

Piezoelectricity and Pyroelectricity in a Copolymer of Vinylidene Fluoride and Tetrafluoroethylene

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ABSTRACT: The piezoelectric constants d_{31} , d_{32} , d_{33}^a were measured for the undrawn and uniaxially drawn copolymer of vinylidene fluoride (80 mol%) and tetrafluoroethylene (20 mol%) as a function of remanent polarization P_r . The data of undrawn samples are consistent with the assumption that the piezoelectric activity mainly arises from macroscopic dimensional changes. Drawn samples show a strong in-plane anisotropy so that d_{31} is much larger than d_{32} . Such an anisotropy is mostly attributable to anisotropic Poisson's ratio. The temperature dependence of the piezoelectric constants is discussed. The pyroelectric constant p_3 was measured as a function of P_r . Using piezoelectric and thermal expansion data, the contribution from the secondary effect was calculated and found to be 1/4 the total activity.

KEY WORDS Ferroelectricity / Piezoelectricity / Pyroelectricity /
Copolymer of Vinylidene Fluoride and Tetrafluoroethylene /

The strong piezoelectric and pyroelectric activities in uniaxially drawn and poled poly(vinylidene fluoride) (PVDF) have stimulated a great deal of interest in this polymer.^{1,2} Several reviews on piezoelectricity and pyroelectricity have been published.³⁻⁶ The copolymer of vinylidene fluoride (VDF) with trifluoroethylene (TrFE) has been of special interest recently because it is ferroelectric toward paraelectric transition. We also investigated piezoelectric and pyroelectric responses of this copolymer. Since the homopolymer and copolymers of VDF are ferroelectric, their piezoelectric and pyroelectric activities are attributable to ferroelectric orientation of the crystalline dipoles.⁷⁻¹⁰

The copolymer of vinylidene fluoride (VDF) with tetrafluoroethylene (TeFE) is known to have a crystalline phase analogous to the β phase of PVDF of as-cast or melt-crystallized films.¹¹ Baise and coworkers have shown that

the copolymer exhibits higher pyroelectric activity than PVDF under the same poling conditions.¹² Davis and Broadhurst measured the piezoelectric constant determined by the change in polarization with hydrostatic pressure and discussed the results on the basis of a molecular theory.¹³ Collins and coworkers measured pyroelectric constants for the 73/27 VDF/TeFE copolymer and showed that the films are not uniformly poled across their thickness and that the response arises from two separate effects.¹⁴ Stefanou reported the film compliance, density, degree of crystallinity and thickness piezoelectricity for copolymers containing 61 to 96% VDF and concluded that the piezoelectric constant can be calculated from the molecular dipole theory where the polarization is derived using a cavity reaction field.¹⁵ Hicks and his coworkers have studied the ferroelectric properties of this copolymer.¹⁶ In comparison with PVDF, VDF/TeFE co-

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polymer has been investigated to a lesser extent.

In this paper, we present further experimental results on piezoelectricity and pyroelectricity in undrawn and/or uniaxially drawn samples of a VDF/TeFE copolymer. In contrast to conventional high temperature poling, we carried out room temperature poling using a slowly changing high electric field and prepared samples with known values of remanent polarization P_r . We determined the transverse and longitudinal piezoelectric constants as a function of P_r . The results allowed us to examine the contribution of the dimensional effect on piezoelectric activity. We also measured the temperature dependence of the piezoelectric constant as well as the dielectric and elastic constants of the copolymer to obtain further information. We also discuss the mechanisms of pyroelectric activity.

EXPERIMENTAL

Sample Preparation

The sample used was an 80/20 copolymer of VDF and TeFE supplied by Daikin Kogyo Co. Ltd. Undrawn film samples were obtained by casting from a methyl ethyl ketone solution and annealed at 120°C for 1 h. The uniaxial drawing was performed at 45°C to 7 times their original length, followed by annealing at 100°C for 1 h. Gold electrodes were evaporated *in vacuo* onto both sides of the samples.

