Macromolecules 1980, *13*, 691-698

Calculation of Elastic and Piezoelectric Constants of Polymer Crystals by a Point Charge Model: Application to Poly(vinylidene fluoride) Form I

Kohji Tashiro,[1a] Masamichi Kobayashi,[1a] Hiroyuki Tadokoro,*[1a] and Eiichi Fukada[1b]

Department of Polymer Science, Faculty of Science, Osaka University, Toyonaka, Osaka, 560, Japan, and the Institute of Physical and Chemical Research, Hirosawa, Wako-shi, Saitama, 351, Japan. *Received December 10, 1979*

ABSTRACT: A theoretical equation for calculating piezoelectric constants (d_{ij}) of polymer crystals based on point charge model has been derived and applied to poly(vinylidene fluoride) form I. The calculated $d_{33} = -2.5 \times 10^{-11}$ C/N is in good agreement with the value of -2×10^{-11} C/N measured by the X-ray method. The calculated d_{31}, -0.025×10^{-11} C/N, is smaller by two digits than d_{33}, consistent with the experimental result that the X-ray (002) spot was not shifted nearly as much by the application of the electrostatic field as in the case of d_{33}. The result is also reasonable from the viewpoint of characteristic mechanical properties of polymer crystals where the Young's modulus along the chain direction is much larger than those in the other directions by two digits. The macroscopic piezoelectric constants $d_{31}{}^{\mathrm{M}}$ and $d_{33}{}^{\mathrm{M}}$ have been estimated by using a model where the piezoelectric crystal form I with a certain degree of orientation is embedded in the nonpiezoelectric amorphous matrix; $d_{31}{}^{\mathrm{M}} = 0.6 \times 10^{-11}$ C/N and $d_{33}{}^{\mathrm{M}} = -1.4 \times 10^{-11}$ C/N at room temperature and $d_{31}{}^{\mathrm{M}} = 4.6 \times 10^{-13}$ C/N and $d_{33}{}^{\mathrm{M}} = -0.5 \times 10^{-11}$ C/N below the glass transition temperature (T_g), respectively. These are in the same order as the values observed both at room temperature and below T_g. In the present estimation, the contribution of crystalline regions to the macroscopic piezoelectricity has been found to be negligible for $d_{31}{}^{\mathrm{M}}$ but significant for $d_{33}{}^{\mathrm{M}}$. The former ($d_{31}{}^{\mathrm{M}}$) has been found to be controlled by the electric and mechanical heterogeneity between amorphous and crystalline regions. Anisotropy of Young's modulus and linear compressibility have also been discussed.

Poly(vinylidene fluoride) [PVDF] is an important polymer both scientifically and industrially because of its combined merits of high elasticity, high processing capacity, and high piezoelectricity.[2,3] But the origin of the "macroscopic" piezoelectric effect of PVDF has not yet been definitely clarified.[4-11] The molecular-theoretical calculation of piezoelectric constants of the "crystalline" phase based on the crystal structure will give us an important criterion for this significant problem.

Although the molecular-theoretical calculation of piezoelectric constants of polymers has been reported in a few papers for polypeptides,[12-14] it concerns only a single chain model, not a three-dimensional crystal. In a previous paper,[15] we derived a general method of calculating the three-dimensional elastic constants of polymer crystals, in which an equation for the atomic displacements induced by an external stress was derived. If each atom has an effective point charge, the polarization of the whole system of the crystal may be changed by the displacements of point charges, resulting in the appearance of the piezoelectric effect. We will derive here the method of calculating "three-dimensional" piezoelectric constants of polymer crystals based on the simple point charge model and apply it to the case of PVDF form I. Different from the case of ionic crystals,[16] we may reasonably consider that the electrostatic long-range interactions hardly affect the properties of the PVDF crystal which are governed primarily by the intermolecular van der Waals interactions. Therefore the influence of the long-range force will be neglected here for simplicity. Based on the calculated results, we will estimate the contribution of the piezoelectric effect for crystalline regions to the macroscopic piezoelectric effect by using the phenomenological equations of macroscopic piezoelectricity and consider the origin of the macroscopic piezoelectric phenomenon of PVDF samples.

Calculation of Piezoelectric Constants

In the following discussion we will use the same notation as that used in the previous paper.[15] On assuming that the ith atom of the mth asymmetric unit in the $\mathbf{k} = (k_1, k_2, k_3)$th unit cell has an effective point charge Q_i, a polarization per unit volume of the whole crystal $\mathbf{P}_0$ may be given as follows

$$\mathbf{P}_0 = (1/N)\sum_{\mathbf{k}}\sum_{m}\sum_{i} Q_i \mathbf{X}(i,m,\mathbf{k})/v \tag{1}$$

where $\mathbf{X}(i,m,\mathbf{k})$ is a Cartesian position vector of the ith atom of the mth unit in the $\mathbf{k}$th unit cell, v is the volume of the unit cell, and N is the number of unit cells considered, respectively. Symbols $\sum_{\mathbf{k}}$, $\sum_m$, and $\sum_i$ mean the summations over all the unit cells in the whole system, all the asymmetric units in the unit cell, and all the atoms contained in the asymmetric unit, respectively.

Now let us consider that an external stress $\mathbf{f}$ is applied to the crystal, just when the change of polarization can be expressed as follows from eq 1,

$$\Delta\mathbf{P} = (1/N)\sum_{\mathbf{k}}\sum_{m}\sum_{i} Q_i[\Delta\mathbf{X}(i,m,\mathbf{k})/v - \mathbf{X}(i,m,\mathbf{k})\Delta v/v^2] = (1/Nv)\sum_{\mathbf{k}}\sum_{m}\sum_{i} Q_i \Delta\mathbf{X}(i,m,\mathbf{k}) - \mathbf{P}_0\Delta v/v \tag{2}$$

where the effective charges are assumed to remain constant after the atoms are displaced by the external mechanical stress. The first term of eq 2 is the polarization change induced by atomic displacements, and the second term indicates the polarization change due to the volume change.

$\Delta\mathbf{X}(i,m,\mathbf{k})$, a Cartesian displacement vector of the ith atom, is represented as below when the external stress $\mathbf{f}$ belongs to the symmetry species Γ of the point group isomorphous to the space group of the crystal:[15]

$$\Delta\mathbf{X}(i,m,\mathbf{k}) = c(m)^{\Gamma}\mathbf{A}(m)\rho^{\Gamma}(i,1) + \mathbf{W}(i,m,\mathbf{k})\mathbf{T}_{\sigma}\Lambda^{\Gamma}\sigma \tag{3}$$

where all of the notations are the same as those used in ref 15. $c(m)^{\Gamma}$ is a character of the symmetry species Γ for the symmetry operation $\mathbf{A}(m)$, $\rho^{\Gamma}(i,1)$ is the internal strain of the ith atom in the first asymmetric unit belonging to the symmetry species Γ, $\mathbf{W}(i,m,\mathbf{k})$ is a matrix concerning the position vectors of constituent atoms, $\mathbf{T}_{\sigma}$ and Λ^{Γ} are matrices concerning the pure strains belonging to the symmetry species Γ, and σ is the strain vector, respectively. Using eq 3, we can write the first term of the polarization

0024-9297/80/2213-0691$01.00/0

change $\Delta \mathbf{P}_1{}^{\Gamma}$ induced by the mechanical deformation belonging to the symmetry species Γ as follows.

$$\Delta \mathbf{P}_1{}^{\Gamma} = (1/Nv)\sum_{\mathbf{k}}\sum_{m}\sum_{i} Q_i[c(m)^{\Gamma}\mathbf{A}(m)\rho^{\Gamma}(i,1) + \mathbf{W}(i,m,\mathbf{k})\mathbf{T}_{\sigma}\Lambda^{\Gamma}\sigma] = (1/v)[\sum_{m} c(m)^{\Gamma}\mathbf{A}(m)] \times [\sum_{i} Q_i\rho^{\Gamma}(i,1)] + (1/Nv)\sum_{\mathbf{k}}\sum_{m}\sum_{i} Q_i\,\mathbf{W}(i,m,\mathbf{k})\mathbf{T}_{\sigma}\Lambda^{\Gamma}\sigma \quad (4)$$

