# Vibrational spectroscopic study of the ferroelectric phase transition in vinylidene fluoride–trifluoroethylene copolymers:

# 1. Temperature dependence of the Raman spectra

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*(Received 3 July 1987; revised 11 August 1987; accepted 24 August 1987)*

Raman spectral changes in the ferroelectric phase transition have been measured for a series of vinylidene fluoride–trifluoroethylene (VDF–TrFE) copolymers with VDF molar contents of 73, 52, 37 and 0%. In the vicinity of the transition temperature, the *trans* band at 845 $cm^{-1}$ decreases in intensity and the *gauche* band at 800 $cm^{-1}$ increases. Such an intensity exchange between the *trans* and *gauche* bands has been found to become more diffuse and incomplete over a wider temperature region as the VDF content decreases. By coupling these Raman spectral data with the X-ray diffraction data (00*l* meridional reflections), the structural regularity in the *gauche*-type crystalline phase has been compared among these copolymer samples. For the copolymer with higher VDF content the regular $TGT\bar{G}$ conformation with a little residue of $TT$ sequences exists in the high-temperature phase; while for the sample with lower VDF content, some *trans* sequences are still included in the polymer chains even in the high-temperature phase and the structure is in a more disordered state. This may be due to the high probability of interrupting the VDF monomer sequences by an intrusion of TrFE units and the resulting stability of the *trans* form relative to the *gauche* form for these lower VDF copolymer samples.

**(Keywords: vinylidene fluoride–trifluoroethylene copolymers; ferroelectric phase transition; *trans–gauche* conformational change; Raman spectra; X-ray diffraction)**

## INTRODUCTION

In a series of papers, we have investigated the structural changes occurring in the ferroelectric phase transition of vinylidene fluoride–trifluoroethylene (VDF–TrFE) copolymers[1-4] and their dependence on the VDF molar ratio, sample preparation conditions, external mechanical and electric fields, etc.[5-9] This phase transition involves three types of crystal phases, i.e. the low-temperature phase, the high-temperature phase and the cooled phase[2,5,6]. For the copolymer samples with high VDF content (> 70%), a clear first-order phase transition occurs between the low-temperature and the high-temperature phases. For example, the lattice spacings *d*, measured by the X-ray diffraction method, change drastically and discontinuously near the Curie transition temperature, and the transition curve (*d* vs. temperature) exhibits a large thermal hysteresis between the heating and cooling processes. The low-temperature phase is constructed with a regular parallel packing of essentially planar zigzag chains with all the monomeric dipoles directed along the *b* axis; the crystal structure is polar and almost equivalent to that of PVDF form I. The all-*trans* zigzag conformation in the low-temperature phase transforms into the *gauche*-type conformation of the paraelectric high-temperature phase at the transition temperature. Such contracted chains, constructed with a statistical combination of $TT$, $TG$ and $T\bar{G}$ rotational isomers, are packed in a non-polar unit cell of pseudo-hexagonal type and rotate around the chain axis through interchange between the $TT$ and $TG$ ($T\bar{G}$) bonds[2,5].

In this way, a clear and discontinuous transition is observed between the low-temperature and high-temperature phases for the copolymers with high VDF content. Strictly speaking, however, this is only for the highly oriented samples obtained by restretching the annealed oriented samples at room temperature[2,5,6]. For the unoriented samples as well as the as-annealed oriented samples of VDF 50–70% copolymers, another type of transition overlaps with it: a phase transition between the cooled phase and the high-temperature phase[2,5,6]. This transition occurs apparently continuously over a relatively wide temperature range compared with the above case. The contribution of this apparently second-order-like phase transition becomes more prominent as the VDF content decreases towards 0%. At the same time, the transition point decreases to lower temperature. For copolymers with VDF content less than 50%, there actually exists only the transition between the cooled phase and the high-temperature phase, irrespective of the oriented or unoriented state of the samples. The cooled phase has a kind of superlattice structure where the long *trans* zigzag segments are aggregated together to form domains with a subcell structure essentially equivalent to that of the low-

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temperature phase[2,5,6]. The domains are bounded with (1 0 0), (1 3 0) or $(1\bar{3}0)$ planes in the lateral direction and by *gauche*-type linkages along the chain axis. These *gauche* bonds are considered to play the role of a kind of nucleus in the crystalline phase transition and make the interchange from *trans* to *gauche* isomers relatively easy, resulting in the apparently continuous transitional behaviour of the cooled phase in the lower-temperature region. The sharpness of the structural transformation from *trans* to *gauche* phases (or vice versa) decreases gradually as the VDF concentration is lowered towards 0%. This has been ascribed to incompleteness of the *trans–gauche* interchange in samples with lower VDF contents, because the *trans* conformation is more stabilized than the *gauche* form for such samples[5]. The cooled phase can be transferred into the low-temperature phase by stretching[2,5] or poling[6,10–13] at room temperature. For VDF 0–40% copolymer, the low-temperature phase can be obtained, though not so perfectly but partly, under mechanical tension[5] or an external electric field[14]. The relaxation of the applied field brings it back to the original cooled phase. Such a forced transition of the cooled phase into the regular low-temperature phase originates from the transformation of the *gauche* bonds included as a structural defect in the chain to the *trans* form under an external field.

As described above, the transitional behaviour of the copolymers is very complicated. But an essential feature of this phase transition is characterized by a large conformational change between the *trans* and *gauche* forms, which governs the drastic changes in the mechanical[15–17] and electrical properties[18,19] in the transition region. As clarified in previous papers[1,2,5,20–22], such important structural information could be obtained by vibrational analysis of the infra-red and Raman spectra coupled with X-ray diffraction measurements. The vibrational spectra are very sensitive to local structural changes in the molecular chain, so one may expect to obtain much more fruitful information concerning the ferroelectric phase transition of VDF–TrFE copolymers by investigating the vibrational spectral data in more detail. In this paper, we will describe the temperature dependence of the Raman spectra for a series of copolymers and analyse it in connection with the above-mentioned structural features. The X-ray diffraction data of the meridional (0 0 *l*) reflections will be coupled with the Raman spectral data to discuss the conformational regularity in this ferroelectric phase transition. In order to discuss the phase transitional behaviour in detail, it may also be necessary to investigate the lower-frequency far-infra-red spectral region, which is difficult to measure by the present Raman spectroscopy because of relatively strong Rayleigh scattering. The experimental results will be reported in the next paper of this series.

## EXPERIMENTAL

### *Samples*

The samples utilized here were copolymers with VDF molar contents of 0 to 73%, which were supplied by Daikin Kogyo Co. Ltd, Japan. The unoriented samples for Raman spectral measurements were prepared by cooling the melt slowly down to room temperature. The uniaxially oriented samples were prepared by elongating the unoriented samples to about five times the original length followed by heat treatment at 100–130°C for 1 h. Orientation of the melt-cooled and drawn samples was checked by X-ray diffraction as well as polarization measurements of the Raman spectra.

### *Measurements*

For the Raman spectral measurements at high temperatures, an optical cell was used. This was a block of metal containing a capillary, into which the sample, tightly bound to a thermocouple, was sealed. The Raman spectra were taken using Japan Spectroscopic Co. R-500 and R-800 Raman spectrophotometers with excitation light from an $Ar^+$ ion laser (wavelength 514.5 nm). The X-ray diffraction measurement of the meridional reflections was made using a position-sensitive proportional counter (PSPC) system with a temperature-controlled sample stage.

