Phase transition at a temperature immediately below the melting point of poly(vinylidene fluoride) form I: A proposition for the ferroelectric Curie point

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A phase transition at a temperature immediately below the melting point of poly(vinylidene fluoride) form I has been found by means of differential scanning calorimetry (d.s.c.) and infra-red (i.r.) vibrational spectroscopy. An endothermic d.s.c. shoulder has been observed at a temperature about 10°C below the melting point, in the vicinity of which the i.r. crystalline *trans* bands decrease in intensity steeply and the crystalline *gauche* bands increase in intensity, indicating the conformational change from all-*trans* to $T_3GT_3\bar{G}$ type. These observations have been found to be detectable more clearly for samples subjected to the poling treatment under a d.c. high voltage. The transition shows the characteristic behaviour essentially identical to those observed for ferroelectric copolymers of vinylidene fluoride and trifluoroethylene, except for the irreversibility of the structural change, suggesting that the phase transformation revealed here may be a ferroelectric-to-paraelectric phase transition of polar form I crystal and that the Curie point may be about 172°C. It is consistent with Micheron's measurement of the temperature dependence of the dielectric constant. Other structural changes in the form I sample occurring in the temperature range from 20° to 170°C have also been discussed based on the i.r. spectral measurements.

Keywords Poly(vinylidene fluoride) form I; phase transition; Curie point; differential scanning calorimetry; infra-red spectra

INTRODUCTION

Poly(vinylidene fluoride) (PVDF) form I crystal has been demonstrated, with an appreciable degree of confirmation, to be a ferroelectric substance by many experimental facts[1]. The Curie point, generally observed for ferroelectric crystals and at which the ferroelectric–paraelectric phase transition occurs, has also been sought for this polymer: the dielectric study[2] suggested a temperature of about 170°C and the remanent polarization measurement[3] pointed out a temperature of about 140°C. At the present stage, therefore, the Curie temperature of PVDF form I has not yet been defined uniquely. Recently a vinylidene fluoride–trifluoroethylene (VDF–TrFE) random copolymer with a VDF monomer content of 55 mol % has been found to show[4] a ferroelectric phase transition at about 65°C. The transition temperature shifts towards the melting point as the VDF content increases[5]. The extrapolation to the VDF homopolymer allows us to predict the occurrence of a ferroelectric transition of PVDF form I crystal at a temperature very close to the melting point, though it is not known whether the transition occurs above or below the melting point[6]. In previous papers[7,8] we proposed the transition mechanism of VDF–TrFE copolymers; the all-*trans* chain conformation on the low-temperature side transforms to the conformation constructed by a statistical combination of TG and T_3G rotational isomers ($T = trans$ and $G = gauche$) above the transition temperature. This conformational change could be detected explicitly in the i.r. and Raman spectra, where the bands characteristic of all-*trans* conformers disappear steeply above the transition point and the bands intrinsic to TG and T_3G conformers increase in intensity. As an extended study of the copolymers, we measured the temperature dependence of i.r. spectra for PVDF form I, and spectral changes similar to those of copolymers could be found, as predicted, at a temperature immediately below the melting point, suggesting the existence of a ferroelectric phase transition of PVDF form I crystal.

EXPERIMENTAL

PVDF samples used were KF 1000 (Kureha Chem. Ind. Co. Ltd) and Kynar 201 (Pennwalt Chem. Co. Ltd). Films of form I with a thickness of ~40 μm were prepared by stretching the melt-quenched films to about four times the original length at ~60°C followed by annealing at 130°–170°C for 100 min under tension. Some film specimens were subjected to the poling treatment by corona charging (from a point ~1 cm distant from the surface of the film; a voltage of about 10 kV; at room temperature). I.r. spectra at high temperature were measured using a Japan Spectroscopic Co. i.r. spectrophotometer type A-3 equipped with a high-temperature optical cell