Measurements

The poling of samples was undertaken at room temperature by applying a sinusoidal high electric field of 100⁻¹ Hz up to 150 MV m⁻¹. By monitoring the induced charges, we obtained a typical hysteresis loop as shown in Figure 1. The remanent polarization P_r was *ca.* 60 mC m⁻², which is much larger than the value reported by Hicks and coworkers.¹⁶ This may be because we applied a much higher field and induced better orientation of the dipoles. The coercive field E_c was found to be 50

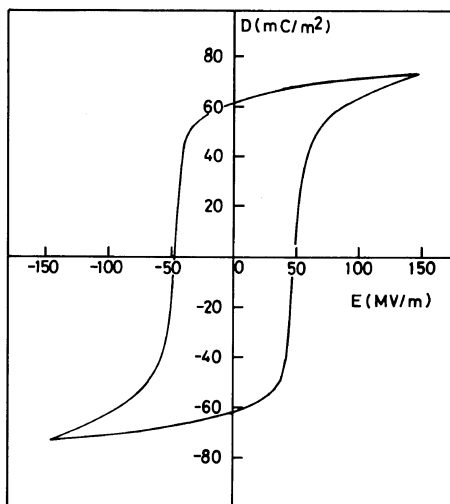


Figure 1. Hysteresis loop of an undrawn 80/20 VDF/TeFE copolymer.

MV m⁻¹. By changing the maximum applied field, we prepared poled samples with various values of P_r .

We studied two types of piezoelectric effects, the transverse effect and longitudinal effect. The transverse effects were observed at 10 Hz by the ratio of charge density generated on the electrode to the applied stress along the drawing direction and/or perpendicular to this direction in-plane of a rectangular sample. Thus, we obtained d_{31} and d_{32} . At the same time, we measured Young's moduli $1/s_{11}$ and $1/s_{22}$ and the dielectric constant ϵ_3/ϵ_0 . We used the Cartesian coordinate system where the 1 axis was taken along the draw direction and the 3 axis, along the thickness [poling direction]. The temperature dependence of the piezoelectric constant was measured from -150 to 100°C. The longitudinal effect was measured by applying a quasi-static stress along the thickness direction to a sample sandwiched between a pair of glass plates. In this configuration, the in-plane deformation of the sample was restricted. Thus, we obtained d_{33}^a rather than the true d_{33} . The pyroelectric constant p_3 was obtained by a conventional technique which measures the change in total

charge on the electrodes due to an increase or decrease in the temperature of a mechanically free sample.

The most commonly used piezoelectric constants are defined by¹⁷

$$d_{3j} = \frac{1}{A} \left(\frac{\partial Q_3}{\partial X_j} \right)_{x_{i \neq j} = 0} \quad (1)$$

$$e_{3j} = \frac{1}{A} \left(\frac{\partial Q_3}{\partial x_j} \right)_{x_{i \neq j} = 0} \quad (2)$$

where X_j is the stress, x_j the strain and Q_3 , the total charge induced on the electrodes of area A . d_{3j} and e_{3j} are related to each other by¹⁸

$$d_{3j} = \sum_{i=1}^3 e_{3i} s_{ij} \quad (3)$$

$$e_{3j} = \sum_{i=1}^3 d_{3i} c_{ij} \quad (4)$$

where s_{ij} is the elastic compliance and c_{ij} , the elastic stiffness. We sometimes used the constants defined by¹⁹

$$d_{3j}^a = \left(\frac{\partial P_3}{\partial X_j} \right)_{x_{i \neq j} = 0} \quad (5)$$

$$e_{3j}^a = \left(\frac{\partial P_3}{\partial x_j} \right)_{x_{i \neq j} = 0} \quad (6)$$

The superscript a denotes the apparent value of these constants because they differ from d_{3j} and e_{3j} in eq 1 and 2 in terms of mechanical boundary conditions. The details are described in a previous paper.¹⁹ Corresponding to eq 3 and 4, we have

$$d_{3j}^a = e_{3j} / c_{jj} \quad (7)$$

$$e_{3j}^a = d_{3j} / s_{jj} \quad (8)$$

We measured three constants: d_{31} and d_{32} and d_{33}^a . The other constants were calculated using eq 3, 4, 7, and 8.

