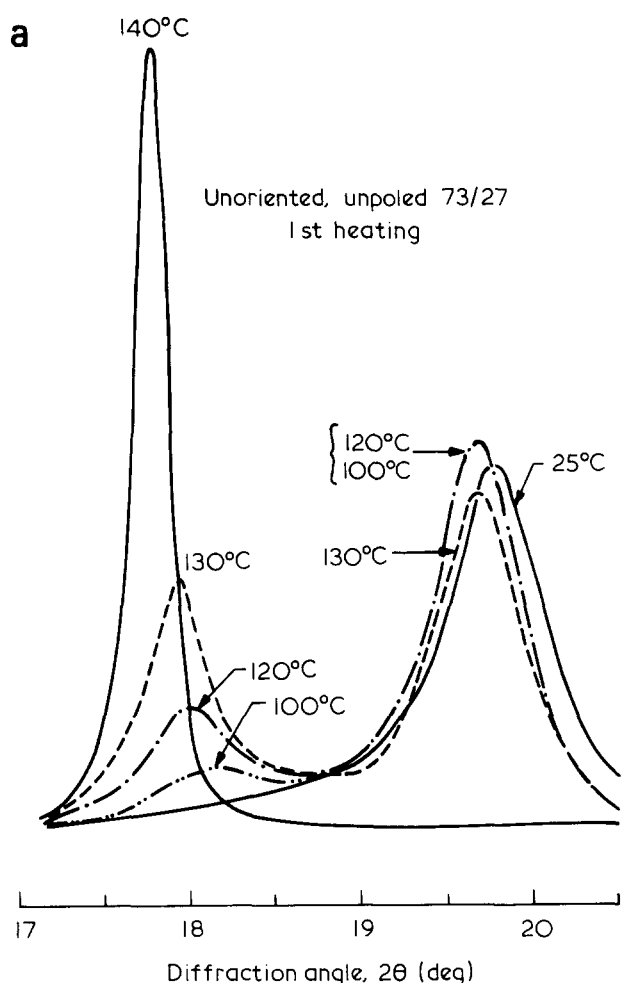


Figure 3 X-ray diffractograms of 73/27 mol% copolymer as functions of temperature, reflecting changes in intermolecular packing associated with the ferroelectric-to-paraelectric transition: (a) first heating, (b) first cooling, and (c) second heating cycles

78/22 mol% copolymer

This is the most interesting composition studied so far, for three reasons: (1) it is very close to being the composition of highest VF₂ content that crystallizes directly into a phase analogous to that of β-PVF₂ (the highest such composition is 80/20 mol%¹⁰, higher ones crystallizing with an α-like unit cell); (2) it is practically the lowest melting of all copolymers of vinylidene fluoride and trifluoroethylene, the region of minimal melting points extending between 77% and 82% VF₂^{8,10,19}, and (3) it is the composition for which Curie temperatures estimated thermally and dielectrically are closest to the melting point^{8,10,19}. For these reasons, the 78/22 mol% copolymer provides the best basis from which we may attempt to discuss meaningfully the existence of a Curie transition in β-PVF₂.

Once again, there is no agreement in the literature as to the temperature of the transition: the dielectric and d.s.c. results of Yamada and Kitayama¹⁰ indicate ~120°C, the early thermal data of Yagi and coworkers¹⁹ yield ~100°C while their later results⁸ do not extend to such a high VF₂ content, although extrapolation of data from lower contents would bring the transition to the vicinity of

150°C, i.e. essentially to the melting point of this copolymer.

As before, we present the initial heating and cooling X-ray data, as well as the second heating curves of the as-crystallized copolymer (see Figure 4). During the first heating cycle (Figure 4a), no indication of transformation is seen below 130°C, and an increase in temperature to 140°C brings only modest diminution of the all-*trans* peak around 20° 2 θ (corresponding again to a hexagonal or pseudo-hexagonal packing with $a = 5.12$ Å at room temperature). It is noteworthy that the bulk of the transformation takes place in the 5°C interval above 140°C, the ferroelectric phase having entirely disappeared by 145°C. Because the peak of the paraelectric phase at 145°C is significantly smaller than the all-*trans* peak at 25°C, we surmise that the Curie transition is indeed under competition from melting at these very high temperatures (and thus partly thwarted).

