Vibrational spectroscopic study on ferroelectric phase transition of vinylidene fluoride–trifluoroethylene copolymers:
2. Temperature dependences of the far-infrared absorption spectra and ultrasonic velocity

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The temperature dependence of far infrared absorption spectra was measured for vinylidene fluoride–trifluoroethylene (VDF–TrFE) copolymers with various VDF contents. For 55, 72 and 82 mol% VDF samples, the *trans–gauche* conformational transition was detected clearly. Near the ferroelectric phase transition temperature of the 55 mol% VDF sample, the band at 116 cm^{-1}, the skeletal torsional mode of the *trans* zig-zag conformation, was observed to transfer continuously to the position of the torsional band of the *gauche* type skeletal conformation at 108 cm^{-1}, suggesting a softening behaviour of the skeletal vibrational mode in the structural transition region. The ultrasonic modulus was found to exhibit an unusual minimum in the same temperature region. This anomalous behaviour was interpreted in terms of the coupling between the optical phonon of the skeletal torsional mode and the acoustic phonon through the piezoelectric and electrostrictive effects.

(Keywords: vinylidene fluoride–trifluoroethylene copolymers; ferroelectric phase transition; *trans–gauche* conformational change; far-infrared spectra; ultrasonic velocity)

INTRODUCTION

Recently much attention has been paid to poly(vinylidene fluoride) (PVDF) and vinylidene fluoride–trifluoroethylene (VDF–TrFE) copolymers because of their unique ferroelectric phase transition, which was discovered for the first time for crystalline synthetic polymers[1–3]. This ferroelectric–paraelectric transition may be characterized by the drastic structural change shown in *Figure 1*, where the all *trans* zig-zag chains change their conformation to the largely contracted *gauche* form above the Curie transition temperature[3–7]. This structural transformation reflects directly on changes in electrical and mechanical properties such as electric polarization, dielectric constant, piezoelectric constant and elastic constant[1,2,8].

In a series of papers we have investigated the vibrational spectroscopic features of this phase transition[3,7]. Corresponding well to the above-mentioned conformational change, the infrared and Raman spectra in the frequency region 200–3200 cm^{-1} were found to change largely between the *trans* and *gauche* phases. In general, a specific phonon is known to play a significant role in the ferroelectric phase transition[9,10]. For example, in the second-order phase transition of ionic crystals, one optical phonon increases its amplitude by an appreciable amount and the vibrational frequency softens toward the zero frequency side; the atoms relating to this soft phonon mode displace their positions under no restoring force and stabilize at new positions, generating a new crystal phase. That is, the soft phonon acts as a driving force for structural change in the phase transition. Such a soft phonon is not limited to second-order type phase transition but exists also in first-order transition. In the latter case, the phonon is softened in the transition region, but before the frequency decreases completely down to zero the other type of phonon begins to appear at the transition temperature. The free energies of the two phases are equalized and the structure changes from one to the other suddenly and discontinuously. So the two phonons coexist at the transition temperature. *Figure 2* illustrates the frequency changes expected for these two types of phase transition mechanism.

In the present copolymer system, it is also important to clarify what type of phonon plays a significant role in the ferroelectric phase transition and what kinds of interaction exist between the phonons in order to understand the above-mentioned characteristic *trans–gauche* transformation mechanism. We have measured optical phonons in the low frequency region of the far infrared spectra and their temperature dependence. A transition mechanism including phonon–phonon coupling will be discussed in connection with the thermal behaviour of the acoustic phonon mode, which is obtained by measurement of the ultrasonic velocity as a function of temperature.

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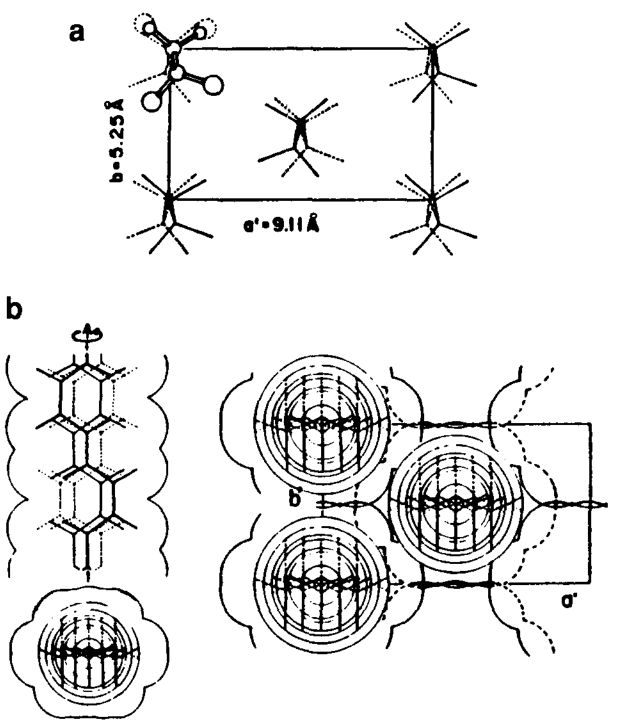

Figure 1 Crystal structures of (a) *trans* and (b) *gauche* phases of the VDF–TrFE copolymers[3]

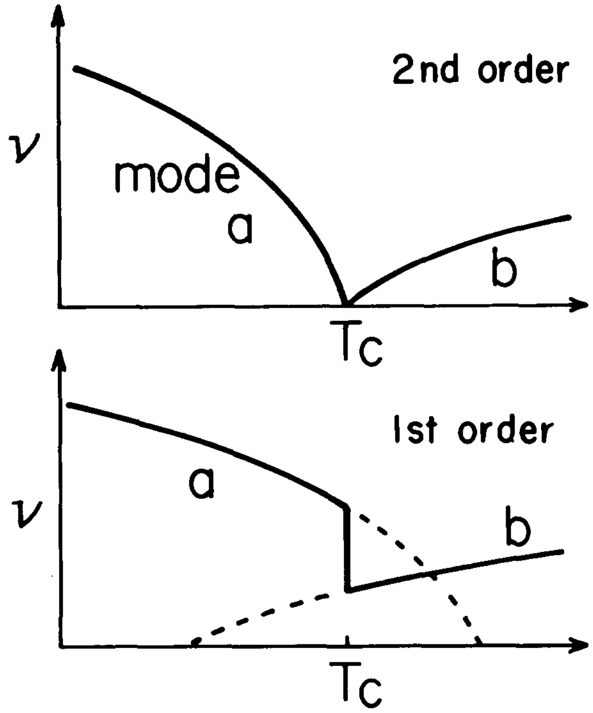

Figure 2 Schematic illustration of temperature dependence of the soft phonon mode in the phase transition region

EXPERIMENTAL

Samples

The samples used were poly(vinylidene fluoride) (PVDF) homopolymer (KF1000), supplied by Kureha Chemical Industry Co. Ltd, Japan, and VDF–TrFE copolymers with VDF molar contents of 0–82%, supplied by Daikin Kogyo Co. Ltd, Japan. Unoriented films of the copolymers were prepared by casting from acetone or methyl ethyl ketone solution at room temperature, followed by heat treatment at ≈135°C for 1 h. The uniaxially oriented films were prepared by drawing the as-cast films to about five times the original length at room temperature and annealing at ≈135°C under clamping between a pair of glass plates. Uniaxially oriented PVDF form I film was prepared by drawing the melt-quenched film to about five times the original length at room temperature. Uniaxially oriented PVDF form II sample was prepared by drawing the melt-quenched film at ≈160°C. Unoriented form III was prepared by casting slowly from the dimethylacetamide solution at ≈60°C (Reference 11). The oriented form III film was difficult to prepare by drawing the cast film at high temperature close to the melting point because it easily transfers to form I under the application of tensile force[12–14]. So it was prepared by annealing the weakly poled form II sample at a temperature immediately below the melting point of ≈180°C for a long time[15]. The polar form II (II_p) of PVDF was prepared by poling the form II film under a d.c. high voltage or corona charging at room temperature[16].

