Polymer Bulletin 2, 397–402 (1980)

Polymer Bulletin

Calculation of Piezoelectric Constants of Poly(Vinylidene Fluoride)

Form I

Kohji Tashiro, Masamichi Kobayashi and Hiroyuki Tadokoro

Department of Polymer Science, Faculty of Science, Osaka University, Toyonaka, Osaka, 560, Japan

Summary

Piezoelectric constants of poly(vinylidene fluoride) form I crystal have been calculated to give a good agreement with observed values; $d_{33} = -2.5 \times 10^{-11}$ C/N (observed: -2×10^{-11} C/N) and $d_{31} = -2.5 \times 10^{-13}$ C/N (observed: ca. 10^{-13} C/N). The macroscopic piezoelectric constants have also been calculated using such a model that the piezoelectric crystal form I is embedded in the non-piezoelectric amorphous matrix to be $d^M_{31} \fallingdotseq 0.6 \times 10^{-11}$ C/N (at room temperature) and 4.6×10^{-13} C/N (below glass transition temperature), and $d^M_{33} \fallingdotseq -1.4 \times 10^{-11}$ C/N and -0.5×10^{-11} C/N, respectively, reproducing well the observed temperature dependence of these constants.

* * *

1. Introduction

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 (HAYAKAWA & WADA 1973; WADA & HAYAKAWA 1976a). But the origin of the "macroscopic" piezoelectric effect of PVDF has not yet been clarified so definitely. The molecular-theoretical calculation of piezoelectric constants of "crystalline" phase based on the crystal structure will give us an important criterion for this basically significant problem. In the present paper, we will report the calculated results of crystalline piezoelectric constants of PVDF form I and estimate the degree of their contribution to the macroscopic piezoelectric effect.

2. Piezoelectric Constants of PVDF Form I Crystal

2.1 Principle of Calculation

0170-0839/80/0002/0397/$01.20

In a previous paper (TASHIRO et al. 1978) we derived a general method of calculating the three-dimensional elastic constants of polymer crystals, in which an equation of atomic displacements induced by an external stress was derived. If each atom has an effective point charge, the polarization of the whole system of crystal may be changed by the displacements of point charges, resulting in the appearence of piezoelectric effect. We may reasonably consider here that, different from the case of ionic crystals, the electrostatic long-range interactions affect hardly the properties of PVDF crystal which is governed primarily by the intermolecular van der Waals interactions. Therefore the influence of the long-range force will be neglected for simplicity. We will explain here only an outline of the theory and discuss the calculated results for the case of PVDF form I. The details will be published elsewhere (TASHIRO et al. 1980).

By 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 $\mathbf{P}_o$ may be given as follows.

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

where $\mathbf{X}(i,m,\mathbf{k})$ is a Cartesian position vector of the i-th atom of the mth unit in the $\mathbf{k}$th unit cell, v is a volume of unit cell, and N is the number of unit cells considered. When an external stress $\mathbf{f}$ is applied to the crystal, the change of polarization can be expressed as follows from eq 1.

$$\Delta\mathbf{P} = (1/Nv) \sum_{\mathbf{k}} \sum_{m} \sum_{i} Q_i \Delta\mathbf{X}(i,m,\mathbf{k}) - \mathbf{P}_o \Delta v/v \qquad (2)$$

Here the effective charges are assumed to remain constant after the atoms are displaced by the external 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. As discussed in reference (TASHIRO et al. 1978) a Cartesian displacement vector $\Delta\mathbf{X}(i,m,\mathbf{k})$ and the volume change Δv can be expressed in terms of the geometrical parameters, force constants, and compliance matrix. A final formula of $\Delta\mathbf{P}^{\Gamma}$, the polarization change belonging to the symmetry species Γ, can be represented as follows.

$$\Delta\mathbf{P}^{\Gamma} = -\{(1/v)[\sum_{m} c(m)^{\Gamma}\mathbf{A}(m)]\mathbf{Q}(\mathbf{F}_{\rho}^{\Gamma})^{-1}\mathbf{F}_{\rho\sigma}^{\Gamma}\mathbf{S}^{\Gamma} + \mathbf{P}_o\mathbf{S}'^{\Gamma}\}\mathbf{f} \qquad (3)$$

where $c(m)^{\Gamma}$ is a character of the symmetry species Γ for the symmetry operation $\underset{\sim}{A}(m)$, which transforms the basic 1st asymmetric unit into the mth unit. $\underset{\sim}{Q}$ is a matrix of effective point charges. The matrices $\underset{\sim}{F}_{\rho}^{\Gamma}$ and $\underset{\sim}{F}_{\rho\sigma}^{\Gamma}$ are constructed from force constants and $\underset{\sim}{B}$ matrix as shown in eq 26 of the previous paper (TASHIRO et al. 1978). $\underset{\sim}{S}^{\Gamma}$ and $\underset{\sim}{S}'^{\Gamma}$ are expressed using the compliance tensor components. On the other hand, the piezoelectric strain constants $\underset{\sim}{d}^{\Gamma}$ belonging to the symmetry species Γ may be defined as

$$\Delta \underset{\sim}{P}^{\Gamma} = \underset{\sim}{d}^{\Gamma}\underset{\sim}{f} \qquad (4)$$

Therefore we can obtain the $\underset{\sim}{d}$-constants from eqs 3 and 4.

