Crystallographic changes characterizing the Curie transition in three ferroelectric copolymers of vinylidene fluoride and trifluoroethylene: 2. Oriented or poled samples

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The effects of uniaxial drawing or poling on the structural changes involved in the ferroelectric-to-paraelectric phase transition in copolymers of vinylidene fluoride and trifluoroethylene were examined and compared to the behaviour of as-crystallized films. The compositions studied were 65/35, 73/27 and 78/22 mol% vinylidene fluoride/trifluoroethylene, all of which crystallize from the melt with a molecular conformation and packing analogous to those of the common piezoelectric β-phase of poly(vinylidene fluoride). Contrary to the previously described behaviour of a 52/48 mol% copolymer, orientation did not induce any significant changes in the structure of these copolymers or in its variation with temperature, primarily because these already crystallize directly from the melt in well-ordered, compact unit cells. On the other hand, electrical poling caused the all-*trans* chains of the ferroelectric phase to be packed more compactly and to survive to higher temperatures, thus shifting the Curie transition closer to the melting points of these copolymers. As a result, competition from melting interfered with the later stages of this solid-state transformation in the 73/27 mol% composition, and aborted it at a very early point in the 78/22 mol% samples. The Curie temperature was found to exhibit hysteresis between heating and cooling parts of the thermal cycle, to extend over a broad range of temperatures, and to involve *intra*molecular changes to the same disordered conformation found in melt-crystallized samples. Our results have allowed reasonable implications to be made concerning the existence and nature of a Curie transition in the piezoelectric β-phase of poly(vinylidene fluoride).

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

INTRODUCTION

The structures and thermal behaviour of 65/35, 73/27 and 78/22 mol% copolymers of vinylidene fluoride and trifluoroethylene have been reported in the preceding paper[1]. Summarized very briefly, all three were found to crystallize directly into a phase closely analogous to the common piezoelectric β-phase of poly(vinylidene fluoride) (PVF_2)[2] (contrary to the behaviour of 52/48 mol% copolymers[3,4]). Structurally, the ferroelectric-to-paraelectric transition was shown to involve *intra*molecular changes through introduction of G and $\bar{G}$ bonds into the original all-*trans* conformation, and to take place over a broad temperature range encompassing typically 30°C and (for the 78/22 copolymer) extending into the melting region.

A major aim of this research is to elucidate why the piezoelectric β-phase of PVF_2 differs from most other ferroelectric materials in not exhibiting unequivocally a Curie transition. From our previous work on as-crystallized specimens[1], we already have a clear indication that this transition may be thwarted by the onset of melting. However, our earlier work on the 52/48 copolymer[3,4] showed that the behaviour of drawn or poled specimens may be significantly different from that of their as-crystallized counterparts. Moreover, β-PVF_2 is not easily obtainable through direct crystallization from the melt, as has been summarized elsewhere.[5] Specifically, at atmospheric conditions, β-PVF_2 is not grown from the melt, except by epitaxial crystallization on potassium bromide[6], and then only as a very thin surface layer; this phase may be obtained by crystallization under high

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pressure[7-9] but this is accompanied by degradation[7] that may sometimes involve explosive dehydrofluorination[8,9]. Finally, for all piezoelectric and pyroelectric applications, β-PVF$_2$ must, of course, first be macroscopically polarized in a high electric field to induce the desired dipolar reorientation normal to the film[5]; most commonly, the film is also oriented, since not only does this treatment yield better mechanical properties and a larger piezoelectric response, but it also makes possible the use of much lower poling fields[10].

For these reasons, we have examined the structure of uniaxially oriented or poled films of vinylidene fluoride/trifluoroethylene copolymers, and its variation with temperature through a number of heating and cooling cycles incorporating the Curie-transition region.

EXPERIMENTAL

The same 65/35, 73/27 and 78/22 mol% copolymers of vinylidene fluoride/trifluoroethylene, prepared by Daikin Kogyo Co., Ltd, Japan, that had been employed in the preceding study[1] were also used here. Thin films prepared by compression moulding were uniaxially drawn at temperatures of 85°–105°C to ratios of 3:1 to 4:1. Similar films were coated with vacuum-evaporated aluminium electrodes and then poled electrically at room temperature for 30 min using fields of 0.9–1.2 MV cm^{-1}; the electrodes were subsequently removed by dissolution in dilute sodium hydroxide. These two types of specimen were examined by X-ray diffraction both diffractometrically (in reflection) and photographically (in transmission) in the manner described previously[1]. Films were mechanically restrained during X-ray recording in order to prevent their relaxation at elevated temperatures.

RESULTS AND DISCUSSION

Drawing and poling were shown[1] to have the same effects in the case of the 52/48 mol% copolymer, for whose partly disordered chains they induced a very regular all-*trans* molecular conformation and caused them to pack in a more compact unit cell. Here, we do not expect such drastic effects, since the molecules are already in a regular *trans* conformation. We present below our findings consecutively for the 65/35, 73/27 and 78/22 copolymers.