Measurement of far infrared absorption spectra

Far infrared spectra in the frequency region 400–30 cm^{-1} were measured by a Hitachi FIS-3 far infrared spectrophotometer equipped with a heating optical cell. To eliminate the thermal emission effect on the infrared absorption spectra at high temperatures, the double-chopping method was applied. The film specimen was sandwiched between a pair of silicon single crystal plates and set into the heating cell. The temperature of the sample was measured by a copper–constantan thermocouple.

Measurement of ultrasonic velocity

The ultrasonic velocity was measured in a transmission fashion using the system described in a previous paper[17]. A block of the copolymer sample was set between a pair of quartz glasses, on the ends of which the PZT piezoelectric transducers were adhered. An electric pulse was applied to the transducer and the propagation time of the ultrasonic pulse thus generated within the sample was measured. The sonic pulse received by a transducer attached at the other end of the sample had the shape of a modulated sine wave with frequency ≈1 MHz. Although it may be necessary, in principle, to separate the contributions of ultrasonic waves with certain vibrational frequencies to estimate the property of each ultrasonic wave exactly, the ultrasonic velocity measured in this experiment is considered to correspond to that at ≈1 MHz, judging from the pattern of the received signals.

RESULTS AND DISCUSSION

Far infrared spectra of the crystal modifications of PVDF

To clarify the vibrational bands characteristic of the *trans* and *gauche* conformers in the low frequency region, the far infrared spectra were measured for various crystal modifications of PVDF homopolymer. *Figure 3* shows the polarized far infrared spectra of forms I, II, II_p and III taken at liquid nitrogen temperature. The molecular conformations of these crystal forms are as

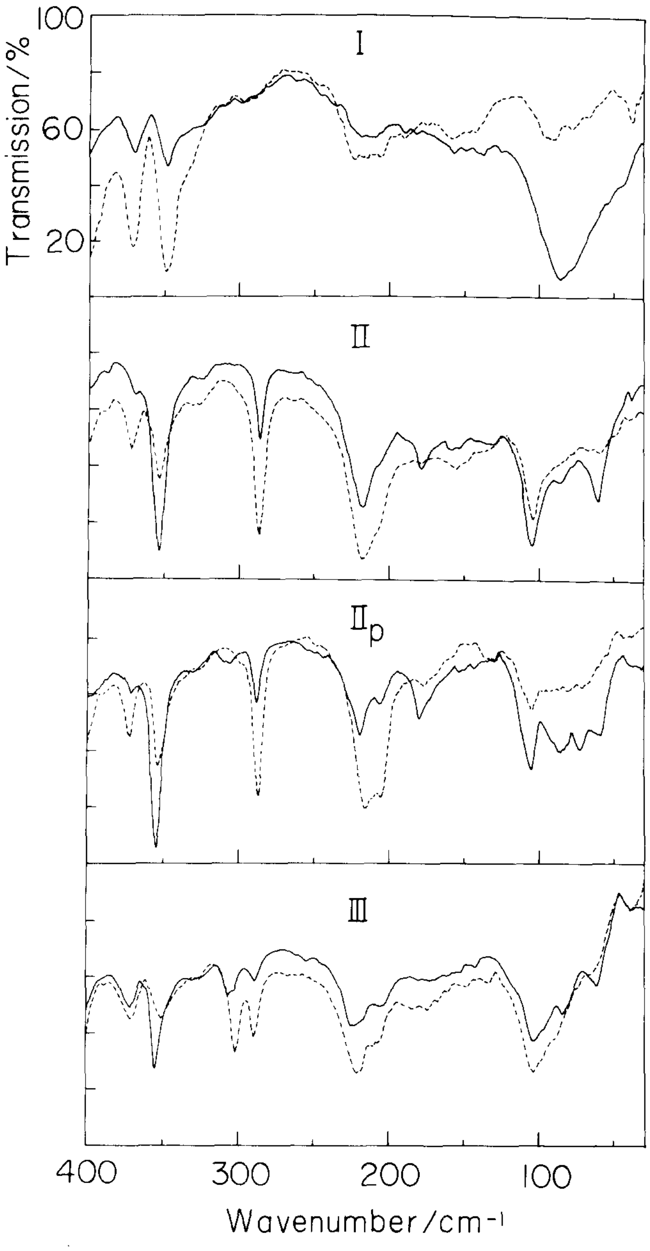

Figure 3 Polarized far infrared spectra of poly(vinylidene fluoride) crystal forms I, II, II_p and III at liquid nitrogen temperature. ———, Electric vector of incident infrared beam perpendicular to the draw direction; – – –, parallel

follows[13,18–23]:

Form I	..TTTT...
Forms II and II_p	..TGT$\bar{G}$...
Form III	..TTTGTTT$\bar{G}$...

The absorption bands characteristic of the *gauche* conformers, which are observed for forms II, II_p and III, are[12,14,24]:

354 cm^{-1} ($\perp$) 287 cm^{-1} ($\parallel$)	CF_2 twisting mode
216 cm^{-1} ($\perp$) 209 cm^{-1} ($\parallel$)	skeletal bending mode
100 cm^{-1} ($\perp$)	skeletal torsional mode

where $\perp$ and $\parallel$ denote the polarization dichroisms of the bands measured with electric vectors of the incident infrared beam perpendicular and parallel to the draw direction, respectively. According to normal modes analysis[12,14,24], the *trans* chain of PVDF form I does not exhibit the infrared active bands in the frequency region 400–100 cm^{-1}. The parallel bands at 350 and 372 cm^{-1} have been assigned to modes which are originally inactive but activated due to the symmetry breakdown of the *trans* zig-zag conformation[12]. The band at 372 cm^{-1} is observed also in the spectra of PVDF forms II, II_p and III, suggesting the existence of some *trans* sequences within the *gauche*-type chains as a kind of structural defect. (The 350 cm^{-1} band overlaps with the strong band of the *gauche* conformation.)