Examination of the initial cooling curves of Figure 4b reveals again the same hysteretic behaviour as before through reappearance of the ferroelectric peak only after the film had been cooled down to 90°C. Interestingly, the peak for the disordered phase at 90°C is not increased in intensity over its value at 145°C suggesting that crystallization from the amorphous melt into the paraelectric phase is not strongly favoured even at high supercoolings. The sharp contraction of the lattice of this phase upon cooling to 90°C is again visible, as is its very rapid transformation back to the ferroelectric phase between 90° and 80°C. Upon further reheating, the same trend towards earlier transformation that we saw for the other two compositions is observed here, too (Figure 4c); as a result, less competition is encountered from melting than during the first heating programme, thus allowing the 145°C peak to increase considerably over its value in Figure 4a. Overall, the above results indicate that the great bulk of crystallographic changes associated with this ferroelectric-to-paraelectric phase transition occurs at very high temperatures (i.e. above 140°C), significantly higher than those reported earlier^{10,19}, and very close to the melting point; this latter finding may be of importance in reinforcing the belief that a similar transition in β -PVF₂ may be overtaken by the occurrence of melting.

A final point concerns the variation of the full diffraction pattern, recorded photographically, of the 78/22 copolymer. Similar diffraction patterns have also been obtained for the other two compositions, but were excluded here to save space. However, presentation of at least one such series is important, because all the earlier results describe only the variations in intermolecular packing associated with the phase transition, but yield no evidence about the concomitant intramolecular conformational changes. This evidence is now depicted in Figure 5. The strong inner reflection at 25°C is the intermolecular-packing reflection sampled diffractometrically in Figure 4; the two outer reflections are due, respectively, to the (001) and (201, 111) planes of an all-*trans* conformation having a *c*-axis repeat of 2.56 (the same as β -PVF₂²¹), whose regularity is manifested in the sharpness of these reflections. At 120°C, the paraelectric phase makes its appearance through a weak innermost ring, although the two reflections associated with the all-*trans* chain conformation remain strong and sharp; the same holds true at 130°C, where the change in packing becomes more noticeable through the increase in intensity of the innermost reflection. The ferroelectric phase is well

