Structural changes in ferroelectric phase transitions of vinylidene fluoride–tetrafluoroethylene copolymers: 1. Vinylidene fluoride content dependence of the transition behaviour

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Structural changes occurring in the ferroelectric phase transitions of vinylidene fluoride–tetrafluoroethylene (VDF–TFE) copolymers with VDF contents of 81–0 mol% have been investigated by X-ray diffraction and i.r. and Raman spectroscopies. In a VDF 81%–TFE sample, the conformational change between the *trans* (low temperature) and *gauche* (high temperature) phases occurs in the temperature region close to the melting point with thermal hysteresis. The VDF 75%–TFE sample shows a similar transition between the low and high temperature phases but via the disordered cooled phase: the behaviour is close to that observed for vinylidene fluoride–trifluoroethylene (VDF–TrFE) copolymer with VDF 65 mol%. As the VDF content decreases, the transition becomes more diffuse: for the VDF 64%–TFE sample the *trans–gauche* conformational change occurs gradually over a wide temperature region with almost no detectable hysteresis. The X-ray fibre diagram taken at room temperature is of the cooled phase, which reversibly transfers into the low temperature phase by the application of tensile force. The same phenomenon is observed for VDF–TrFE copolymer with VDF 37%. In this way the transition behaviour of VDF–TFE copolymers with VDF contents of 60–80% corresponds to that of VDF–TrFE copolymers with *lower* VDF content. As the VDF content decreases, the low temperature phase is stabilized more due to the effect of the TFE monomeric units. The as-drawn VDF 41%–TFE sample shows an X-ray fibre pattern characteristic of the low temperature phase, which transforms irreversibly to the cooled phase by heating above 110°C. Tensile force causes the transition to the original low temperature phase irreversibly. VDF 23%–TFE sample exists in the stable 'untilted' all-*trans* chain conformation above room temperature. Below −40°C, the X-ray fibre diagram changes into an overlap of the patterns of the poly(vinylidene fluoride) planar zigzag structure and of the poly(tetrafluoroethylene) helical structure. The transitional behaviour has been discussed in comparison with that of VDF–TrFE copolymers and the factors governing these structural phase transitions have been investigated.

(Keywords: vinylidene fluoride–tetrafluoroethylene copolymers; ferroelectric phase transition; X-ray diffraction; i.r. spectra; Raman spectra; monomer composition)

INTRODUCTION

Recently a lot of attention has been paid to fluorine polymers because of their excellent electrical properties, such as dielectricity, piezoelectricity and pyroelectricity[1–3]. Among these polymers, poly(vinylidene fluoride) (PVDF), in particular, crystal form I, is the most important in connection with its ferroelectric property[4,5]. In general ferroelectric materials are characterized by dipole inversion under an electric field and ferroelectric phase transition. Many experiments confirmed the ferroelectricity of the PVDF form I crystal phase: inversion current[2,3]; D-E hysteresis loop[2,3]; and reorientation of the polar *b*-axis under an electric field[6–13]. On the other hand, the ferroelectric phase transition had been sought through measurements of the temperature dependence of the dielectric constant, electric polarization, etc., but with ambiguous results[14–17]. About a decade ago, a clear ferroelectric phase transition was discovered for the vinylidene fluoride–trifluoroethylene (VDF–TrFE) copolymer[18–20]: this was the first time such a transition had been found for synthetic polymer materials. Since then many investigations have been carried out to clarify the relationship between the structure and physical properties of this copolymer.

As discussed later, the structure and phase transition behaviour of this copolymer changes remarkably depending on the sample preparation conditions and the VDF molar content. In other words the introduction of TrFE monomer units into the PVDF chain causes a large perturbation on the structural phase transition in the VDF chains. Such a consideration makes us speculate that a substitution of TrFE units by other types of comonomer might modify the phase transitional behaviour observed in the VDF–TrFE copolymers. In

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fact the copolymers of VDF and tetrafluoroethylene (TFE) were found to show a ferroelectric phase transition similar to but different from that of the VDF–TrFE samples[21–26]. The X-ray diffraction measurements have already been reported for a series of VDF–TFE copolymers by Lovinger *et al.*[21–23]. They measured mainly the temperature dependence of the (200, 110) lattice spacing and determined some roles of the TFE units in the ferroelectric phase transition. Green and Rabolt measured the temperature dependence of the Raman spectra for the VDF 81% copolymer sample and found a *trans–gauche* conformational change which is essentially the same as that observed in VDF–TrFE copolymers[24]. However the detailed structural characteristics and the transitional behaviour of VDF–TFE copolymers have not been clarified so well as in the case of VDF–TrFE copolymers. A comparison of the transitional features between these two types of copolymer will provide important information for the understanding of the ferroelectric phase transition of fluorine copolymers in a more organized and systematic way. In this paper the structural changes occurring in the phase transition will be investigated in detail for a series of VDF–TFE copolymers with various VDF contents by means of X-ray diffraction and i.r. and Raman spectroscopies. The results obtained will be compared with those of the VDF–TrFE copolymers with similar VDF contents, from which the factors governing the phase transition will be extracted.

CHARACTERISTIC FEATURES OF STRUCTURAL PHASE TRANSITIONS IN VDF–TrFE COPOLYMERS

A review of the transitional behaviour of VDF–TrFE copolymers will help us to understand the characteristic features observed for the VDF–TFE copolymers discussed below.

Structural characteristics[27–33]. One of the most characteristic structural features in this transition is a large conformational change of the chains between the *trans* and *gauche* forms. The planar zigzag molecular chains of the low temperature ferroelectric phase transfer into *gauche*-type molecular chains in the high temperature paraelectric phase constructed by statistical combination of TG, $T\bar{G}$, T_3G and $T_3\bar{G}$ rotational isomers along the chain axis. Such a large conformational change results in the disappearance of electrical polarization at high temperature[3], the softening of the Young's modulus and elastic constants[34–37], the dimensional change of the bulk samples[38,39], the large change in the thermal conductivity[40], etc.

VDF content dependence of transitions[27,30,31,33]. The transitional behaviour depends sensitively on the VDF content of the copolymers. For VDF–TrFE copolymers with VDF content >70 mol%, a clear and discontinuous transition occurs over a relatively narrow temperature region, attendant with a large thermal hysteresis, i.e. a thermodynamically first-order transition. As the VDF content increases towards 100 mol%, the Curie temperature increases and gradually approaches the melting point. In the PVDF homopolymer, the *trans–gauche* conformational change occurs in the temperature region quite close to the melting point and overlaps partly with the melting phenomenon[41–43]. For VDF 50–65% copolymers, two kinds of ferroelectric *trans* phase coexist at room temperature, the relative amounts of which depend on the VDF content as well as on the sample preparation conditions. One is the so-called low temperature phase where the *trans* zigzag chains are packed regularly in the compact unit cell, just as in the PVDF form I crystal. The other is the cooled phase with an irregular structure. The characteristic features of the X-ray fibre pattern of the cooled phase are the shift of the reflection positions from the horizontal layer lines, i.e. the so-called tilting phenomenon of the polymer chains and the diffuseness of the reflections compared with those of the low temperature phase. According to X-ray structural analysis[32], this phase exhibits a kind of superstructure consisting of a statistical aggregation of domains. The unit cell structure of each domain is essentially the same as that of the low temperature phase. The *trans* zigzag chains tilt from the draw axis by ~18° in the (130) plane. The domain boundary is composed of a sequence of *trans* and *gauche* bonds. Application of tension or high electric field changes the *gauche* boundary linkage to the *trans* structure, resulting in the transformation from the irregular and tilted cooled phase to the regular and extended low temperature phase. Inversely, heating causes the transition from the *trans* to *gauche* form and then the low temperature phase changes into the high temperature phase via the cooled phase. The high temperature phase does not transfer back to the low temperature phase but to the cooled phase because of a 'freezing-in' of some *gauche* bonds between the long *trans* segments. For the copolymer sample of VDF 0–40%, the low temperature phase is no longer detectable under the usual conditions: at room temperature the cooled phase transfers into the low temperature phase only under tension[32,33] or under high electric field[44,45]. The phase transition between the cooled phase and the high temperature phase occurs gradually over a wide temperature region. The transformation from *trans* to *gauche* form is localized in the VDF sequence and the TrFE segments remain in the *trans* form even at high temperature. That is to say, the conformational change occurs imperfectly[46]. In the VDF 0% copolymer or polytrifluoroethylene (PTrFE), the conformational transition does not occur.

EXPERIMENTAL

Samples

The samples used were VDF–TFE random copolymers with VDF molar contents of 81, 75, 64, 41, 23 and 0% (Daikin Kogyo Co. Ltd, Japan). The melting points measured by d.s.c. (5°C min^{-1}) are given in *Table 1*. Unoriented films of the VDF 81–23% contents were prepared by casting from acetone solution at room temperature. Oriented films of the VDF 81–64% copolymers, used in the i.r. measurements, were prepared by stretching the unoriented films three to five times the original length at room temperature. Oriented films of VDF 41 and 23% copolymers were difficult to prepare

Table 1 Melting points for the VDF–TFE copolymers

VDF (%)	81	75	64	41	23	0
Melting point (°C)	124	128	160	215	280	325

by stretching the as-cast films and they were prepared by rolling the original powder specimens at room temperature. Oriented rod samples used in the Raman and X-ray diffraction measurements were prepared by drawing melt-quenched samples at a high temperature.