In the frequency region of the external lattice modes the spectra are different largely in the crystal forms. The broad perpendicular band located around 70–80 cm^{-1} in the spectra of PVDF form I comes from the librational lattice mode of the *trans* zig-zag chains in the crystal lattice. The broadness of this band might come from the structural disorder in the molecular packing within the crystal cell. A librational lattice mode of the *gauche* chain appears at 53 cm^{-1} at room temperature and 60 cm^{-1} at liquid nitrogen temperature for PVDF form II[12]. Form II_p takes a molecular conformation essentially the same as that of form II and, therefore, the infrared spectra in the fingerprint region are very close to each other[16]. In the far infrared frequency region, however, form II_p exhibits some different spectral features from those of form II, especially in the lattice vibrational frequency region. The lattice vibrational band appears at ≈65 cm^{-1} at room temperature and 73 cm^{-1} at liquid nitrogen temperature. *Figure 4* shows the far infrared spectral change observed in the transition process of form II → polar form II → form I, which is caused by poling treatment at high voltage. As the poling proceeds, the bands intrinsic to form II (e.g. 60 cm^{-1} at liquid nitrogen temperature) begin to decrease in intensity and the lattice band of form II_p (indicated by arrows) appears and increases in intensity. At the same time, the band of form I also begins to increase in intensity. Splitting between the perpendicular and parallel bands near 220 cm^{-1} is observed uniquely for the II_p form. The form II_p contains two chains in the unit cell[2,16] and the intermolecular interactions may cause band splitting through the following phase correlation, where the crystal structure is assumed to have a space group of C_s^2:

Molecular chain	Site group	Space group
C_s	C_s	C_s
$A'(\perp, \parallel)$	$A'(\perp, \parallel)$	$A'(\perp, \parallel)$
$A''(\perp)$	$A''(\perp)$	$A''(\perp)$

This correlation table predicts the bands of the A' symmetry species split into two A' bands with parallel or perpendicular polarization. The bands located near 210 cm^{-1} may correspond to such a correlation splitting.

The lattice vibrational bands of form III have not yet been clearly identified. The perpendicular band at 55 cm^{-1} at room temperature (63 cm^{-1} at liquid nitrogen temperature) may be one of them. In the far infrared spectra of form III are contained bands characteristic of both local *trans* and *gauche* structures. Detailed assignments are referred to in Reference 14.

Far infrared spectra of VDF–TrFE copolymers at room temperature

Figure 5 shows the polarized far infrared spectra measured at room temperature for copolymer samples

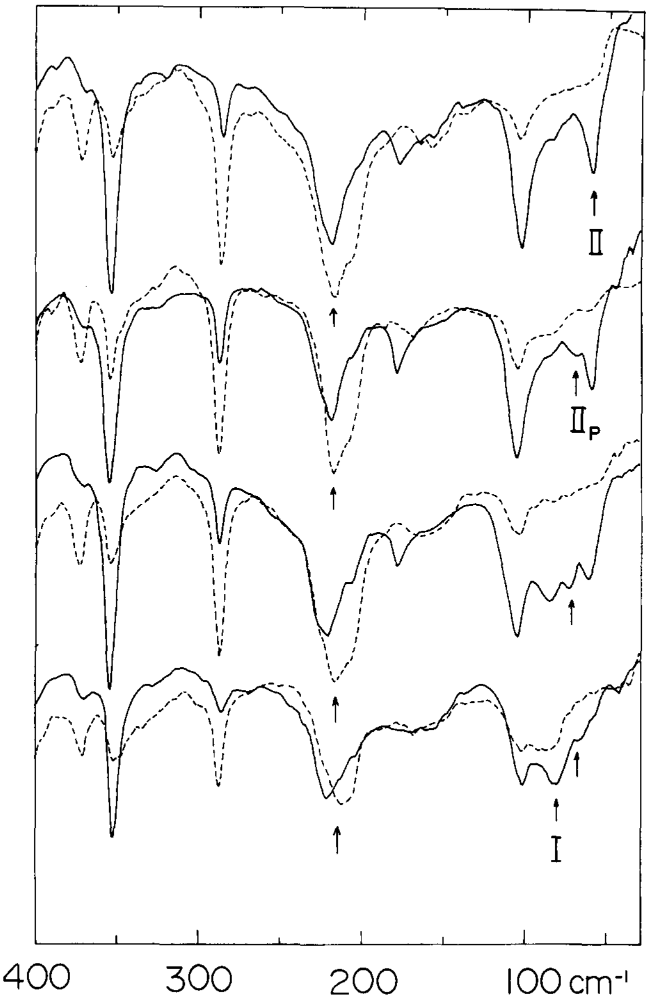

Figure 4 Polarized far infrared spectral changes induced by the poling treatment of the uniaxially oriented PVDF form II film (spectra were taken at liquid nitrogen temperature). ———, Electric vector of incident infrared beam perpendicular to the draw direction; ----, parallel

with various VDF contents. The perpendicularly polarized band at 70 cm^{-1} of PVDF form I (the librational lattice mode around the chain axis) decreases in intensity and shifts to lower frequency as VDF content decreases (indicated by bars in this figure). This suggests a gradual weakening of the intermolecular interactions due to the lattice expansion induced by the introduction of TrFE monomers into the molecular chains[2,6]. When the VDF content decreases further, this band cannot be observed within the spectral region detectable by the present FIS-3 spectrophotometer. For copolymer samples with VDF content $<60\%$, the broad band is observed below 150 cm^{-1}. This may be assigned to the torsional vibrational mode of the planar zig-zag conformation, which is originally inactive in the infrared spectra but spectroscopically activated due to the breakdown of the translational symmetry along the copolymer chains[12,25]. This assignment comes from the frequency dispersion curves and frequency distribution function calculated for PVDF form I, where the peak of the out-of-phase skeletal torsional mode appears around 120 cm^{-1}. The bands located in the 200–300 cm^{-1} region increase in intensity for the samples of lower VDF content. They are considered to originate from vibrational modes characteristic of TrFE monomer sequences. The parallel band at 350 cm^{-1} increases in intensity with an increment of the VDF content. Since the copolymer samples with VDF content $<75\%$ crystallize in the *trans* conformation, this band is assigned to the mode characteristic of the *trans* segment of the VDF monomeric sequences, as already stated in the preceding section. The half width of this band becomes broader with a decrease in VDF content, consistent with the X-ray and Raman data, showing the higher structural irregularity of the VDF *trans* sequences in the copolymer chains with lower VDF content[3,7].

Temperature dependence of far infrared spectra of the copolymers

Figures 6 and *7* show the polarized far infrared spectra taken below and above the ferroelectric transition temperature for 72 and 55% VDF copolymers, respectively. Above the transition temperature, the bands characteristic of VDF *trans* sequence decrease in intensity and the *gauche* bands at 310 ($\perp$), 290 ($\parallel$), 210 ($\parallel$) and 100 ($\perp$) cm^{-1} increase in intensity, while keeping a clear polarization character. Such a spectral change was also reported by Petzelt *et al.*[25]. For the 72% VDF sample, the lattice band at ≈ 60 cm^{-1} disappears above the transition point. For the 55% VDF copolymer, the band near 110 cm^{-1} at room temperature shifts apparently continuously toward the lower frequency position of the *gauche* band at 100 cm^{-1}, which will be discussed later. The perpendicularly polarized band at 230 cm^{-1}, characteristic of TrFE units, does not disappear even above the transition temperature, suggesting that the TrFE parts do not experience a *trans–gauche* conformational change as discussed in the previous paper[3].