RESULTS

The β -phase of PVDF is usually obtained by drawing melt crystallized films. Since the VDF/TeFE copolymer was assumed to have a

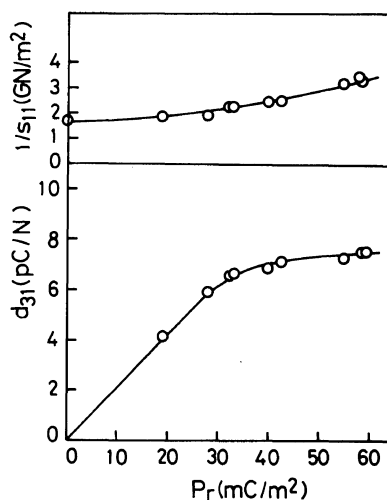


Figure 2. Dependence of the transverse piezoelectric constant d_{31} and the Young's modulus $1/s_{11}$ on the remanent polarization P_r in an undrawn VDF-TeFE copolymer.

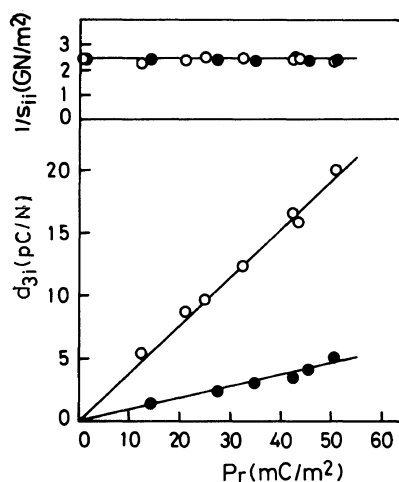


Figure 3. Dependence of d_{31} and the Young's modulus $1/s_{11}$ on P_r in uniaxially drawn VDF/TeFE copolymer. \circ , for d_{31} and $1/s_{11}$ respectively; \bullet , for d_{32} and $1/s_{22}$, respectively.

crystalline structure similar to the β -PVDF of as-cast or melt-crystallized films, we could observe a square D - E hysteresis loop and piezoelectric and pyroelectric activities in undrawn samples. Figure 2 shows the dependence of the piezoelectric constant d_{31} and Young's modulus $1/s_{11}$ on the remanent po-

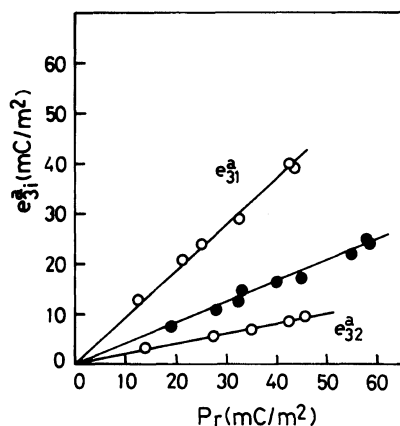


Figure 4. Dependence of e_{3i}^a on P_r in undrawn and uniaxially drawn VDF/TeFE copolymers. ●, for e_{31}^a of an undrawn copolymer.

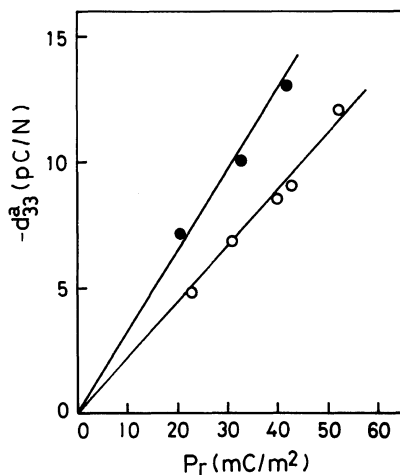


Figure 5. Dependence of e_{33}^a on P_r in undrawn and uniaxially drawn VDF/TeFE copolymers: ○, for an undrawn copolymer; ●, for a drawn copolymer.

larization P_r in an undrawn 80/20 copolymer. The Young's modulus gradually increases with increasing remanent polarization P_r . Although the piezoelectric constant d_{31} initially increases with increasing P_r , it tends to saturate at high P_r .