I.r., Raman and X-ray measurements

The i.r. spectra were obtained using Japan Spectroscopic Co. (JASCO) FT/IR 5MP- and 8000-type Fourier-transform i.r. spectrophotometers in the frequency range of 4000–400 cm^{-1}. The temperature dependence of the i.r. absorption spectra was measured using a high temperature optical cell (20–300°C) and a cryostat (−150 to +260°C) with temperature fluctuation of <0.5°C. The Raman spectra were measured by a JASCO R-500 Raman spectrophotometer equipped with a heating cell or a cryostat. The 514.5 nm line from an Ar^{+} ion laser was used as an excitation light source. The X-ray fibre patterns were taken by a cylindrical camera with an incident X-ray beam of the Cu-Kα line. The X-ray photographs at high temperature were taken using a home-made heating cell. The low-temperature X-ray fibre diagrams were taken by blowing cooled nitrogen gas onto the sample. The temperature dependence of the X-ray diffraction curves was measured using a Rigaku Rotaflex goniometer system.

RESULTS AND DISCUSSION

VDF 81%–TFE copolymer

The X-ray fibre diagram taken at room temperature indicates that this copolymer exists in the crystal form of the low temperature phase, essentially the same as that of PVDF form I[47]. *Figure 1* shows the temperature dependence of the polarized i.r. spectra measured for the oriented VDF 81% sample. In *Figure 2* the i.r. absorbance, reduced by the value at room temperature, is plotted against temperature. The bands characteristic of the *trans* conformation in the VDF sequence are observed at 1323, 842, 510 cm^{-1}, etc.[10,48,49]. In the heating process, these *trans* bands decrease in intensity largely at the transition point located just below the melting temperature. Correspondingly, the 925 cm^{-1} i.r. band and the 810 cm^{-1} Raman band, which are attributed to the *gauche* form[48,49], increase in intensity at the transition point with the polarization reserved. These crystalline *gauche* bands disappear above the melting point. An apparent maximum in the intensity *versus* temperature curve of the i.r. *gauche* band indicates a partial overlap of the *trans*-to-*gauche* solid-state transition with the melting process (*Figure 2*). In the cooling process from the melt, the *gauche* band appears first and transfers into the *trans* form, being observed as the peak of the intensity–temperature curve of the *gauche* band and the corresponding steep increase of the *trans* band intensity. Such behaviour observed in the i.r. and Raman spectra is consistent with the X-ray results reported by Lovinger *et al.*[21–23]. *Figure 3* shows the i.r. spectral pattern in the region of 550–700 cm^{-1}, where the 610 cm^{-1} *gauche* band is found to appear at high temperature. This *gauche* band is also observed typically for PVDF forms II and III[49]. The i.r. 619 cm^{-1} band and the Raman 833 cm^{-1} band are assigned to the vibrational modes characteristic of the TFE sequence or the boundary between VDF and TFE segments (see later). Different to the bands intrinsic of VDF segments, these TFE bands gradually decrease in intensity even in the *trans–gauche* transition region and disappear above the melting point. This tendency can be detected more clearly for copolymers with lower VDF contents, as shown below.

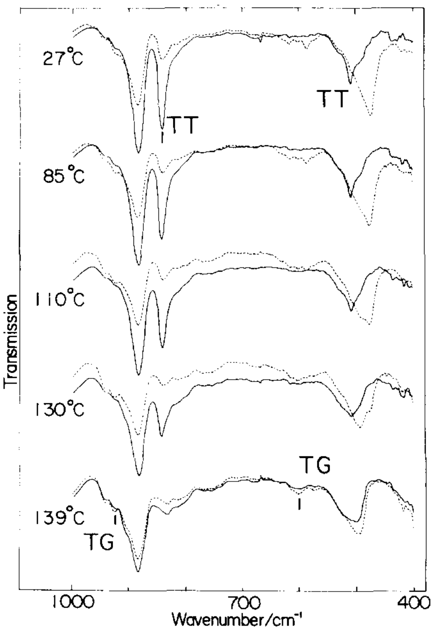

Figure 1 Temperature dependence of the polarized i.r. spectra of VDF 81%–TFE copolymer: (——) electric vector ⊥ orientation direction; (– – –) electric vector ∥ orientation direction

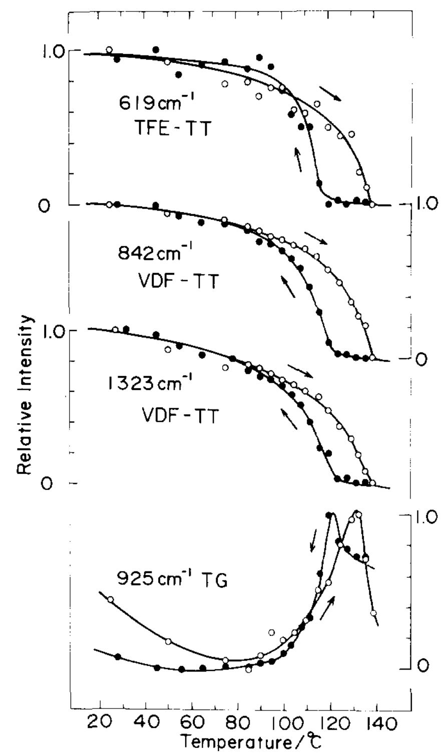

Figure 2 Temperature dependence of the reduced absorbance of the various i.r. bands of VDF 81%–TFE copolymer

VDF 75%–TFE copolymer

Figure 4 shows the temperature dependence of the lattice spacing of (200, 110) planes measured for the VDF

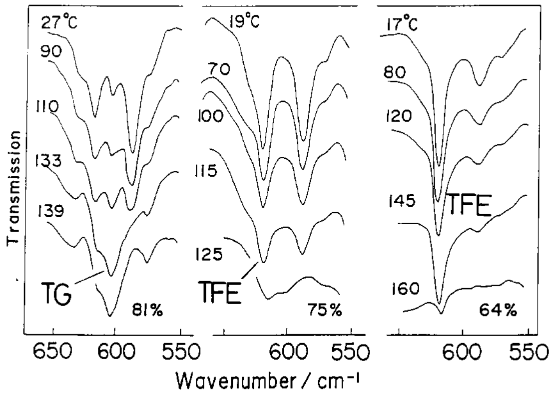

Figure 3 Temperature dependence of the i.r. spectra of the VDF 81, 75 and 64%-TFE copolymers in the frequency region of 550–700 cm^{-1} (heating process)

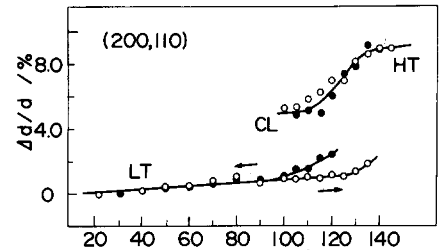

Figure 4 Temperature dependence of the lattice spacing $d(200, 110)$ measured for the unoriented VDF 75%-TFE copolymer. The value at room temperature is taken as a standard

75%-TFE sample. As the temperature rises, the reflection intensity of the low temperature phase decreases and a new reflection begins to appear and gradually shifts its position. In the high temperature region, a single reflection is observed, the position of which corresponds to that of the high temperature phase. This behaviour is very similar to that observed for the unoriented VDF 65%-TrFE copolymer[33]; the low temperature phase and the cooled phase coexist at room temperature and the transition occurs between the low and high temperature phases via the cooled phase. *Figure 4* indicates therefore that the unoriented VDF 75%-TFE copolymer may experience a transition similar to that of the VDF 65%-TrFE sample by the following route:

$$\text{low temperature phase} \overset{\text{discontinuous}}{\rightleftharpoons} \text{cooled phase} \overset{\text{continuous}}{\rightleftharpoons} \text{high temperature phase}$$

Confirmation of this transition route can be made more clearly for the uniaxially oriented sample of the VDF 41%-TFE copolymer, as discussed later.