For 82% VDF copolymer, the crystal polymorphism and the transition behaviour are largely dependent on the sample preparation conditions[11,26]. For example, melt-quenching gives the almost pure form II sample, while the sample obtained by slow cooling of the melt gives the *trans* zig-zag form I with some *gauche* form content. *Figure 8* shows the temperature dependence of the far infrared spectra of the VDF 82 copolymer sample obtained by slow cooling of the melt. In the cooling process from the melt (165°C), a spectral pattern similar to PVDF forms II or III is obtained at 125°C (the characteristic bands at 310, 210 and 100 cm^{-1}); i.e. the 82% VDF copolymer crystallizes first in the high temperature *gauche* form. As the temperature is lowered further, these *gauche* bands decrease in intensity and instead the spectral pattern changes into that of the *trans* form stable at room temperature. In the heating process, the *trans–gauche* transition occurs at a temperature close to but still *below* the melting point (see the spectra at 150°C). These spectral data indicate clearly that the *trans–gauche* phase transition occurs *below* the melting point, quite consistent with the X-ray diffraction and infrared spectral data reported before[3,26]. *Figure 9* shows the temperature dependence of the band located at ≈ 110 cm^{-1} measured for the unoriented VDF 52% copolymer. In *Figure 10* the peak frequency is plotted against temperature. The *trans* band at 116 cm^{-1} appears to shift continuously to the lower frequency side and transfer gradually to the *gauche* band position (108 cm^{-1}) near the transition temperature. As one of the possible candidates for interpreting this spectral behaviour, the following mechanism might be proposed. As pointed out in the previous section, the *trans* band at 116 cm^{-1} is considered to come from the originally inactive torsional mode with the phase angle π between the neighbouring monomeric units along the chain axis.

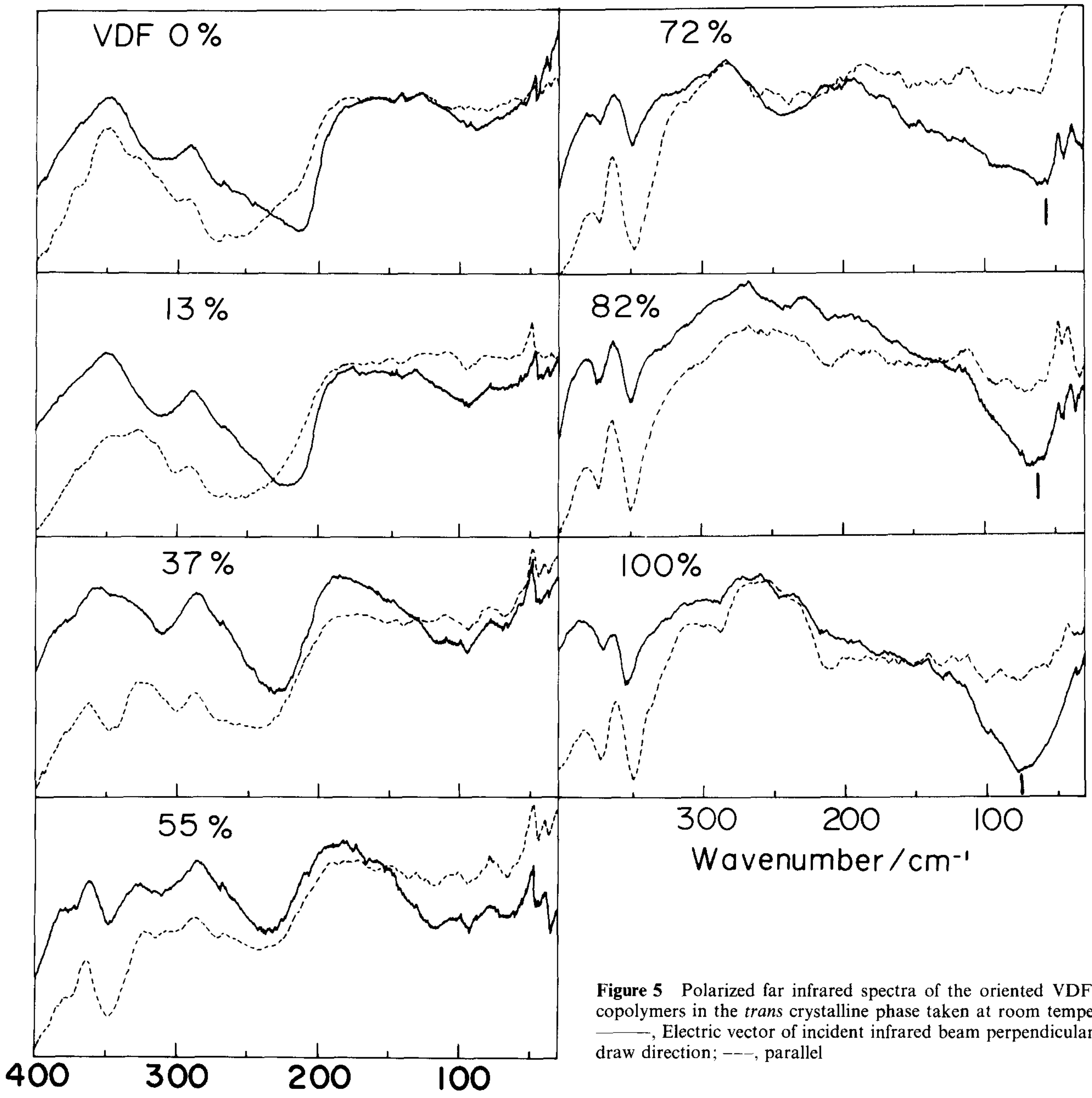

Figure 5 Polarized far infrared spectra of the oriented VDF–TrFE copolymers in the *trans* crystalline phase taken at room temperature. ———, Electric vector of incident infrared beam perpendicular to the draw direction; – – –, parallel