The first term in eq 4 represents the net piezoelectric effect originating from the atomic displacements *not affine to* the uniform deformation of crystal lattice (internal strain ρ). The second term does not contribute to the piezoelectric effect because it is canceled out over the whole crystal. Therefore we obtain

$$\Delta \mathbf{P}_1{}^{\Gamma} = (1/v)[\sum_{m} c(m)^{\Gamma}\mathbf{A}(m)][\sum_{i} Q_i\rho^{\Gamma}(i,1)] = (1/v)[\sum_{m} c(m)^{\Gamma}\mathbf{A}(m)]\mathbf{Q}\rho^{\Gamma} \quad (5)$$

where

$$\sum_{i} Q_i\rho^{\Gamma}(i,1) = \begin{bmatrix} Q_1 & 0 & 0 & \cdots & Q_p & 0 & 0 \\ 0 & Q_1 & 0 & \cdots & 0 & Q_p & 0 \\ 0 & 0 & Q_1 & \cdots & 0 & 0 & Q_p \end{bmatrix} \begin{bmatrix} \rho^{\Gamma}(1,1) \\ \rho^{\Gamma}(2,1) \\ \cdot \\ \cdot \\ \rho^{\Gamma}(p,1) \end{bmatrix} = \mathbf{Q}\rho^{\Gamma} \quad (6)$$

Internal strain ρ^{Γ} is given in the following equation, which is obtained from such a physical condition that the atoms change their relative positions in the unit cell so as to minimize the energy increment due to the external deformation; $\partial V^{\Gamma}/\partial\rho^{\Gamma}(i) = 0$ where V^{Γ} is a potential energy of the deformation of the unit cell[15]

$$\rho^{\Gamma} = -(\mathbf{F}_{\rho}{}^{\Gamma})^{-1}\mathbf{F}_{\rho\sigma}{}^{\Gamma}\sigma = -(\mathbf{F}_{\rho}{}^{\Gamma})^{-1}\mathbf{F}_{\rho\sigma}{}^{\Gamma}\mathbf{S}^{\Gamma}\mathbf{f} \quad (7)$$

where the relationship between the stress and strain, $\sigma = \mathbf{S}^{\Gamma}\mathbf{f}$, is utilized. $\mathbf{S}^{\Gamma}$ is a compliance tensor matrix belonging to the symmetry species Γ. $\mathbf{F}_{\rho}{}^{\Gamma}$ and $\mathbf{F}_{\rho\sigma}{}^{\Gamma}$ are expressed in terms of force constants and the **B** matrix as shown in eq 26 of the previous paper.[15] Therefore from eq 5 and 7, we obtain the following equation for $\Delta \mathbf{P}_1{}^{\Gamma}$.

$$\Delta \mathbf{P}_1{}^{\Gamma} = -(1/v)[\sum_{m} c(m)^{\Gamma}\mathbf{A}(m)]\mathbf{Q}(\mathbf{F}_{\rho}{}^{\Gamma})^{-1}\mathbf{F}_{\rho\sigma}{}^{\Gamma}\mathbf{S}^{\Gamma}\mathbf{f} \quad (8)$$

The second term of the polarization change in eq 2 can be expressed as below. When the external stress **f** is applied to the crystal, the three perpendicular axes are deformed by the strains σ_1, σ_2, and σ_3, respectively, and these strains can be represented by using the compliance constants s_{ij} as

$$\begin{aligned} \sigma_1 &= s_{11}f_1 + s_{12}f_2 + \cdots + s_{16}f_6 \\ \sigma_2 &= s_{21}f_1 + s_{22}f_2 + \cdots + s_{26}f_6 \\ \sigma_3 &= s_{31}f_1 + s_{32}f_2 + \cdots + s_{36}f_6 \end{aligned} \quad (9)$$

When the cross terms such as $s_{ij}s_{kl}$ are neglected, the volume change can be written as

$$\Delta v/v \fallingdotseq \sigma_1 + \sigma_2 + \sigma_3 = (s_{11} + s_{21} + s_{31})f_1 + (s_{12} + s_{22} + s_{32})f_2 + \cdots + (s_{16} + s_{26} + s_{36})f_6 = \mathbf{S}'^{\Gamma}\mathbf{f}$$

where $\tilde{\mathbf{S}}'^{\Gamma} = [s_{11} + s_{21} + s_{31}, s_{12} + s_{22} + s_{32}, \cdots, s_{16} + s_{26} + s_{36}]$ and $\tilde{\mathbf{f}} = [f_1, f_2, \cdots, f_6]$. Thus the second term of eq 2 may be expressed as

$$\Delta \mathbf{P}_2{}^{\Gamma} = -\mathbf{P}_0(\Delta v/v) = -\mathbf{P}_0\mathbf{S}'^{\Gamma}\mathbf{f} \quad (10)$$

Therefore from eq 2, 8, and 10, we can write $\Delta \mathbf{P}^{\Gamma}$ as

$$\Delta \mathbf{P}^{\Gamma} = \Delta \mathbf{P}_1{}^{\Gamma} + \Delta \mathbf{P}_2{}^{\Gamma} = -\{(1/v)[\sum_{m} c(m)^{\Gamma}\mathbf{A}(m)]\mathbf{Q}(\mathbf{F}_{\rho}{}^{\Gamma})^{-1}\mathbf{F}_{\rho\sigma}{}^{\Gamma}\mathbf{S}^{\Gamma} + \mathbf{P}_0\mathbf{S}'^{\Gamma}\}\mathbf{f} \quad (11)$$

The piezoelectric strain constants $\mathbf{d}^{\Gamma}$ belonging to the symmetry species Γ may be defined as

$$\begin{bmatrix} \Delta P_x \\ \Delta P_y \\ \Delta P_z \end{bmatrix} = \begin{bmatrix} d_{11} & d_{12} \cdots d_{16} \\ d_{21} & d_{22} \cdots d_{26} \\ d_{31} & d_{32} \cdots d_{36} \end{bmatrix} \begin{bmatrix} f_1 \\ f_2 \\ \cdot \\ \cdot \\ \cdot \\ f_6 \end{bmatrix}$$

or

$$\Delta \mathbf{P}^{\Gamma} = \mathbf{d}^{\Gamma}\mathbf{f} \quad (12)$$

Comparing eq 11 and 12, we obtain the final equation of piezoelectric strain constants as follows.

$$\mathbf{d}^{\Gamma} = -\{(1/v)[\sum_{m} c(m)^{\Gamma}\mathbf{A}(m)]\mathbf{Q}(\mathbf{F}_{\rho}{}^{\Gamma})^{-1}\mathbf{F}_{\rho\sigma}{}^{\Gamma}\mathbf{S}^{\Gamma} + \mathbf{P}_0\mathbf{S}'^{\Gamma}\} \quad (13)$$

Application to Poly(vinylidene fluoride)

In a previous paper[17] we calculated the normal-mode frequencies of lattice vibrations of PVDF forms I, II, and III and analyzed their infrared and Raman spectra. In the present calculations of mechanical and piezoelectric constants of PVDF form I, most of the basic parameters used are transferred directly from the previous paper,[17] although some modifications are added.

A. Crystal Structure. Although the actual chains are deflected more or less from the planar-zigzag conformation,[18] the calculated results are not much affected by such a small deflection, as will be discussed later. Therefore the model adopted here is as follows:[17] the planar-zigzag chains are packed in the unit cell with the dimensions of $a = 8.58$ Å, $b = 4.91$ Å, and c (fiber axis) $= 2.56$ Å and the space group of $Cm2m\text{-}C_{2v}{}^{14}$.

B. Force Fields and Point Charges. Intramolecular force constants are the valence-force-field type and the numerical values are transferred from the previous paper.[17] We have not yet found well-established intermolecular potential functions concerning a fluorine atom. We used here the repulsive terms of Lennard-Jones 6–12 potentials[19] and electrostatic potentials (point charge model). The second derivatives of these potential functions with respect to interatomic distance were used for intermolecular force constants

$$f(\text{mdyn/Å}) = 1.08386\alpha/r^{14} + 4.614q_1q_2/(\epsilon r^3)$$

where q_1 and q_2 are the effective point charges on a pair of atoms in the elementary charge unit (4.803×10^{-11} cgs esu) and the dielectric constant $\epsilon = 4.0$ is used.[20] The interatomic distance r is in ångstrom units. The values of parameters α, q_1, and q_2 are listed in Table I. The atomic pairs considered are H···F, F···F, C···F, H···C, and H···H for distances shorter than 4 Å.

The intrinsic polarization $\mathbf{P}_s{}^0$ of the PVDF form I unit cell is calculated to be

$$\mathbf{P}_s{}^0 = \begin{bmatrix} 0.0 \\ 0.140 \\ 0.0 \end{bmatrix} \text{C/m}^2 \quad (14)$$

In the following sections we will discuss the calculated results of lattice vibrations, elastic constants, and piezoelectric constants, all of which can be calculated at the same time by using the common **B** and **F** matrices.