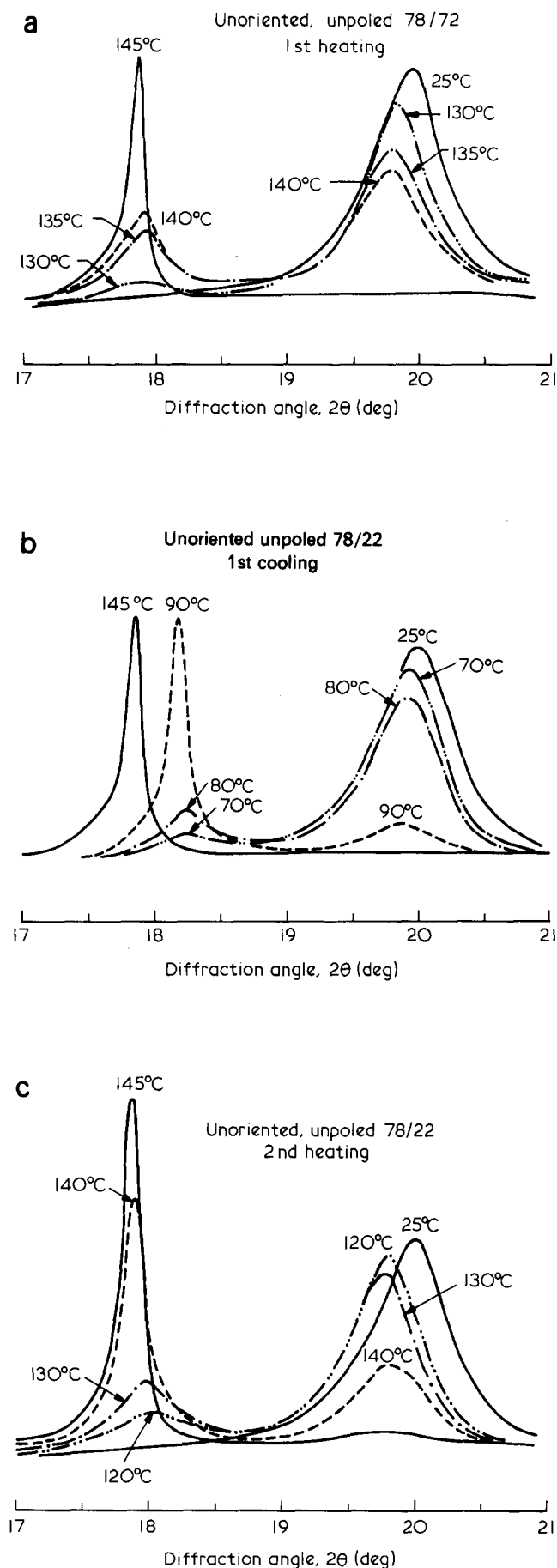


Figure 4 X-ray diffractograms of 78/22 mol% copolymer as functions of temperature, reflecting changes in intermolecular packing associated with the ferroelectric-to-paraelectric transition: (a) first heating, (b) first cooling, and (c) second heating cycles