The temperature dependence of the Raman spectra measured for the unoriented VDF 75% sample is shown in *Figure 5*. As temperature increases, the *trans* band at 839 cm^{-1} decreases in intensity while the *gauche* band at 805 cm^{-1} increases. The intensity of the band at 822 cm^{-1}, which is assignable to the VDF–TFE boundary, remains almost unchanged. *Figure 6* shows the temperature dependence of the polarized i.r. spectra in the heating and cooling processes. The reduced absorbances of the bands are plotted against temperature in *Figure 7*. As in the VDF 81%-TFE sample, the *trans* bands at 842 and 1325 cm^{-1} decrease in intensity and the *gauche* band at 926 cm^{-1} (and 610 cm^{-1}) increases with the polarization characters reserved. The apparent maximum at ~125°C indicates competition between the *trans*-to-*gauche* transformation and the melting process. A similar maximum can also be observed in the cooling

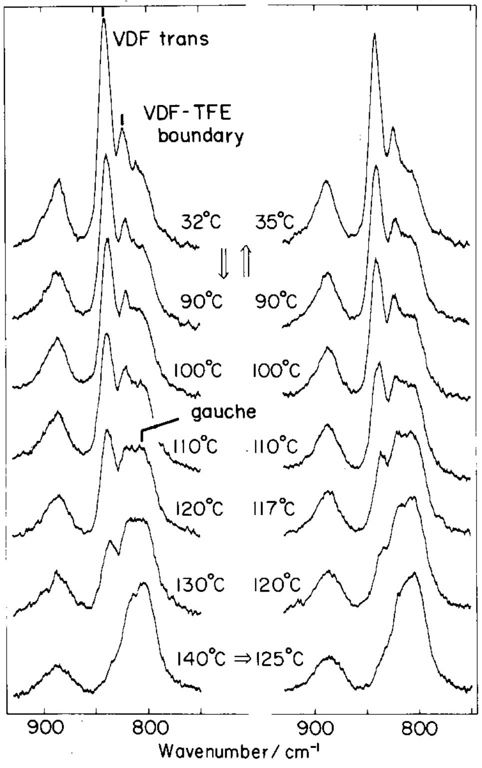

Figure 5 Temperature dependence of the Raman spectra of VDF 75%-TFE copolymer in the frequency region 700–1000 cm^{-1}

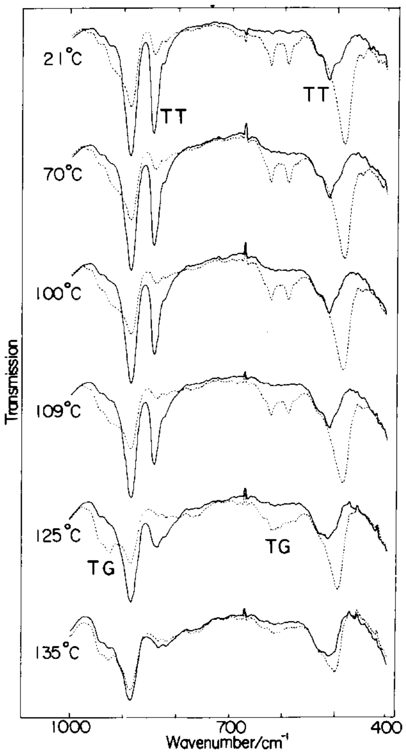

Figure 6 Temperature dependence of the polarized i.r. spectra of VDF 75%-TFE copolymer in the heating process: (——) electric vector ⊥ orientation direction; (- - -) electric vector ∥ orientation direction

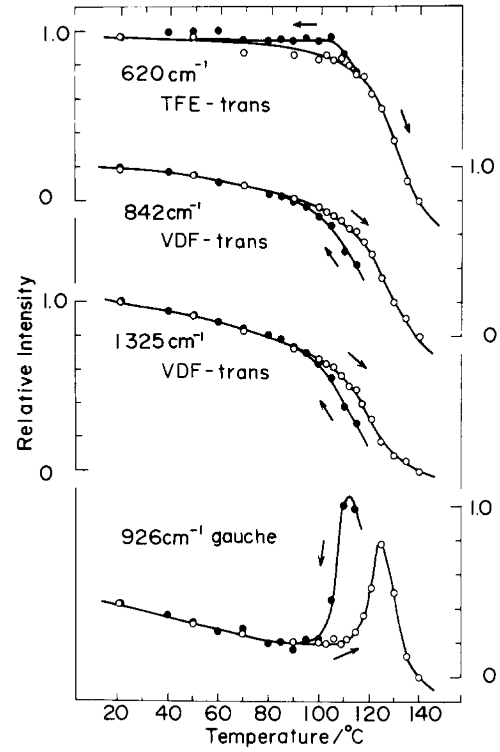

Figure 7 Temperature dependence of the reduced i.r. absorbance of the various bands of VDF 75%–TFE copolymer

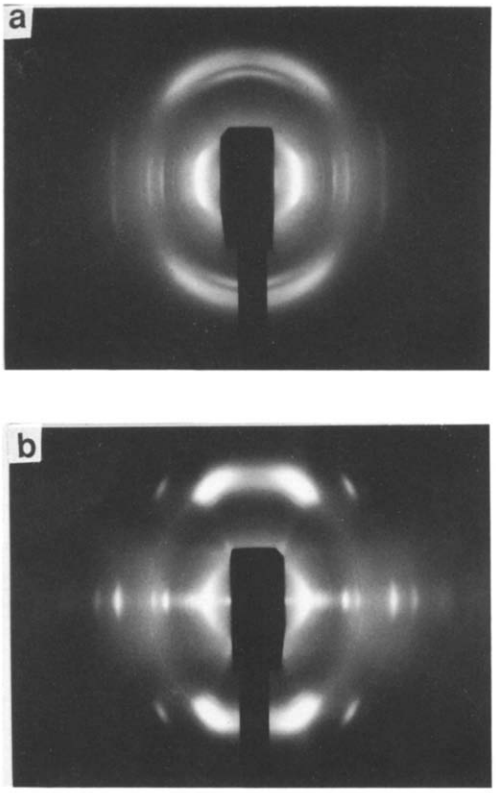

Figure 8 X-ray fibre diagram of the VDF 64%–TFE copolymer taken under (a) relaxed and (b) strained conditions at room temperature

process: crystallization occurs in the crystalline form of the high temperature *gauche* phase and then the *gauche*-to-*trans* structural transition is observed in the lower temperature region. This is consistent with the X-ray results in *Figure 4*.

VDF 64%–TFE copolymer

Different from the VDF 75%–TFE sample, the X-ray fibre diagram of the uniaxially oriented VDF 64% sample shows the pattern of the cooled phase at room temperature (*Figure 8a*)[33]. This cooled phase transfers into the low temperature phase by applying a tensile strain of 5–10% but returns immediately into the original cooled phase when the tension is relaxed (*Figure 8b*). Such a stress-induced transformation between the cooled phase and the low temperature phase has been observed mainly for the VDF–TrFE copolymer with VDF content $<40\%$[33].

The temperature dependences of the polarized i.r. and Raman spectra are shown in *Figures 9* and *10*, respectively. *Figure 11* plots the temperature dependence of the polarized i.r. absorbance of the various bands. The bands characteristic of the VDF *trans* sequence at 835 and 1340 cm^{-1} gradually decrease in intensity over a wide temperature range. The thermal hysteresis between the heating and cooling processes is almost undetectable. The polarized i.r. band at 939 cm^{-1} and the 800 cm^{-1} Raman band increase their intensity at high temperature but the rate of the increment is quite low compared with the VDF 81 and 75% samples (the steep increase around 150°C is due to the crystal melting). The 621 cm^{-1} i.r. band and the 820 cm^{-1} Raman band, characteristic of the TFE segmental parts, hold their polarization character and do not show a large intensity change during the *trans–gauche* conformational transition in the VDF sequences and decrease in intensity for the first time above the melting point (*Figures 3* and *9*). From these figures it may be said that the *trans–gauche* conformational change of the VDF 64%–TFE sample occurs only partly over a wide temperature region and the TFE segments remain essentially in a *trans* form over the whole

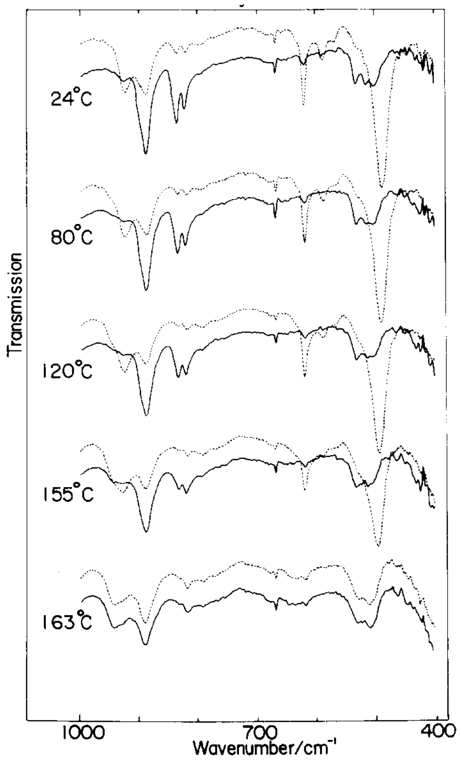

Figure 9 Temperature dependence of the polarized i.r. spectra of VDF 64%–TFE copolymer: (——) electric vector ⊥ orientation direction; (– – –) electric vector ∥ orientation direction

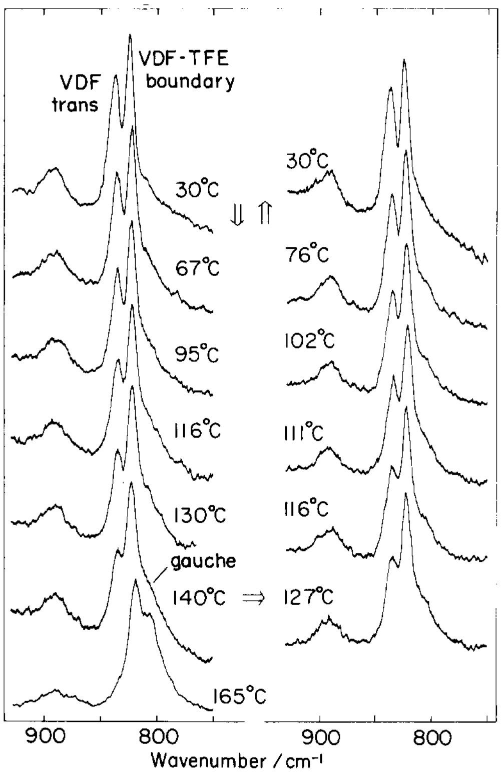

Figure 10 Temperature dependence of the polarized Raman spectra of VDF 64%–TFE copolymer