Lattice Vibrations

The optical unit cell of PVDF form I contains only one molecular chain so that there should appear only one op-

Table I
Numerical Parameters for Nonbonded Interatomic Force Constant $f(\mathrm{mdyn/Å}) = 1.08386\alpha/r^{14} + 4.614q_1q_2/(\epsilon r^3)$

atomic pair	α^a	$q_1{}^b$	$q_2{}^b$
H···F	15 350	−0.219	0.067
F···F	43 000	−0.219	−0.219
F···C(F)	126 200	−0.219	0.538
F···C(H)	126 200	−0.219	−0.134
H···C(H)	56 000	0.067	−0.134
H···C(F)	56 000	0.067	0.538
H···H	7180	0.067	0.067

[a] After ref 19. Units of kcal Å^{12}/mol. [b] In elementary charge unit (4.803 × 10^{-10} cgs esu).

tically active external vibration (librational mode around the chain axis). The calculated wavenumber is 83 cm^{-1}, about 10 cm^{-1} higher than the previously reported value of 72 cm^{-1} which was calculated by using intermolecular potential functions different from the present ones.[17] Considering that the observed infrared and Raman bands of lattice vibrations of form I are very broad, widely ranging from 30 cm^{-1} to 120 cm^{-1} with the center at about 74 cm^{-1}, caused by the lattice disorder in crystallites,[17] the agreement between the calculated and observed frequencies is still satisfactory. The calculated frequencies of the internal vibrations hardly vary from the previous values, in good agreement with the observed ones.

Elastic Constants

The calculated values of elastic and compliance constants are listed below.

$$C = \begin{bmatrix} 23.60 & 1.92 & 3.98 & & & \\ 1.92 & 10.64 & 2.19 & & 0 & \\ 3.98 & 2.19 & 238.24 & & & \\ & & & 4.40 & & \\ & 0 & & & 6.43 & \\ & & & & & 2.15 \end{bmatrix} \text{GPa} \quad (15)$$

$$S = \begin{bmatrix} 4.31 & -0.76 & -0.07 & & 0 & \\ -0.76 & 9.55 & -0.08 & & & \\ -0.07 & -0.08 & 0.42 & & & \\ & & & 22.75 & & \\ & 0 & & & 15.56 & \\ & & & & & 46.45 \end{bmatrix} \times 10^{-11}\ \text{Pa}^{-1} \quad (16)$$

Using these values, we can calculate the anisotropy of Young's modulus $E(\theta)$ in the direction of an angle θ measured from the a axis within the ab plane normal to the chain axis by the equation

$$1/E(\theta) = s_{11}\cos^4\theta + s_{22}\sin^4\theta + (2s_{16} + s_{66})\cos^2\theta\sin^2\theta \quad (17)$$

The calculated result is shown in Figure 1. Sakurada et al. measured the Young's moduli of PVDF form I in the direction normal to the chain axis by the X-ray method.[21] For the overlapped spot of the (110) and (200) reflections E = 6.4 GPa, and for that of (020) + (310) E = 7.4 GPa, respectively. According to the crystal structure of Hasegawa et al.,[18] the intensity ratios for these X-ray reflections are calculated as[22]

$$I(110)/I(200) \fallingdotseq 1372/408$$

and

$$I(310)/I(020) \fallingdotseq 708/403$$

Therefore the reflection from the (110) plane may be considered to contribute mainly to the overlapped spot of (110) + (200), and the reflections from both (020) and (310) planes contribute almost equally to the overlapped spot of (020) + (310), respectively. Thus the three independent vaules of Young's modulus [6.4 GPa for (110) and 7.4 GPa for (020) and (310)] are used for determining the anisotropy curve, the result being shown in Figure 1. The calculated anisotropy of Young's modulus in the a direction larger than that in the b direction is consistent with the observed anisotropy, though the calculated magnitude itself is rather large in the a axis compared with the observed one. In the actual crystal structure of form I, the molecular conformation and/or the chain packing are disordered more or less as revealed in the previous paper.[17] We calculated the anisotropy of Young's modulus in the ab plane by assuming four kinds of models shown in Figure 2: (a) and (b) for deflected chains (deflection angle ±7°), and (c) and (d) for disordered chain packing (setting angle of a chain from the b axis ±7°), respectively. However these models gave almost the same results as the present one, not affecting essentially the anisotropy of mechanical properties. In the actual crystallites such a disorder may be much more complicated than that with the models used here.

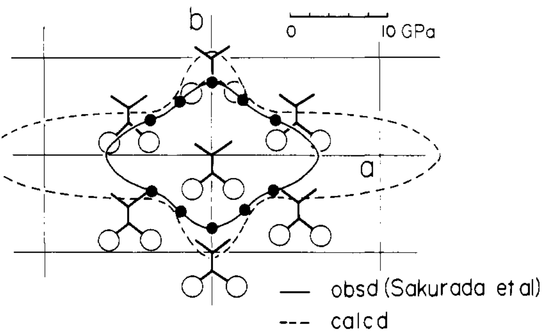

Figure 1. Anisotropy of Young's modulus of PVDF form I in the ab plane normal to the chain axis. The solid line represents the observed values by Sakurada et al.[21] and the broken line shows the calculated result.

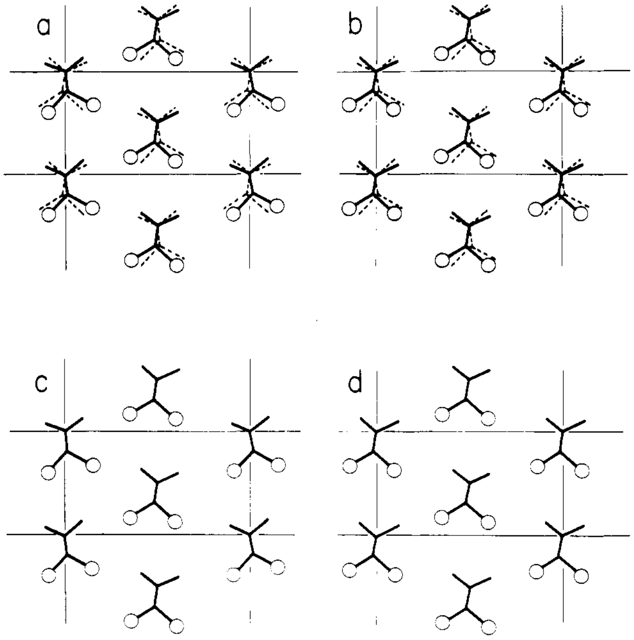

Figure 2. Four kinds of models with regular structure for the statistically disordered structure of PVDF form I: (a) and (b), alternately deflected chain models; (c) and (d), planar-zigzag models.

The calculated Young's modulus Y in the chain direction is about 237.0 GPa, rather larger than the value of 177 GPa

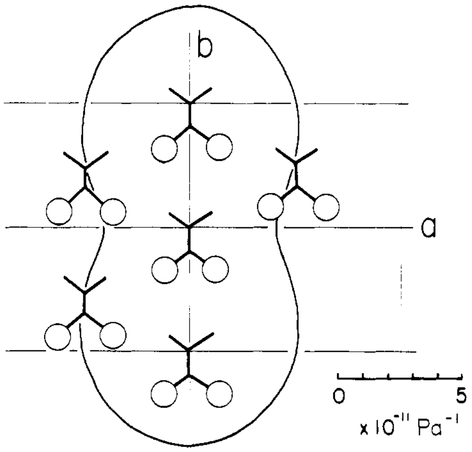

Figure 3. Calculated anisotropy of linear compressibility of PVDF form I in the *ab* plane.

observed by Sakurada et al.[21] We tried to calculate Y for the deflected chain stated above, giving the theoretical value of about 222 GPa. Such a deflection affects the Y only slightly as well as the above-mentioned Young's modulus in the direction normal to the chain axis, so that we must consider another reason for the smaller value of observed modulus than that of the calculated one. Recently Takahashi et al.[23] proposed the existence of kink bands within the crystallites of planar-zigzag form I by analyzing the diffuse scattering appearing on the fiber diagram of cold-drawn sample. Such kink bands may lower the Young's modulus Y from the value of the planar-zigzag chain. Another reason concerns the assumption of the series model in the X-ray method. As discussed for many kinds of polymer samples such as polyethylene,[24,25] poly(oxymethylene),[26] poly(tetrafluoroethylene),[27] and so on, the Young's moduli Y measured by the X-ray method[28] show appreciably smaller values than those obtained by the spectroscopic methods of Raman and neutron scatterings,[29] the latter being in good agreement with the theoretical values. The reason has been considered to be due to the inhomogeneous stress distribution in the polymer specimens.[26,27] The same circumstances may be applied to the present case of PVDF form I.