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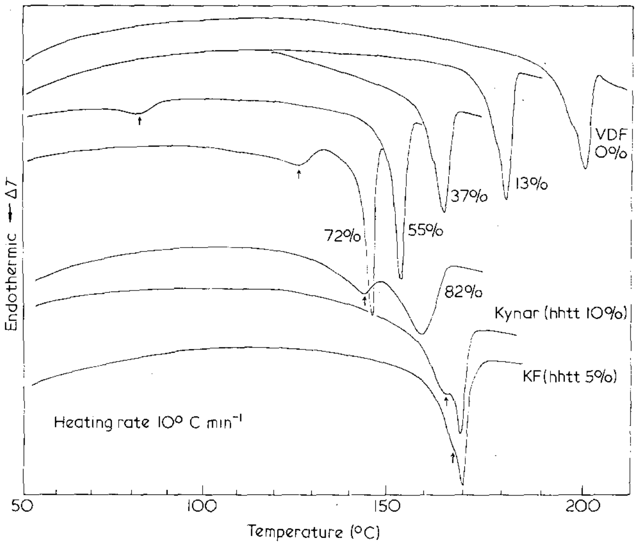

Figure 1 D.s.c. thermograms for a series of VDF–TrFE copolymers and PVDF form I (Kynar and KF samples). The arrows indicate the phase transition points

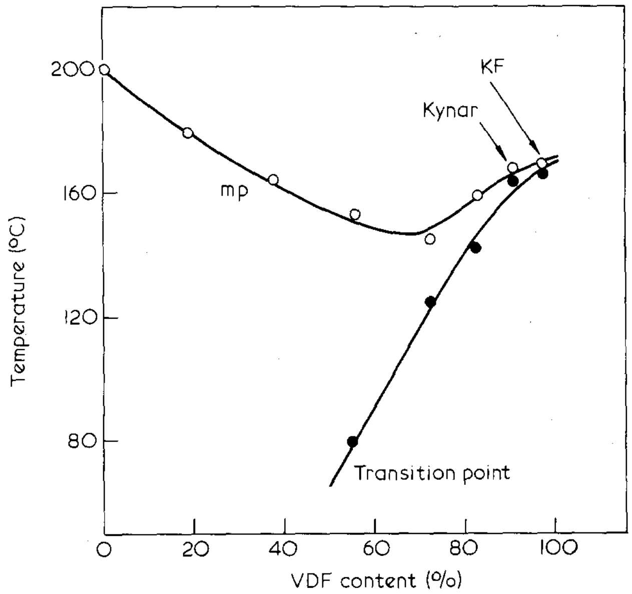

Figure 2 Dependence of melting and transition points on VDF mole content of VDF–TrFE copolymers and PVDF form I

(temperature accuracy ±0.5°C at 160°C). D.s.c. thermograms were measured by a Rigaku Denki thermoflex low-temperature type with the heating rate of 2°–10°C min^{-1}.

RESULTS AND DISCUSSION

Ferroelectric phase transition

D.s.c. measurements. In *Figure 1* are shown the d.s.c. thermograms for a series of VDF–TrFE copolymers and PVDF form I, where the sample tested was a thick plate, not a bundle of thin filaments or powder, in order to avoid the apparent broadening of the peaks due to poor thermal conductivity. As seen in the figure, PVDF form I sample has a shoulder on the low-temperature side of the melting peak. The shoulder is more prominent for the Kynar sample (having a head-to-head and tail-to-tail abnormal linkage of about 10%) than for the KF sample (about 5% abnormal linkage). Here the amount of abnormal linkage was estimated from ^{19}F n.m.r.[9] In *Figure 2* are plotted these temperature points along with those measured for VDF–TrFE copolymers as a function of VDF mole content. The observed shoulders of PVDF form I correspond well to the extrapolated points of VDF–TrFE copolymers. Furthermore, they can be observed only for form I samples, not for the samples of pure form II or III. We might assign the shoulders to the phase transition in a similar way to that of VDF–TrFE copolymers, but cannot do so unequivocally from these d.s.c. data only.

I.r. spectral measurements at high temperatures. In *Figure 3* is shown the temperature dependence of polarized i.r. spectra for PVDF form I (KF sample). The bands corresponding to long *trans* sequence[10], e.g. 1280, 840, 470 and 445 cm^{-1}, decrease in relative intensity in the vicinity of 172°C, close below the melting point. The bands at 810, 614 and 488 cm^{-1}, which correspond to the *gauche* bands of TG and T_3G, increase in intensity at high temperature, though not so appreciably. After cooling down to 135°C, the spectra do not give the profile of original form I but the profile of *oriented* crystalline form III. Several weak bands of form II are also observed at room temperature. Additionally it should be noticed that the polarization of the bands remains detectable throughout these changes. These spectral changes are essentially identical to those of VDF–TrFE copolymers except for the irreversibility of the transition. For Kynar samples the drastic interchange of *trans* and *gauche* bands is observed at 160°C and the polarized spectra of form III are obtained after cooling down to 150°C.