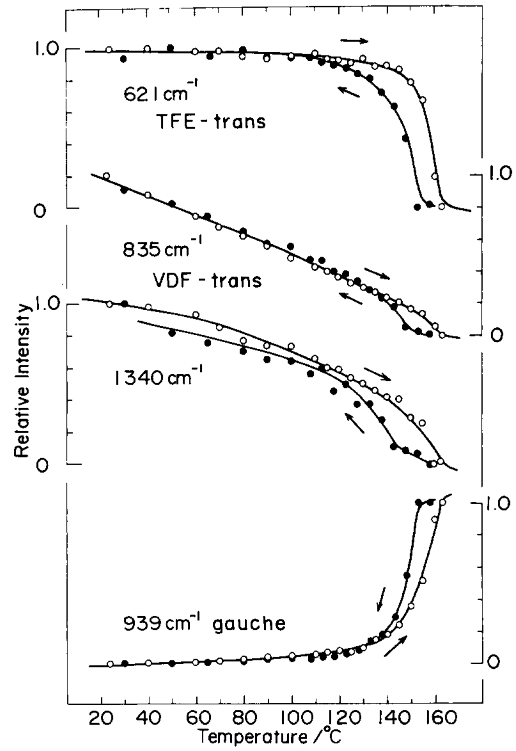

Figure 11 Temperature dependence of the reduced i.r. absorbance of the various bands of VDF 64%–TFE copolymer

temperature region below the melting point. In other words, in the high temperature region the long *trans* sequences are considered to spread over the VDF and TFE segments and only a small amount of *gauche* bonds are generated between these *trans* chain segments. The X-ray fibre pattern taken at 140°C is consistent with this structural model; the pattern is still of the cooled phase although the layer lines become diffuse possibly because of a conformational disordering along the chain axis.

Comparison between the TFE and TrFE copolymers with VDF 60–80%

Figure 12 shows the temperature dependence of the i.r. *trans* band intensity of the VDF–TrFE and VDF–TFE copolymers with similar VDF contents. For the copolymers with high VDF content, the *trans–gauche* conformational change is observed relatively sharply in a definite transition temperature region. The transition point is very close to the melting point for the VDF–TFE copolymers and the hysteresis is appreciably smaller than that of the corresponding VDF–TrFE copolymer. As the VDF content decreases, the transition occurs gradually over a wide temperature region and the thermal hysteresis becomes smaller. In more detail, the conformational change becomes less perfect and occurs only partly in the VDF segments. The TFE and TrFE segments remain in a *trans* form. Such a tendency is typically seen for the VDF 64%–TFE sample, which is rather similar to that

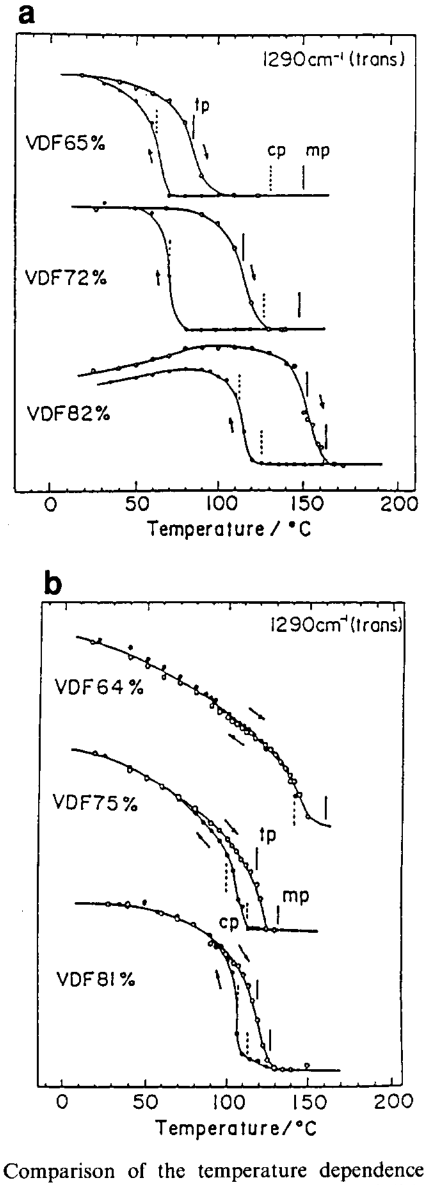

Figure 12 Comparison of the temperature dependence of the i.r. intensity (*trans* band) between (a) VDF–TrFE and (b) VDF–TFE copolymers: mp, melting point; cp, crystallization point; tp, transition point

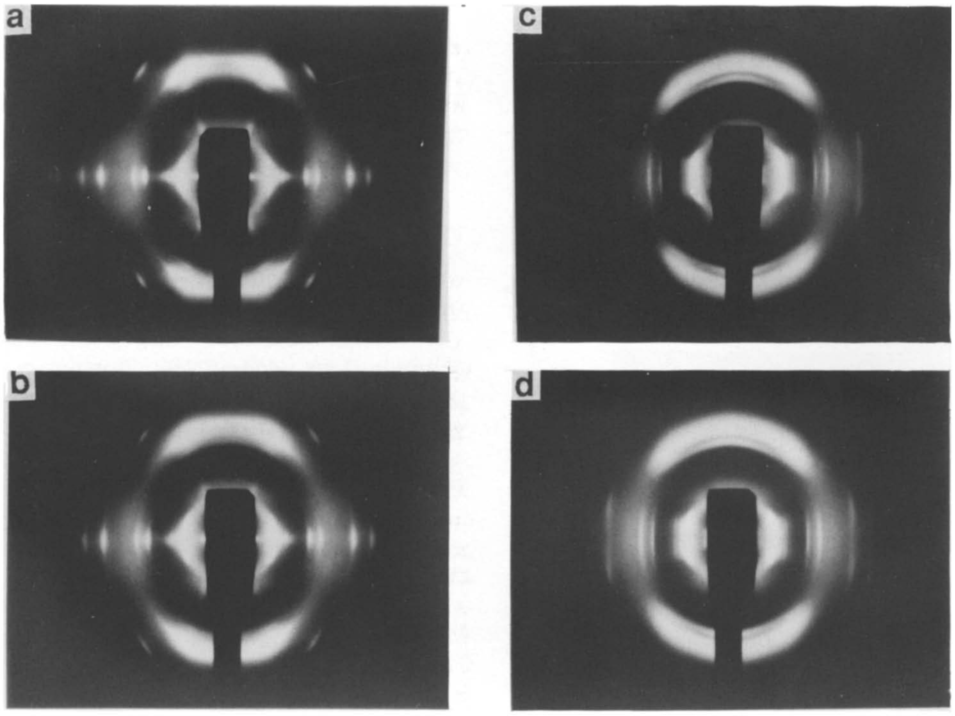

Figure 13 Dependence of the X-ray fibre diagram of VDF 41%–TFE copolymer on the annealing temperature: (a) unannealed; (b) 100°C; (c) 120°C; (d) 150°C. Measurements were made at room temperature

of the VDF–TrFE copolymer with VDF 37% content[33]. The cooled phase of the VDF 64%–TFE copolymer transforms to the low temperature phase only under the application of the tensile force. This is also coincident with the behaviour of the VDF 37%–TrFE copolymer. In a similar way, the temperature dependence of the X-ray reflections of the VDF 75%–TFE sample is close to that of the VDF 65%–TrFE sample (*Figure 4*)[33]. Summarizing these experimental facts allows us to say that the transitional behaviour of VDF–TFE copolymers with VDF 60–80% content corresponds to that of the VDF–TrFE copolymers with *lower* VDF content. A detailed discussion of this correspondence will be given later.

VDF 41%–TFE copolymer

As stated in the Introduction, all the VDF–TrFE copolymers with VDF content <40% show the X-ray fibre pattern of the cooled phase at room temperature[33]. Judging from the correspondence between the VDF 64%–TFE and the VDF 37%–TrFE copolymers, it should be naturally speculated that the VDF–TFE copolymers with VDF content <64% also exhibit the X-ray pattern of the cooled phase. The actually observed X-ray fibre diagram of the as-drawn VDF 41% sample gives the pattern of the low temperature phase with sharp reflections and no tilting phenomenon at room temperature. This sample transfers to the cooled phase on annealing above 110°C (*Figure 13*). This temperature is found to correspond to the phase transition point from the low temperature phase to the cooled phase as shown in *Figure 14*, where the temperature dependence of the X-ray fibre diagram is reproduced starting from the low temperature phase. The cooled phase begins to appear around 110°C overlapping with the original low temperature phase and the original low temperature phase disappears in the higher temperature region (see the change in the pattern in the equatorial and first-layer lines in *Figure 14*). After cooling the sample, only the cooled phase is observed at room temperature. Restretching this sample transfers the cooled phase into the original low temperature phase, which does not return to the cooled phase even when not under tension. The behaviour shown in *Figures 13* and *14* has been typically observed for the VDF–TrFE copolymer with VDF 55% content[32]:

$$\text{low temperature phase} \underset{\text{stretching}}{\overset{\text{heating}}{\rightleftarrows}} \text{cooled phase} \underset{\text{cooling}}{\overset{\text{heating}}{\rightleftarrows}} \text{high temperature phase}$$

The temperature dependence of the polarized i.r. spectra of the VDF 41%–TFE sample was measured in the high temperature region. The absorption intensities of the 836 cm^{-1} band (characteristic of the VDF *trans* sequence), the 824 cm^{-1} band (the VDF–TFE boundary) and the *gauche* band at ~930 cm^{-1} are plotted against temperature in *Figure 15*. With a rise in temperature the *trans* bands decrease in intensity and a deflection of the curves is found around 110°C, where the *gauche* band begins to increase in intensity. In the vicinity of 180–190°C, the 836 cm^{-1} band almost disappears and a decrease in the 824 cm^{-1} band intensity and an increase in the 930 cm^{-1} band intensity become steeper, suggesting partial melting of the crystalline region although the i.r. dichroism is still reserved.