As for the anisotropy of linear compressibility shown in Figure 3, the check by X-ray measurement under hydrostatic pressure would be hoped. The calculated volume compressibility κ is 12.48×10^{-11} Pa^{-1} and the linear compressibility in the chain direction is 0.282×10^{-11} Pa^{-1}. The values may be reasonable, judging from the order of the experimental values for the various kinds of polymers.[30]

Piezoelectric Strain Constants

The calculated piezoelectric strain constants (d constants) are shown below.

$$\mathrm{d} = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & -0.428 \\ -0.405 & -2.519 & -0.025 & 0 & 0 & 0 \\ 0 & 0 & 0 & -3.070 & 0 & 0 \end{bmatrix} \times 10^{-11}\ \mathrm{C/N} \quad (18)$$

For the sake of convenience, the tensor is transformed to the usually used coordinate system of (1 // c, 2 // a, 3 // b).

$$\mathrm{d} = \begin{bmatrix} 0 & 0 & 0 & 0 & -3.070 & 0 \\ 0 & 0 & 0 & -0.428 & 0 & 0 \\ -0.025 & -0.405 & -2.519 & 0 & 0 & 0 \end{bmatrix} \times 10^{-11}\ \mathrm{C/N} \quad (19)$$

We will discuss mainly the values of d_{31} and d_{33} here, which may be very important for the comparison with the observed values.

(i) d_{33}. Recently Odajima et al.[31] measured the converse piezoelectric effect of the (020) X-ray reflection of form I and estimated d_{33} as ca. -2×10^{-11} C/N, which is in good agreement with the above calculated value of -2.5×10^{-11} C/N both in sign and in magnitude. Calculated from the internal displacements ρ (not the total displacements) of the constituent atoms induced by the application of tensile stress of $f_{33} = 1$ GPa in the b direction, the dipole moment of the monomeric unit pointing along the b axis decreases from 0.75×10^{-29} C m to 0.68×10^{-29} C m. The volume of the unit cell, on the other hand, increases from 107.85 to 117.16 Å^3 by the tensile stress f_{33}. Therefore, as a total, the polarization of the unit cell changes from 0.140 to 0.117 C/m^2. This is a negative change of polarization and results in a negative value of the piezoelectric constant d_{33}, -2.5×10^{-11} C/N.

(ii) d_{31}. In this case the dipole moment of the monomeric unit increases from 0.75×10^{-29} to 0.77×10^{-29} C m by the tensile force (f_{11}) of 30 GPa along the chain direction, while the volume changes from 107.85 to 116.47 Å^3, resulting in the polarization change of 0.140 to 0.132 C/m^2. Therefore the piezoelectric strain constant d_{31} becomes about -0.025×10^{-11}C/N. Odajima et al. reported a negligibly small X-ray shift of (002) reflection by the application of the electrostatic field,[31] consistent with our calculated value of d_{31}, which was smaller by two digits than d_{33}. Our calculated value is reasonable from the viewpoint of characteristic mechanical properties of polymer chains, constructed generally by the strong covalent linkages, which are packed together by weak van der Waals interactions, that is, very high stiffness in the chain direction compared with the stiffness in the other directions. In order to explain more clearly the converse piezoelectric effect will be taken into consideration now. If we apply the electrostatic field E in the direction of the 3 axis (the b axis), the strain induced in the direction of the 1 (chain axis) or the 3 axis can be expressed as follows (see Figure 4).

$$\begin{aligned} \sigma_1 &= \sigma_{11} = d_{311}E_3 = d_{31}E_3 \\ \sigma_3 &= \sigma_{33} = d_{333}E_3 = d_{33}E_3 \end{aligned} \quad (20)$$

Therefore

$$\frac{\text{strain in the chain direction}}{\text{strain normal to the chain direction}} = \frac{\sigma_1}{\sigma_3} = \frac{d_{31}}{d_{33}} \quad (21)$$

Substitution of theoretical values of $d_{31} = -0.025 \times 10^{-11}$ C/N and $d_{33} = -2.50 \times 10^{-11}$ C/N into eq 21 results in

$$\sigma_1/\sigma_3 \fallingdotseq 1/100$$

That is to say, the electric field induces the deformation of crystal mainly in the direction normal to the chain axis because of a much higher Young's modulus in the chain direction than the moduli normal to the chain axis.

The macroscopic piezoelectric strain constant $d_{31}{}^{\mathrm{M}}$ of the PVDF form I sample is about of the order of 10^{-11} C/N,[2,3] much larger than that of the crystalline region. If we use the macroscopic constants of $d_{31}{}^{\mathrm{M}}$ and $d_{33}{}^{\mathrm{M}}$ in eq 21, the ratio of strains becomes

$$\sigma_1{}^{\mathrm{M}}/\sigma_3{}^{\mathrm{M}} \fallingdotseq -1$$

Almost the same magnitude of strain in the directions of the chain axis (or draw axis) and of the axis normal to it suggests that the amorphous region may play a significantly large role in the deformation induced by the electrostatic field and also in the appearance of piezoelectric

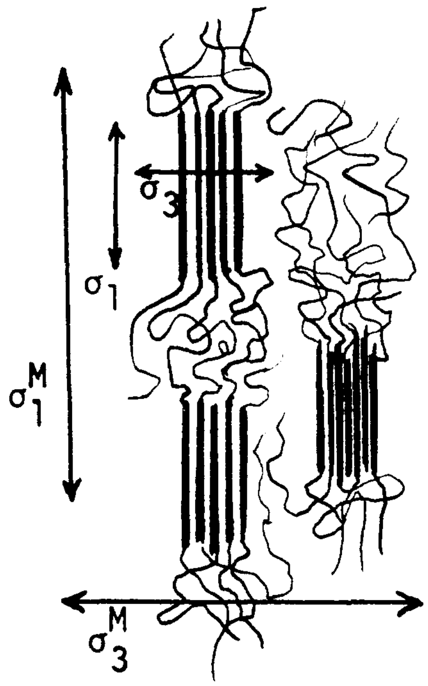

Figure 4. Illustration of strains working on the various parts of the macroscopic sample of PVDF form I: σ_1 and σ_3 for the crystalline part, and σ_1^M and σ_3^M for the whole system, respectively.

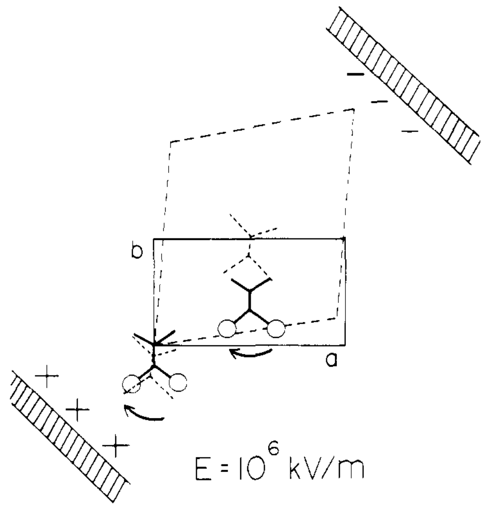

Figure 5. Calculated structural change of PVDF form I with the application of electrostatic field in the *ab* plane.

phenomenon of the sample, which will be discussed in detail as below.

Atomic Displacements Induced by Electric Field

Figure 5 shows the atomic displacements induced by the electric field into the various directions (converse piezoelectric effect). The atomic displacements $\Delta\mathbf{X}^{\Gamma}(i,m,\mathbf{k})$ belonging to the symmetry species Γ are expressed as follows by using eq 3 and 7 and the equation of converse piezoelectric effect $\sigma = \tilde{\mathbf{d}}\mathbf{E}$ where $\mathbf{E}$ is an electrostatic field vector.

$$\begin{aligned}\Delta\mathbf{X}^{\Gamma}(i,m,\mathbf{k}) &= c(m)^{\Gamma}\mathbf{A}(m)\rho^{\Gamma}(i,1) + \mathbf{W}(i,m,\mathbf{k})\mathbf{T}_{\sigma}\mathbf{\Lambda}^{\Gamma}\sigma = \\ &[\mathbf{W}(i,m,\mathbf{k})\mathbf{T}_{\sigma}\mathbf{\Lambda}^{\Gamma} - c(m)^{\Gamma}\mathbf{A}(m)(\mathbf{F}_{\rho}^{\Gamma})^{-1}\mathbf{F}_{\rho\sigma}^{\Gamma}]\sigma = \\ &[\mathbf{W}(i,m,\mathbf{k})\mathbf{T}_{\sigma}\mathbf{\Lambda}^{\Gamma} - c(m)^{\Gamma}\mathbf{A}(m)(\mathbf{F}_{\rho}^{\Gamma})^{-1}\mathbf{F}_{\rho\sigma}^{\Gamma}]\tilde{\mathbf{d}}\mathbf{E} \quad (22)\end{aligned}$$