The uniaxial drawing resulted in a strong in-plane anisotropy of the piezoelectric constant, as shown in Figure 3. The value of d_{31} is much larger than that of d_{32} at a given P_r . Both d_{31} and d_{32} are linearly proportional to P_r .

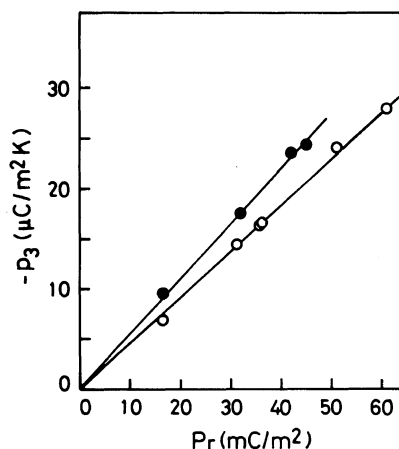


Figure 6. Dependence of the pyroelectric constant p_3 on P_r in undrawn and uniaxially drawn VDF/TeFE copolymers. ○, for an undrawn copolymer; ●, for a drawn copolymer.

Young's moduli $1/s_{11}$ and $1/s_{22}$ are identical to each other and independent of P_r . Similar behavior has been reported for uniaxially drawn and poled PVDF.²⁰

Figure 4 shows the dependence of piezoelectric constants e_{31}^a and e_{32}^a on P_r for undrawn and uniaxially drawn VDF/TeFE copolymers. Both e_{31}^a and e_{32}^a are linearly proportional to P_r . The ratio of e_{31}^a/P_r for the undrawn sample is about 0.42, which is very close to the value reported for undrawn VDF/TrFE copolymers.¹⁹ The ratios of e_{31}^a/P_r and e_{32}^a/P_r for uniaxially drawn samples are 0.9 and 0.2 respectively. These values are similar to those in drawn PVDF and VDF rich copolymers with TrFE. The results indicate a similarity in the mechanism of piezoelectric activity of these polymers.

Figure 5 shows the dependence of the longitudinal piezoelectric constant d_{33}^a on P_r for undrawn and uniaxially drawn samples. The values of d_{33}^a are linearly proportional to the remanent polarization P_r . At a given value of P_r , uniaxially drawn samples have larger values of d_{33}^a than undrawn samples.

The pyroelectric constants of undrawn and drawn copolymers were determined as a func-

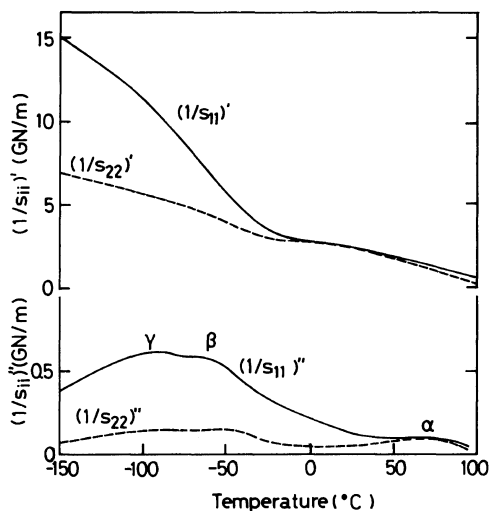


Figure 7. Temperature dependence of real and imaginary parts of Young's moduli of drawn VDF/TeFE copolymer.

tion of P_r , and the results are shown in Figure 6. A linear relationship between p_3 and P_r is observed. The drawn samples have slightly larger pyroelectric activity than undrawn samples.