65/35 mol% copolymer

The above expectation of little change is indeed substantiated for the oriented specimens of this composition. As seen in *Figure 1*, the position of the 25°C peak moves only very slightly to higher angles compared to the melt-crystallized copolymer (*Figure 1a* of the preceding paper[1]), thus showing only minimal contraction of the unit cell from $a = 5.24$ Å to 5.23 Å. The thermal behaviour is essentially the same as in the undrawn case, i.e. the first indications of transformation are seen in the 80°C curve, and the temperature must be raised to 110°C to bring the sample fully to its paraelectric state. Cooling behaviour also shows the hysteresis observed in as-crystallized specimens (*Figure 1b* of preceding paper[1]). We can see this in the photographic diffraction patterns of *Figure 2*, which are included primarily to show the conformational changes that are not sampled by the diffractometric traces. The initial room-temperature diffraction pattern of oriented 65/35 copolymer is seen in *Figure 2* to exhibit the strong equatorial reflection attributable to its hexagonal cell base, plus a sharp meridional reflection at 2.56 Å accompanied by its off-meridional (201, 111) counterparts; the latter two outermost reflections uniquely identify the molecular conformation as all-*trans*. In addition, a very slight diffuseness is visible in the meridional region between these two outermost reflections; the diffuse scattering is observed more clearly at the higher temperatures, and is attributable to the small extent of conformational disorder existing in this drawn copolymer. At 80°C, the transformation has begun, but is noted only by the somewhat increased diffuseness of the meridional region and by the introduction of a new equatorial reflection just inside (and partly overlapping with) the original equatorial reflection. At 90°C, this new equatorial peak is now clearly seen, while all reflections attributable to the regular *trans* phase are fading away; their last traces are barely visible at 100°C, and by 110°C the ferroelectric-to-paraelectric transition is seen to be complete. At this temperature, the meridional region contains exclusively the broad, diffuse arc centred at 2.30 Å and identifying the paraelectric conformation as discussed immediately below. If this sample is now cooled to 70°C, the hysteresis-like behaviour observed for the as-crystallized specimens is obvious here, too: it is only at 60°C that the equatorial and meridional reflections of the all-*trans* phase reappear.

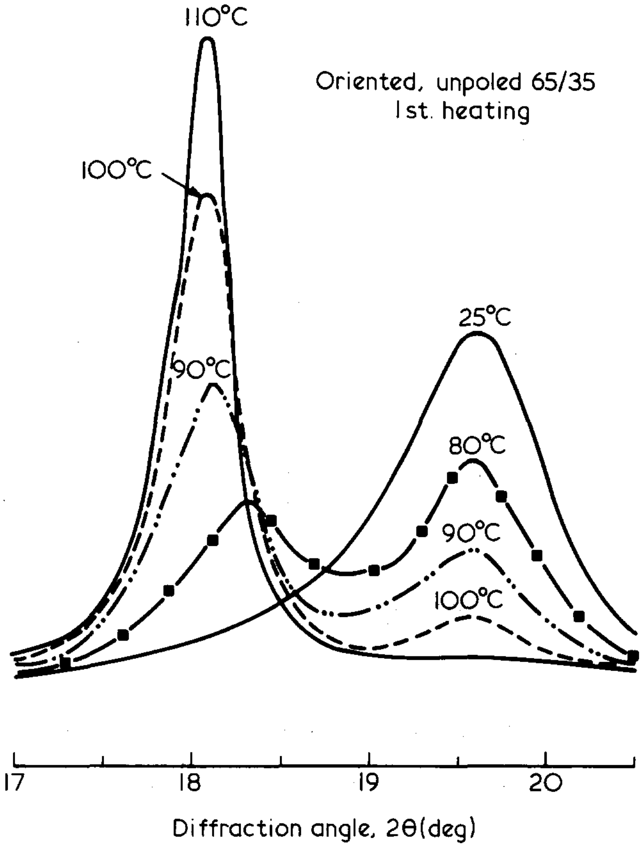

Figure 1 X-ray diffractograms during initial heating of oriented, unpoled 65/35 mol% copolymer

The molecular conformation of the paraelectric phase is the same for this and all other copolymers studied by us (52, 65, 73 and 78 mol% VF$_2$). Its meridional reflection at 2.30 Å is consistent with a number of regular arrangements of *TG*, $T\bar{G}$, and *TT* groups (e.g. $TGT\bar{G}$, $(TG)_3$, $(T\bar{G})_3$,