The electrostatic field vector $\mathbf{E}$ is assumed to be applied in the *ab* plane

$$\mathbf{E} = \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix} = \begin{bmatrix} E\cos\theta \\ E\sin\theta \\ 0 \end{bmatrix} \quad (23)$$

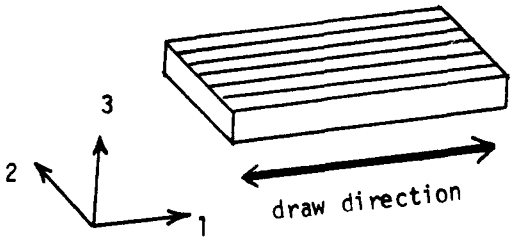

Figure 6. Cartesian coordinates fixed on the macroscopic sample of PVDF form I.

where θ is the angle between the direction of application and the *a* axis. As shown in Figure 5 the molecular chains tend to rotate into the direction of the positive electrode, accompained by the resultant preferred orientation of the *b* axis of the unit cell. Thus we can illustrate a model of change of the *b* axis orientation on the poling process reported by X-ray[22,32] and infrared methods.[33,34]

Macroscopic Piezoelectric Effects of PVDF Form I Samples

Based on the calculated results for the form I crystal, we will consider to what extent the piezoelectric property of crystallites may contribute to the macroscopic piezoelectric effect. We now set up a model such that the form I crystallites are embedded in the nonpiezoelectric amorphous matrix. Hayakawa and Wada[35] proposed a phenomenological theory for the piezoelectric stress constant e_{31}^M for the model of a polymer film, where the spherical charges are dispersed in the nonpiezoelectric polymer matrix. This theory will be utilized here with some modifications.

According to their derivations, the charge on the electrode on the film surface is in general given by

$$Q_e = AD/4\pi = A(\epsilon E + 4\pi\bar{P}_s)/4\pi \quad (24)$$

where A is the area of the electrode, D is the electric displacement, ϵ is the dielectric constant, E is the electric field, and $\bar{P}_s$ is the spontaneous polarization along the 3 axis, respectively. The definition of Cartesian coordinate axes fixed on the film sample is shown in Figure 6. The dielectric constant ϵ is written as follows by using the dielectric constant ϵ^a of the amorphous matrix and ϵ^c of the spherical particles,

$$\epsilon = \epsilon^a\left[1 + \frac{3(\epsilon^c - \epsilon^a)}{2\epsilon^a + \epsilon^c}\phi\right] \quad (25)$$

where ϕ is the volume fraction of particles and is given by

$$\phi = NV/(Al)$$

Here N is the total number of particles in the volume $A \times l$, l is the thickness of the film, and V is the volume of a particle. The spontaneous polarization $\bar{P}_s$ in eq 24 is expressed as

$$\bar{P}_s = \frac{3\epsilon^a}{2\epsilon^a + \epsilon^c}\phi P_s \quad (26)$$

where the particle is assumed to have the spontaneous polarization of P_s.

The tensile stress f_1 is now applied to the film along the draw direction and as a result the sample is deformed by the macroscopic strain σ_1^M. Then the macroscopic piezoelectric stress constant of the film defined by

$$e_{31}{}^{\mathrm{M}} = \frac{1}{A}\left(\frac{\partial Q_e}{\partial \sigma_1{}^{\mathrm{M}}}\right)_{\mathrm{E}=0}$$

is finally given by the following equation, which is obtained from eq 24–26.

$$e_{31}{}^{\mathrm{M}} = \phi\frac{3\epsilon^{\mathrm{a}}}{2\epsilon^{\mathrm{a}} + \epsilon^{\mathrm{c}}}\left[P_{\mathrm{s}}\left\{\frac{\epsilon^{\mathrm{c}}}{2\epsilon^{\mathrm{a}} + \epsilon^{\mathrm{c}}}\left(\frac{\kappa_{31}{}^{\mathrm{a}}}{\epsilon^{\mathrm{a}}} - \frac{\kappa_{31}{}^{\mathrm{c}}}{\epsilon^{\mathrm{c}}}\right) + m + \frac{1}{V}\frac{\partial V}{\partial \sigma_1{}^{\mathrm{M}}}\right\} + \frac{\partial P_{\mathrm{s}}}{\partial \sigma_1{}^{\mathrm{M}}}\right] \quad (27)$$

This equation is the same as the equation derived by Hayakawa and Wada.[35] Here $\kappa_{31}{}^{\mathrm{a}}$, for example, is the electrostriction constant of the amorphous phase

$$\kappa_{31}{}^{\mathrm{a}} = \partial\epsilon^{\mathrm{a}}/\partial\sigma_1{}^{\mathrm{M}}$$

and

$$m = -\frac{1}{l}\left(\frac{\partial l}{\partial \sigma_1{}^{\mathrm{M}}}\right)$$

In the present case of the PVDF sample, the spherical charge is replaced by the polar crystallite of form I. As Hayakawa and Wada stated,[35] the macroscopic strain $\sigma_1{}^{\mathrm{M}}$ is the strain for the whole sample and not the strain of the crystallites. Therefore we must rewrite $\partial P_{\mathrm{s}}/\partial\sigma_1{}^{\mathrm{M}}$ in eq 27 as follows because it does not represent the intrinsic piezoelectric effect of the crystal.

$$\frac{\partial P_{\mathrm{s}}}{\partial \sigma_1{}^{\mathrm{M}}} = \sum_{i=1}^{6}\frac{\partial P_{\mathrm{s}}}{\partial \sigma_i}\frac{\partial \sigma_i}{\partial \sigma_1{}^{\mathrm{M}}} \quad (28)$$

The terms $\partial P_{\mathrm{s}}/\partial\sigma_{\mathrm{i}}$ represent the intrinsic piezoelectric effect of the crystal. It is now necessary to take into consideration the effect of orientation of crystallites on the macroscopic piezoelectric constants. We should principally carry out the transformation of tensors and the averaging of them over the Eulerian angles representing the orientation of crystallites. But, for simplicity, we introduce here such an effect of orientation in the form that the polar crystallites of form I with their three principal axes parallel to the macroscopic coordinate axes (Figure 6) have the spontaneous polarization P_{s} smaller than the intrinsic polarization $P_{\mathrm{s}}{}^0$ of the original crystal by a factor χ (see Appendix);

$$P_{\mathrm{s}} = \chi P_{\mathrm{s}}{}^0 \qquad (\chi < 1) \quad (29)$$

Then $\partial P_{\mathrm{s}}/\partial\sigma_{\mathrm{i}}$ is written as

$$\frac{\partial P_{\mathrm{s}}}{\partial \sigma_{\mathrm{i}}} = \chi\frac{\partial P_{\mathrm{s}}{}^0}{\partial \sigma_{\mathrm{i}}} = \chi e_{3\mathrm{i}} \quad (30)$$

where $e_{3\mathrm{i}}$ is a piezoelectric stress constant of the form I crystal and is given by the equation $\mathbf{e} = \mathbf{dC}$. As seen in eq 19, only three of the constants (e_{31}, e_{32}, and e_{33}) are not zero. Thus, from eq 28, 29, and 30,

$$\frac{\partial P_{\mathrm{s}}}{\partial \sigma_{\mathrm{i}}} = \chi\left(e_{31}\frac{\partial \sigma_1}{\partial \sigma_1{}^{\mathrm{M}}} + e_{32}\frac{\partial \sigma_2}{\partial \sigma_1{}^{\mathrm{M}}} + e_{33}\frac{\partial \sigma_3}{\partial \sigma_1{}^{\mathrm{M}}}\right) \quad (31)$$

If we assume a mechanical series model of crystalline and amorphous phases in the tensile direction and the Young's modulus of the crystalline phase $Y_1{}^{\mathrm{c}}$ (= $1/s_{11}$) is assumed to be much larger than that of the amorphous phase $Y_1{}^{\mathrm{a}}$, the macroscopic Young's modulus $Y_1{}^{\mathrm{M}}$ and $\partial\sigma_i/\partial\sigma_1{}^{\mathrm{M}}$ (i = 1, 2, and 3) can be, respectively, written as

$$Y_1{}^{\mathrm{M}} = \frac{Y_1{}^{\mathrm{a}}Y_1{}^{\mathrm{c}}}{Y_1{}^{\mathrm{c}} + (Y_1{}^{\mathrm{a}} - Y_1{}^{\mathrm{c}})\phi} \doteq \frac{Y_1{}^{\mathrm{a}}}{1 - \phi} \quad (32)$$

$$\frac{\partial \sigma_1}{\partial \sigma_1{}^{\mathrm{M}}} = \frac{Y_1{}^{\mathrm{a}}}{(Y_1{}^{\mathrm{a}} - Y_1{}^{\mathrm{c}})\phi + Y_1{}^{\mathrm{c}}} = \frac{Y_1{}^{\mathrm{M}}}{Y_1{}^{\mathrm{c}}} = Y_1{}^{\mathrm{M}}s_{11} \quad (33)$$

Using Poisson's relation of $\sigma_2/\sigma_1 = s_{21}/s_{11}$ for the tensile stress f_1,

$$\frac{\partial \sigma_2}{\partial \sigma_1{}^{\mathrm{M}}} = \frac{\partial \sigma_1}{\partial \sigma_1{}^{\mathrm{M}}}\frac{s_{21}}{s_{11}} = Y_1{}^{\mathrm{M}}s_{21} \quad (34)$$

$$\frac{\partial \sigma_3}{\partial \sigma_1{}^{\mathrm{M}}} = \frac{\partial \sigma_1}{\partial \sigma_1{}^{\mathrm{M}}}\frac{s_{31}}{s_{11}} = Y_1{}^{\mathrm{M}}s_{31} \quad (35)$$

We must notice here that the compliance tensor components (s_{11}, s_{21}, and s_{31}) used above are based on the coordinate system of $(1//c,2//a,3//b)$ and derived from eq 16.