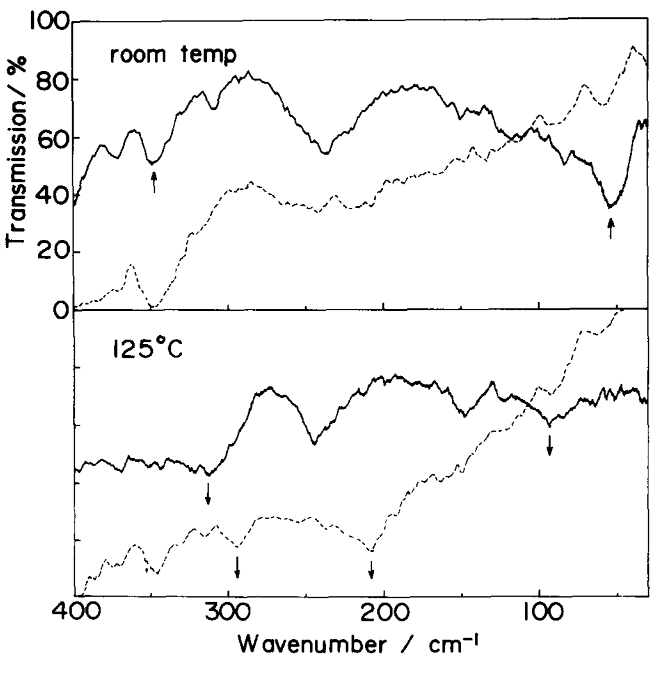

Figure 6 Polarized far infrared spectra of 72% VDF copolymer taken at room temperature and 125°C. ———, Electric vector of incident infrared beam perpendicular to the draw direction; – – –, parallel

As the temperature approaches the transition point, anharmonicity of the torsional mode becomes larger, the vibrational amplitude is increased and the frequency is softened. As indicated in *Figure 2*, the vibrational frequency begins to decrease toward the zero frequency side and approaches the frequency position intrinsic to the *gauche* conformer (108 cm^{-1}). The amplitude of the torsional mode of the *trans* form becomes large enough to reach the level of the *gauche* position of the CF_2 groups, just when the molecular chain is trapped by a potential well of the *gauche* form and stabilized as a thermodynamically stable *gauche* crystalline phase. *Figure 11* illustrates such a situation schematically. It is unclear at present whether the continuous frequency change in *Figure 10* is real (second order) or apparent due to the weighted overlapping of the *trans* and *gauche* bands of slightly different frequencies (first order). Even when the transition is of the first order type, however,

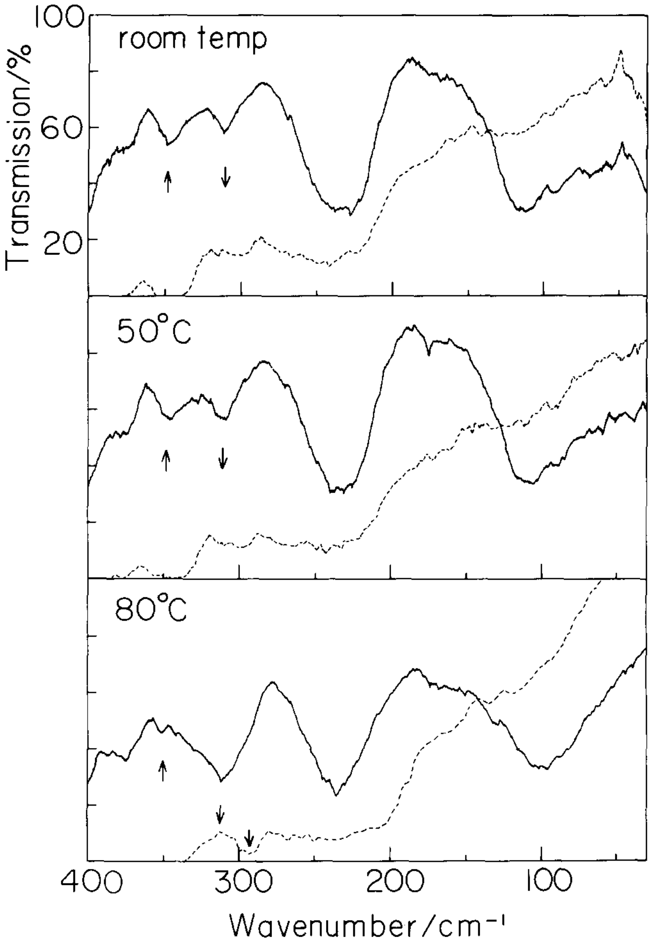

Figure 7 Polarized far infrared spectra of 55% VDF copolymer taken at room temperature, 50°C and 80°C. ———, Electric vector of incident infrared beam perpendicular to the draw direction; ---, parallel

softening of the *trans* vibrational mode could occur and a new band intrinsic to the *gauche* phase might appear before the wavenumber of the *trans* band decreases completely down to zero, as explained in the introduction. In such a sense, therefore, softening of the *trans* form and the vibrational motion of enhanced amplitude are considered to be one of the plausible mechanisms for conformational structure transition, irrespective of the type of phase transition, continuous or discontinuous. (In the ideal case of phase transition caused by softening of the phonon modes, the wavenumber of the vibrational mode should increase again in the newly generated crystal phase because of the hardening of the mode[9,10]. In the present case, however, the *gauche* band decreases slightly to the lower frequency side in the higher temperature region. It is not clear at present whether this is just inconsistent with the idea of mode hardening or whether it results from an overlap of mode-hardening during the transition to the new phase and softening of the anharmonic force field caused by the thermal effect.)

Coupling of optical and acoustic phonons

Figures 12 and *13* show the temperature dependences of the ultrasonic velocity measured for the 65 and 73% VDF copolymer samples compared with those of the infrared intensities of the *trans* and *gauche* bands (and also of the inverse dielectric constant for the latter case). *Figures 14* and *15* show the temperature dependences of the ultrasonic velocity measured for a series of VDF–TrFE copolymers[27]. As seen in *Figures 12* and *13*, the ultrasonic velocity shows an anomalous behaviour near the ferroelectric *trans–gauche* transition temperature. Such an observation was made also by Matsushige *et al.*[28], Tanaka *et al.*[29] and Krüger *et al.*[30]. As shown in *Figures 14* and *15*, the anomalous behaviour of the