Figure 7 shows the temperature dependence of the real and imaginary parts of Young's moduli $1/s_{11}$ and $1/s_{22}$ of drawn VDF/TeFE copolymer. Three relaxations are observed, and designated as α , β , and γ in order of decreasing temperature. The α process near 60°C is attributable to the molecular motions in the crystalline regions. The β process reflects micro-Brownian motions of the molecular chain backbone in the noncrystalline regions.²¹ The γ process is related to local motions of the molecular chains. At low temperatures, the Young's modulus along the drawn direction is much larger than that perpendicular to the drawn direction.

Figure 8 shows the temperature dependence of the dielectric constant measured at 10 Hz for the drawn copolymer. Two relaxation processes are observed near 60 and -40°C corresponding to the α and β processes, respectively. The γ process is not clearly ob-

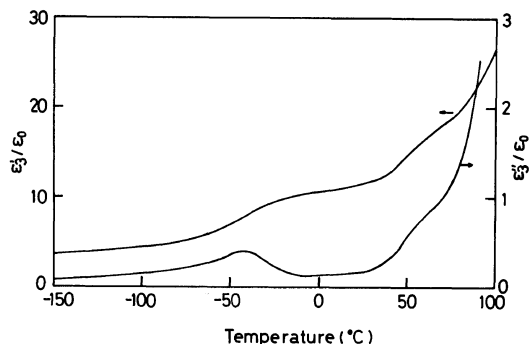


Figure 8. Temperature dependence of the dielectric constant of drawn VDF/TeFE copolymer.

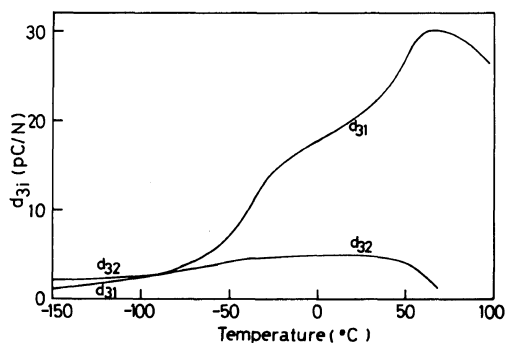


Figure 9. Temperature dependence of the d_{31} and d_{32} in an uniaxially drawn VDF/TeFE copolymer.

served.

Figure 9 shows the temperature dependence of the piezoelectric constants, d_{31} and d_{32} , measured at 10 Hz for the drawn copolymer having a remanent polarization $P_r = 53 \text{ mC m}^{-2}$. The value of d_{31} is very small at low temperatures and increases rapidly around the glassy transition temperature T_g of *ca.* -40°C . Above 60°C , d_{31} gradually decreases with increasing temperature because of depolarization. After heating to 100°C , the remaining d_{31} was about 1/3 of the original value. Such an anisotropy of d_{31} and d_{32} is very similar to that of PVDF.²²

Below -90°C , d_{32} is larger than d_{31} . However, d_{32} shows only a small increase with temperature. At a room temperature, d_{32} is much smaller than d_{31} . The sharp decrease in d_{32} above 60°C also reflects depolarization of

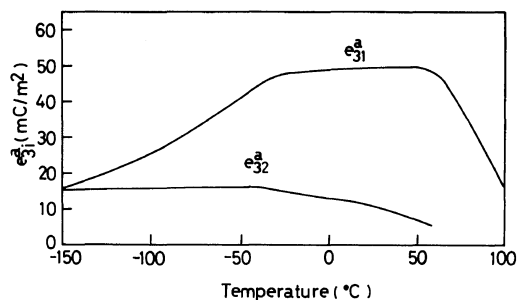


Figure 10. Temperature dependence of e_{31}^a and e_{32}^a in an uniaxially drawn VDF/TeFE copolymer.

crystalline regions.