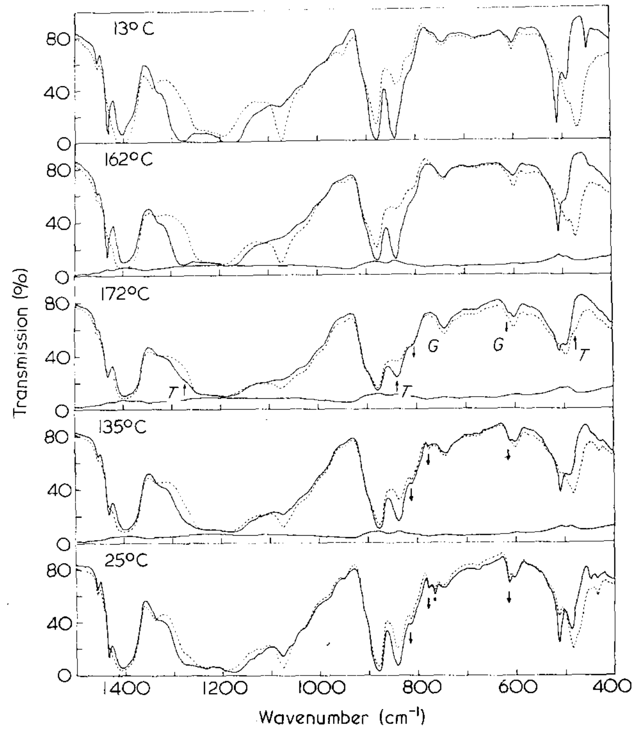

Figure 3 Temperature dependence of polarized i.r. spectra of unpoled PVDF form I (KF sample): ——, incident electric vector perpendicular to the draw direction; – – – –, incident electric vector parallel to the draw direction. The emission spectra near 0% transmission lines are also indicated for high-temperature spectra

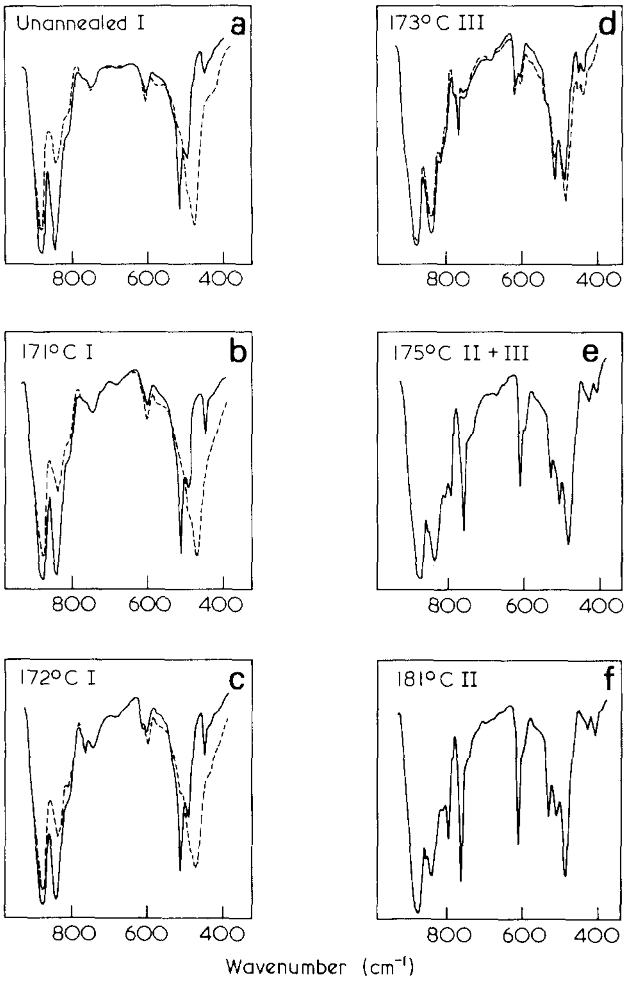

Figure 4 I.r. spectral changes of PVDF form I (KF sample) induced by heat treatment at the various annealing temperatures: ——, incident electric vector perpendicular to the draw direction; – – – –, incident electric vector parallel to the draw direction