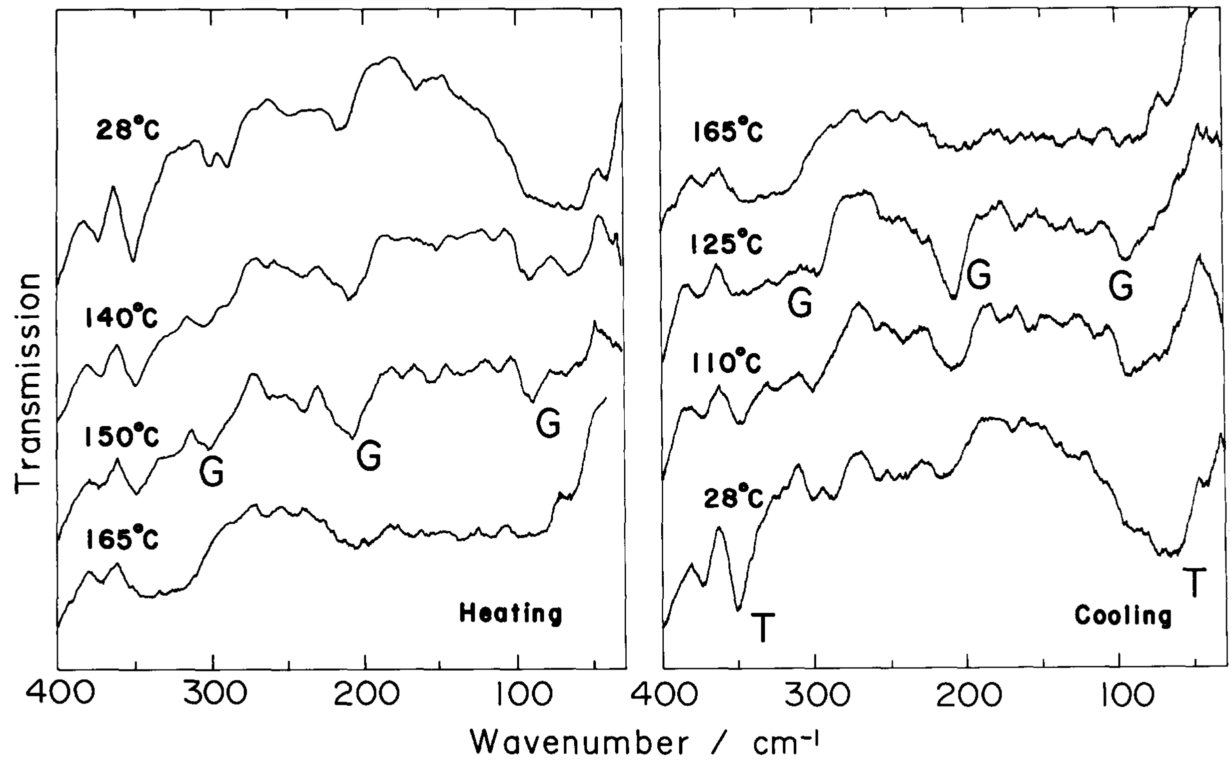

Figure 8 Temperature dependence of the far infrared spectra of unoriented 82% VDF copolymer

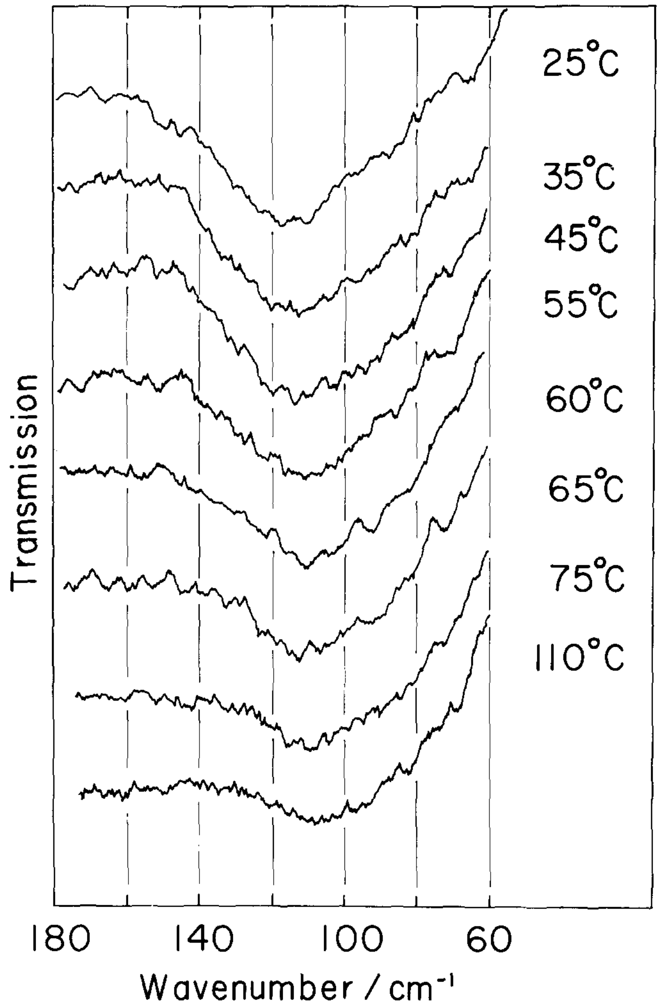

Figure 9 Temperature dependence of the far infrared spectra of unoriented 52% VDF copolymer in the 60–180 cm^{-1} region

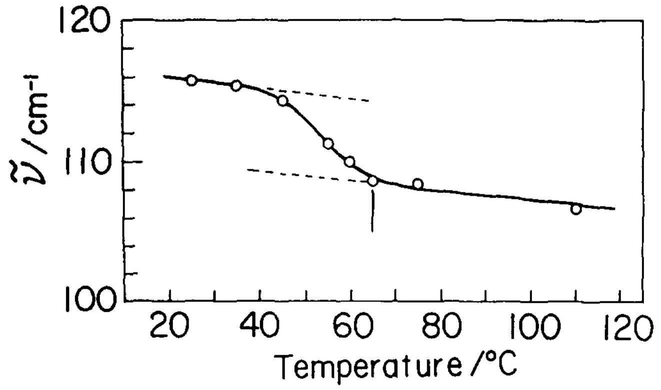

Figure 10 Temperature dependence of the far infrared band frequency of the 52% VDF sample of *Figure 9*

ultrasonic velocity is not limited to the cases of the 65 and 73% VDF samples, but is found to occur in the structural transition region for all copolymer samples, although the drastic change in ultrasonic velocity becomes more ambiguous as the VDF content decreases down to 0%. Such an anomaly may be interpreted phenomenologically in terms of coupling between the electric polarization P and mechanical strain ε. We will assume that the Helmholtz free energy is expressed by the following equation using the variables P and ε[31]:

$$A = A_0 + \tfrac{1}{2}c^{\mathrm{P}}\varepsilon^2 + \tfrac{1}{2}a_2P^2 + \tfrac{1}{4}a_4P^4 + \tfrac{1}{6}a_6P^6 + \cdots + \beta P\varepsilon + \gamma P^2\varepsilon + \delta P\varepsilon^2 \qquad (1)$$

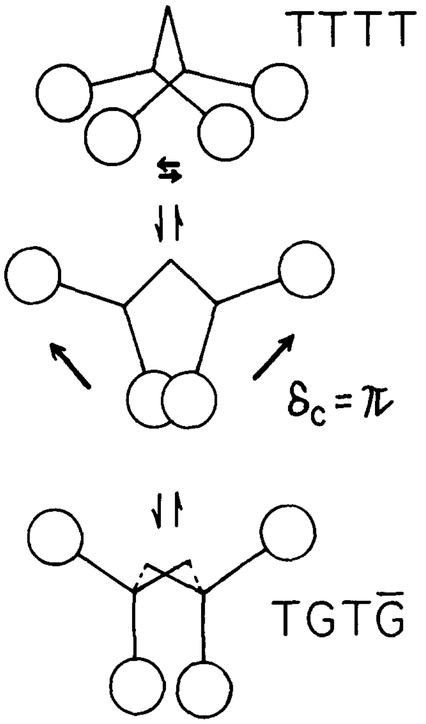

Figure 11 Conformational change between the *trans* and *gauche* forms via a skeletal torsional mode with phase angle π between neighbouring CF$_2$ units