Correspondence between the X-ray and i.r. data around 110°C is important to notice. The X-ray fibre pattern of the cooled phase begins to appear near 110°C (*Figure 14*) and the intensity of the *gauche* i.r. band begins to increase in the same temperature region (*Figure 15*). This correspondence is considered to support a

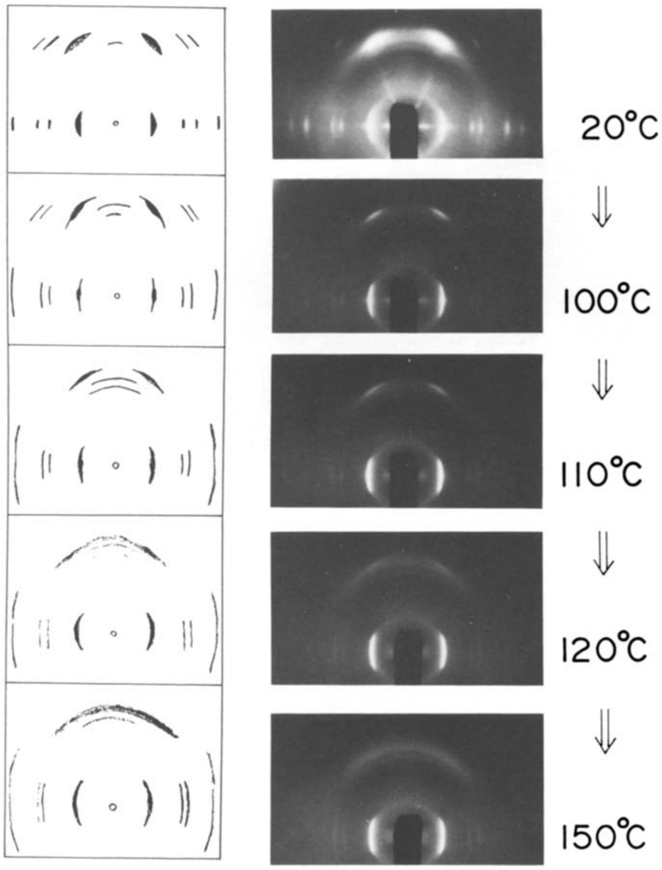

Figure 14 Temperature dependence of the X-ray fibre diagram of the as-drawn VDF 41%–TFE copolymer

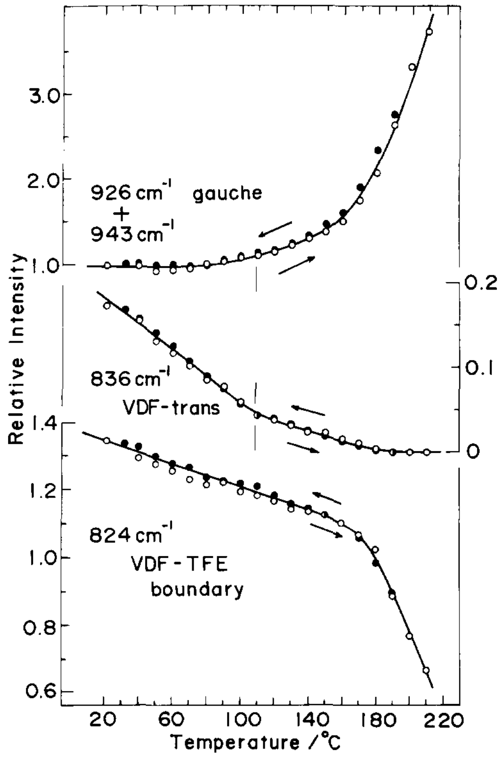

Figure 15 Temperature dependence of the i.r. absorbance of VDF 41%–TFE copolymer

mechanism proposed for VDF–TrFE copolymers; the cooled phase is generated at high temperature by the introduction of *gauche* bonds into long *trans* segments[32,33]. Besides, it is also checked that the tilting phenomenon characteristic of the cooled phase may be related to the existence of the *gauche* bonds generated within the *trans* zigzag skeletal chains. The 824 cm^{-1} band characteristic of the VDF–TFE boundary decreases the intensity gradually but without any deflection at $\sim$110°C and disappears steeply as the temperature approaches the melting point. This indicates that the VDF–TFE boundary (... VDF–VDF–*VDF–TFE*–TFE–...) remains in the *trans* conformation as pointed out above. In other words, the long *trans* sequences from the TFE and VDF–TFE boundary region can exist even at high temperatures. This is consistent with the X-ray fibre pattern taken at 190°C, which is essentially that of the *trans* phase although the layer reflections are broad and diffuse because of disorder in the conformation and packing modes.

VDF 23%–TFE copolymer

The X-ray pattern of the VDF 23% sample indicates the low temperature phase of the *trans* zigzag chain as seen in *Figure 16*; the typical reflection is the sharp (311, 021) reflection observed on the first layer line. In this X-ray photograph the diffuse reflections are detected at positions corresponding to the second, seventh and

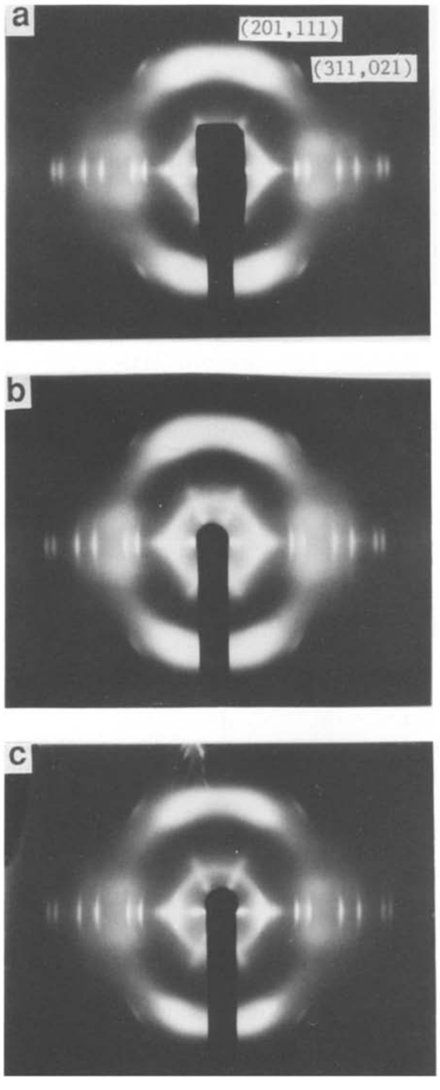

Figure 16 X-ray fibre diagrams of the VDF 23%–TFE copolymer annealed at different temperatures: (a) unannealed; (b) 100°C; (c) 200°C

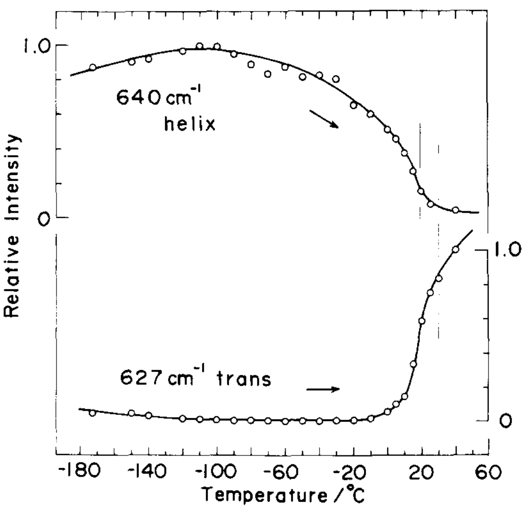

Figure 17 Temperature dependence of the reduced i.r. absorbance of PTFE sample

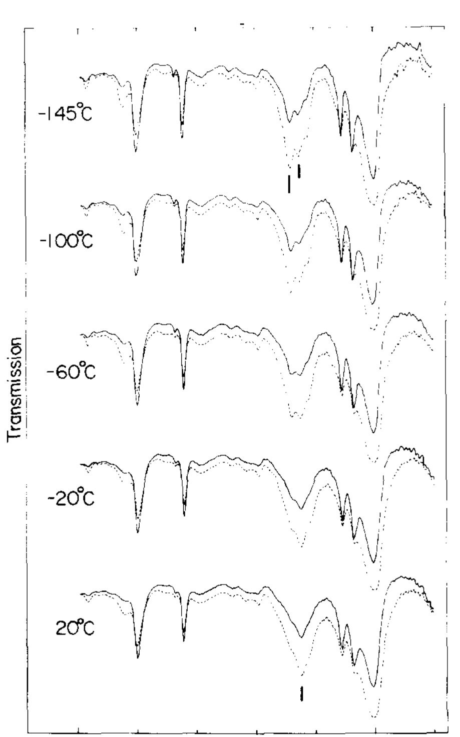

Figure 18 Temperature dependence of the polarized i.r. spectra of VDF 23%-TFE copolymer: (——) electric vector ⊥ orientation direction; (– – –) electric vector ∥ orientation direction