## RESULTS AND DISCUSSION

### *Polarized Raman spectra at room temperature*

In *Figure 1* are shown the polarized Raman spectra ((*zz*) component) taken at room temperature for a series

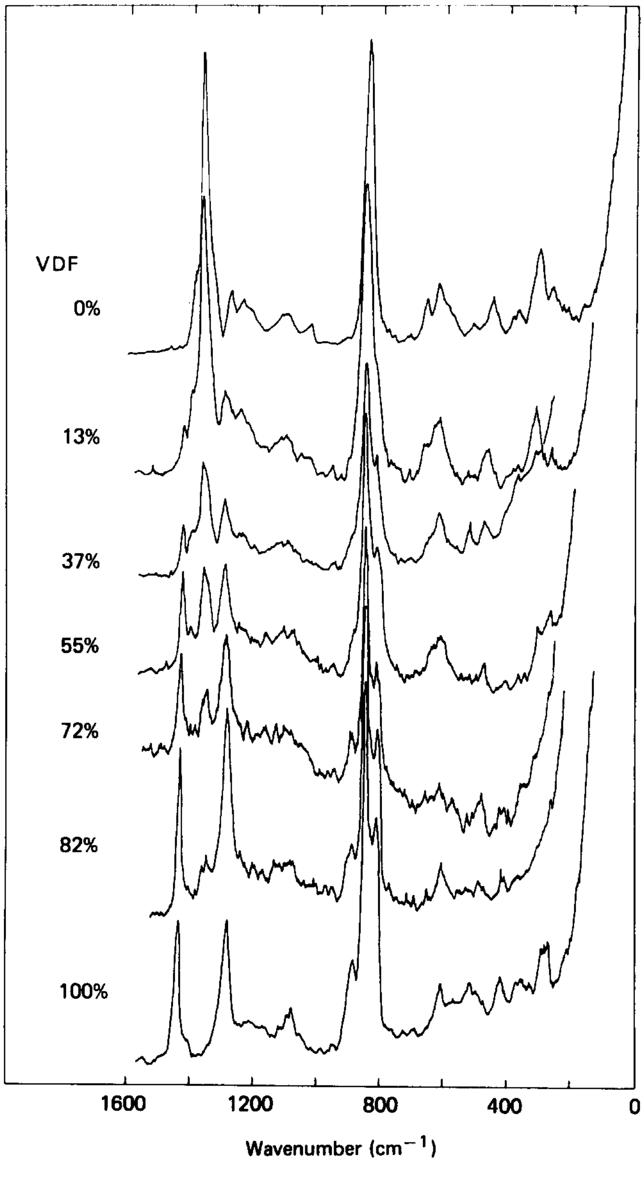


**Figure 1** Polarized Raman spectra ((*zz*) component) of a series of uniaxially oriented VDF–TrFE copolymers taken at room temperature

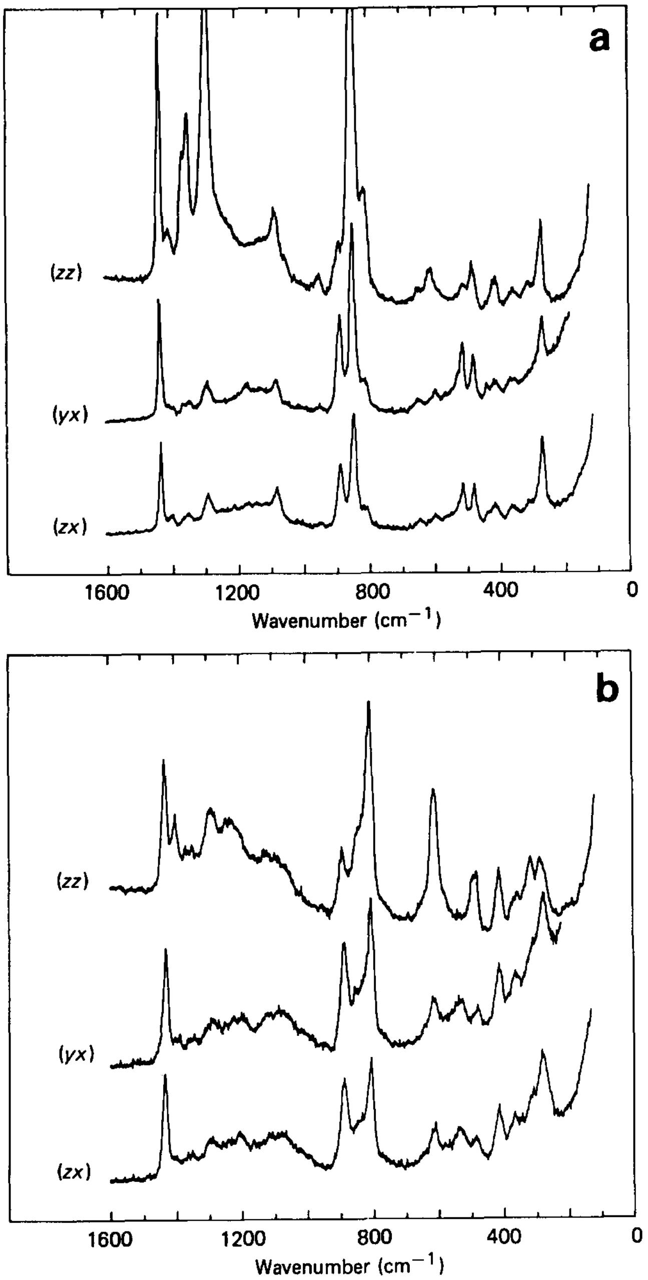


**Figure 2** Polarized Raman spectra of uniaxially oriented VDF 73% copolymer taken at (a) room temperature (27°C) and (b) 120°C

of oriented copolymers with various VDF contents, where the $z$ axis is parallel to the orientation axis. Using the X-ray diffraction method, these uniaxially oriented samples are found to be in a crystal form of all-*trans* conformation, as in PVDF form I[23,24]. As seen in *Figure 1*, PVDF form I shows a strong Raman band at 840 cm$^{-1}$, which is assigned to the symmetric stretching mode of the $CF_2$ groups in the all-*trans* conformation[25,26]. This band can be observed commonly for all copolymers, consistent with the all-*trans* conformation of the skeletal chains revealed by X-ray diffraction. The Raman band at 1280 cm$^{-1}$ (a coupling of $CF_2$ stretching and skeletal CC stretching modes) is also characteristic of the all-*trans* conformation. The relative intensity of this band decreases with a decrease in the VDF molar content. Therefore, it is considered to correlate intimately with the *trans*-type VDF monomer sequences in the copolymer chains. The band at 1430 cm$^{-1}$ is assigned to the $CH_2$ deformation mode characteristic of the VDF sequence, while the band at 1380 cm$^{-1}$ is due to the CH bending mode of the TrFE group because it increases in intensity with TrFE content. A Raman band characteristic of the VDF monomeric unit is also observed at 880 cm$^{-1}$, which is assigned to the $CH_2$ rocking mode[25-27]. We may utilize these bands at 1380 and 1430 (or 880) cm$^{-1}$ for quantitative analysis of the VDF/TrFE monomer ratio in the copolymer chains, as in the infra-red analysis[5].

### *Temperature dependence of the Raman spectra of VDF 73% copolymer*

*Figure 2* shows the polarized Raman spectra of oriented VDF 73% copolymer measured at room temperature and 120°C. In *Figure 3* is shown the

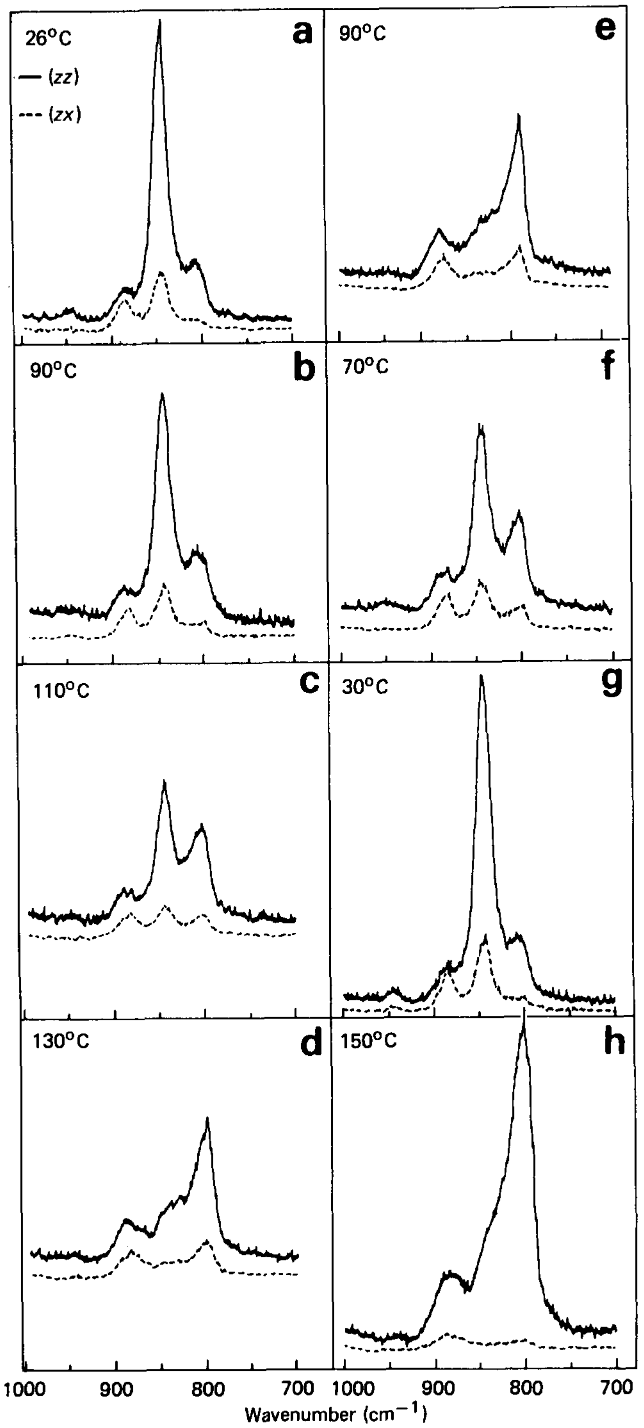


**Figure 3** Temperature dependence of polarized Raman spectra of uniaxially oriented VDF 73% copolymer in the frequency region 700–1000 cm$^{-1}$