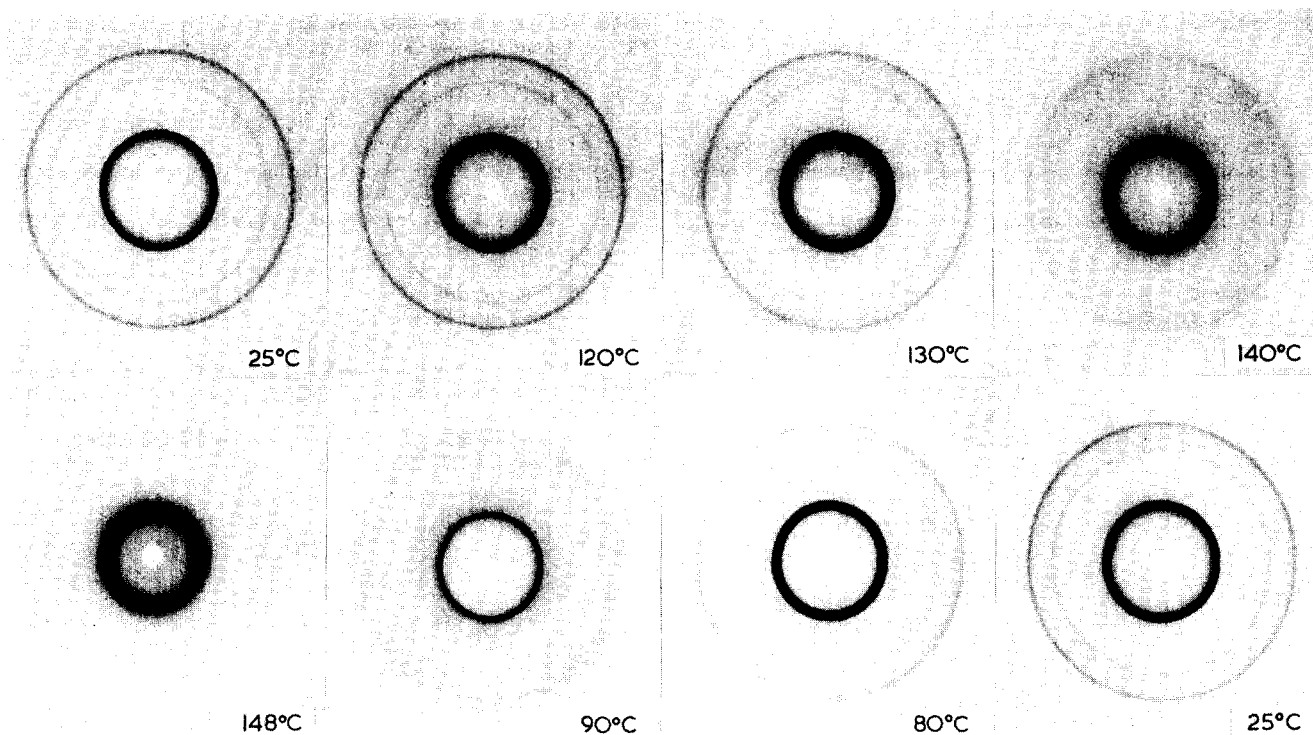


Figure 5 X-ray diffraction patterns obtained during the initial heating-and-cooling cycle of a 78/22 mol% copolymer and reflecting intra- and intermolecular changes accompanying the Curie transition

on its way to disappearance at 140°C, but now this becomes quite clear also in the *intramolecular* sense, as the two outer reflections are greatly weakened; they are bridged by a diffuse ring centred at 2.3 Å (this is barely visible in the photographic print) and attributed to the disordered conformation growing at the expense of the *trans* sequences. This specimen was heated to 148°C, whereupon all crystalline reflections disappeared, and only amorphous rings were seen; the striking difference in the diffraction patterns at 140° and 148°C confirms clearly the proximity of the ferroelectric and melting transitions. Subsequent cooling to 90°C shows the paraelectric phase in isolation: this time, the weak and broad outer ring reflecting the intramolecularly disordered conformation is clearly visible. Cooling down to 80°C brings back all reflections attributable to the ferroelectric lattice, while return to room temperature removes essentially all visible traces of the paraelectric phase. Consequently, we see that the aforementioned discussion based on molecular packing is fully supported by *intrachain* evidence.

CONCLUSIONS

The three copolymers investigated in the as-crystallized state, 65/35, 73/27 and 78/22 mol% VF₂, all show great similarities among themselves and diverge from the behaviour exhibited by the 52/48 composition. Contrary to that copolymer, they adopt the well-ordered all-*trans* structure directly upon crystallization, without the need for drawing or poling. Whereas in their ferroelectric phase their chains are packed hexagonally (or pseudo-hexagonally) in unit cells of different dimensions (increasing with decreasing VF₂ content), above the phase

transition they *all* (including the 52/48 copolymer) pack into the *same* unit cell: that is an enlarged hexagonal cell whose molecular chains adopt a partly disordered arrangement of *TG*, *T \bar{G}* and *TT* sequences. The phase transition extends over a wide temperature range, encompassing at least 30°C in the 65/35 and 73/27 copolymers, and about 15°C in the 78/22; the smaller range of the latter is attributed to competition from melting. As for the 52/48 composition, so here, too, the mechanism of the ferroelectric-to-paraelectric phase change is primarily *intramolecular*. However, contrary to the 52/48 copolymer, a hysteresis-like behaviour is observed here upon cooling, causing the disordered conformation to persist to lower temperatures than during heating; this is presumably a result of the higher energy needed to re-adopt the well-ordered all-*trans* conformation and packing.

Our results, stemming from copolymers of high VF₂ content that crystallize in essentially the same manner as β -PVF₂, indicate a high probability that this polymer should also be capable of undergoing the same type of ferroelectric-to-paraelectric transition, i.e. through the introduction of *intramolecular* disorder. Moreover, the close proximity of this transition in the 78/22 composition to its melting point renders most credible the hypothesis that, if such a transition does indeed exist in β -PVF₂, it lies in its melting region. This possibility is further examined and clarified in the following paper¹⁶ with the aid of our results from drawn or poled specimens.

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