Structural study on ferroelectric phase transition of vinylidene fluoride–trifluoroethylene random copolymers

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In the present situation of much discussion concerning the ferroelectricity of poly(vinylidene fluoride) [PVDF] form I crystal, the random copolymer of vinylidene fluoride (VDF) and trifluoroethylene (TrFE) has been recently found to show a phase transition in the crystalline region between the ferroelectric and paraelectric phases through a so-called Curie temperature (e.g. 65°C for a copolymer with a VDF monomer content of 55 mol%) based on the following experimental facts revealed by Fukada *et al.*[1]. (1) The dielectric anomaly and the disappearance of remnant polarization estimated from the hysteresis loop of electric displacement vs. electric field have been observed at the transition temperature, where the piezoelectric constant has also vanished simultaneously. The reciprocal dielectric constant $1/\varepsilon'$ is linearly related to the temperature and the Curie–Weiss law holds [$1/\varepsilon' \propto T-T_c$, $T_c \doteqdot 65°C$]. (2) The lattice spacing of the crystal changes steeply in the vicinity of the transition point, and the amount of change of spacing Δd is linearly proportional to the square of remnant polarization, indicating the existence of spontaneous deformation induced by the parallel arrangement of dipoles in the ferroelectric crystal phase.

Although the ferroelectric characteristics of the crystal transition have been established in this way, the detailed crystal structures of both phases of ferroelectric and paraelectric as well as the transition mechanism have not yet been clarified. A series of these copolymers stands as a typical model compound for solving the relationship between structure and ferroelectric property of PVDF form I crystal. We report here the experimental results for the crystalline phase transition of these copolymers using X-ray diffraction, infra-red and Raman spectroscopic methods and propose one possible mechanism of the transition.

Experimental

In this communication the copolymer sample with VDF monomer content of 55 mol% was mainly used, which was supplied by Daikin Kogyo Co., Ltd. (m.pt. at about 153°C). Unoriented films were obtained by casting from an acetone solution at room temperature or by melt-quenching. Uniaxially oriented samples were prepared by elongating them at room temperature (elongation ratio 500%). These samples were annealed at 110°C for 3 h. Measurements of X-ray diffraction and Raman spectra at high temperatures were carried out by blowing hot air onto the sample under the operation of a temperature controller (accuracy: ±0.4°C at 60°C and ±1.0°C at 100°C). The temperature dependence of infra-red spectra was measured by using a high-temperature optical cell equipped with KBr windows.

Results and discussion

Temperature dependence of X-ray fibre diagram. At room temperature the 55% copolymer gives an X-ray fibre diagram essentially identical to that of PVDF form I (*Figure 1*)[2]. The equatorial relfections can be indexed by a rectangular unit cell of $a'=9.11$ Å and $b'=5.25$ Å. The fibre period is 2.55 Å, suggesting an extended zigzag conformation for this polymer molecule. As the temperature rises closely to the transition point (65°C), the equatorial reflections split slightly up and down from a horizontal line, implying occurrence of a tilting