Utilization of irreversibility of phase transition. In contrast to the case of copolymers, the i.r. spectral changes are irreversible. So we expect that the phase transition occurring at high temperature can also be deduced, though indirectly, from the following experiments. A cold-drawn sample is annealed at a certain temperature for a constant time of 1 h. Then the sample is cooled down to room temperature, at which the i.r. spectral measurements are carried out. Since the transition is irreversible, one may speculate from these spectral data on the structural change occurring at the annealing temperature. In *Figure 4* are shown the i.r. spectra measured at room temperature for the KF samples annealed at 160°–180°C and cooled rapidly down to room temperature. Annealing at a temperature lower than 171°C gives only the spectra of crystalline form I. In the very narrow annealing temperature range of 171°–174°C the spectra obtained correspond to those of *oriented* form III. When annealed above 174°C, the samples begin partly to melt and so, at room temperature, the form II bands increase their intensity and the polarization gradually becomes unrecognizable. The spectra of the sample annealed at 181°C are essentially the same as those of the melt-quenched sample. (It should be noted that the annealing time is about 1 h in this experiment and that rapid cooling of the melt (181°C) gives predominantly the crystal form II. But when the sample is annealed at 181°C for a longer time of about 1 day, the melt-recrystallization of form III occurs very slowly and the unpolarized i.r. spectra of this form are obtained[11]. Thus obtained form III sample melts at about 187°C and the form II spectra are given after cooling down to room temperature[26].) From *Figure 4* the following structural change is considered:

———— 171°C ———— 174°C ————

oriented form I	oriented *gauche* form	*gauche* form (molten)
Cooling ↓	↓	↓
oriented form I (more crystalline)	oriented form III	unoriented form II

These annealing effects on the irreversible structural change of PVDF form I can be also seen in the d.s.c. measurements. In the heating process of the d.s.c. scanning we held the sample for a while at the temperature where the shoulder was observed as shown in *Figure 1* and then cooled it down to room temperature. When the sample was heated again, it did not exhibit any shoulder but gave only one sharp melting peak at a temperature about 5°C higher than the original one, corresponding well to the i.r. spectral changes shown in *Figure 4.*

Poling effect. The above-mentioned phenomena are detected more explicitly when the corona-poled form I sample is used in the i.r. measurement at high temperatures. The result is reproduced in *Figure 5.* In the temperature range 170°–180°C the crystalline-sensitive bands characteristic of form III (3016 and 774 cm^{-1}) appear clearly with remarkable polarization. In parallel, the crystalline *trans* bands of form I (3013 and 445 cm^{-1}) decrease strongly in intensity. Above a temperature of about 180°C, the crystalline form III bands disappear by