eighth layer lines of polytetrafluoroethylene (PTFE)[50]. In the case of the PTFE homopolymer, these X-ray reflections change to spots on cooling the sample to low temperature via the several stages of the phase transition. According to the X-ray structural analysis[50] and the i.r. and Raman spectral analyses reported so far[51,52], the PTFE chain experiences an active thermal motion attendant with large conformational change between the right- and left-handed helices via the *trans* zigzag conformation. This motion is considered to occur because of a very low potential energy barrier between the right- and left-handed helices[53]. The *trans* zigzag part behaves as a boundary between the right- and left-handed helical domains and the relative amount of this boundary region increases with a rise in temperature. This structural change was proposed on the basis of the vibrational spectral data[51,52]. In fact, as shown in *Figure 17*, the 627 cm^{-1} band of the *trans* sequence begins to steeply increase in intensity near 0°C and the 640 cm^{-1} band characteristic of the helical conformer decreases. At higher temperatures the spectral pattern becomes more like the *trans* type. The X-ray fibre diagram taken at 200°C supports this interpretation. The intense layer reflections observed at low temperature are smeared into the apparently single but diffuse reflection at high temperature, the position of which is close to that of the *trans* zigzag conformation[54].

Such a structural change in the TFE segments may be expected also to occur in the VDF 23% copolymer. At an ambient temperature, the TFE segment exists predominantly in the *trans* form but with some coexistence of helical form. This is supported by the i.r. spectral data. *Figure 18* shows the temperature dependence of the polarized i.r. spectra of the VDF 23% sample. As discussed elsewhere, the 625 cm^{-1} band, which increases in intensity with an increase in TFE content, is coincident with the peak position of the *trans* form of the PTFE homopolymer[51,52]. As seen in *Figure 18* this TFE *trans* band decreases gradually at lower temperature and the 642 cm^{-1} band characteristic of the TFE helical segment increases in intensity. *Figure 19* shows this situation clearly. While these bands characteristic of the TFE sequence exhibit an intensity exchange over a wide temperature range from 0 to −100°C, the VDF *trans* bands at 824 and 902 cm^{-1} change in intensity monotonically. This indicates a structural change occurring from the *trans* to helical form within the TFE monomer sequence, while the VDF sequences remain in the *trans* form. Such a structural change can also be detected in the X-ray photograph of the VDF 23%-TFE sample. *Figure 20* shows the X-ray fibre diagrams taken at room temperature and at −70°C. The diffuse reflections observed at room

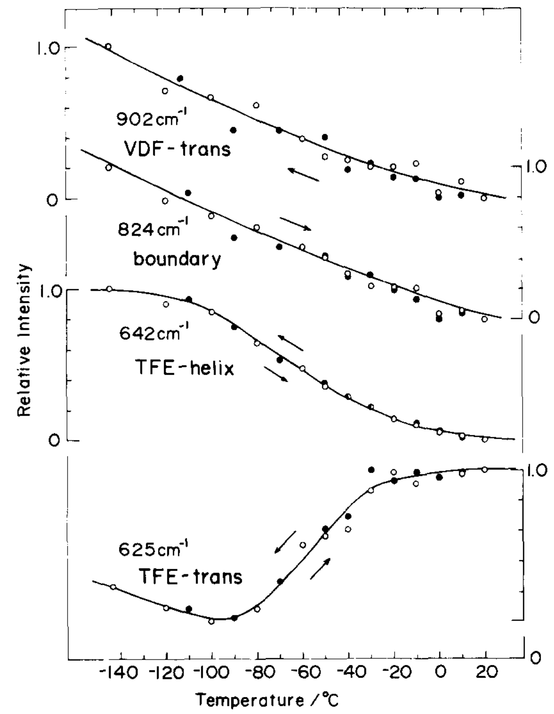

Figure 19 Temperature dependence of the reduced i.r. absorbance measured for VDF 23%-TFE copolymer

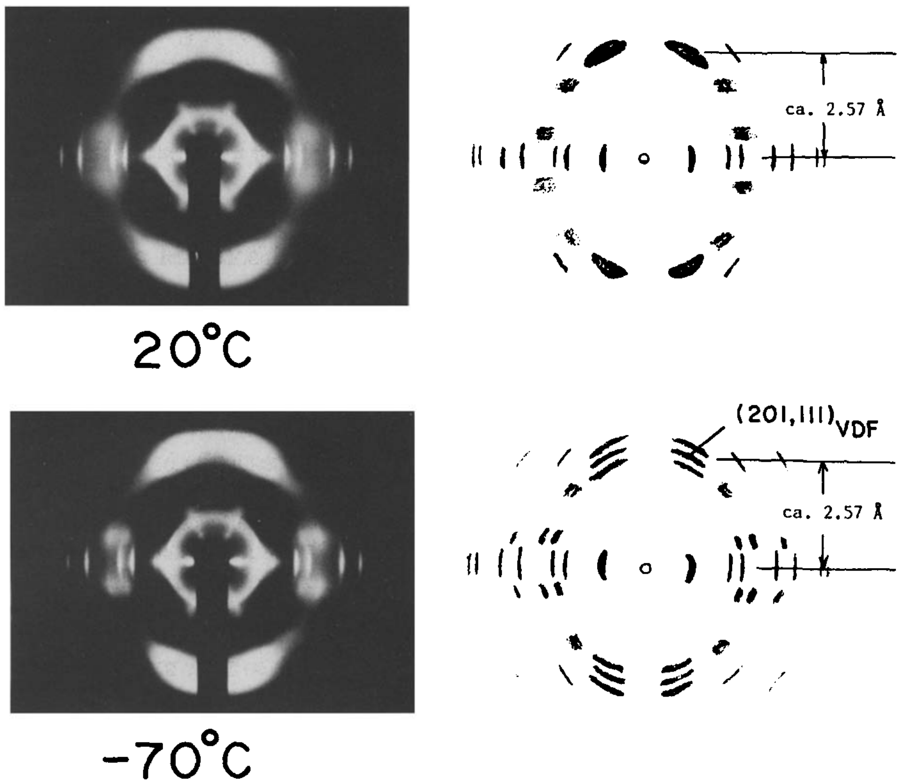

Figure 20 X-ray fibre diagrams of VDF 23%–TFE copolymer taken at 20°C and −70°C together with schematic diagrams

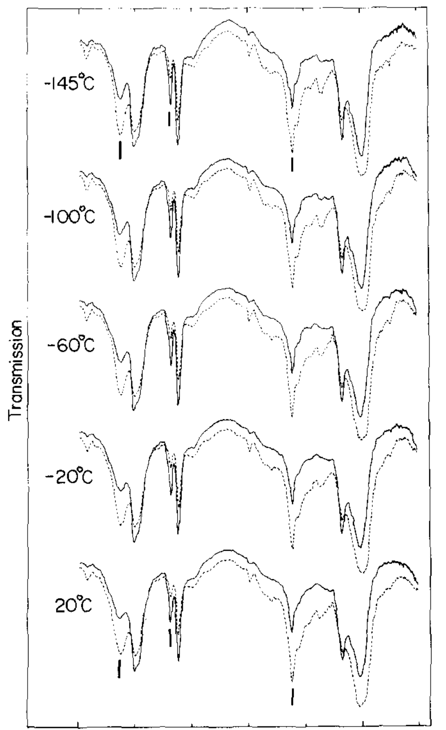

Figure 21 Temperature dependence of the polarized i.r. spectra of VDF 41%–TFE copolymer in the low temperature region

temperature become spot-like and the innermost intense reflection on the first layer line changes to a group of three sharp reflections, which were found to correspond to the reflections of the first layer line of the planar zigzag chain and the seventh and eighth layer lines of the uniform PTFE helical chain. Combining these i.r. and X-ray data, it may be said that a conformational change occurs in the TFE segments from *trans* to helical with keeping the *trans* form of the VDF sequence. Strictly speaking, the relative intensity of the (201, 111) reflection of the *trans* form at −70°C is lower than that measured at room temperature. This suggests a decrease in the *trans* content possibly because some VDF sequences are engulfed into the helical part, for example. It should be noticed here that the equatorial reflections are not a simple overlap of the differently positioned reflections coming from the independent VDF and TFE sequences but are unique for this copolymer. This indicates, as one plausible possibility, that both the *trans* zigzag and helical sequences are included in a coherent fashion within a unique unit cell, although we cannot now neglect another possibility such as phase separation to a PTFE-rich phase and a VDF-rich phase with a common basal lattice.