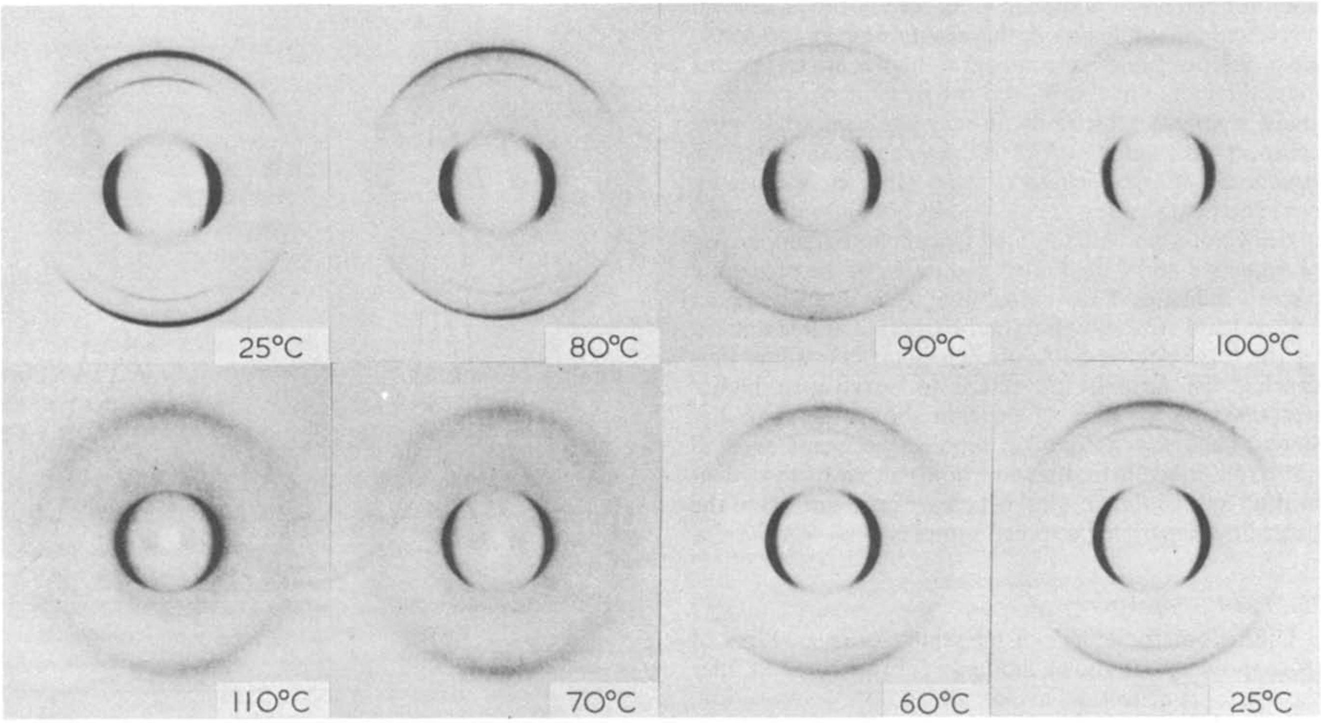

Figure 2 X-ray diffraction patterns of oriented, unpoled 65/35 mol% copolymer showing *intra*- and *inter*molecular changes during the initial heating and cooling cycle

$(TG)_2(T\bar{G})_2$, $T_3GT_3\bar{G}$, $T_5GT\bar{G}$, etc.) or with an irregular succession of such groups. The fibre diffraction pattern of this paraelectric phase is closely analogous[3] to that of trifluoroethylene *homo*polymer, the latter having been identified previously[11] with a 3/1 helical conformation (i.e. $(TG)_3$ or $(T\bar{G})_3$) on the basis of energy calculations and X-ray diffraction; we therefore referred to the paraelectric conformation as a 'disordered 3/1 helix', the disorder being evident in the breadth and diffuseness of the meridional reflection. We have now attempted to get a better understanding of this conformation by heavily overexposing diffraction patterns to seek out weak reflections at intermediate layer lines (see *Figure 3*). The very broad streak-like reflections oriented parallel to the meridian, together with the sharp appearance of all equatorial reflections, confirm our earlier conclusions[1,3,4] that the chains are severely disordered *intra*molecularly, yet are packed *inter*molecularly on a well-ordered lattice. A completely random arrangement of TG, $T\bar{G}$ and TT sequences would place the 2.30 Å reflection on the first layer line, whereas a regular combination of such groups would cause this reflection to lie on a higher layer line; the locations of the first layer line for the cases that this meridional reflection lies on the second, third, or fourth lines are marked in *Figure 3* as 1/2, 1/3 and 1/4, respectively. It appears from this figure that diffuse reflections are localized on the line marked 1/2 and very possibly on the other two as well (although their breadth and diffuseness do not permit definitive determination). We therefore conclude that the conformation of the paraelectric phase is a partly disordered arrangement of TG, $T\bar{G}$ and TT groups that have a tendency to organize themselves in longer sequences of two, three, or four such groups.