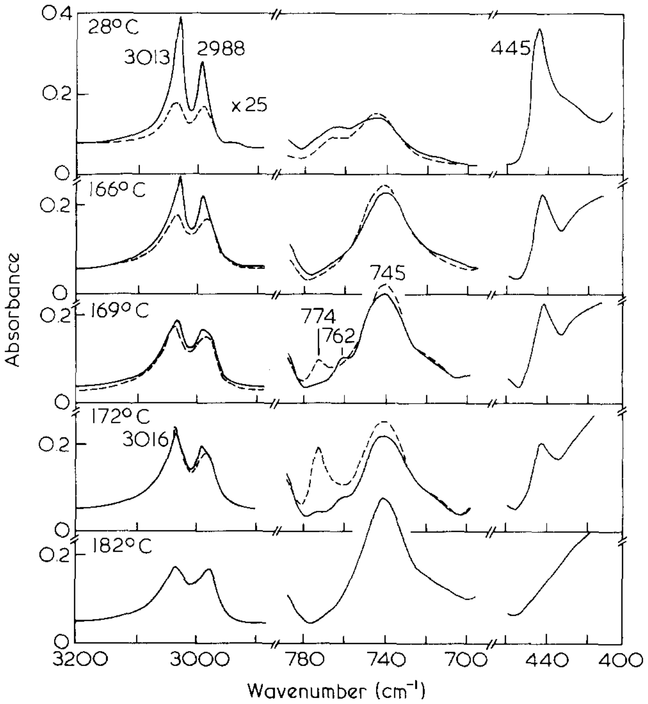

Figure 5 Temperature dependence of polarized i.r. spectra of poled PVDF form I (KF sample): ——, incident electric vector perpendicular to the draw direction; – – – –, incident electric vector parallel to the draw direction

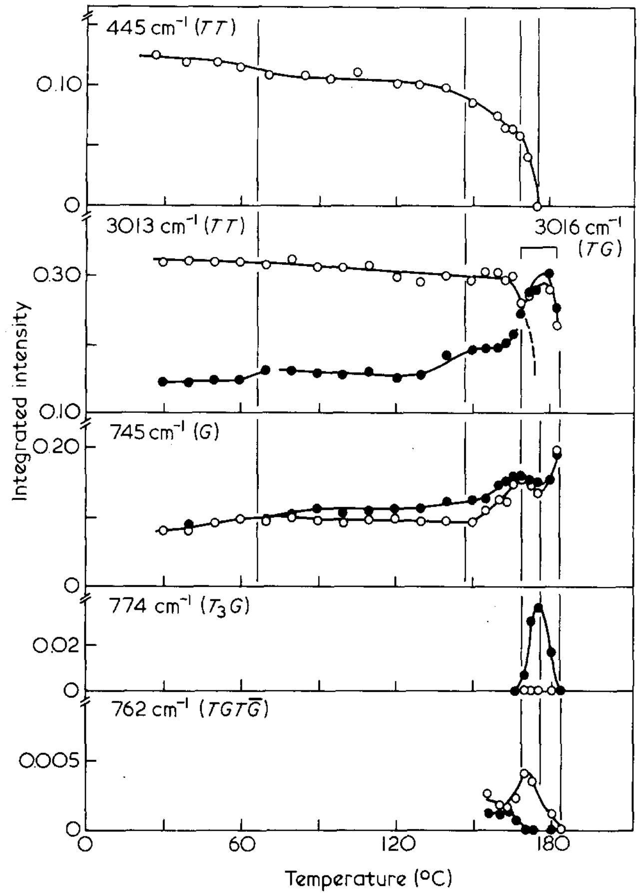

Figure 6 Temperature dependence of i.r. absorbances of poled PVDF form I (KF sample) estimated from *Figure 5*: ○, incident electric vector perpendicular to the draw direction; ●, incident electric vector parallel to the draw direction

the melting of the crystals. As in the case of unpoled samples, some polarized bands of form II (762 cm^{-1}) are also observed, though only a little, along with those of form III at a temperature of 165°–180°C, suggesting the coexistence of small amounts of $TGT\bar{G}$ conformational sequences within the crystals with $T_3GT_3\bar{G}$ conformational chains.[10] In *Figure 6* is shown the temperature dependence of relative absorbances measured from *Figure 5*.

The possibility of a ferroelectric phase transition. Taking into consideration the parallel relationship between the d.s.c. thermograms (*Figures 1* and *2*) and the temperature dependence of i.r. spectra (*Figures 3–6*), together with the close similarity of the transition phenomenon to that of VDF–TrFE copolymers, we may conclude that the crystalline phase transition, accompanied by the molecular structural change from all-*trans* conformation to the conformation constructed by T_3G and $T_3\bar{G}$ sequences, occurs at a temperature immediately below the melting point of PVDF form I. Multiple melting peaks are sometimes observed in the d.s.c. thermograms of some polyesters[12], which are said to originate from the melt-recrystallization of incomplete and small crystallites within the sample specimens. These peaks, however, change their position and profile according to the conditions of heat treatment. In the d.s.c. thermograms of PVDF form I, the shoulder under discussion appears constantly at a temperature a few degrees below the melting peak. Thus such an idea of melt-recrystallization cannot be assumed suitable for the present case, judging from all the experimental results stated above.