2.2 Application to PVDF Form I Crystal

Although the actual chains are deflected more or less from the planar-zigzag conformation in the crystal cell, the present calculation adopts the model of planar-zigzag chains 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 $Cm2m\text{-}C_{2v}^{14}$ (Figure 1). Intramolecular force constants are valence-force-field type, and for the intermolecular force constants are used the second derivatives of the repulsive terms of Lennard-Jones 6-12 potentials and the electrostatic potentials with respect to the interatomic distance shorter than 4 Å, the numerical values of which will be given elsewhere (TASHIRO et al. 1980). The calculated piezoelectric strain and stress constants are given below.

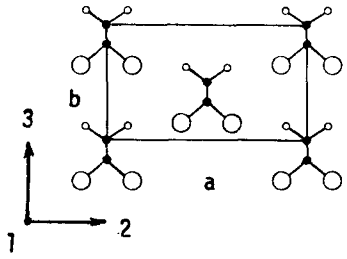

Figure 1. Crystal structure of PVDF form I (HASEGAWA et al. 1972).

$$\underset{\sim}{d} = \begin{bmatrix} 0 & 0 & 0 & 0 & -3.070 & 0 \\ 0 & 0 & 0 & -0.428 & 0 & 0 \\ -0.025 & -0.405 & -2.519 & 0 & 0 & 0 \end{bmatrix} \times 10^{-11}\ \mathrm{C/N} \qquad (5)$$

$$\underset{\sim}{e} = \begin{bmatrix} 0 & 0 & 0 & 0 & -0.135 & 0 \\ 0 & 0 & 0 & -0.009 & 0 & 0 \\ -0.130 & -0.145 & -0.276 & 0 & 0 & 0 \end{bmatrix} \ \mathrm{C/m^2} \qquad (6)$$

Here the tensors are defined in the coordinate system of (1 // c, 2 // a, 3 // b).

Odajima et al. (1978) 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 calculated value of -2.5×10^{-11} C/N. The calculated d_{31} is smaller by two digits than d_{33}, consistent with the experimental result by Odajima et al. (1978), i.e., the negligibly small x-ray shift of (002) reflection by the application of electro-static field. When the electrostatic field E_3 is applied along the b axis, the ratio of strains induced in the directions of the 1 and 3 axes is given by $\sigma_1/\sigma_3 = (d_{31}E_3)/(d_{33}E_3) = d_{31}/d_{33} \doteqdot 1/100$, that is, the strain along the chain axis is much smaller than the strain in the b axis. It is reasonable from the view-point of characteristic mechanical property of polymer chains, constructed generally by the strong covalent linkages, which are packed together by the weak van der Waals interactions.

Compared with the crystalline piezoelectric constant d_{31} ($\doteqdot 10^{-13}$ C/N), the macroscopic constant d^M_{31}, about 10^{-11} C/N (WADA & HAYAKAWA 1976a), is much larger, suggesting that the amorphous region may play a significantly important role on the appearence of piezoelectric phenomenon of the bulk sample.

3. Macroscopic Piezoelectric Effects of PVDF Sample

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 set up such a model that the form I crystallites are embedded in the non-piezoelectric amorphous matrix. Based on the theory by HAYAKAWA & WADA (1976b), we can derive the macroscopic piezoelectric constants d^M_{31} and d^M_{33} by assuming a mechanical series model;

$$d^M_{31} = \frac{3\varepsilon^a}{2\varepsilon^a+\varepsilon^c}\left[\frac{\phi(1-\phi)}{Y^a_1}\chi P^\circ_s\left(\frac{\varepsilon^c}{2\varepsilon^a+\varepsilon^c}\frac{\kappa^a_{31}}{\varepsilon^a} + m\right) + \phi\chi\sum_{i=1}^{3} e_{3i}s_{i1}\right] \tag{7}$$

$$d^M_{33} = \frac{3\varepsilon^a}{2\varepsilon^a+\varepsilon^c}\left[\frac{\phi\chi}{Y^M_3}P^\circ_s\left(\frac{\varepsilon^c}{2\varepsilon^a+\varepsilon^c}\frac{\kappa^a_{33}}{\varepsilon^a} - 1\right) + \phi\chi\sum_{i=1}^{3} e_{3i}s_{i3}\right] \tag{8}$$

where $Y^M_3 = Y^a_3Y^c_3/[(Y^a_3-Y^c_3)\phi + Y^c_3]$. The definition of parameters is listed in Table I. The polarization P_s of a crystallite is assumed to be reduced by the parameter χ from the intrinsic polarization P_s^o ($P_s = \chi P_s^o$) because of incomplete orientation of crystallites and so on. In eqs 7 and 8 the first terms are originated from the difference in mechanical and electrical properties between amorphous and crystalline phases and the second terms are from the intrinsic piezoelectric effect of crystalline phase itself, respectively.