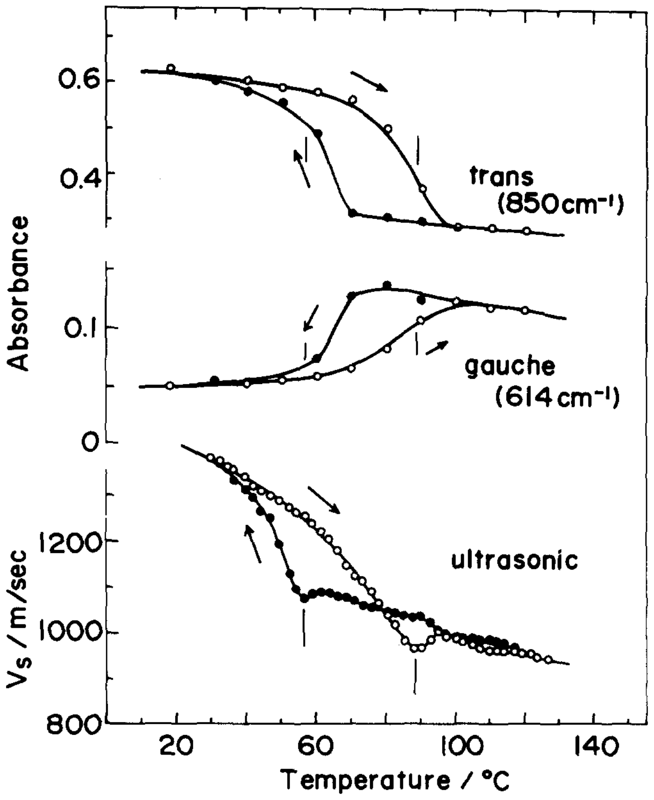

Figure 12 Temperature dependence of the ultrasonic velocity measured for unoriented 65% VDF copolymer compared with temperature dependences of the infrared intensities

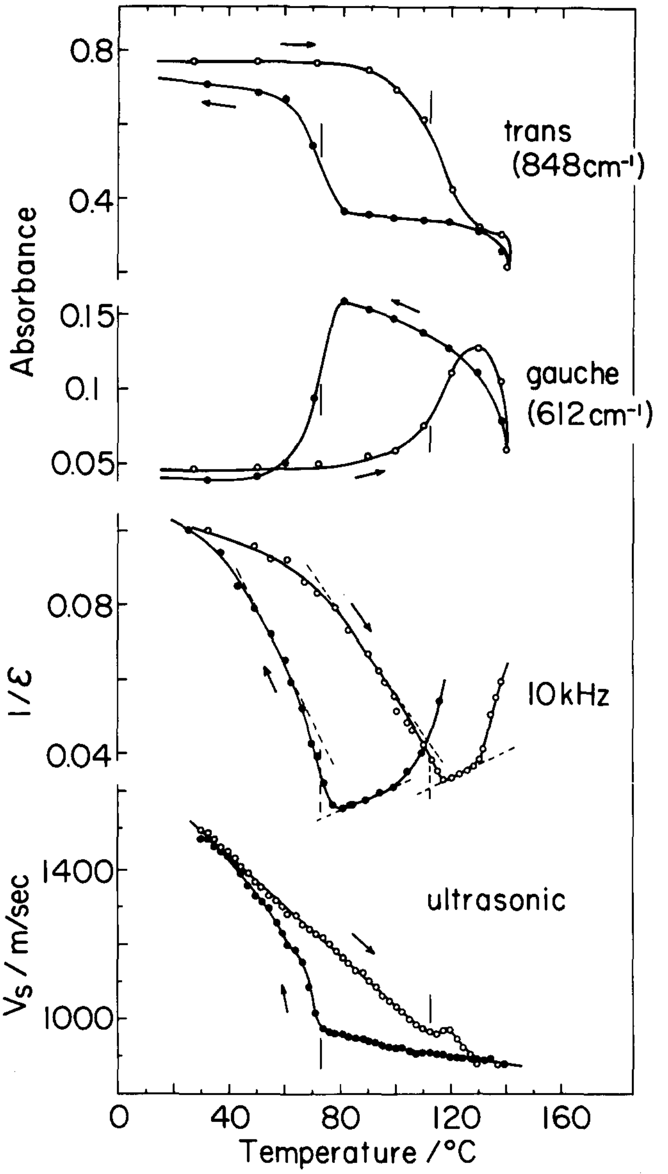

Figure 13 Temperature dependence of the ultrasonic velocity measured for unoriented 73% VDF copolymer compared with temperature dependences of the infrared intensities and inverse dielectric constant

where $a_2 = \alpha(T - T_c)$, c^P is the elastic modulus under a constant polarization, and β, γ and δ are the coupling constants between P and ε. The elastic constant c^E under a constant electric field is given by

$$c^E = (\partial^2 A/\partial \varepsilon^2)_E \qquad (2)$$

where electric field E is defined as

$$E = \partial A/\partial P \qquad (3)$$

From equations (1)–(3), c^E can be expressed as follows:

$$c^E = c^P - (\partial^2 A/\partial \varepsilon\, \partial P)^2 \chi^\varepsilon \qquad (4)$$

where χ^ε is an electric susceptibility defined as

$$\chi^\varepsilon = (\partial^2 A/\partial P^2)_\varepsilon^{-1} = (\partial E/\partial P)_\varepsilon^{-1} \qquad (5)$$

Some results obtained for equation (4) are as follows[31]. For continuous transition ($a_4 > 0$, $a_6 = 0$), for example, c^E for linear coupling $\beta P \varepsilon$ is expressed by

$$\begin{array}{lll} c^E = c^P - \beta^2 \chi^\varepsilon = c^P - \beta^2/[\alpha(T - T_c)] & T > T_c & \\ \quad = c^P - \beta^2/[2\alpha(T - T_c)] & T < T_c & \end{array} \qquad (6)$$

Similarly, for coupling $\gamma P^2 \varepsilon$,

$$\begin{array}{ll} c^E = c^P & T > T_c \\ \quad = c^P - \gamma^2/(2a'_4) & T < T_c \quad (a'_4 = a_4 - 2\gamma^2/c^P) \end{array} \qquad (7)$$

and for coupling $\delta P \varepsilon^2$ with positive δ

$$c^E = c^P + 2\delta P \qquad (8)$$

Results calculated on the basis of these equations are illustrated in *Figure 16* for the first ($a_4 < 0$) and second