In the case of VDF–TrFE copolymers, the ferroelectric phase transition includes the molecular conformational change from *trans* to *gauche* forms. being the origin of the disappearance of spontaneous polarization above the Curie temperature[7,8]. If it is possible to extend the idea to the case of PVDF form I, the phase transition revealed here may be a *ferroelectric* phase transition of form I crystal and then the Curie point is considered to be about 172°C. It is also consistent with Micheron's observation[2] that the inverse of dielectric permittivity ε intersects the temperature scale axis at about 170°C ($1/\varepsilon \propto T - T_c$; $T_c \simeq 170°\mathrm{C}$). Lovinger[13] reported the existence of non-polar form III crystal from an X-ray diffraction study on the annealing effect of polar form II. If the transition is ferroelectric as explained, the high-temperature phase has the possibility of being a paraelectric crystal; in other words, the crystal form III obtained from polar form I may be a new and non-polar phase, different from the already-reported crystal form III with polar structure[14], although the molecular conformations are essentially the same as each other judged from the vibrational spectra. That is to say, there may exist two kinds of possible packing modes for the molecular chains of form III:

$$\text{non-polar form II} \xrightarrow{\text{annealing}} \text{III (polar)}^{14}$$

$$\text{polar form I} \longrightarrow \text{III (non-polar ?)}$$

In addition to the experimental results presented here, we also found that the X-ray fibre diagram of form I changed greatly at about 174°C for the poling-treated sample, providing the possibility of clarifying the crystal structural change definitely[15].

The role of poling in the phase transition. As seen in *Figures 5* and *6*, the crystallization-sensitive i.r. bands of form III can be detected much more clearly when the original form I sample is subjected to the poling treatment under a d.c. high voltage. Servet and Rault[16] reported that the thermally induced transformation from form II to form III is promoted by the poling of original form II. An almost pure and unpoled form II sample does not, on the other hand, transform even when annealed immediately below the melting temperature for a long time. *Figure 7* shows that the content of form III, X(III),[17] newly generated by the thermal transition of form II, is dependent on the relative amount of form III contained in the original sample, $X(\mathrm{III})^0$. Here the original samples with various ratios of forms II and III, prepared by slow cooling of the melt, were annealed at 175°C for 44 h. The difference $\Delta X = X(\mathrm{III}) - X(\mathrm{III})^0$ or the degree of transformation from forms II to III becomes maximal for the $X(\mathrm{III})^0$ value of about 0.3. That is to say, the transformation from form II to form III is considered to be promoted by the presence of an amount of originally existing form III segments, which may act as a kind of nucleus for crystal transformation. It is, however, difficult to clarify the state of these nuclei only from the spectral data: they may exist in a form of T_3G conformational sequence within a form II chain of $TGT\bar{G}$ $(\ldots TGT\bar{G}TGTTTGT\bar{G}TG\ldots)$[18] or they may exist at the interspherulitic boundaries between forms II and III.[19] The consideration of requiring the existence of a nucleus for acceleration of the phase transition may also be