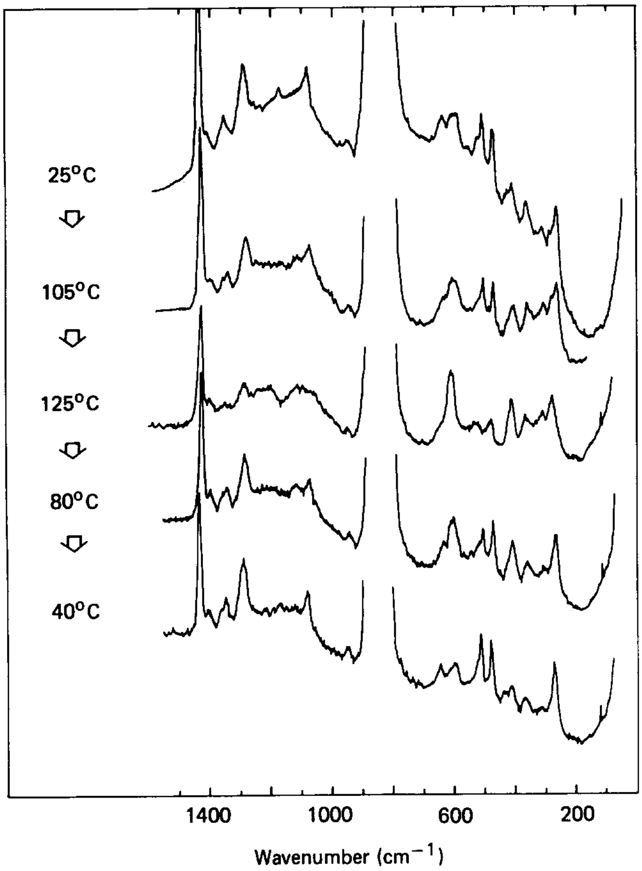


**Figure 4** Temperature dependence of Raman spectra of unoriented VDF 73% copolymer sample in the frequency region 0–1500 cm$^{-1}$

temperature dependence of the polarized Raman spectra in the frequency region 700–1000 cm$^{-1}$ measured for the uniaxially oriented VDF 73% copolymer sample. In *Figure 4* is shown the temperature dependence of the relatively weak Raman bands measured for the unoriented VDF 73% copolymer sample. In *Figure 5* is plotted the peak intensity of the *trans* (844 cm$^{-1}$) and *gauche* (800 cm$^{-1}$) bands against temperature. The Raman spectral pattern at room temperature, shown in *Figure 2a*, is characteristic of the *trans* crystal form, very similar to the spectra of PVDF form I. As the temperature rises towards the transition point of ~110°C, the *trans* bands decrease in intensity and the *gauche* bands increase, as seen in *Figures 3–5*. In the high-temperature phase, as shown in *Figure 2b*, the Raman bands at 410, 530, 610 and 800 cm$^{-1}$, etc., are prominent. (It should be noted here that the Raman bands characteristic of the *gauche* form are observed relatively strongly compared with the corresponding infra-red bands with low intensity[5].) These Raman bands exhibit a high degree of polarization character, indicating the occurrence of the crystal phase transition without any loss in orientation character, as already clarified by the X-ray diffraction study. Roughly speaking, the Raman spectral feature of the high-temperature phase resembles that of PVDF form II[25,27], but the sharpness of the bands is not so high as in form II and the *trans* band at 844 cm$^{-1}$ remains as a shoulder even above the transition point, where the X-ray diffraction from the original *trans* crystal phase is not detected. This suggests that the molecular conformation of the high-temperature phase is not so regular as that of PVDF form II ($TGT\bar{G}$) but some *trans* isomers ($TT$) still reside even above the transition temperature. Such a tendency is more remarkable for the copolymer sample with lower VDF content, as discussed later.

*Figure 6* shows the Raman spectra measured in the frequency region of 3000 cm$^{-1}$. The symmetric and antisymmetric $CH_2$ stretching bands (2970 and 3007 cm$^{-1}$, respectively) decrease in intensity and broaden above the transition temperature. In particular, the polarization components including the $x$ or $y$ axis perpendicular to the chain axis ($\alpha_{yx}$, $\alpha_{zx}$) become much broader in their halfwidth. This may be due to conformational irregularity and thermally activated rotational motion of the molecular chains around the chain axis[28,29].

In *Figure 7* are shown the polarized Raman spectra taken for the molten state (about 160°C) of VDF 73% copolymer. Comparing the spectral pattern with that of the high-temperature phase at 120°C (*Figure 2b*), we may say that these two spectra are similar to each other, although the crystalline *gauche* bands at 410, 530 and 610 cm$^{-1}$, etc., disappear and the halfwidth of the $CH_2$ stretching bands broadens much more in the molten state. As stated above, the possible local molecular conformation in the high-temperature phase of VDF 73% copolymer consists of $TGT\bar{G}$ sequences with some $TT$ bonds. But the whole molecular state is rather close to that of the melt. In other words, the high-temperature phase may be assumed to be a kind of conformationally disordered phase ('condis' phase)[30]. Such a 'condis' phase has also been reported for polyethylene, where the orthorhombic phase transfers to the pseudohexagonal phase at high temperature under high pressure (for

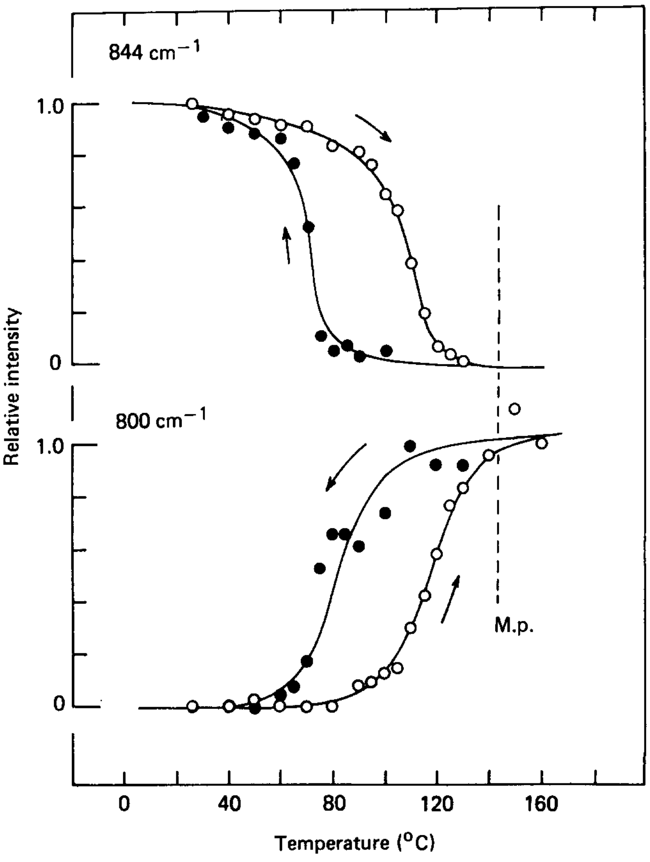


**Figure 5** Temperature dependence of the relative Raman intensity of the *trans* (844 cm$^{-1}$) and *gauche* (800 cm$^{-1}$) bands for VDF 73% copolymer