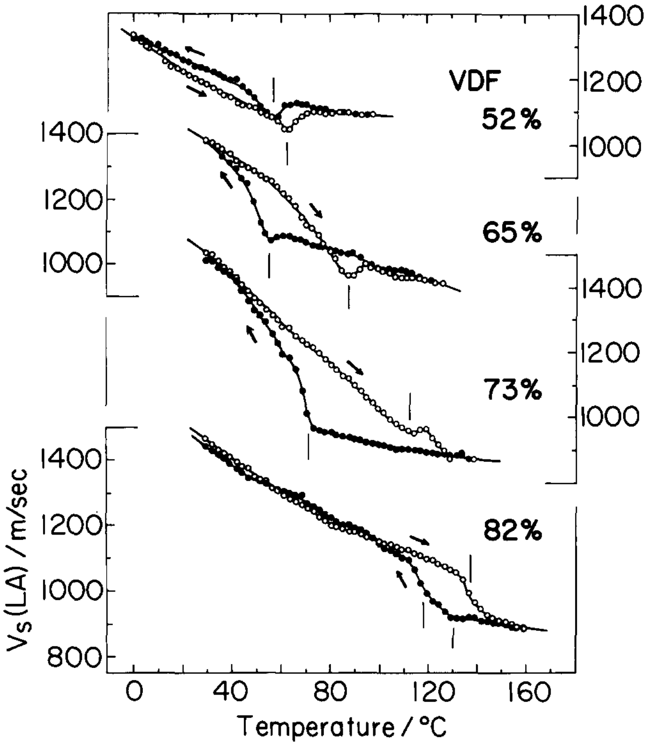

Figure 14 Temperature dependence of the ultrasonic velocity measured for 52, 65, 73 and 82% VDF unoriented samples

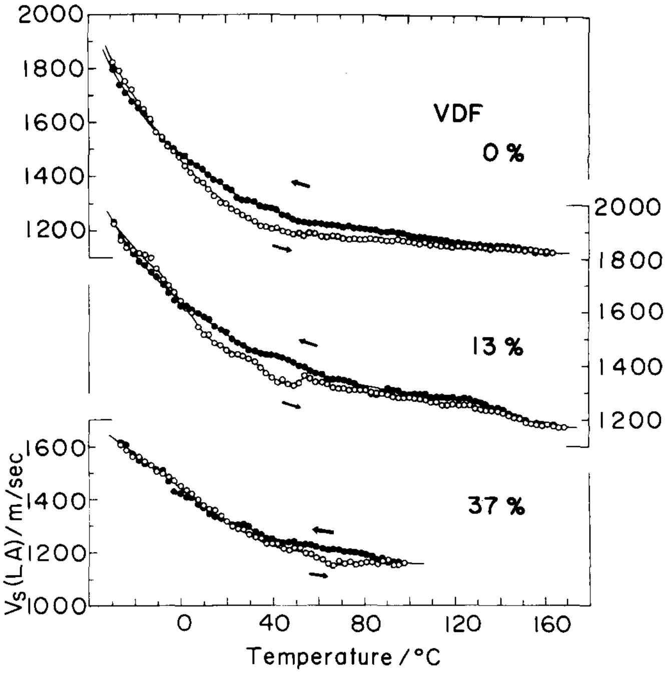

Figure 15 Temperature dependence of the ultrasonic velocity measured for 0, 13 and 37% VDF unoriented samples

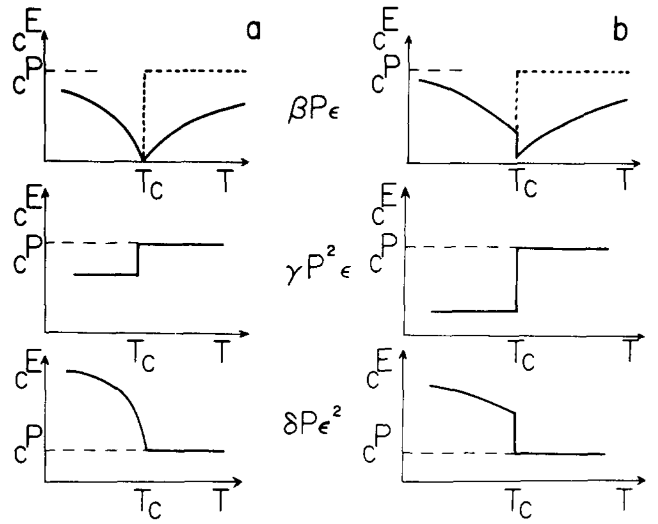

Figure 16 Calculated temperature dependence of the elastic modulus for various coupling conditions: (a) second-order; (b) first-order phase transition. In the top two figures: ———, $\beta \neq 0$; ----, $\beta = 0$ above the transition point. The curves for the coupling $\delta P\varepsilon^2$ are calculated for positive δ

($a_4 > 0$) type of transition. The linear coupling of P and ε, $\beta P\varepsilon$, represents the piezoelectric effect on the elastic constant c^E (the coefficient β corresponds to piezoelectric constant). The coupling of P^2 and ε, $\gamma P^2\varepsilon$, is due to the electrostrictive effect. In the present copolymer case, the polarization P decreases to zero and the piezoelectric constant β disappears above the Curie transition temperature[1]. As seen in *Figures 14–16*, the appearance of the minimum in the ultrasonic velocity at the Curie transition point can be reproduced qualitatively by taking into account the couplings between P and ε. The observed curves of velocity *versus* temperature are apparently similar to those calculated for the couplings $\beta P\varepsilon$ and $\delta P\varepsilon^2$ (Reference 2). But a quantitative estimation of the contribution of these coupling effects is difficult, because the observed ultrasonic velocity was for the unoriented bulk samples and includes the contribution from the amorphous phase more or less, although the crystalline phase seems to play a significant role in the transition temperature region. (A close interrelation between the bulk sample and the crystalline region in the transition region has already been reported for measurements of the dimensional changes[32,33].) The electric polarization P comes from the parallel arrangement of CF_2 dipoles. The temperature dependence of P reflects the disordering of these CF_2 dipole arrays induced by the large structural change between the *trans* and *gauche* conformations. As discussed in the previous section, such a conformational change correlates well with the optical phonon of the skeletal torsional modes. In other words, the temperature change in electric polarization P may originate from the thermal behaviour of these optical phonons. The anomalous thermal behaviour of the ultrasonic velocity may be interpreted in such a way that these optical phonons are coupled with the acoustic phonons through the piezoelectric interaction and so on, as explained above.

CONCLUSIONS

In this paper we have discussed the characteristic features of far infrared spectra for various crystal modifications of PVDF and VDF–TrFE copolymers. In the far infrared region, the skeletal deformation and torsional modes predominate. The large structural change between *trans* and *gauche* skeletal conformations in the ferroelectric phase transitions could be detected clearly as the remarkable far infrared spectral change. In particular, a large frequency shift has been found between the torsional modes of the *trans* and *gauche* forms in the 55% VDF copolymer. This experimental result leads us to speculate on a structural transition mechanism based on the soft mode concept: the increase in the vibrational amplitude of the torsional mode of the *trans* chain and softening into the stable *gauche* conformational position.

The anomalous temperature dependence of the acoustic phonon (or the ultrasonic velocity) has been detected for a series of copolymers and could be interpreted qualitatively in terms of electromechanical coupling between the optical and acoustic phonons. But the observed sonic velocity is for the bulk samples and not for the isolated crystalline region.

A more direct detection of such a phonon–phonon coupling occurring in the crystalline region might be obtained by measuring the phonon dispersion curves over the whole Brillouin zone and their temperature dependence by means of inelastic coherent neutron scattering, for example. The method is not so promising, however, for neutron experiments with refined results for broad and irregular polymer crystal systems.

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