This more-or-less unchanged behaviour of oriented samples from that of their as-crystallized counterparts

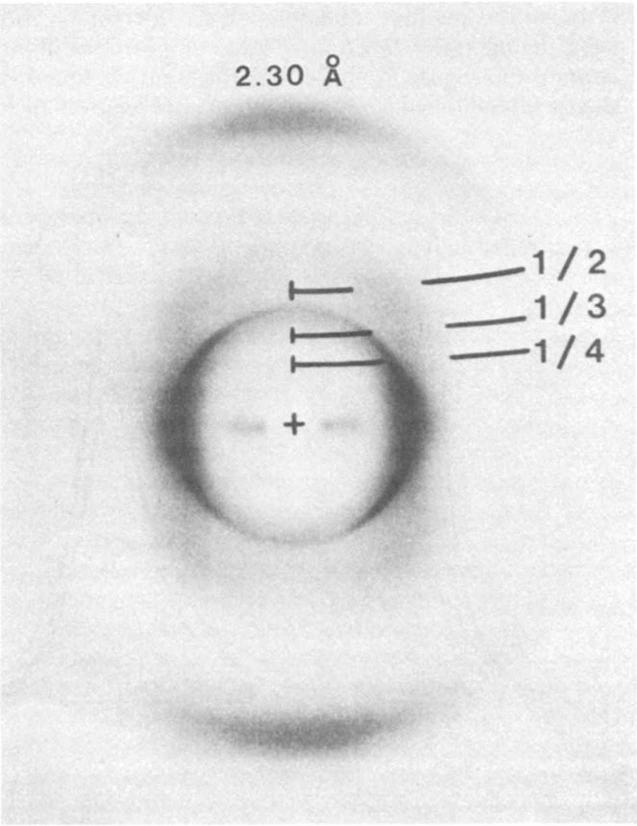

Figure 3 X-ray diffraction pattern typical of the paraelectric phase of these vinylidene fluoride/trifluoroethylene copolymers. The sample is oriented, unpoled 65/35 mol% copolymer held at 130°C

does not extend to poled films. As seen in the equatorial diffractograms of *Figure 4*, the all-*trans* peaks are somewhat narrower and have moved to higher angles; poling must therefore have improved the packing of crystalline chain segments, which now fit within a somewhat more compact unit cell ($a = 5.18$ Å). More significantly, the structural changes characterizing the ferroelectric-to-paraelectric transition are delayed by ~ 10°C with respect to drawn or otherwise unpoled specimens, as comparison of *Figures 4* and *1* (and, also, *Figure 1a* of the preceding paper[1]) indicates. This is attributed to the more compact and ordered structure imparted by poling and stabilized by the local electric fields of each polar crystallite, thus causing the ferroelectric phase to survive to higher temperatures. Cooling of the film shows the same hysteretic behaviour as found in unpoled specimens, and will not be described here; the same holds also for subsequent heating and cooling cycles, which are as described in the preceding paper[1] for unpoled samples.

73/27 mol% copolymer

Diffractometric traces of uniaxially oriented films of this copolymer are shown in *Figure 5*. From these we infer the same conclusions as for the 65/35 composition, namely that drawing improves the molecular packing only slightly, and that the temperature range and structural characteristics of the transformation are essentially those exhibited by the as-crystallized samples (*Figure 3a* of the preceding paper[1]).

On examination of poled films (*Figure 6a*), we first observe that—contrary to the 65/35 copolymer—this 73/27 composition shows no significant improvement of molecular packing as a result of the poling treatment. This is due to the fact that, already upon direct crystallization from the melt, the 73/27 and 78/22 compositions do not contain the slight amount of disorder that we found for their melt-solidified 65/35 counterpart (see again *Figure 2* of the preceding paper[1]). Nevertheless, poling once again appears to offer greater stability to the all-*trans* phase, causing it to survive above 140°C (*Figure 6a*), at which temperature all traces of this phase had disappeared in drawn (*Figure 5*) and as-crystallized (*Figure 3a* of the preceding paper[1]) samples. Moreover, if we increase the temperature to 148°C to complete the transformation in poled films, we notice that there is now competition from melting: the 148°C peak is quite low in *Figure 6a*, because at this temperature (nominally ~2°C below the melting point), there is sufficient driving force to transform a great number of *trans* chains all the way to the amorphous conformation, rather than to an already defect-ridden intermediate structure. This conclusion is further substantiated by inspection of the cooling curves for the same specimen (*Figure 6b*): lowering the temperature (to anywhere between 135° and 90°C) causes a strong increase in the intensity of the peak for the disordered paraelectric phase, implying crystallization directly into that phase from the melt. For the sake of clarity, *Figure 6b* does not show traces obtained at temperatures higher than 90°C (which is where the well-ordered *trans* phase makes its reappearance, showing once again the by now expected hysteresis upon cooling). At lower temperatures, the behaviour is again typical of unpoled samples of this copolymer.