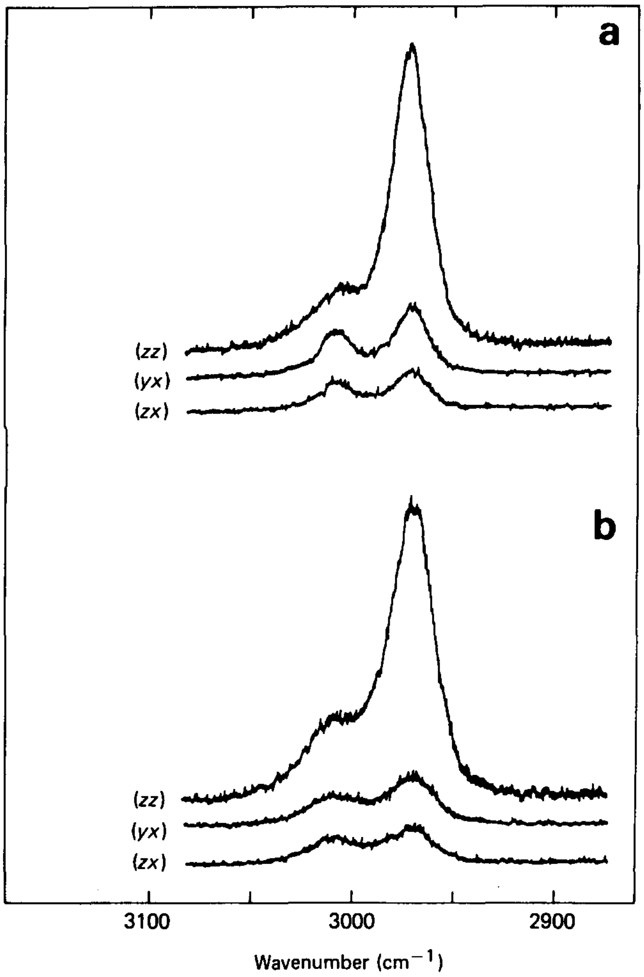


**Figure 6** Polarized Raman spectra of uniaxially oriented VDF 73% copolymer taken at (a) room temperature (27°C) and (b) 120°C in the frequency region 2900–3100 cm$^{-1}$

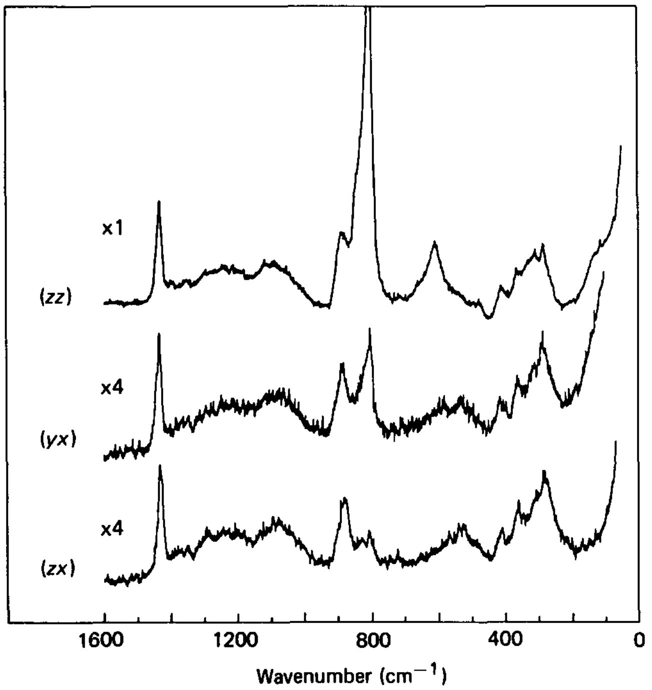


**Figure 7** Polarized Raman spectra of molten VDF 73% copolymer sample taken at 160°C

example, at 230°C under 3–5 kbar)[31,32]. In that case the Raman spectra of the high-temperature phase consist of the mixing of the *trans* and *gauche* bands and is very close to that of the molten state[33,34], indicating that the molecular conformational state is actually in the molten state although the X-ray diffraction data showed some degree of crystalline order in the high-temperature phase[35]. In the case of VDF 73% copolymer, the 'condis' phase or the high-temperature phase is not so disordered as in polyethylene, as understood from the observation of crystalline *gauche* bands in *Figures 2–4*. Such a difference in the conformational regularity in the 'condis' phase between VDF–TrFE copolymer and polyethylene may reflect on the thermal data. The ratio of the transition enthalpy $\Delta H_t$ to the melting enthalpy $\Delta H_m$, that is $\Delta H_t/\Delta H_m$, is 0.2–0.8 for the VDF–TrFE copolymers[36], while it is about 2.3 for polyethylene[37]. The entropy ratio $\Delta S_t/\Delta S_m$ is 0.3–0.8 for the copolymers and about 2.3 for polyethylene. That is to say, in the case of polyethylene, the thermal change in the ortho→'condis' transition is overwhelmingly larger than that in the 'condis'→melt transition. This indicates that the regularity in the crystalline state, especially in the molecular conformation, decreases drastically in the phase transition from ortho to 'condis' phases and the long-range conformational regularity is lost as in the molten state. On the contrary, small ratios of $\Delta H_t/\Delta H_m$ and $\Delta S_t/\Delta S_m$ may indicate that the conformational state in the high-temperature phase of VDF–TrFE copolymer is also disordered but not so much as that in the molten state, compared with the case of polyethylene. This could be supported by the observation of a relatively clear X-ray diffraction pattern of the high-temperature phase, as already reported for the copolymers.

### *Transitional behaviour of copolymers with different VDF contents*

*Raman spectral changes.* In *Figures 8–10* are shown the temperature dependences of the Raman spectra measured for the unoriented VDF–TrFE copolymers with 52, 37 and 0% VDF contents, respectively. At room temperature these copolymer samples exhibit a strong band at ~850 cm$^{-1}$, indicating that they exist in the *trans* form, as pointed out in the above section. As the temperature rises, the *trans–gauche* intensity exchange can be detected for VDF 52 and 37% samples. But the *trans* bands do not disappear completely even above the transition point. In *Figure 11* is compared the spectral change for VDF 73, 52 and 37% samples in the frequency range 700–950 cm$^{-1}$. In *Figure 12* is plotted the temperature dependence of the Raman intensity for the *trans* and *gauche* bands of these copolymer samples. As the VDF content decreases, the temperature region of the intensity change becomes broader and the *trans* band still has some intensity even above the transition point. That is to say, the intensity ratio of the *trans/gauche* Raman bands becomes higher and thus the *trans*-to-*gauche* conformational change above the transition temperature is less complete for copolymers with lower VDF contents. In other words, the conformational structure of the molecular chains in the high-temperature phase becomes less ordered for the copolymers with lower VDF contents. For the VDF 0% copolymer, i.e. polytrifluoroethylene, no conformational transition is observed up to the melting point.