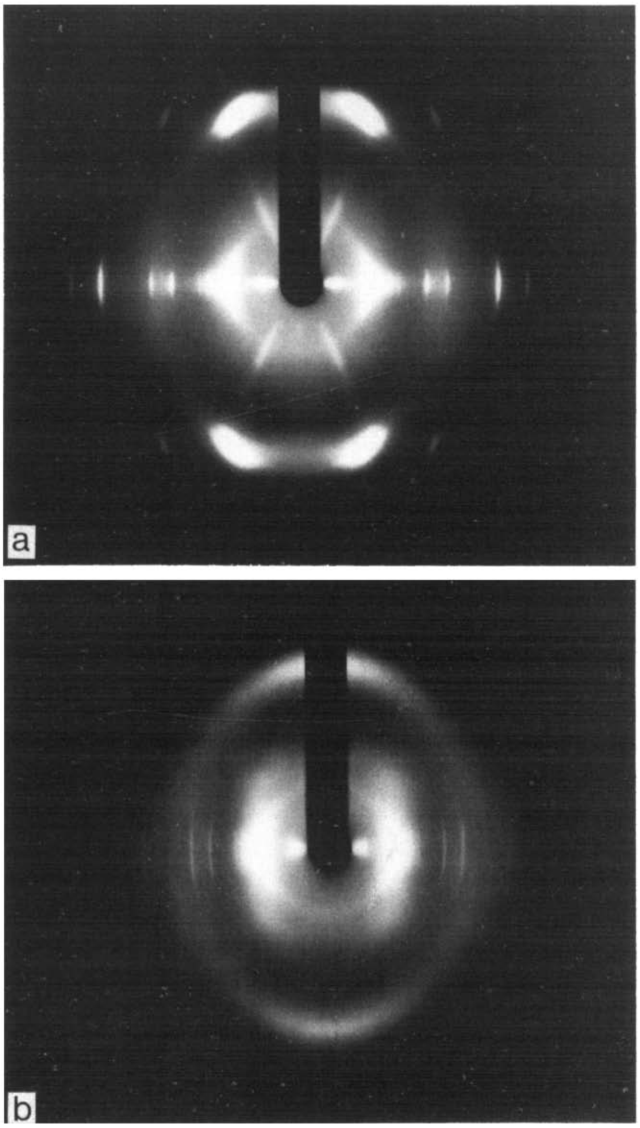

Figure 1 **X-ray fibre diagrams for (a) low- (21°C) and (b) high-temperature (81°C) phases of 55% copolymer**

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phenomenon[3]. At the temperature higher than the transition point the tilting phenomenon vanishes. The equatorial reflections are still sharp but the layer lines become gradually diffuse. The high-temperature phase is of a hexagonal type with $a'=9.75$ Å and $b'=5.63$ Å at 89°C. A new reflection is found to appear, though weak and broad, just in the middle between the equatorial and the first layer lines and corresponds well to the position of the (021) reflection of PVDF form II[2] and the (102) reflection of PVDF form III[4,5]. The interlayer spacing is estimated to be about 4.62 Å. The (00*l*) reflections measured in Weissenberg photographs indicate that the fibre repeating period is a multiple of 2.31 Å. If the new layer line is assigned to the first layer and the observed Weissenberg (00*l*) reflections are of $l=2$ and 4, the repeating period along the chain axis is about 4.62 Å. After cooling down to room temperature, the tilting photograph is obtained but the layer lines are still diffuse. Detailed structure analyses of these low- and high-temperature phases will be reported later.

Temperature dependence of infra-red and Raman spectra. *Figure 2* shows the temperature dependence of infra-red spectra for the 55% copolymer film. In *Figure 3* the temperature dependence of relative absorbances for several bands is shown. In a previous paper[6] we have identified the infra-red bands characteristic of T_m ($m \geqslant 3$), TG, and T_3G conformational sequences (T:*trans*, G:*gauche*) based on detailed normal coordinate treatments of PVDF forms I, II, and III. For example, 1288 and 350 cm^{-1} for T_m ($m \geqslant 4$), 850 cm^{-1} for T_m ($m \geqslant 3$), 870 and 614 cm^{-1} for TG, and 300 cm^{-1} for T_3G. It can be easily seen from *Figures 2* and *3* that as the temperature rises from room temperature to the higher temperature over the transition point the bands corresponding to the long *trans* sequences decrease in their intensity while those of TG and T_3G bands increase the intensity appreciably. Additionally the distinct polarizations of the bands are kept unchanged even after the transition, and the *gauche* bands appearing at the high temperatures also reveal remarkable polarizations, indicating that the interchange between the *trans* and *gauche* conformers occurs within the crystalline region, not in the amorphous region (this can be definitely recognized also from the X-ray fibre diagrams shown in *Figure 1*). The similar spectral changes are also observed in the Raman spectra.