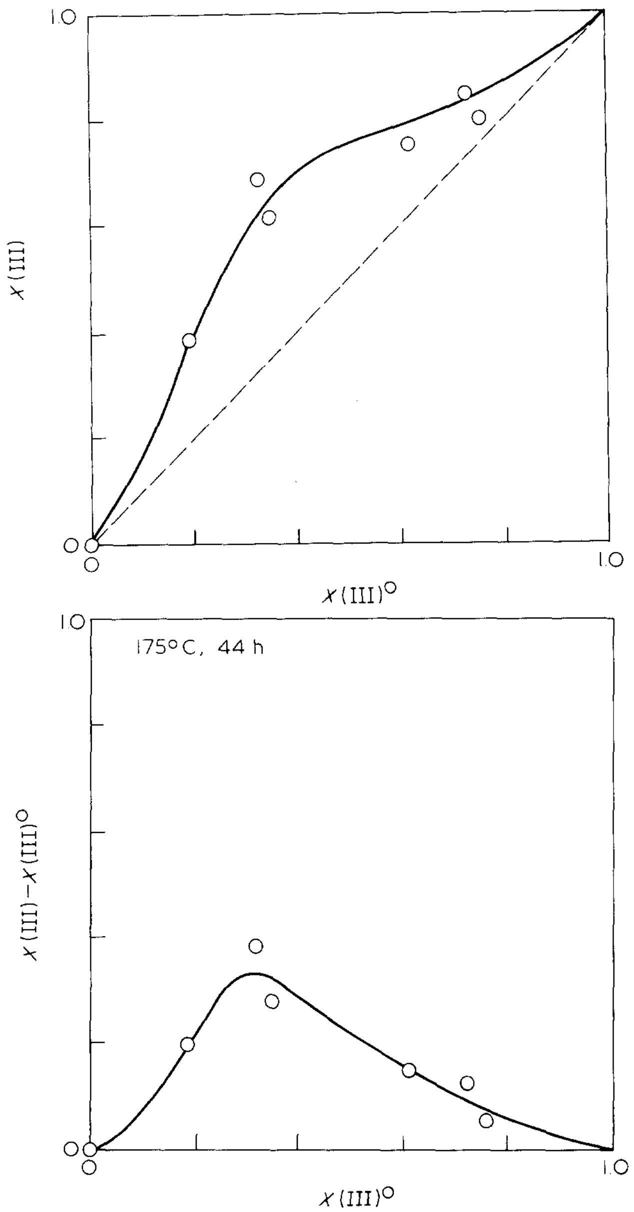

Figure 7 Dependence of mole fraction X(III) of PVDF form III produced by the thermally induced structural change from form II to form III upon the initial content X(III)^0 of form III contained in the original samples

applied to the present case of form I to form III. The more explicit observation of phase transition from form I to form III for the poled sample implies that the poling process may promote the production of such nuclei; for example, the poling treatment may generate some *gauche* sequences within the long *trans* sequences, as a kind of kink structure[20], by twisting the all-*trans* chain into the direction of the electric field, and such *guache* segments of T_3G may act as a nucleus for the conformational transformation from form I to form III. In the case of an unpoled sample, such nuclei necessary for transformation may be generated by the thermal agitation of the all-*trans* conformation at high temperature. Then the whole system may be appreciably disordered even after the crystalline transformation from form I to form III, this being a reason why the crystallization-sensitive bands of form III were difficult to detect in the high-temperature i.r. spectra of the unpoled sample, although the interchange of *trans* and *gauche* band intensities could be observed and the polarized form III spectra were obtained as shown in *Figure 3*.

Spectral changes induced by other thermally occurring structural changes of PVDF form I

As shown in *Figure 6* the i.r. spectra of PVDF form I (poled sample) show the specific changes in the temperature regions other than the above-mentioned ones.

(i) 70°C: The temperature corresponds to the crystalline dispersion point of form I[21], where the decrease in intensity of crystallization-sensitive band (445 cm^{-1}) and the intensity increment of *gauche* band originating from amorphous or disordered structure (745 cm^{-1}, abbreviated as disordered *gauche* band) are observed[22]. The polarization of the latter band begins to be recognized.

(ii) 140°C: At this point a further decrease in intensity of *trans* crystalline band and an increment of disordered *gauche* band intensity are observed. The remanent polarization of the poled film is reported to become very small but does not disappear completely[3,23]. In the temperature regions of (i) and (ii), the X-ray diffraction pattern is essentially of all-*trans* type, though the relative intensities of reflections are appreciably changed[15].

(iii) 170°C: A steep disappearance of crystalline *trans* bands and the appearance of crystalline form III bands are observed. The disordered *gauche* band decreases transiently in intensity. At 175°C these spectral changes become maximal. The i.r. polarization is still reserved. The X-ray pattern also changes drastically[15], indicating the crystal structural transformation, consistent with the vibrational observation explained in the previous section.

(iv) 181°C: All the crystalline bands disappear completely, just when the i.r. polarization cannot be detected for all the bands. The intensity of disordered *gauche* band increases greatly.