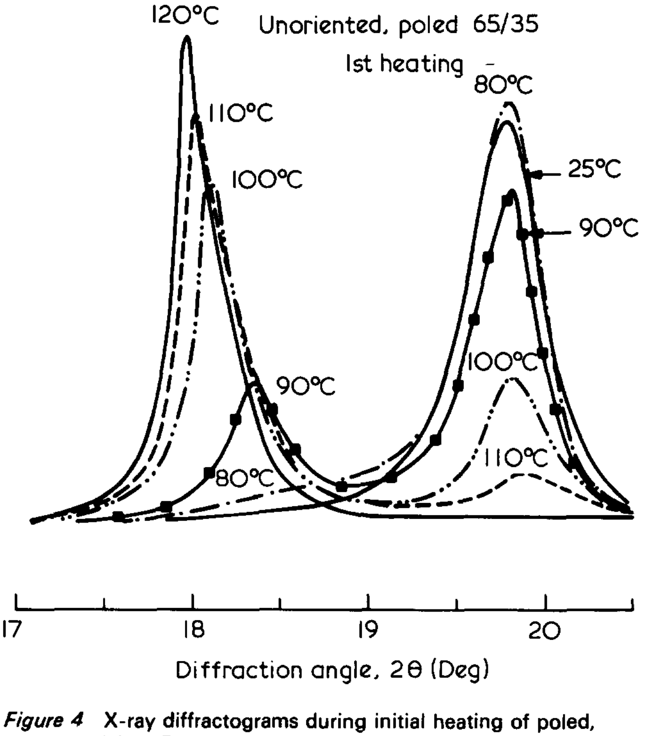

Figure 4 X-ray diffractograms during initial heating of poled, unoriented 65/35 mol% copolymer

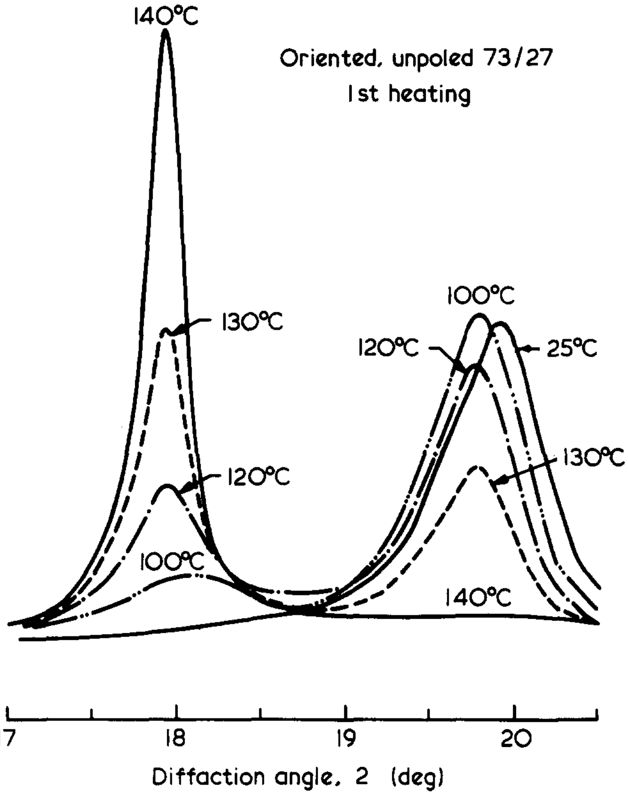

Figure 5 X-ray diffractograms during initial heating of oriented, unpoled 73/27 mol% copolymer

78/22 mol% copolymer

It will be recalled from the study of as-crystallized specimens[1] that this was found to be the most interesting composition, not only because its high VF_2 content renders it the closest to β-PVF_2 but also because its phase transition extends into the melting range of this lowest melting[12–14] of all vinylidene fluoride/trifluoroethylene