At high temperature, such as 200°C, the X-ray diagram becomes rather diffuse but still retains the *trans* pattern. In the i.r. spectra measured at high temperature the TFE *trans* band at 625 cm^{-1} is observed with a clear polarization character but the TFE helical band at 640 cm^{-1} is not observed. The *trans* bands of the VDF (902 cm^{-1}) and VDF–TFE boundary (824 cm^{-1}) decrease in intensity only gradually. These data indicate the predominant existence of the *trans* zigzag conformation at high temperature.

Such structural transformation in the TFE sequences detected for VDF 23%–TFE copolymer is not found for the VDF–TFE copolymers with VDF contents of >41%. The polarized i.r. spectra (*Figure 21*) and X-ray fibre diagram of the uniaxially oriented VDF 41%–TFE copolymer do not change their essential patterns even at low temperature but remain in the *trans* type (with tilting phenomenon). The short TFE segments are considered to be stabilized in the *trans* form by the restraining effect

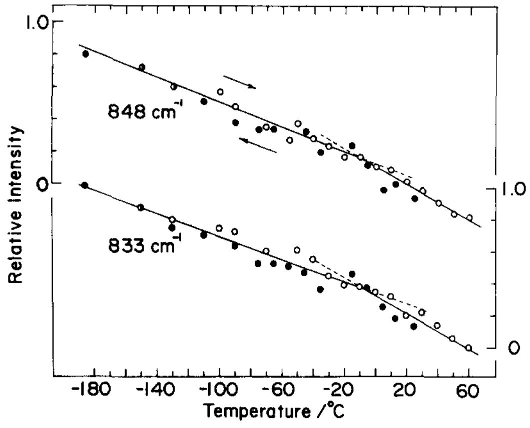

Figure 22 Temperature dependence of the i.r. absorbance of PTrFE sample

of neighbouring VDF *trans* sequences and therefore do not experience any such conformational change as observed for the VDF 23%-TFE sample having longer TFE sequences. This type of conformational change in TFE monomer sequences is not observed for the case of TrFE monomeric units. For example, *Figure 22* shows the temperature dependence of the i.r. absorbance measured for the 833 and 848 cm^{-1} bands of polytrifluoroethylene (VDF 0%-TrFE copolymer). No spectral change can be detected over the whole temperature region. Deflection from the linear lines detected near 0°C may be due to the occurrence of rotational motion of the chain in the crystalline region, as pointed out in references 33 and 55.

Comparison of the structure and phase transition between TrFE and TFE copolymers

As discussed above, the structure and phase transitional behaviour of the copolymer remarkably depend on the VDF content as well as on the type of comonomer (TrFE or TFE). *Figure 23* summarizes the characteristic features of the copolymers.

Crystal form at room temperature. Figure 24 shows the Weissenberg (00*l*) reflections taken at room temperature for a series of annealed VDF-TFE copolymers with VDF contents of 81-0%. The low temperature phase giving unsplit (00*l*) reflections is obtained at room temperature for annealed VDF-TFE copolymers with VDF contents of >75%. This is similar to the case of VDF-TrFE copolymers. In VDF-TrFE copolymers, the cooled phase with split (00*l*) reflections is obtained for a wide range of VDF content (0-50%). There exists a boundary in the vicinity of VDF 55-65%, where the cooled phase *coexists* with the low temperature phase. In VDF-TFE copolymers, on the other hand, the cooled phase appears for the sample with VDF content of 40-65%. In particular the behaviour of the VDF 64%-TFE sample is much different from the corresponding VDF 65%-TrFE copolymer sample. That is, the VDF 64%-TFE copolymer exists as the pure cooled phase (under no tension), which is rather similar to the behaviour of the VDF 37%-TrFE sample. As the TFE content increases, the cooled phase is difficult to obtain as typically illustrated for the samples of VDF 20-40% content. They exist as the *untilted trans* structure at room temperature. In the case of the VDF 41%-TFE sample, heating causes the generation of *gauche* isomers within the *trans* chain, resulting in the transition to the cooled phase. In the case of the VDF 23%-TFE sample, on the contrary, stabilization of the *trans* structure is enhanced and the cooled phase is not detected even at 200°C.

Local structure of comonomer. As seen from the temperature dependence of the X-ray reflection and i.r. and Raman spectra, the TrFE segments exist essentially in a *trans* conformation even above the transition temperature. The same situation can also be seen for the TFE segments. As the TFE sequential length is longer, however, the characteristic behaviour begins to appear. Just as in PTFE, the long TFE segments experience thermal motion around the chain axis through internal rotation via the *trans* form. Such thermal motion is frozen-in at low temperature and then the more stable helical form is attained in the long TFE sequences, as observed for the VDF 23%-TFE sample and PTFE. The short TFE segments included in the copolymers of higher VDF content take the *trans* form. This is possibly due to the restraint of the TFE structure by the neighbouring *trans*-type VDF segments as pointed out above.

Phase transition behaviour. In the case of VDF-TrFE copolymers with VDF 70-100% content, the sharp and discontinuous phase transition of first-order type occurs between the low and high temperature phases with a large thermal hysteresis between the heating and cooling processes. Such a transition can be observed for the VDF-TFE copolymers with VDF contents of >75%, although the transition point is close to the melting point and the thermal hysteresis is small. For the VDF-TrFE copolymers with VDF contents of <50%, the broad and apparently continuous phase transition of the second-

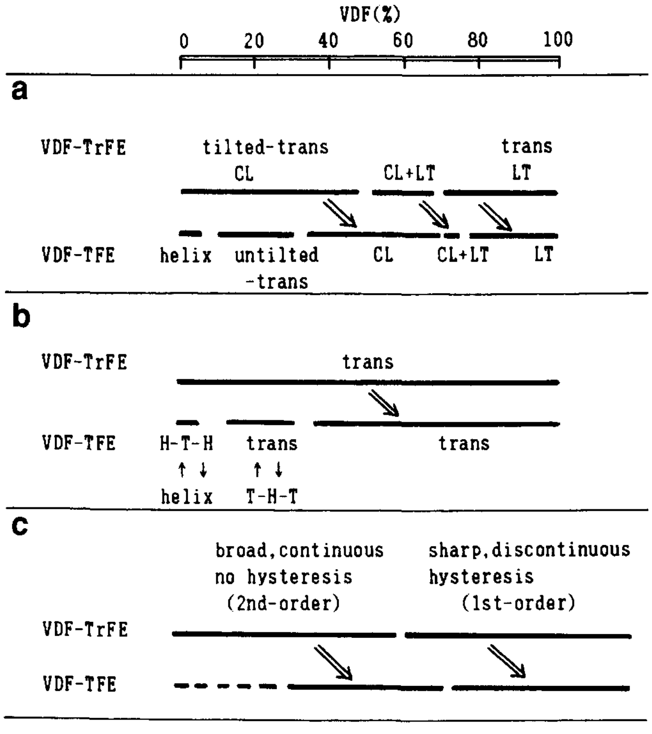

Figure 23 Comparison between the VDF-TrFE and VDF-TFE copolymers: (a) crystal form at room temperature; (b) structure of comonomer parts; (c) phase transition behaviour

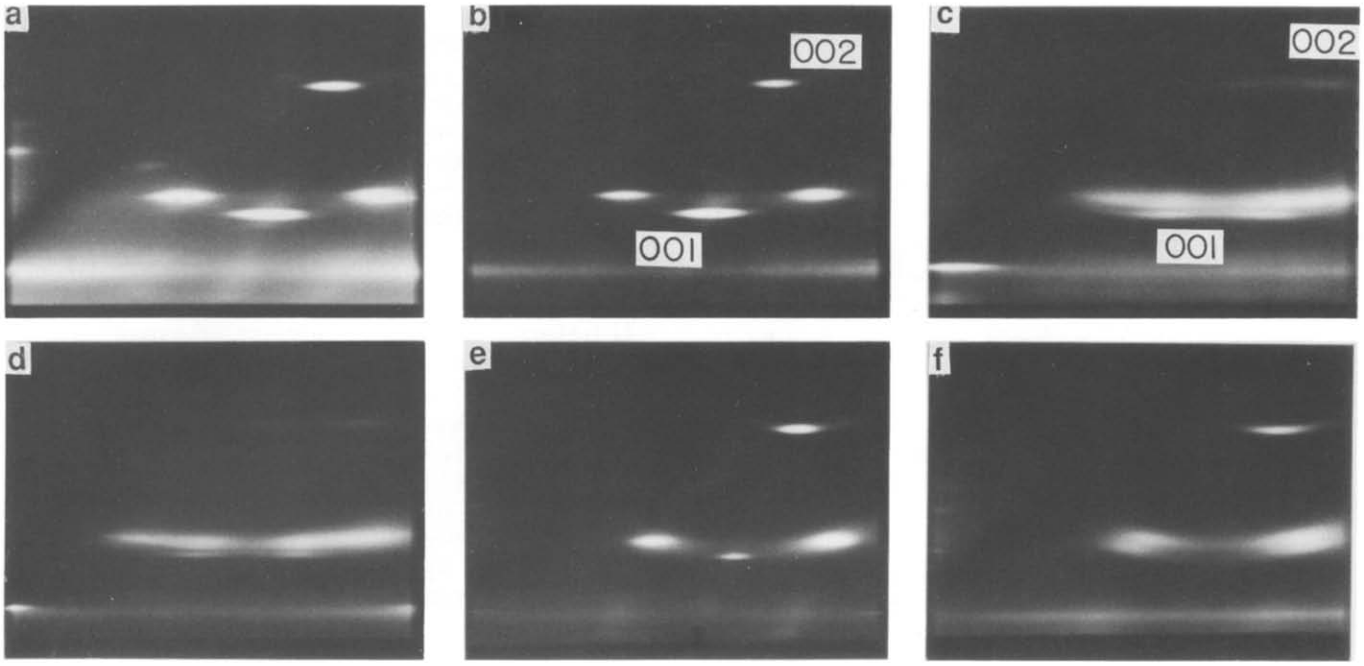

Figure 24 Weissenberg photographs for the (00*l*) reflections measured for a series of uniaxially oriented VDF–TFE copolymers at room temperature: (a) VDF 81%; (b) VDF 75%; (c) VDF 64%; (d) VDF 41%; (e) VDF 23%; (f) PTFE. In the low temperature phase the (001) and (002) reflections do not split but in the cooled phase they split into two because of the tilting phenomenon of the zigzag chains[44]