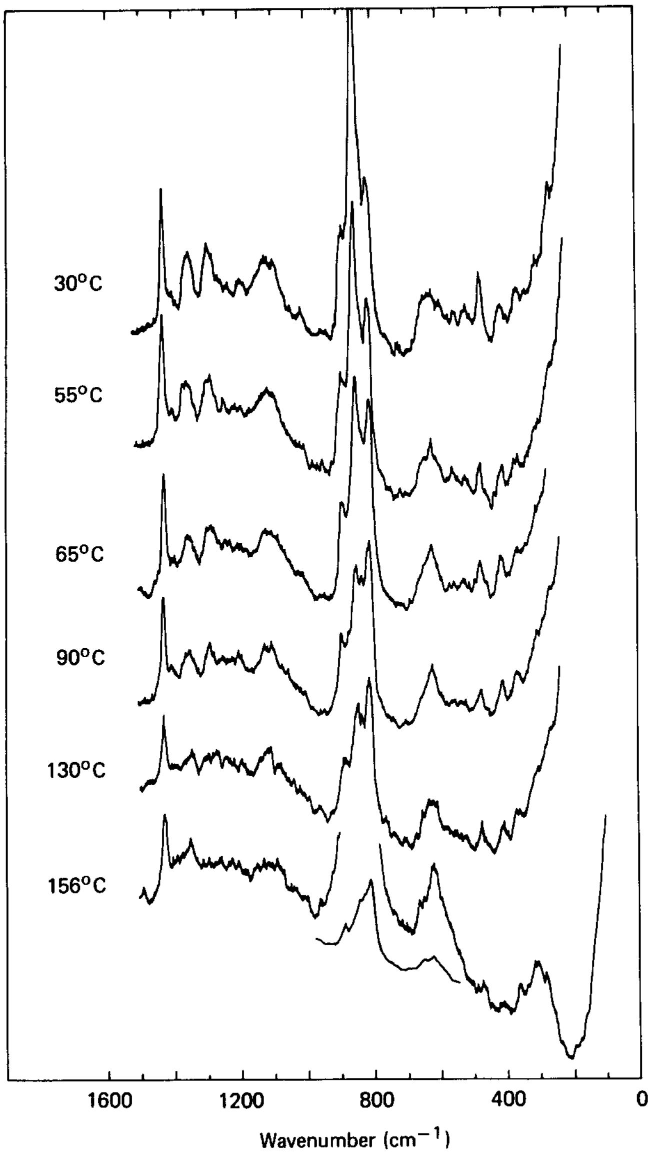


**Figure 8** Temperature dependence of Raman spectra of unoriented VDF 52% copolymer sample

The difference in the conformational state of chains in the high-temperature phase also reflects on the position of the Raman bands in the frequency region 800–850 cm$^{-1}$. In *Figure 13* are compared the Raman spectra of the high-temperature phase for a series of copolymers with those of PVDF forms I, II and III, the molecular conformations of which are all-*trans*, $TGT\bar{G}$ and $TTTGTTT\bar{G}$, respectively[38]. The positions of the main $\nu_s(CF_2)$ bands for PVDF forms I, II and III are as follows[25–27]:

| | |
|---|---|
| $TTTT$ | 840 cm$^{-1}$ |
| $TGT\bar{G}$ | 800 cm$^{-1}$ |
| $TTTGTTT\bar{G}$ | 816 cm$^{-1}$ |

As seen here, the band characteristic of the *gauche* bond neighbouring the long *trans* segment tends to appear at higher frequency. In the high-temperature phase of the copolymers, the main Raman bands in this frequency region are:

VDF 73%: 801, 845 cm$^{-1}$ VDF 52%: 814, 848 cm$^{-1}$
VDF 37%: 814, 850 cm$^{-1}$ VDF 0%: 850 cm$^{-1}$