From eq 27–35, we obtain the expression for the macroscopic piezoelectric strain constant $d_{31}{}^{\mathrm{M}}$ as follows

$$d_{31}{}^{\mathrm{M}} = \frac{e_{31}{}^{\mathrm{M}}}{Y_1{}^{\mathrm{M}}} = \frac{3\epsilon^{\mathrm{a}}}{2\epsilon^{\mathrm{a}} + \epsilon^{\mathrm{c}}}\frac{\phi(1 - \phi)}{Y_1{}^{\mathrm{a}}}\chi P_s{}^0\left(\frac{\epsilon^{\mathrm{c}}}{2\epsilon^{\mathrm{a}} + \epsilon^{\mathrm{c}}}\frac{\kappa_{31}{}^{\mathrm{a}}}{\epsilon^{\mathrm{a}}} + m\right) + \frac{3\epsilon^{\mathrm{a}}}{2\epsilon^{\mathrm{a}} + \epsilon^{\mathrm{c}}}\phi\chi(e_{31}s_{11} + e_{32}s_{21} + e_{33}s_{31}) \quad (36)$$

where the derivatives of volume ($\partial V/\partial\sigma_1{}^{\mathrm{M}}$) and of dielectric constant ($\partial\epsilon^{\mathrm{c}}/\partial\sigma_1{}^{\mathrm{M}} \equiv \kappa_{31}{}^{\mathrm{c}}$) of the crystallite with respect to the stain $\sigma_1{}^{\mathrm{M}}$ are neglected because of the larger stiffness of the crystal phase.

Quite similarly to the case of $e_{31}{}^{\mathrm{M}}$, we can obtain the equation of $e_{33}{}^{\mathrm{M}}$ as

$$e_{33}{}^{\mathrm{M}} = \frac{1}{A}\left(\frac{\partial Q_e}{\partial \sigma_3{}^{\mathrm{M}}}\right)_{E=0} = \phi\frac{3\epsilon^{\mathrm{a}}}{2\epsilon^{\mathrm{a}} + \epsilon^{\mathrm{c}}}\left[P_s\left\{\frac{\epsilon^{\mathrm{c}}}{2\epsilon^{\mathrm{a}} + \epsilon^{\mathrm{c}}}\left(\frac{\kappa_{33}{}^{\mathrm{a}}}{\epsilon^{\mathrm{a}}} - \frac{\kappa_{33}{}^{\mathrm{c}}}{\epsilon^{\mathrm{c}}}\right) - 1 + \frac{1}{V}\frac{\partial V}{\partial \sigma_3{}^{\mathrm{M}}}\right\} + \frac{\partial P_s}{\partial \sigma_3{}^{\mathrm{M}}}\right] \doteq \phi\frac{3\epsilon^{\mathrm{a}}}{2\epsilon^{\mathrm{a}} + \epsilon^{\mathrm{c}}}\left[P_s\left(\frac{\epsilon^{\mathrm{c}}}{2\epsilon^{\mathrm{a}} + \epsilon^{\mathrm{c}}}\frac{\kappa_{33}{}^{\mathrm{a}}}{\epsilon^{\mathrm{a}}} - 1\right) + \frac{\partial P_s}{\partial \sigma_3{}^{\mathrm{M}}}\right] \quad (37)$$

Using the expressions for the mechanical series model,

$$Y_3{}^{\mathrm{M}} = \frac{Y_3{}^{\mathrm{a}}Y_3{}^{\mathrm{c}}}{Y_3{}^{\mathrm{c}} + (Y_3{}^{\mathrm{a}} - Y_3{}^{\mathrm{c}})\phi} \quad (38)$$

$$\frac{\partial P_s}{\partial \sigma_3{}^{\mathrm{M}}} = \sum_{i=1}^{6}\frac{\partial P_s}{\partial \sigma_i}\frac{\partial \sigma_i}{\partial \sigma_3{}^{\mathrm{M}}} = \chi\left(e_{31}\frac{\partial \sigma_1}{\partial \sigma_3{}^{\mathrm{M}}} + e_{32}\frac{\partial \sigma_2}{\partial \sigma_3{}^{\mathrm{M}}} + e_{33}\frac{\partial \sigma_3}{\partial \sigma_3{}^{\mathrm{M}}}\right) \quad (39)$$

$$\frac{\partial \sigma_3}{\partial \sigma_3{}^{\mathrm{M}}} = \frac{Y_3{}^{\mathrm{a}}}{(Y_3{}^{\mathrm{a}} - Y_3{}^{\mathrm{c}})\phi + Y_3{}^{\mathrm{c}}} = \frac{Y_3{}^{\mathrm{M}}}{Y_3{}^{\mathrm{c}}} = Y_3{}^{\mathrm{M}}s_{33} \quad (40)$$

$$\frac{\partial \sigma_2}{\partial \sigma_3{}^{\mathrm{M}}} = \frac{\partial \sigma_3}{\partial \sigma_3{}^{\mathrm{M}}}\frac{s_{23}}{s_{33}} = Y_3{}^{\mathrm{M}}s_{23} \quad (41)$$

$$\frac{\partial \sigma_1}{\partial \sigma_3{}^{\mathrm{M}}} = \frac{\partial \sigma_3}{\partial \sigma_3{}^{\mathrm{M}}}\frac{s_{13}}{s_{33}} = Y_3{}^{\mathrm{M}}s_{13} \quad (42)$$

We obtain the macroscopic piezoelectric strain constant $d_{33}{}^{\mathrm{M}}$ as

$$d_{33}{}^{\mathrm{M}} = \frac{e_{33}{}^{\mathrm{M}}}{Y_3{}^{\mathrm{M}}} = \frac{3\epsilon^{\mathrm{a}}}{2\epsilon^{\mathrm{a}} + \epsilon^{\mathrm{c}}} \frac{(Y_3{}^{\mathrm{a}} - Y_3{}^{\mathrm{c}})\phi + Y_3{}^{\mathrm{c}}}{Y_3{}^{\mathrm{a}} Y_3{}^{\mathrm{c}}} \phi \chi P_s{}^0 \left(\frac{\epsilon^{\mathrm{c}}}{2\epsilon^{\mathrm{a}} + \epsilon^{\mathrm{c}}} \frac{\kappa_{33}{}^{\mathrm{a}}}{\epsilon^{\mathrm{a}}} - 1 \right) + \frac{3\epsilon^{\mathrm{a}}}{2\epsilon^{\mathrm{a}} + \epsilon^{\mathrm{c}}} \phi \chi (e_{31} s_{13} + e_{32} s_{23} + e_{33} s_{33}) \quad (43)$$

In eq 36 and 43, the first terms originate from the difference in mechanical and electrical properties between the amorphous and crystal phases and the second terms are from the intrinsic piezoelectric effect of the crystal, as stated by Hayakawa and Wada.[35]