In parallel with these intensity changes, the degree of orientation of CH_2CF_2 dipoles of the zigzag chain is also observed to change in the temperature ranges stated above. We started from the sample subjected to the poling treatment, which has some degree of parallel arrangement of *trans* dipoles into the direction normal to the film surface, and measured the lowering of the degree of dipole orientation as a function of temperature. In *Figure 8* is shown the temperature dependence of a quantity $p = D_{\perp}(\nu_s)/D_{\perp}(\nu_{as})$, where $D_{\perp}$ means the i.r. absorbance component measured with the electric vector of the incident i.r. beam perpendicular to the chain direction and ν_s and ν_{as} represent the CH_2 symmetric and antisymmetric stretching modes, respectively. The ratio p is a measure of the degree of orientation of *trans* chain dipoles in the plane perpendicular to the chain direction: a completely parallel alignment of dipoles along the external electric field or along the normal to the film surface gives a value of $p = 0$ and the value becomes larger as the degree of orientation is lowered. As shown in *Figure 8*, the value of p is found to increase greatly in the vicinity of 70°C and 140°C, where the changes in vibrational band intensity are observed as described above and the mechanical and dielectric parameters have also been reported to change[21]. The lowering of the degree of parallel alignment of dipoles at 70°C was already reported by Odajima *et al.*[24] based on the X-ray diffraction method and was

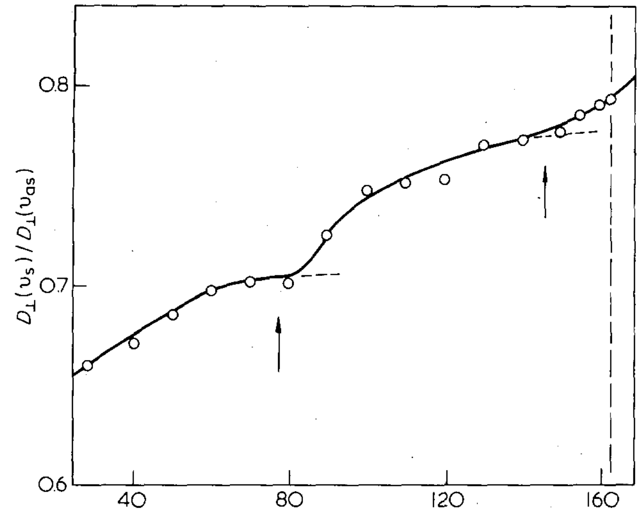

Figure 8 Temperature dependence of $D_\perp(\nu_s)/D_\perp(\nu_{as})$ for poled PVDF form I. The notation $D_\perp$ is defined in the text

related to the decrease in macroscopic piezoelectric constant e_{33}.

Interpretation of these observations of *Figures 6* and *8* along with the mechanical and electrical data published so far[3,21–24] allows us to consider the following structural changes occurring in the sample in the various temperature ranges. At 70°C the disordered *gauche* segments, with some degree of orientation along the draw direction, begin to increase at, for example, the defective points of the crystallites or the interfaces of crystal and amorphous regions. Simultaneously the *trans* segments decrease their relative amounts and the parallel dipole alignment in the plane perpendicular to the chain direction is disordered. At 140°C the large-scale rotational motion of chains begins to occur, accompanied by an appreciable increase in the amount of *gauche* segments. These *gauche* segments show clear i.r. polarization and so are considered to be generated within the oriented crystallites. In the vicinity of 170°C, the crystal phase transition from form I to form III begins to occur with conformational change from *trans* to *gauche* forms. Some parts of *disordered gauche* segments are organized into the *ordered gauche* sequences (i.e. T_3G regular conformation) as understood from the transient decrease in 745 cm^{-1} i.r. band intensity. Above 180°C, the crystallites melt and disappear.

Yoon *et al.*[3] assigned the point 140°C to the Curie temperature of PVDF form I from the measurement of remanent polarization. But the remanent polarization has been reported to become not completely zero at this temperature[3,23], and the piezoelectric constant d_{31} also does not reduce to zero and shows thermally stable behaviour up to 150°C[25]. The temperature 140°C is rather considered to be a disordering point of *trans*-dipole orientation induced by the large increment of *gauche* segments within crystallites as discussed above. The Curie point of PVDF form I *crystal* should be considered to be located at about 172°C as discussed in the previous section. The temperature 140°C seems too low, when compared with the transition curve of *Figure 2*, to interpret PVDF form I as an ultimate member of a series of ferroelectric VDF–TrFE copolymers.

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