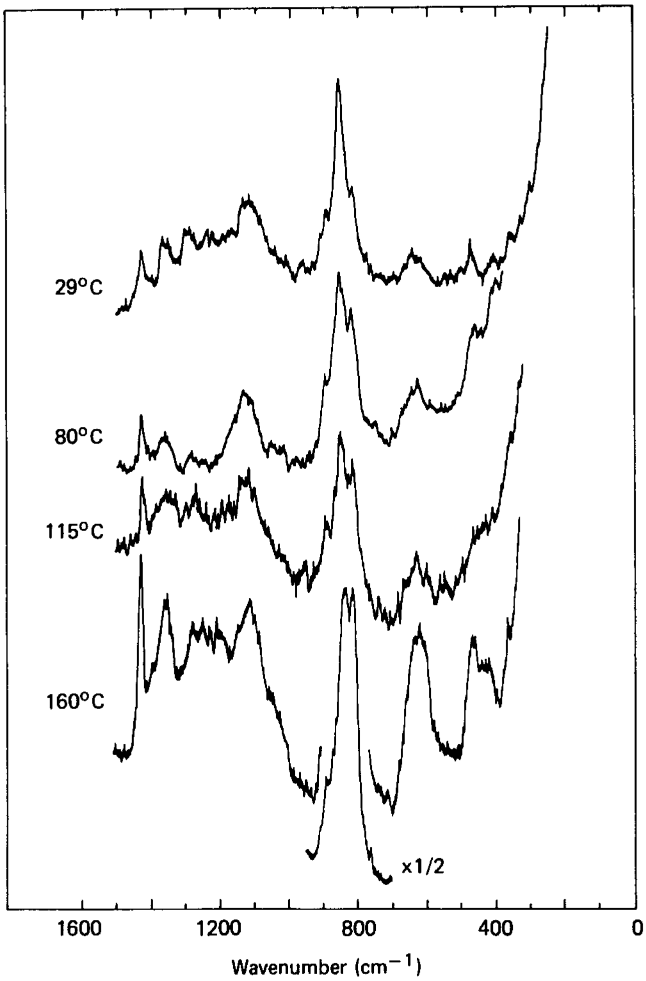


**Figure 9** Temperature dependence of Raman spectra of unoriented VDF 37% copolymer sample

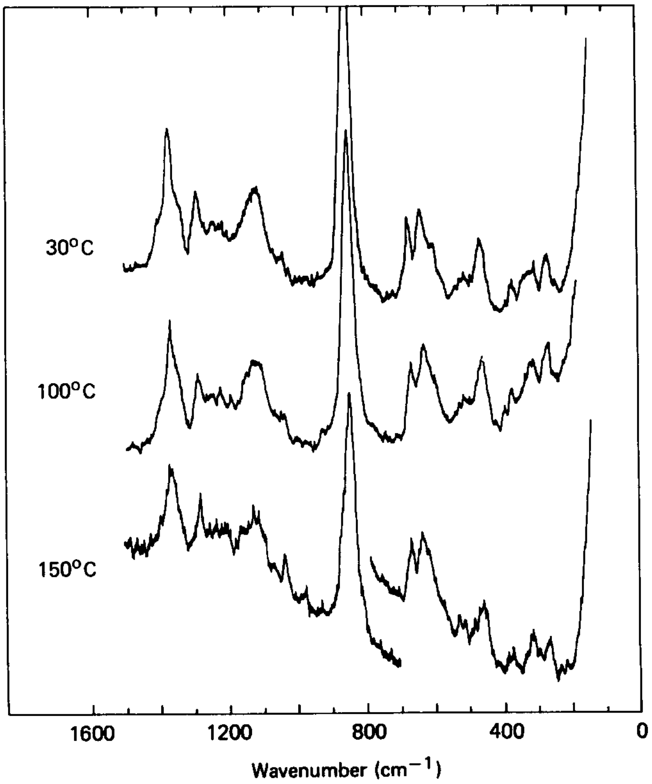


**Figure 10** Temperature dependence of Raman spectra of unoriented VDF 0% copolymer or polytrifluoroethylene sample

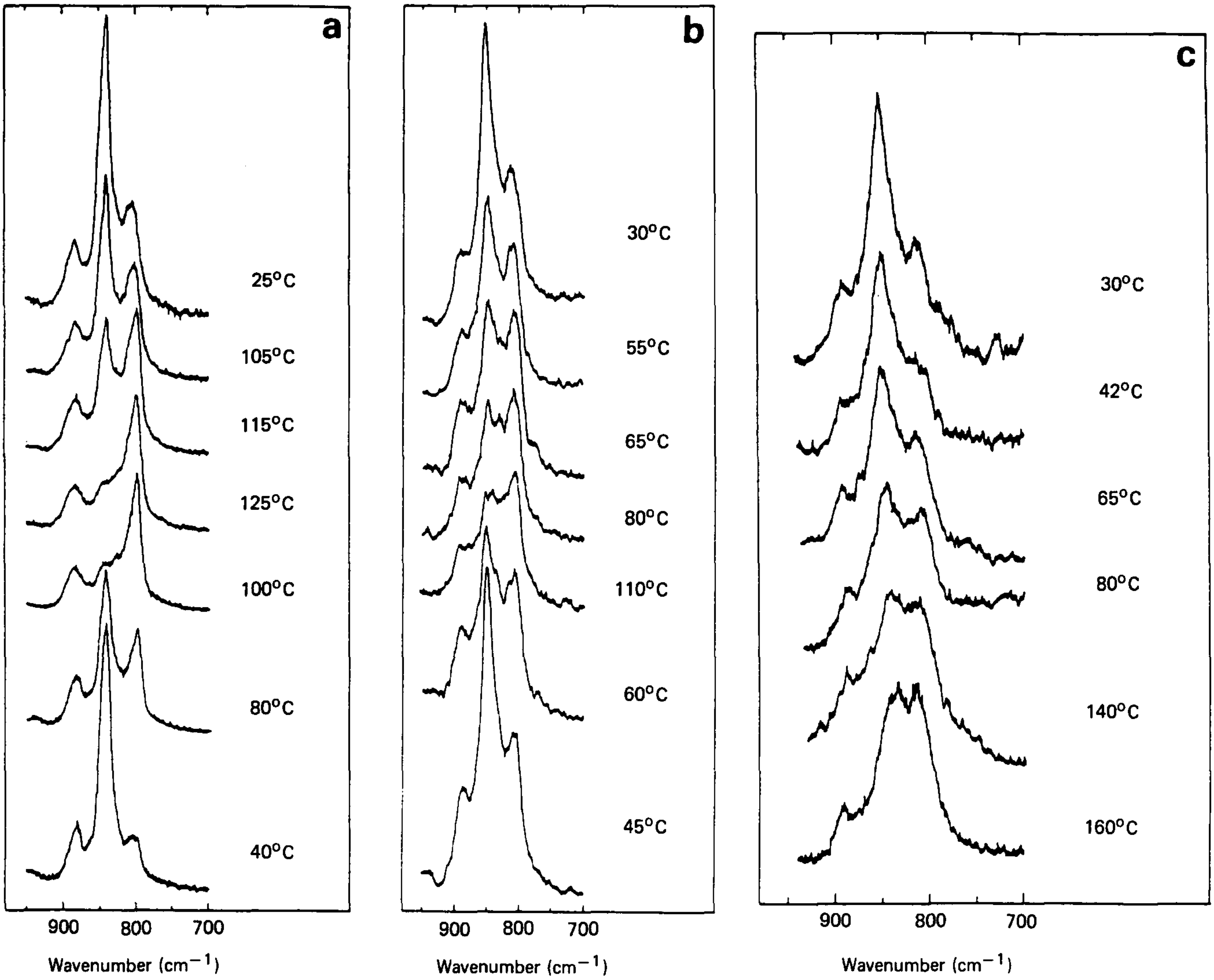


**Figure 11** Temperature dependence of Raman spectra of unoriented copolymer samples in the frequency region 700–1000 cm$^{-1}$: (a) VDF 73%; (b) VDF 52%; (c) VDF 37%

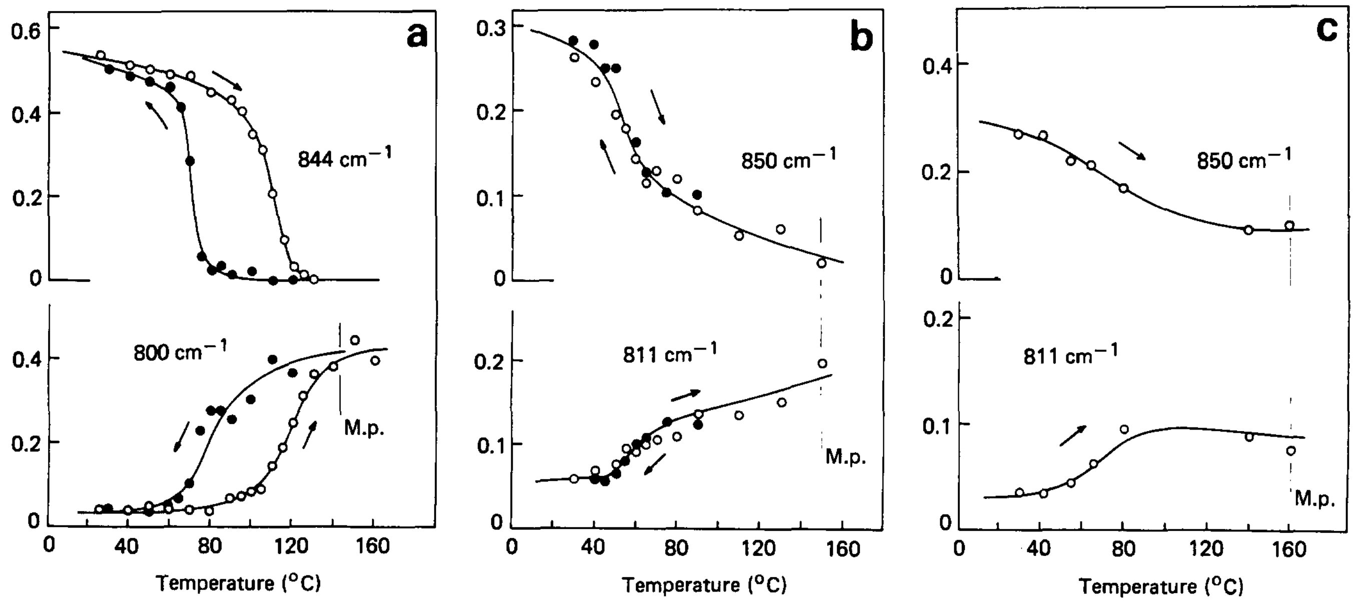


**Figure 12** Temperature dependence of relative Raman intensity of the *trans* (850 cm$^{-1}$) and *gauche* (800 and 811 cm$^{-1}$) bands for the copolymers: (a) VDF 73%; (b) VDF 52%; (c) VDF 37%

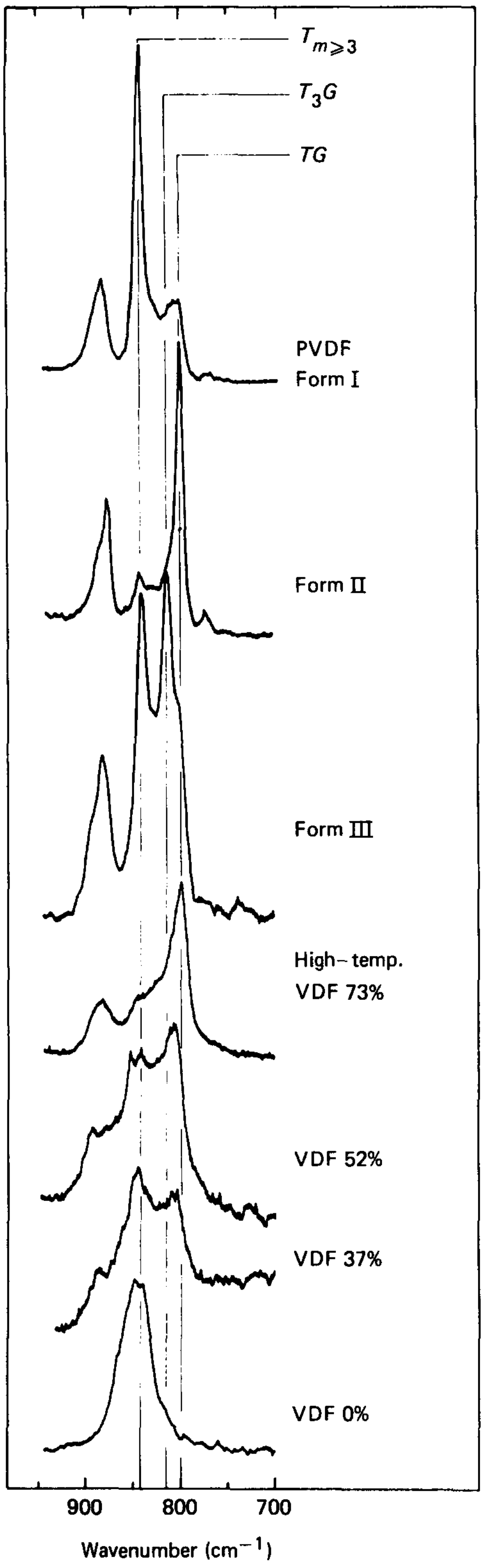


**Figure 13** A comparison of Raman spectral patterns for PVDF forms I, II and III and the high-temperature phase of VDF 73, 52, 37 and 0% (PTrFE) copolymer samples

(A weak 830 cm$^{-1}$ band, which overlaps with these two bands, might be from the amorphous phase.) As discussed later, in the VDF 73% sample, the high-temperature phase contains rather long and regular $TGT\bar{G}$ sequences in the molecular chain. For the VDF 52% sample, on the contrary, the *gauche* form includes a larger contribution from some long *trans* segments, and so the conformational segments such as $TTTT$... and $TTTGTTT\bar{G}$... are contained in irregular molecular chains. The frequency position of the *gauche* bands observed for the high-temperature phase of VDF 37% (814 cm$^{-1}$), 52% (814 cm$^{-1}$) and 73% (801 cm$^{-1}$) may be consistent with such a local conformational state of the chains.