Estimation of $d_{31}{}^{\mathrm{M}}$

Now we will try to estimate the order of $d_{31}{}^{\mathrm{M}}$ based on eq 36. Some parameters in eq 36 are replaced by the typical values obtained experimentally by many authors;[2–11] i.e., $\phi \fallingdotseq 0.5$ m $\fallingdotseq 0.5$, $Y_1{}^{\mathrm{a}} \fallingdotseq 1$ GPa. For the value of $\kappa_{31}{}^{\mathrm{a}}/\epsilon^{\mathrm{a}}$ we used the macroscopic electrostriction constant, about 2.0 at room temperature. Taking into consideration that the macroscopic dielectric constant ϵ, measured at 20 °C, is 12.9[10] and that the macroscopic dielectric constant at −100 °C, 3.4, may be assumed equal to that of the crystalline region (ϵ^{c}), the dielectric constants ϵ^{a} and ϵ^{c} can be estimated as $\epsilon^{\mathrm{a}}/\epsilon^{\mathrm{c}} \fallingdotseq 10$ based on eq 25. The spontaneous polarization $\bar{P}_{\mathrm{s}}$ in eq 26 is assumed to be nearly equal to the residual polarization P_{r}, about 2×10^{-2} C/m^2. From eq 26 and 29 and $P_{\mathrm{s}}{}^0 = 0.140$ C/m^2, the parameter χ becomes about 0.2. The piezoelectric stress constants e_{31}, e_{32}, and e_{33} of the crystal phase calculated from the equation $\mathbf{e} = \mathbf{dC}$ are $e_{31} = -0.13$ C/m^2, $e_{32} = -0.14$ C/m^2, and $e_{33} = -0.28$ C/m^2, respectively. The compliance constants of the crystal are derived from eq 16 as $s_{11} = 0.42 \times 10^{-11}$ Pa^{-1}, $s_{21} = -0.07 \times 10^{-11}$ Pa^{-1}, and $s_{31} = -0.08 \times 10^{-11}$ Pa^{-1}, respectively. Just then the macroscopic piezoelectric constant $d_{31}{}^{\mathrm{M}}$ is calculated from eq 36 to be

$$d_{31}{}^{\mathrm{M}} \fallingdotseq (0.6 \times 10^{-11}) - (0.3 \times 10^{-13}) \fallingdotseq 0.6 \times 10^{-11}\ \mathrm{C/N} \quad (44)$$

which is of the same order as the experimental values measured at room temperature, $(0.2\text{–}3) \times 10^{-11}$ C/N.[2,3] In eq 44 the contribution of the intrinsic piezoelectric effect (the second term) is almost neglected. The macroscopic piezoelectric effect $d_{31}{}^{\mathrm{M}}$ is found to be almost governed by the mechanical and electric heterogeneity between the amorphous and crystalline phases (the first term).

It has been clarified so far experimentally[3,5,6,10,11] that the macroscopic $d_{31}{}^{\mathrm{M}}$ (and $e_{31}{}^{\mathrm{M}}$) is almost proportional to the electrostriction constant of the amorphous phase $\kappa_{31}{}^{\mathrm{a}}$, to the degree of crystallinity ϕ ($\phi < 0.5$) and to the magnitude of P_{s} (and therefore $\bar{P}_{\mathrm{s}}$), which can be easily understood from eq 36.

Estimation of $d_{33}{}^{\mathrm{M}}$

Quite similarly, the following parameters are used for the calculation of $d_{33}{}^{\mathrm{M}}$: $Y_3{}^{\mathrm{a}} = 1$ GPa, $Y_3{}^{\mathrm{c}} = 10$ GPa (calculated value), $s_{13} = -0.08 \times 10^{-11}$, $s_{23} = -0.76 \times 10^{-11}$ Pa^{-1}, and $s_{33} = 9.55 \times 10^{-11}$ Pa^{-1} (calculated values). Although the electrostriction constant $\kappa_{33}{}^{\mathrm{a}}$ has not yet been measured, we may utilize the observed value of $\kappa_{32}/\epsilon \fallingdotseq \kappa_{32}{}^{\mathrm{a}}/\epsilon^{\mathrm{a}} \fallingdotseq -0.2$.[2] Assuming Poisson's ratio $(-\partial\sigma_3{}^{\mathrm{M}}/\partial\sigma_2{}^{\mathrm{M}})$ of 0.5, $\kappa_{33}{}^{\mathrm{a}}/\epsilon^{\mathrm{a}}$ becomes

$$\frac{\kappa_{33}{}^{\mathrm{a}}}{\epsilon^{\mathrm{a}}} = \frac{1}{\epsilon^{\mathrm{a}}} \frac{\partial \epsilon^{\mathrm{a}}}{\partial \sigma_3{}^{\mathrm{M}}} = \frac{1}{\epsilon^{\mathrm{a}}} \frac{\partial \epsilon^{\mathrm{a}}}{\partial \sigma_2{}^{\mathrm{M}}} \frac{\partial \sigma_2{}^{\mathrm{M}}}{\partial \sigma_3{}^{\mathrm{M}}} = \frac{\kappa_{32}{}^{\mathrm{a}}}{\epsilon^{\mathrm{a}}} \frac{\partial \sigma_2{}^{\mathrm{M}}}{\partial \sigma_3{}^{\mathrm{M}}} \fallingdotseq 0.4 \quad (45)$$

The calculated $d_{33}{}^{\mathrm{M}}$ becomes as follows at room temperature

$$d_{33}{}^{\mathrm{M}} \fallingdotseq (-1.1 \times 10^{-11}) - (0.3 \times 10^{-11}) = -1.4 \times 10^{-11}\ \mathrm{C/N} \quad (46)$$

which agrees well with the observed values in order and also in sign.[7] Contrary to the case of $d_{31}{}^{\mathrm{M}}$, $d_{33}{}^{\mathrm{M}}$ contains a comparable amount of contribution from both terms in eq 43.

Temperature Dependence of $d_{31}{}^{\mathrm{M}}$ and $d_{33}{}^{\mathrm{M}}$

Fukada and Sakurai[4] and Burkard and Pfister[36] measured the temperature dependence of $d_{31}{}^{\mathrm{M}}$, which decreases to 10^{-12} to 10^{-13} C/N below the glass transition temperature ($T_{\mathrm{g}} \fallingdotseq -40$ °C), lower by one to two digits than the value at room temperature. Fukada et al.[10] ascribed it to the lowering of $\kappa_{31}{}^{\mathrm{a}}/\epsilon^{\mathrm{a}}$, almost zero below T_{g}, because of the stopping of the segmental motion in the amorphous region. On the other hand, $d_{33}{}^{\mathrm{M}}$ has almost the same value both at room temperature and below T_{g}.[7] Such a difference in temperature dependence between $d_{31}{}^{\mathrm{M}}$ and $d_{33}{}^{\mathrm{M}}$ can be explained definitely by using eq 36 and 43.

Assuming now $\kappa_{3i}{}^{\mathrm{a}} \fallingdotseq 0$ (i = 1 and 3), $Y_i{}^{\mathrm{a}} = 10$ GPa, and $\epsilon^{\mathrm{a}} = \epsilon^{\mathrm{c}}$ below T_{g} results in the following calculated values

$$d_{31}{}^{\mathrm{M}} \fallingdotseq (5.0 \times 10^{-13}) - (0.4 \times 10^{-13}) = 4.6 \times 10^{-13}\ \mathrm{C/N}$$

$$d_{33}{}^{\mathrm{M}} \fallingdotseq (-0.2 \times 10^{-11}) - (0.3 \times 10^{-11}) = -0.5 \times 10^{-11}\mathrm{C/N} \quad (47)$$

That is, $d_{31}{}^{\mathrm{M}}$ decreases from 10^{-11} to 10^{-13} C/N and $d_{33}{}^{\mathrm{M}}$ does not change detectably as the temperature was lowered, in good agreement with the observed behavior of these constants. Comparison of eq 47 with eq 44 and 46 reveals that the first term decreases largely at low temperature and the contribution of the crystalline phase (the second term) gradually becomes large.

About the Role of Space Charge

In the above discussion, the contribution of space charges to the macroscopic piezoelectric effect has not been taken into consideration. But we may consider that the parameter χ in $P_{\mathrm{s}} = \chi P_{\mathrm{s}}{}^0$ contains such an effect indirectly. As a first example, let us consider that, when the samples are poled, the space charges are injected from the metal electrode and trapped on the surface of crystallites so as to reduce the polarization $P_{\mathrm{s}}{}^0$ of the crystal, resulting in the decrease of $d_{31}{}^{\mathrm{M}}$ (eq 36). If so, the prevention of charge transfer from the metal electrode to the polymer sample should not reduce the $P_{\mathrm{s}}{}^0$ and therefore the d constant should become larger than that of the sample poled conventionally. But this prediction is inconsistent with the experimental results made by Murayama et al.[5,6] and Sussner et al.,[8] i.e., the samples poled by means of the so-called blocking electrode covered with SiO$_2$ insulators exhibit much smaller values of $d_{31}{}^{\mathrm{M}}$ (and $d_{33}{}^{\mathrm{M}}$) than the cases of the samples poled without such a blocking. Thus the space charges should be considered to increase the parameter χ or P_{s}. There may be some factors leading to a mechanism for increasing P_{s}; for example, (i) there may exist heterocharges with a sign equal to the polarity of crystallites, or (ii) the charges may propose a kind of "field" for revising the degree of orientation of crystallites in the sample,[37] and so on.