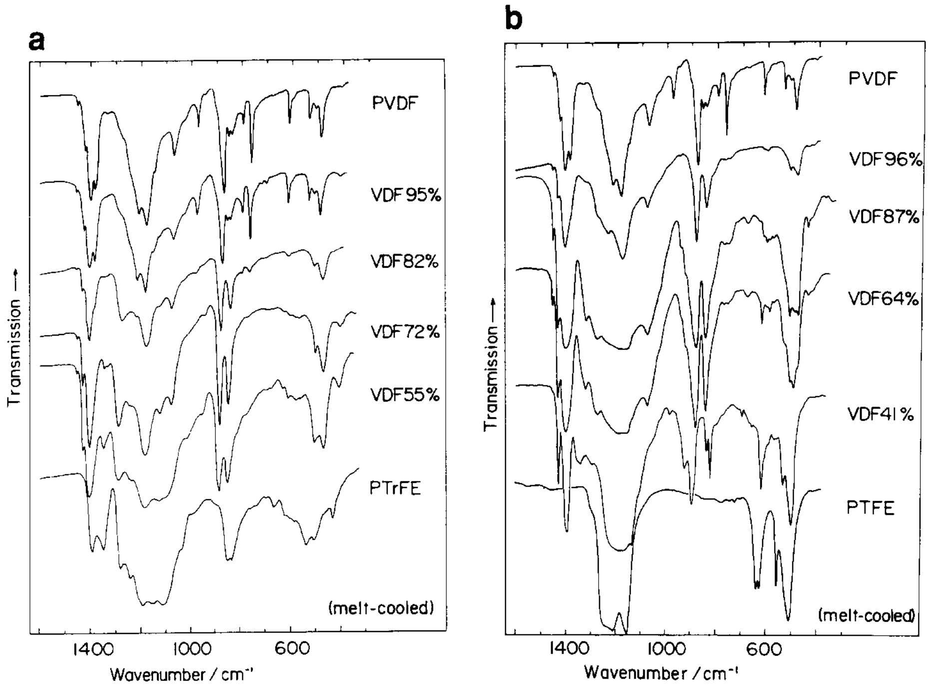

Figure 25 Comparison of the VDF content dependence of the i.r. spectra of the melt-cooled samples between (a) VDF–TrFE and (b) VDF–TFE copolymers

order type occurs with almost negligibly small thermal hysteresis. Such a transition is observed in the VDF–TFE samples with VDF contents of 40–65%. In the case of VDF–TrFE copolymers the conformational change in the VDF segments becomes imperfect for the copolymer with lower VDF content possibly because of the *trans* stabilization effect of the TrFE units. Such a phenomenon can also be seen in the case of the TFE copolymer system with a much stronger influence. In fact, as reported above, the TFE *trans* band of the VDF 64% sample, for example, remains up to a higher temperature than that of the VDF 65%–TrFE sample. In this way, the co-operative nature and the completeness of the conformational transition are reduced by cutting off the continuous VDF arrays due to the introduction of comonomer units into the chain.

As discussed here, the structure and phase transitional behaviour depend on the relative amount of TrFE or TFE comonomer units in the chain. We will now consider why such a difference may be generated between these two copolymers. As seen in *Figure 25*, where the i.r. spectra of the melt and slowly cooled samples are compared at room temperature for both types of copolymer, the i.r. pattern of the *gauche* conformation is easily obtained for the VDF–TrFE copolymers with VDF contents of >80%. That is, the VDF 95%–TrFE sample gives a spectral pattern typical of PVDF form II ($TGT\bar{G}$) and the VDF 82%–TrFE sample still exhibits the bands of form II although the relative intensity of these bands is low and the spectra characteristic of the all-*trans* form I are predominant. The corresponding VDF–TFE copolymers exhibit the i.r. pattern containing richer *trans* structure; that is, the all-*trans* pattern for the VDF 87% sample and the $TTTGTTT\bar{G}$ pattern (form III) for the VDF 96% sample. (A similar tendency can also be observed for the samples cast from solution.) Hence VDF–TFE copolymers more easily take the *trans* conformation than VDF–TrFE copolymers; a TFE unit can stabilize the *trans* conformer of a VDF chain more effectively than a TrFE unit. This is also supported by the larger steric hindrance of the fully substituted TFE groups. According to Hopfinger[56], the non-bonded F...F interatomic interaction in a VDF–TrFE chain is reduced to about half that in a VDF–TFE chain. This might clarify the difference in the conformational stability between the TFE and TrFE copolymers and explains the reason why the VDF–TFE copolymer exhibits a transition behaviour similar to that of the VDF–TrFE copolymer with a *higher* TrFE content. The mobility of the comonomer unit must also be taken into account. In VDF–TFE copolymers, the *trans* band intensity decreases gradually even over a temperature region much lower than the co-operative conformational transition point. As discussed above, PTFE experiences a rather active librational motion around the chain axis over a comparatively low temperature region. The thermal librational motion originates from a low energy barrier for internal rotation about the CF_2–CF_2 bond. This type of thermal motion is considered to occur also in the TFE segmental parts of a VDF–TFE copolymer chain. Such a motion in the TFE parts may induce fluctuation of the end region of the adjacent VDF segments, while the inner parts of the segments are held in the *trans* form. The expansion of the unit cell by the introduction of more bulky CF_2CF_2 groups may also make it easier to induce such a thermal motion. Thermal fluctuations may progress into the inner parts of the VDF segments and result in a gradual decrease in the i.r. *trans* band intensity with a rise in temperature. Such an effect may also be seen in VDF–TrFE copolymers. The torsional barrier is considered to be higher for CHF–CF_2 bonds[56]. The small thermal hysteresis of the transition in VDF–TFE copolymers may be also interpreted by the idea of easier thermal motion of the TFE segments.

At this stage we must interpret why the cooled phase is more easily observed for the VDF 64%–TFE copolymer compared with the case of the VDF 65%–TrFE copolymer. As understood from the crystal structure, a small amount of *gauche* bonds within the stable *trans* segments is needed for the generation of the cooled phase. Many experimental facts support this idea: (1) heating of the low temperature phase gives the cooled phase as seen in the VDF 55%–TrFE copolymer and the VDF 41%–TFE copolymer. In the transition temperature region from the low temperature phase to the cooled phase, the *gauche* content increases slightly with a large amount of *trans* segments remaining; (2) the stretching of the cooled phase gives the low temperature phase (stress-induced *gauche*-to-*trans* change) and cooling from the high temperature *gauche* phase results in the cooled phase; (3) in the VDF 37%–TrFE copolymer, the local transition between *trans* and *gauche* bonds occurs in the cooled phase near room temperature. This cooled phase is transformed to the low temperature phase only under tension. Relaxation of the stress brings the low temperature phase back to the original cooled phase, because the thermally activated *trans–gauche* conformational change occurs at room temperature as stated above.

The active thermal motion of the TFE segments will become a kind of trigger for generating *gauche* bonds in the neighbouring VDF sequences and hence for the appearance of the cooled phase as in the VDF 37%–TrFE copolymer case. It should be kept in mind that the phenomenon occurs only for VDF 41–64% samples of the VDF–TFE copolymers. As the relative content of TFE units increases furthermore, the *trans* conformation is stabilized overwhelmingly and then the generation of the *gauche* bonds is suppressed strongly. Such a situation is not seen for the VDF–TrFE copolymers because of the weaker *trans* stabilization effect of TrFE monomeric units. This difference is observed actually between the VDF 23%–TFE copolymer and VDF 0–37%–TrFE copolymers: at room temperature the VDF 23%–TFE copolymer exists in the untilted *trans* form but the VDF–TrFE samples exist in the tilted *trans* form or the cooled phase.

In this way the effect of *trans* stabilization and thermal mobility of the comonomer component are considered to be important factors in governing the structure and transitional behaviour of the VDF copolymers. In the ferroelectric transition a dipole–dipole interaction also plays an important role. The dipole moment of the *trans* zigzag VDF chain is partly cancelled or diluted by the introduction of a comonomer. A non-polar TFE unit has a larger effect than a TrFE unit with a small dipole moment. In order to clarify these situations, energetical calculations will be required.

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