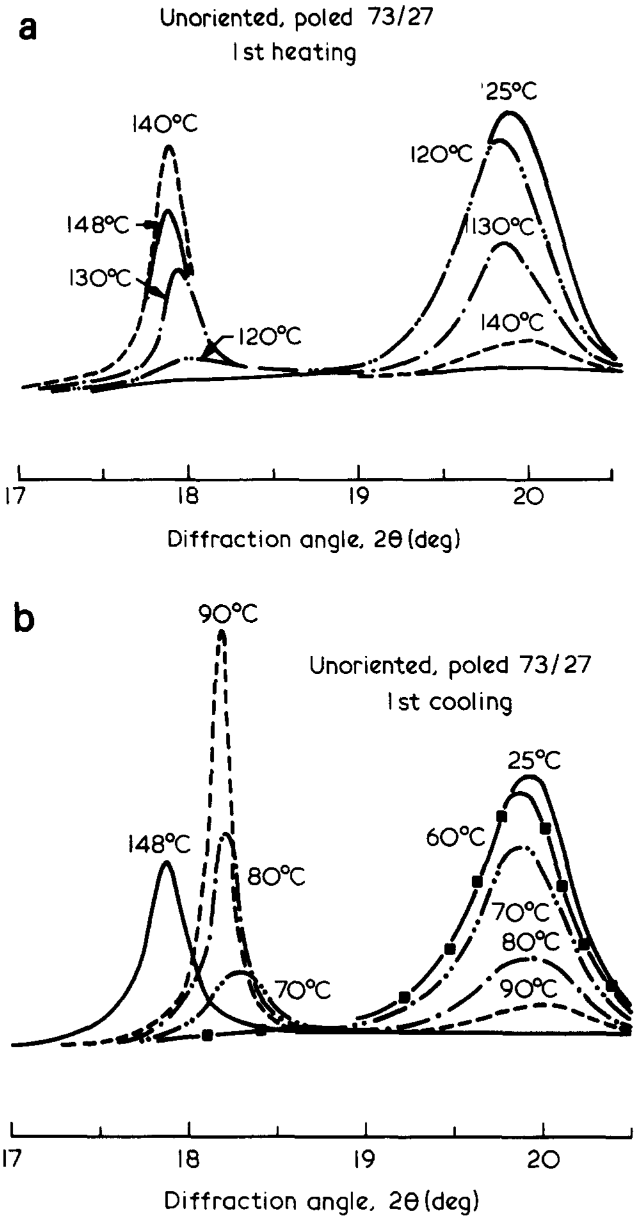

Figure 6 X-ray diffractograms of poled, unoriented 73/27 mol% copolymer during initial (a) heating and (b) cooling

copolymers. Uniaxially oriented films behave in the same manner as their melt-crystallized counterparts: their structural changes as functions of temperature upon heating and cooling are in all respects equivalent to the results presented in *Figure 4* of the preceding paper[1], and will consequently not be repeated here. Poled samples, on the other hand, display a more interesting behaviour, which is summarized below.

The heating part of the first thermal cycle for electrically polarized 78/22 copolymer films is seen in *Figure 7a*. Owing to the already compact packing of essentially defect-free all-*trans* chains in this copolymer of high VF_2 content, there is no reduction in the cell base upon poling. However, poling seems to impart an exceptional stability to this packing, as evidenced by the lack of decreases of the *trans* peak at all temperatures up to 145°C (which is only 4°C below the nominal melting point of this copolymer). Nevertheless, a small peak is seen to be growing at low angles above a temperature of 130°C. This can be due only in part to ferroelectric chains undergoing transformation (since the all-*trans* peak remains essentially unchanged), unless at high temperatures there is favourable reorientation of such chains that were originally in a non-diffracting position. Another possibility is that transformation begins in the amorphous regions, e.g. in chain segments that due to steric reasons become frozen into strained conformations during crystallization or poling; with the expansion of the unit cell at high temperatures and the onset of relaxational motions, these chain segments might then become free to adopt the disordered conformation of the paraelectric phase (a process similar to annealing).

When the poled specimen is heated above 145°C, e.g. to 148°C, there is a most pronounced drop in the intensity of *both* the all-*trans* and disordered-phase peaks (see *Figure 7a*). Thus, the solid-state ferroelectric-to-paraelectric transformation in poled 78/22 copolymer is essentially