Appendix. Effect of Orientation on Piezoelectric Constants of Crystal

The piezoelectric constants are third-rank tensors so that they should be canceled if the sample in hand is unoriented or uniaxially oriented around the chain direction. We calculate the dependence of d constants upon the degree of orientation of the crystal by employing an assumed

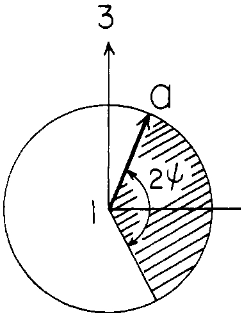

Figure 7. Assumed orientation function of the crystal: $n(\theta) = 1$, where θ is an angle between the a axis of the crystal and the 2 axis of the film. In the figure, the a axis orients in the range of an angle $+\psi$ to $-\psi$ around the draw axis (= the c axis).

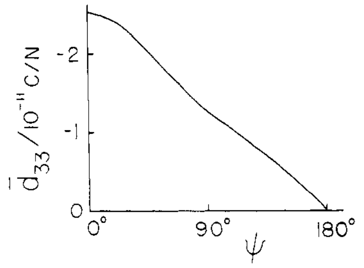

Figure 8. The averaged piezoelectric strain constant $\bar{d}_{33}$ as a function of an angle ψ (see Figure 7).

simple orientation function shown in Figure 7, where the c axis of the crystallites is completely arrayed along the draw direction and the a axis is oriented preferably in the range of an angle $+\psi$ to $-\psi$ ($0 < \psi < \pi$) around the draw direction. The averaged d constants based on the sample coordinates are represented as follows by using the d constants of the crystal.

$$\bar{d}_{ijk} = \sum_{l}\sum_{m}\sum_{n} \langle \omega_{il}\omega_{jm}\omega_{kn}\rangle d_{lmn} \tag{A.1}$$

where ω_{il}, for example, is the direction cosine between the axes i and l. In the case of the orientation function of Figure 7, eq A.1 can be expressed as

$$\begin{aligned} \bar{d}_{31} &= \langle \cos\theta\rangle_{\psi} d_{31} \\ \bar{d}_{33} &= \langle \cos^3\theta\rangle_{\psi} d_{33} + \langle \cos\theta \sin^2\theta\rangle_{\psi}(d_{32} + d_{24}) \end{aligned} \tag{A.2}$$

where θ is an angle between the a axis of the crystal and the 2 axis of the film, and

$$\begin{aligned} \langle \cos\theta\rangle_{\psi} &= \frac{1}{2\psi}\int_{-\psi}^{+\psi} \cos\theta \, d\theta = \frac{1}{\psi}\sin\psi \\ \langle \cos^3\theta\rangle_{\psi} &= \frac{1}{2\psi}\int_{-\psi}^{+\psi} \cos^3\theta \, d\theta = \frac{1}{\psi}\left(\sin\psi - \frac{1}{3}\sin^3\psi\right) \\ \langle \cos\theta\sin^2\theta\rangle_{\psi} &= \frac{1}{2\psi}\int_{-\psi}^{+\psi} \cos\theta\sin^2\theta \, d\theta = \frac{1}{3\psi}\sin^3\psi \end{aligned} \tag{A.3}$$

The calculated $\bar{d}_{33}$ as a function of ψ is shown in Figure 8, indicating that the $\bar{d}_{33}$ decreases almost linearly with the gradual lowering of the degree of orientation. Thus we may represent $\bar{d}_{33}$ as a linear function of d_{33} in a good approximation,

$$\bar{d}_{33} = kd_{33} \tag{A.4}$$

As to $\bar{d}_{31}$, it is clearly the linear function of d_{31} as shown in eq A.2.

$$\bar{d}_{31} = \langle \cos\theta\rangle_{\psi} d_{31} = k'd_{31} \tag{A.5}$$

From the definition of $d_{3i} = \partial P_s/\partial f_i$, we express the polarization P_s as shown in eq 29,

$$P_s = \chi P_s^0 \tag{A.6}$$

Acknowledgment. We wish to thank Professor Yasaku Wada of University of Tokyo for his useful advice to our study.

References and Notes

(1) (a) Osaka University; (b) the Institute of Physical and Chemical Research.
(2) R. Hayakawa and Y. Wada, *Adv. Polym. Sci.*, **11**, 1 (1973).
(3) Y. Wada and R. Hayakawa, *Jpn. J. Appl. Phys.*, **15**, 2041 (1976).
(4) E. Fukada and T. Sakurai, *Polym. J.*, **2**, 656 (1971).
(5) N. Murayama, *J. Polym. Sci., Polym. Phys. Ed.*, **13**, 929 (1975).
(6) N. Murayama, T. Oikawa, T. Katto, and K. Nakamura, *J. Polym. Sci., Polym. Phys. Ed.*, **13**, 1033 (1975).
(7) H. Ohigashi, *J. Appl. Phys.*, **47**, 949 (1976).
(8) H. Sussner and K. Dransfeld, *J. Polym. Sci., Polym. Phys. Ed.*, **16**, 529 (1978).
(9) M. G. Broadhurst, G. T. Davis, J. E. McKinney, and R. E. Collins, *J. Appl. Phys.*, **49**, 4992 (1978).
(10) T. Furukawa, J. Aiba, and E. Fukada, *J. Appl. Phys.*, **50**, 3615 (1979).
(11) S. Tasaka, M. Sato, S. Miyata, and E. Fukada, *Polym. Prepr., Jpn.*, **28**, 450 (1979).
(12) K. Kasai, *J. Phys. Soc. Jpn.*, **27**, 1268 (1969).
(13) E. Fukada and S. Takashita, *Jpn. J. Appl. Phys.*, **10**, 722 (1971).
(14) K. Namiki, R. Hayakawa, and Y. Wada, *Rep. Prog. Polym. Phys. Jpn.*, **21**, 539, 543 (1978).
(15) K. Tashiro, M. Kobayashi, and H. Tadokoro, *Macromolecules*, **11**, 908, 914 (1978).
(16) M. Born and K. Huang, "Dynamical Theory of Crystal Lattices", Oxford University Press, London, 1954.
(17) M. Kobayashi, K. Tashiro, and H. Tadokoro, *Macromolecules*, **8**, 158 (1975).
(18) R. Hasegawa, Y. Takahashi, Y. Chatani, and H. Tadokoro, *Polym. J.*, **3**, 600 (1972).
(19) A. E. Tonelli, *Macromolecules*, **9**, 547 (1976).
(20) R. Hasegawa, M. Kobayashi, and H. Tadokoro, *Polym. J.*, **3**, 591 (1972).
(21) K. Kaji, Doctoral Thesis, Kyoto University (1970); *Seni-to-Kogyo*, **3**, 555 (1970).
(22) N. Takahashi and A. Odajima, *Rep. Prog. Polym. Phys. Jpn.*, **21**, 141 (1978).
(23) Y. Takahashi, H. Tadokoro, and A. Odajima, *Polym. Prepr., Jpn.*, **28**, 1970 (1979).
(24) R. F. Schaufele and T. Shimanouchi, *J. Chem. Phys.*, **47**, 3605 (1967).
(25) G. R. Strobl and R. Eckel, *J. Polym. Sci., Polym. Phys. Ed.*, **14**, 913 (1976).
(26) J. F. Rabolt and B. Fanconi, *J. Polym. Sci., Polym. Lett. Ed.*, **15**, 121 (1977).
(27) J. F. Rabolt and B. Fanconi, *Polymer*, **18**, 1258 (1977).
(28) I. Sakurada and K. Kaji, *J. Polym. Sci., Part C*, **31**, 57 (1970).
(29) L. Holliday and J. W. White, *Pure Appl. Chem.*, **26**, 545 (1971).
(30) T. Ito, *J. Soc. Fiber Sci. Technol., Jpn.*, **32**, P-42 (1976).
(31) N. Takahashi, A. Odajima, K. Nakamura, and N. Murayama, *Polym. Prepr., Jpn.*, **27**, 364 (1978).
(32) R. G. Kepler and R. A. Anderson, *J. Appl. Phys.*, **49**, 1232 (1978).
(33) M. Date and E. Fukada, *Rep. Prog. Polym. Phys. Jpn.*, **20**, 339 (1977).
(34) D. Naegele and D. Y. Yoon, *Appl. Phys. Lett.*, **33**, 132 (1978).
(35) R. Hayakawa and Y. Wada, *Rep. Prog. Polym. Phys. Jpn.*, **19**, 321 (1976).
(36) H. Burkard and Pfister, *J. Appl. Phys.*, **45**, 3360 (1974).
(37) B. Stoll, *Kolloid Z. Z. Polym.*, **256**, 521 (1978).