*X-ray meridional reflection data.* The above considerations of the conformational regularity may also be supported by the X-ray diffraction data. In *Figure 14* is shown the temperature dependence of the meridional (00*l*) reflections measured for the uniaxially oriented VDF 72, 55 and 37% copolymers. We can easily see the difference in the sharpness of the intensity change for these samples; a clear change in VDF 72% and a diffuse change in VDF 37%. In the latter case, the crystal at room temperature exists in the form of the cooled phase and the degree of regularity is rather low. The (001) reflection is observed as a broad shoulder on the (201, 111) reflection[5]. As the temperature is raised, the (001) reflection of the cooled phase decreases in intensity and the (201, 111) reflection transforms to the (002) reflection of the high-temperature phase apparently in a continuous manner. Such a change has already been observed in the temperature dependence of the X-ray fibre diagram. In the case of VDF 55% copolymer, the initial sample in *Figure 14* is the low-temperature phase and the transition is comparatively sharp in the heating process, whereas in the cooling process the high-temperature phase does not transfer back to the original low-temperature phase but into the disordered cooled phase[2,5]. The intensity and halfwidth of the (001) reflection become weak and broad, respectively, at room temperature. The thermal behaviour of the (001) reflection in the cooling process is very similar to that observed in the VDF 37% sample.

In *Figure 15* is shown the halfwidth of the (002) reflection of the high-temperature phase for the various copolymer samples. The halfwidth becomes broader as the VDF content decreases towards 37%, suggesting that structural regularity in the high-temperature phase decreases gradually as the VDF content is lowered. This result is consistent with the conclusion deduced from the above-mentioned vibrational spectral data.

In *Figure 16* is plotted the temperature dependence of the halfwidth of the (001) reflection of the *trans* phase. In the case of the VDF 72% sample, the halfwidth is almost constant up to the transition temperature and returns to almost the same value after cooling to room temperature. In the case of VDF 55%, the halfwidth of the initial low-temperature phase broadens largely in the vicinity of the transition point. The cooled phase, obtained in the cooling process, has a much broader halfwidth of the (001) reflection than the initial value for the low-temperature phase. The VDF 65% sample shows intermediate behaviour between the VDF 55 and 72% samples. *Figure 17* shows the temperature dependence of the lattice spacing of the (001) meridional reflection $d_{001}$ measured for the *trans* phase of the uniaxially oriented VDF 75, 55 and 0% copolymers. The $d_{001}$ value was found to shrink beyond the usual thermal contraction of the chain in the vicinity of the *trans–gauche* conformational transition point. This may be due to the effect of invasion and migration of the *gauche* linkage into the *trans* segments. The $d_{001}$ value of the VDF 55% cooled phase is less than that of the initial low-

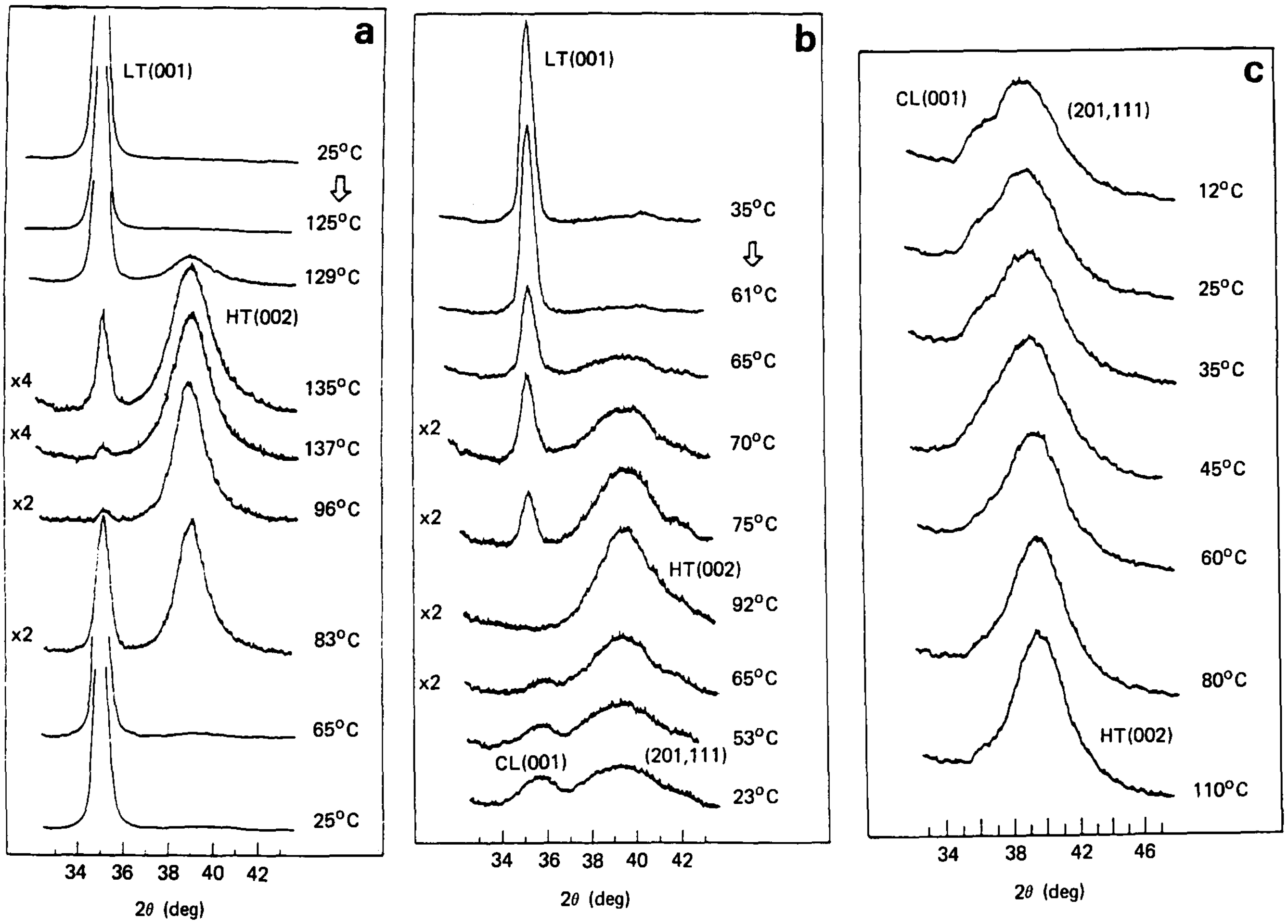


**Figure 14** Temperature dependence of X-ray (0 0 *l*) meridional reflections taken for the uniaxially oriented copolymer samples: (a) VDF 72%; (b) VDF 55%; (c) VDF 37%. The starting sample of VDF 55% copolymer is in the crystalline form of the low-temperature phase. CL, LT and HT denote the cooled phase, the low-temperature phase and the high-temperature phase, respectively

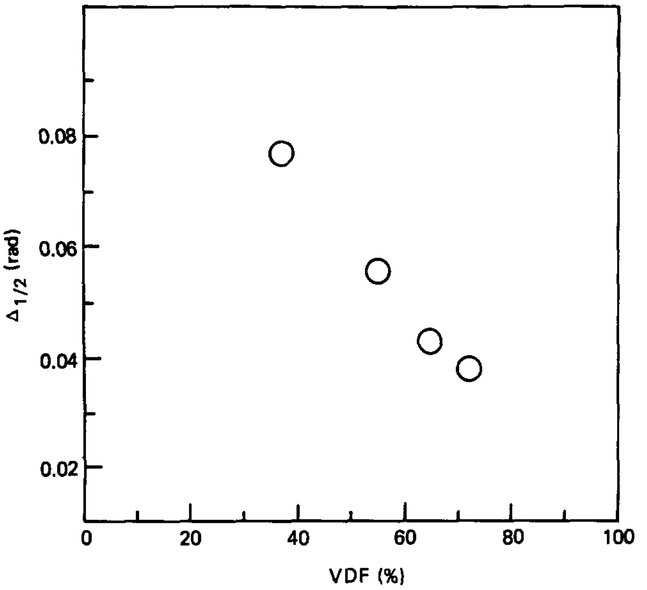


**Figure 15** The integrated halfwidth of the X-ray (0 0 2) reflection of the high-temperature phase for the various VDF–TrFE copolymer samples

temperature phase because of the coexistence of *gauche* bonds in the *trans*-type chain.