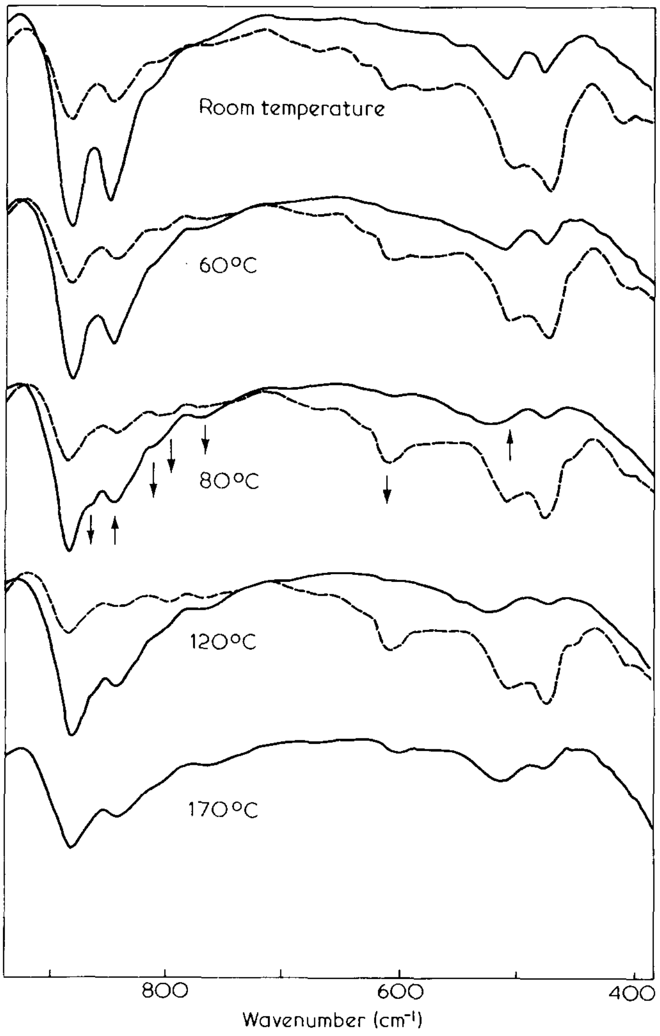

Figure 2 Temperature dependence of polarized infra-red spectra of 55% copolymer: (——) electric vector ⊥ orientation axis, (– – –) electric vector // orientation axis

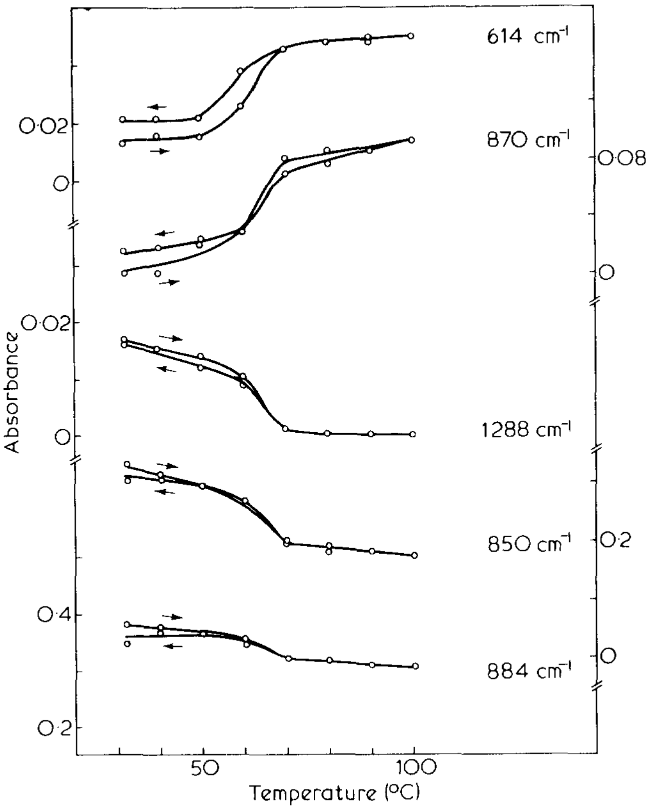

Figure 3 Temperature dependence of relative absorbances for 55% copolymer

Structural change in phase transition of 55% copolymer. From all the experimental results stated above, we may consider the structural change occurring in the phase transition of 55% random copolymer as follows. At room temperature this polymer has a crystal structure similar to that of PVDF form I: the molecular chain is essentially all-*trans* conformation and the crystal lattice is polar. As the temperature rises, the *trans* sequences are cut short by an invasion of newly generated *gauche* bonds as would be understood from the spectral changes in *Figures 2* and *3*. Prior to the phase transition the tilting phenomenon is observed. At the temperature above the transition point