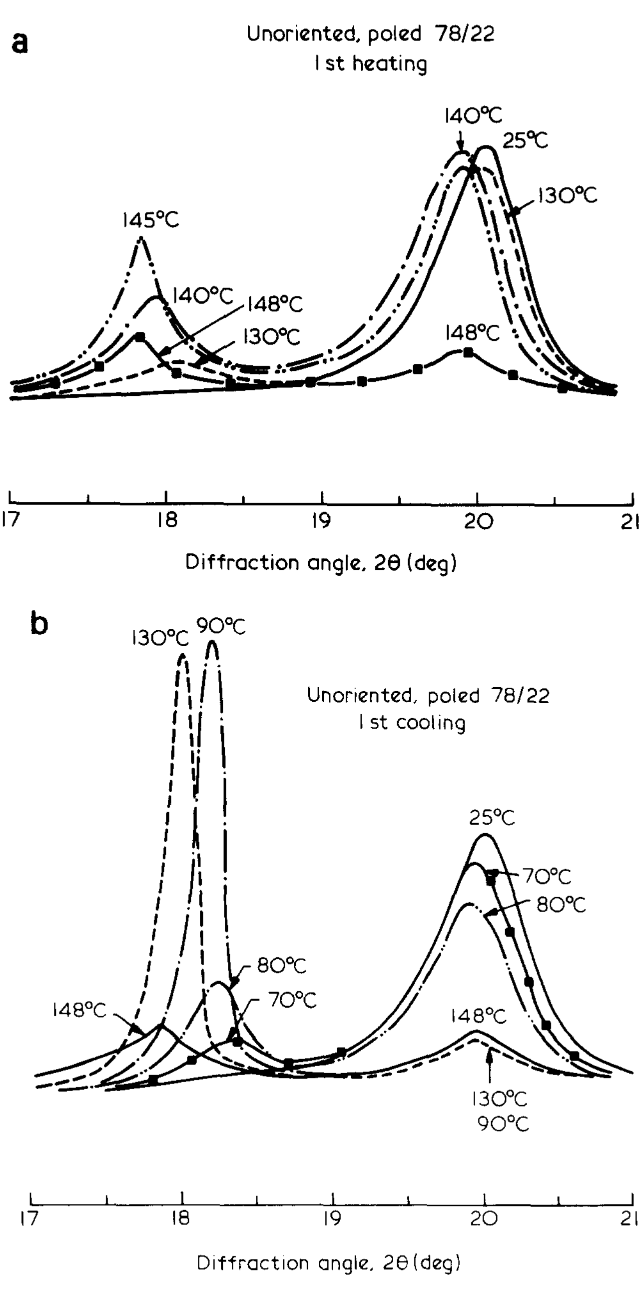

Figure 7 X-ray diffractograms of poled, unoriented 78/22 mol% copolymer during initial (a) heating and (b) cooling

aborted by the melting process before it has had the opportunity to proceed to a significant extent; this is the strongest evidence so far that a similar, but even earlier, thwarting may be responsible for the lack of a clearly observable Curie transition in β-PVF$_2$. Returning now to the poled 78/22 copolymer, we conclude by examining the cooling part of the first cycle in *Figure 7b*. The paraelectric crystalline phase is seen to appear strongly when the specimen is cooled to 130°C and to survive unchanged in the documented hysteresis-like fashion to temperatures as low as 90°C. Down to those temperatures there is no increase in the small amount of *trans* phase surviving at 148°C. Return to this ferroelectric phase is seen first at 80°C, with the great majority of molecular segments participating; most of the remaining ones are transformed by 70°C.

CONCLUSIONS

Electrical poling of 65/35, 73/27 and 78/22 mol% copolymers was seen to induce significant changes to the samples, increasing the order of the all-*trans* ferroelectric phase, packing the molecular chains more compactly (except in the already highly ordered 78/22 composition), and stabilizing the polar phase to higher temperatures. On the other hand, mechanical orientation causes no major changes to the behaviour found in melt-crystallized films. Thermal treatment revealed hysteretic behaviour of the structural changes in heating and cooling parts of the cycle. A most important finding is the stabilization of the ferroelectric phase by poling, to an extent that raises the Curie point significantly; for the 73/27 copolymer, this causes melting to catch up to the final stages of the Curie transition, while for the 78/22 samples it practically aborts this transition at its very beginning.

This latter finding has important implications with respect to the basic question of whether the common piezoelectric β-phase of PVF$_2$ undergoes such a Curie transition, as found in most ferroelectric materials. Only one study[15], not confirmed by other laboratories, has reported a ferroelectric-to-paraelectric transition in β-PVF$_2$, occurring around 140°C; most investigators have suspected that such a transition may in fact be preceded by melting of this polymer. Our results do not support the possibility of a 140°C transition in β-PVF$_2$; the transition region was found to move to higher temperatures with increasing VF$_2$ content, and for the 78/22 mol% copolymer it is already clearly above 140°C. This variation of Curie temperature with composition, based on our results, is summarized in *Figure 8* for both poled and unpoled specimens. Each bar covers the range of the transition region that was observed by X-ray diffraction (i.e. from the first appearance of a paraelectric peak to the disappearance of the ferroelectric peak). Data points on each bar correspond to the temperatures of maximal rate of transformation (based on our X-ray findings), and are in excellent agreement with our dielectric results[16] indicated in this figure. If we now fit these data points to the best straight line (through linear regression) and extrapolate to 100% VF$_2$, we obtain for poled and unpoled β-PVF$_2$ assumed Curie transitions at 205°–207°C. Of course, these numbers cannot be regarded absolutely, nor is there any certainty that the solid-state Curie transition would continue to vary linearly with composition at very high VF$_2$ contents. Nevertheless, we believe that the basis for extrapolation to 100% VF$_2$ is valid because of the close analogy between β-PVF$_2$ and these copolymers both on the microscopic level (molecular and crystalline structure) and the macroscopic (piezoelectric and pyroelectric behaviour). Moreover, the ability of the melting process to abort such ferroelectric-to-paraelectric crystalline transitions at both their early and late stages has now been definitely established by our findings from the 73/27 and 78/22 mol% copolymers. It is also interesting to observe that, if the 205°–207°C Curie temperature is valid for β-PVF$_2$, and if this hypothetical transition extends over a similarly broad temperature range as found here for the copolymers, then the earliest signs of the transition might occur just below the melting point of β-PVF$_2$ (the highest T_m observed for folded-chain crystals of this polymorph is 191°C in pressure-crystallized samples[8,17]).