Using the parameters listed in Table I the piezoelectric strain constants are calculated at room temperature to be

$$\begin{aligned} d_{31}^M &\doteqdot 0.6 \times 10^{-11} - 0.3 \times 10^{-13} \doteqdot 0.6 \times 10^{-11} \text{ C/N} \\ d_{33}^M &\doteqdot -1.1 \times 10^{-11} - 0.3 \times 10^{-11} = -1.4 \times 10^{-11} \text{ C/N} \end{aligned} \qquad (9)$$

The observed values at room temperature are $d_{31}^M \doteqdot 0.2 \sim 3 \times 10^{-11}$ C/N and $d_{33}^M \doteqdot -1 \times 10^{-11}$ C/N (WADA & HAYAKAWA 1976a), being reproduced well in the calculation. In eq 9 we can say that the macroscopic piezoelectric effect of d_{31}^M is almost determined by the mechanical and electrical heterogeneity between amorphous and crystalline phases and the intrinsic piezoelectric effect of crystalline part contributes to it only negligibly, while d_{33}^M contains comparable degrees of contribution from both terms.

Table I

Parameters used in eqs 7 & 8 at room temperature[a]

Dielectric constant: $\varepsilon^a/\varepsilon^c = 10.0$

Electrostriction constant: $\kappa_{31}^a/\varepsilon^a = 2$, $\kappa_{33}^a/\varepsilon^a = 0.4$

Young's modulus: $Y_1^a = Y_3^a = 1$ GPa, $Y_3^c = 10$ GPa

Crystallinity: $\phi = 0.5$, Poisson's ratio: $m = 0.5$

Intrinsic polarization: $P_s^o = 0.140$ C/m^2, $\chi = 0.2$

Compliance constants ($\times 10^{-11}$ Pa^{-1}): $s_{11} = 0.42$, $s_{12} = -0.07$, $s_{13} = -0.08$, $s_{23} = -0.76$, $s_{33} = 9.55$

---

[a] Superscripts "a" and "c" mean "amorphous" and "crystal" phases, respectively; the coordinate axes are defined as 1//(draw axis), 3⊥(film plane), 2⊥(1 & 3).

The macroscopic piezoelectric constant d_{31}^{M} decreases from 10^{-11} C/N to $10^{-12} \sim 10^{-13}$ C/N as the temperature lowers from 20°C to the glass transition temperature (T_g = -40°C), while d_{33}^{M} has almost the same order of value above and below T_g (OHIGASHI 1976). Such a difference in temperature dependence between these two constants can be explained definitely using eqs 7 & 8.

Among the parameters in Table I, the following quantities are assumed to change below T_g (FURUKAWA et al. 1979); $\kappa_{3i}^{a} = 0$ (i = 1 & 3), Y_i^a = 10 GPa, and $\varepsilon^a/\varepsilon^c = 1$. Then the piezoelectric constants are calculated as

$$d_{31}^{M} \doteqdot 5.0 \times 10^{-13} - 0.4 \times 10^{-13} = 4.6 \times 10^{-13} \text{ C/N}$$
$$d_{33}^{M} \doteqdot -0.2 \times 10^{-11} - 0.3 \times 10^{-11} = -0.5 \times 10^{-11} \text{ C/N} \tag{10}$$

which are in good agreement with the observed results. Comparison of eq 10 with eq 9 reveals that the first term decreases largely at low temperature and the contribution of crystalline phase (the second term) becomes gradually large.

The role of space charges present in the film on the macroscopic piezoelectric effect of PVDF will be discussed elsewhere (TASHIRO et al. 1980).

The authors wish to thank Dr. Eiichi Fukada of the Institute of Physical and Chemical Research and Professor Yasaku Wada of the University of Tokyo for their useful advices.

4. References

FURUKAWA, T., J. AIBA, and E. FUKADA, J. Appl. Phys., 50, 3615 (1979)
HASEGAWA, R., Y. TAKAHASHI, Y. CHATANI, and H. TADOKORO, Polym. J., 3, 600 (1972)
HAYAKAWA, R. and Y. WADA, Adv. Polym. Sci., 11, 1 (1973)
HAYAKAWA, R., and Y. WADA, Rep. Progr. Polym. Phys. Jpn. , 19, 321 (1976)
ODAJIMA, A., et al., Polym. Preprints, Jpn., 27, 364 (1978)
OHIGASHI, H., J. Appl. Phys., 47, 949 (1976)
TASHIRO, K., M. KOBAYASHI, and H. TADOKORO, Macromolecules, 11, 908 (1978)
TASHIRO, K., M. KOBAYASHI, and H. TADOKORO, Macromolecules, to be published
WADA, Y. and R. HAYAKAWA, Jpn. J. Appl. Phys., 15, 2041 (1976)

Received February 20, 1980
Accepted March 4/ 10, 1980