*Incomplete structural change and irregular conformation.* As clarified in the above two subsections, for the copolymer samples with lower VDF content, the molecular conformations both in the cooled phase and in the high-temperature phase are disordered due to the coexistence of *trans* and *gauche* sequences: in the cooled phase the *gauche* linkages are included within the long *trans* segments and in the high-temperature phase the regular *gauche* sequences are interrupted by *trans* bonds along the chain axis. For the copolymer with high VDF content, such as 73%, the crystalline phases are relatively ordered, the low-temperature phase having long *trans* sequences and the high-temperature phase having $TGT\bar{G}$ sequences. Such a difference in structural regularity as well as the transitional behaviour among copolymers may originate from the difference in monomer sequential distribution in the copolymer chains. In the copolymer with high VDF content, the long VDF monomer sequences are included along the chain and the conformational change may occur cooperatively throughout the VDF sequences. The TrFE sequential part is assumed not to experience any conformational change, as pointed out in *Figure 10*. On the other hand, the copolymer sample with lower VDF content does not include such long VDF sequences, which are interrupted by TrFE monomers. The conformational change in the VDF sequences does not occur so cooperatively, but scarcely and over a wide temperature range, resulting in the incomplete conformational transition. The conformational stability of the *trans* form relative to the *gauche* form for the copolymer chain with higher TrFE content

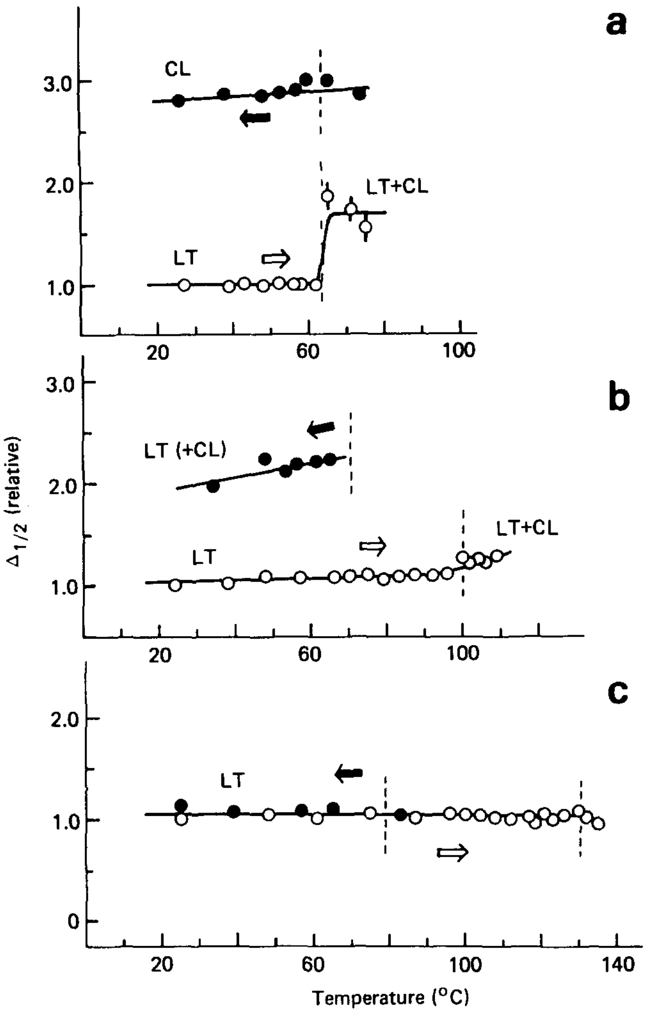
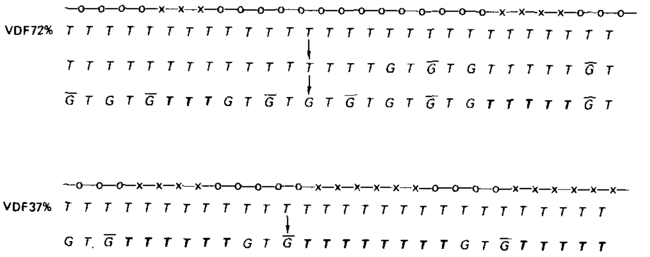


**Figure 16** Temperature dependence of the integrated halfwidth of the X-ray (0 0 1) reflection taken for the *trans* phase of the copolymer samples: (a) VDF 55%; (b) VDF 65%; (c) VDF 72%. The vertical broken lines indicate the transition temperatures. CL and LT denote the cooled phase and the low-temperature phase, respectively

may accelerate such a tendency[5,38]. A schematic illustration of the transitional behaviour for these copolymers is given below:



## CONCLUSIONS

In the present paper the temperature dependence of the Raman spectra has been measured for a series of VDF–TrFE copolymers with different VDF contents. When the samples are heated, the intensity of the *trans* band ($845\,\text{cm}^{-1}$) decreases and that of the *gauche* band ($800\,\text{cm}^{-1}$) increases in the vicinity of the transition temperature. Such an intensity exchange between the *trans* and *gauche* bands becomes incomplete and diffuse as the VDF content decreases down to 0%. Correspondingly, the regularity in the structure of the *trans* and *gauche* phases is lowered for the low VDF content copolymers, as understood from the coupled experimental data of Raman and X-ray diffraction measurements. The diffuse and non-cooperative transition behaviour and the low degree of structural order in the low VDF copolymer may come from the irregular distribution of the short VDF monomer sequences in the copolymer chains.

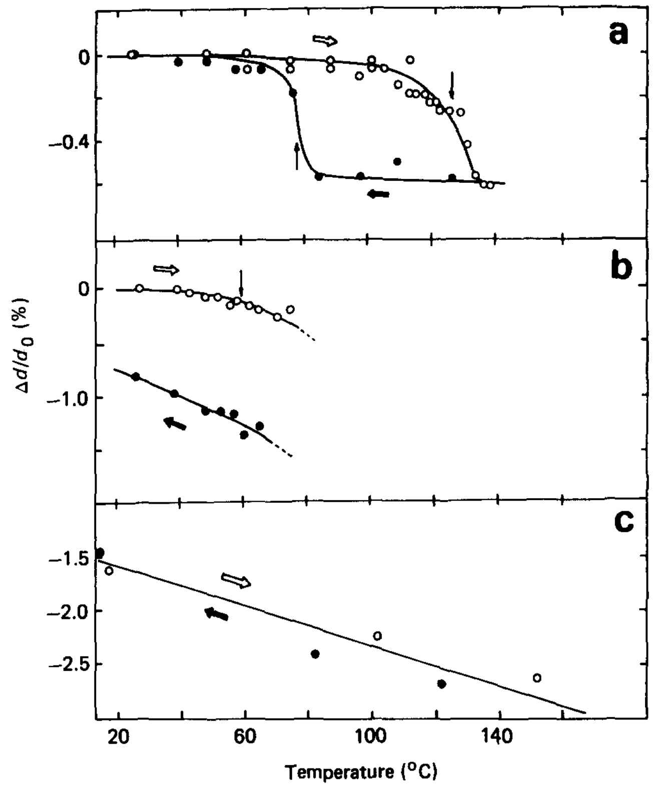


**Figure 17** Temperature dependence of lattice spacing $d$ measured for the (0 0 1) reflection of the *trans* phase of the copolymer samples: (a) VDF 72%; (b) VDF 55%; (c) VDF 0% (PTrFE). $d_0 = 2.555$ Å (all-*trans*) is taken as a standard initial value

In previous papers we investigated the *trans–gauche* conformational changes by means of infra-red spectroscopy, where the relatively weak *gauche* bands were analysed quantitatively. Such a conformational change could be detected much more clearly by the present Raman spectral measurement, as typically observed in the frequency region $700\text{–}900\,\text{cm}^{-1}$. More detailed study of the Raman spectra will contribute significantly to clarification of an essential feature of this unique ferroelectric phase transition of VDF–TrFE copolymers from the molecular theoretical point of view.

## ACKNOWLEDGEMENTS

The authors are indebted to Daikin Kogyo Co. Ltd, Japan, for supplying the samples of VDF–TrFE copolymers. They are also grateful to Emeritus Professor Hiroyuki Tadokoro for his continuing encouragement. This work was supported in part by a Grant-in-Aid on Special Project Research for 'Organic Thin Films for Information Conversion' from the Ministry of Education, Science and Culture of Japan.

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