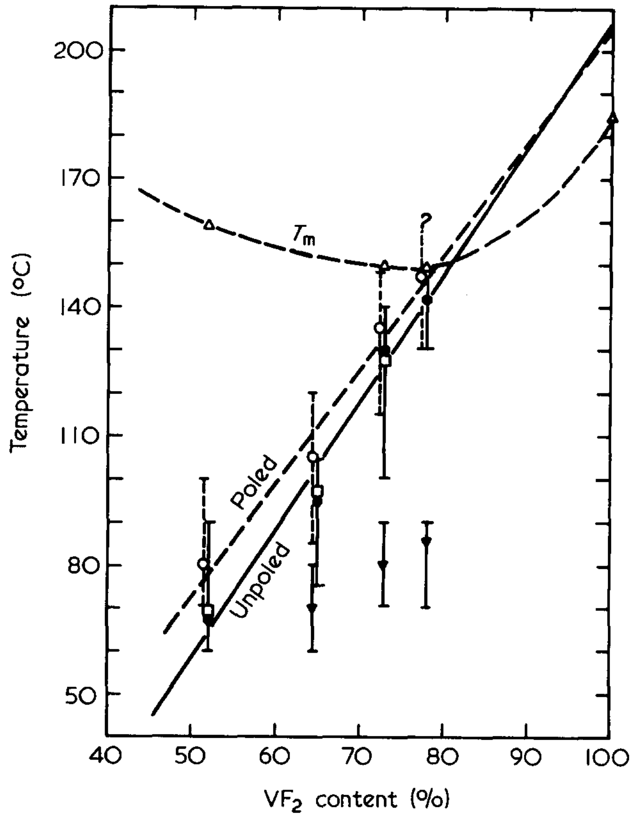

Figure 8 Variation of melting and ferroelectric transitions in copolymers of vinylidene fluoride and trifluoroethylene with composition. Bars denote the entire range of X-ray changes during the ferroelectric transition, and circles the temperatures of maximal rate of transformation: ●, unpoled specimens (heating); ○, poled specimens (heating); ▼, cooling-cycle data; □, dielectric peaks (from ref. 16); and △, optical melting temperatures for unoriented unpoled copolymers and oriented unpoled β-PVF$_2$ (Kureha KF-1100 mechanically restrained during heating)

As a final point, we may speculate on the nature of the solid-state Curie transition in β-PVF$_2$ if it were not masked by the onset of melting: would it then involve *inter*molecular or *intra*molecular processes? Clearly, all our findings from 52/48, 65/35, 73/27 and 78/22 copolymers indicate an *intra*molecular mechanism for the overall process of transformation, although dielectric results[4,16] show that rotational motions also play a role. Even in those copolymers for which the solid-state transition is thwarted by melting, the paraelectric state that would have been expected makes its appearance by crystallizing from the melt at high temperatures when the copolymers are subsequently cooled. In the copolymers, this phase is non-polar and has molecules consisting of TG, $T\bar{G}$ and, possibly, TT sequences. It is interesting to note that when the β-phase of PVF$_2$ is cooled after melting, it also crystallizes predominantly in a non-polar phase having molecules with TG and $T\bar{G}$ sequences (the α-phase). Of course, despite these similarities, the α-phase should not be considered a paraelectric counterpart to β-PVF$_2$, the main reason being that it does not transform spontaneously to the ferroelectric β-phase at lower temperatures. Also, in a strict sense, the α-phase, while not polar, is not paraelectric: it is anti-polar (and probably anti-ferroelectric). Another polymorph obtained as a minority during crystallization of PVF$_2$ is the γ-phase; however, its unit cell is polar (although an antipolar analogue has been suggested[18]), and it, too, does not transform to the β-phase on further cooling. What, then, could be a reasonable structure of a paraelectric phase of β-PVF$_2$? In view of the facts that copolymers containing as high a proportion of vinylidene fluoride as 78% crystallize with the same all-*trans* conformation as β-PVF$_2$ and adopt a partly disordered conformation containing TG, $T\bar{G}$ and TT groups above the Curie transition, it is reasonable to expect that a similar conformational transition would also characterize PVF$_2$ if melting had not interfered. Since rotational molecular motions also accompany the Curie transformation in copolymers[4,16], they could also play a similar role in β-PVF$_2$.

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