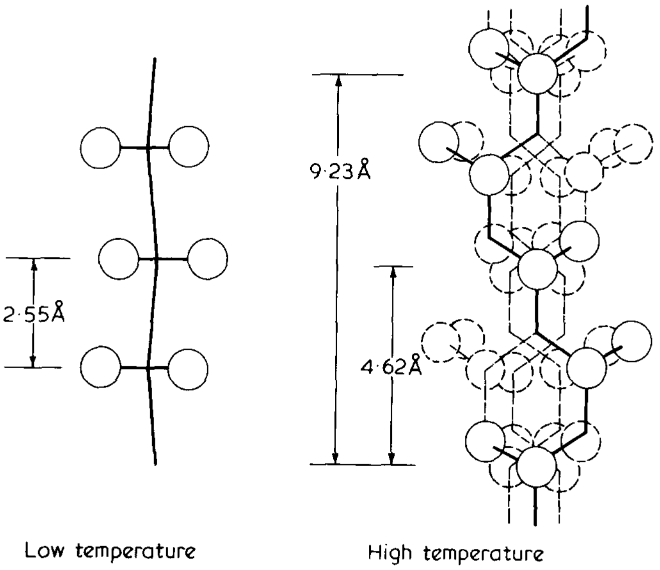

Figure 4 Molecular models for low- and high-temperature phases of 55% copolymer. For simplicity, only the VDF sequences are illustrated

the long *trans* sequences almost disappear and the molecular structure changes from all-*trans* extended form to the conformation constructed by the random combination of TG, $T\bar{G}$, T_3G, and $T_3\bar{G}$ sequences. Such a molecular chain with statistically distributed sequences of T_3G and TG units gives an averaged repeating period of 4.62 Å, coincident with the value for PVDF form II ($TGT\bar{G}$, 4.62 Å)[2] and with a half of that for PVDF form III ($T_3GT_3\bar{G}$, 9.23 Å),[4,5] and might correspond to the newly appearing layer line in the high-temperature X-ray fibre diagram shown in *Figure 1*. In *Figure 4* the molecular structural models for low- and high-temperature phases are illustrated. The latter molecular chains may be packed in a hexagonal fashion at the high temperature and the polarization of unit cell vanishes. That is to say, the crystal transforms from the polar phase into non-polar one. Such a structural change in the crystalline region may be responsible for the temperature dependence of macroscopic polarization measured by Fukada *et al.*[1].

The phase transition is reversible but a slight hysteresis is observed in *Figure 3*, i.e., some *gauche* bands remain observable after cooling the sample down to room temperature and the degree of crystallinity decreases appreciably.

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Origin of the pressure variation of front factor in rubber elasticity*

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The application of the Gaussian statistics to a macromolecular network results in the familiar force law

$$f = GA_0(\alpha - V/V_0\alpha^2) \qquad (1)$$

where α is L/L_0 and L_0, A_0, V_0 are respectively the length, cross-sectional area and volume of the sample at zero force f, zero pressure, and T, L and V correspond to the situation at P, f and T. G is the shear modulus defined as $G = (NkT/V_0)(\overline{r_i^2}/\overline{r_o^2})$. In the latter bracket frequently denoted as a front factor, $\overline{r_i^2}$ and $\overline{r_o^2}$ are respectively, the mean square end-to-end distances of a network chain at volume V_0 and of the free chain. Since the reference (unperturbed) dimensions $\overline{r_o^2}$ are frequently assumed to be a function of temperature only the modulus G should also depend on T.

Tobolsky and Shen[1] proposed a modified equation of state which takes into account the possible effect of the volume change on shear modulus using the relation $G' = G(V/V_0)^{\gamma}$. This modification implies the variation of $\overline{r_0^2}$ with the sample volume or pressure. Some accepted relations from the theory of rubber elasticity are affected by the introduction of this concept. The adjustable empirical parameter γ can be determined from volume dilatation, force-pressure or thermoelastic measurements. A non-zero value of γ is reported for several polymeric networks[2]. In this communication the molecular interpretation of the nature of the parameter γ is proposed together with an estimation of its value for polymethylene network.

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