Figure 10 shows the temperature dependence of piezoelectric constants e_{31}^a and e_{32}^a for the same sample. The e_{31}^a value shows a gradual increase up to -30°C and then levels off. Above 60°C , e_{31}^a suddenly decreases because of depolarization. The temperature dependence of e_{31}^a for the drawn VDF/TeFE copolymer is very similar to that of β -PVDF.²³ The depolarization occurs more rapidly in the copolymer than in PVDF because the former has a lower melting point ($\sim 130^\circ\text{C}$) than the latter ($\sim 170^\circ\text{C}$).

e_{32}^a has the same value as e_{31}^a at -150°C and rather decreases with increasing temperature around room temperature (above T_g).

DISCUSSION

Various mechanisms have been proposed to explain the piezoelectric activity in PVDF. Broadhurst and coworkers have considered a model consisting of polarizable and liberating dipoles.¹⁷ Wada and Hayakawa developed a theory on piezo- and pyroelectricity for a semicrystalline polymer with polar crystals.²⁴ Although their theoretical consideration is based on different models, they have derived a common mechanism called the dimensional effect which assumes the consistent dipoles to be rigid when a sample is subjected to deformation. The expected change in induced charges on deformation may be proportional

to a change in thickness. Therefore, the e constants are given as follows:

$$e_{31} = e_{32} = 0. \quad (9)$$

$$e_{33} = -P_r \quad (10)$$

We usually carry out direct measurements on the d constant rather than on the true e constant. The apparent e^a constant is easily obtained from the d constant *via* eq 8. The dimensional effect leads to the expression for e^a as follows:

$$e_{31}^a = P_r v_{31}, \quad (11)$$

$$e_{32}^a = P_r v_{32}, \quad (12)$$

$$e_{33}^a = -P_r. \quad (13)$$

These expressions are independent of the choice of model. If the piezoelectric constants are measured as a function of macroscopic polarization P_r , the contribution of the dimensional effect is estimated by eq 9–13.

We previously investigated the piezoelectricity and pyroelectricity in VDF/TrFE copolymers in detail,¹⁹ and found the piezoelectric activity in undrawn copolymers primarily to arise from macroscopic dimensional change, indicating the molecular dipoles to be relatively rigid. The additional contribution from the electrostrictive coupling has been shown important in drawn copolymers of equimolar composition.

We measured various piezoelectric constants in the 80/20 VDF/TeFE copolymer as a function of P_r . In undrawn samples, we obtained the ratio of e_{31}^a/P_r of 0.42. This value may be close to Poisson's ratio in usual semicrystalline polymers. Thus, the piezoelectric activity in undrawn VDF/TrFE is primarily attributable to the dimensional effect.

To evaluate true piezoelectric constants e_{31} and e_{33} , we used the following equations¹⁹

$$e_{33} = \frac{1 - \nu}{(1 - 2\nu)(1 + \nu)} \frac{d_{33}^a}{s} \quad (14)$$

$$e_{31} = \frac{1}{1-\nu} e_{31}^a + \frac{\nu(1-\nu)}{(1-2\nu)(1+\nu)} \frac{d_{33}^a}{s} \quad (15)$$

where s is the elastic compliance and ν , the Poisson's ratio; these are two independent quantities characterizing an isotropic elastic body. For the case of $P_r = 50 \text{ mC m}^{-2}$, we have $d_{33}^a = -11 \text{ pC N}^{-1}$ from the results in Figure 5 and $1/s = 2.8 \text{ GN m}^{-2}$ from Figure 2. Assuming that ν is 0.38, we obtain e_{33} as -58 mC m^{-2} , which is only 20% greater than P_r . Thus, the value of d_{33}^a is also consistent with the prediction of the dimensional effect.

The drawing of the copolymer results in a piezoelectric anisotropy indicating d_{31} to be much larger than d_{32} . Because Young's moduli $1/s_{11}$ and $1/s_{22}$ are identical, there is the same anisotropy, $e_{31}^a \gg e_{32}^a$. From Figure 4, we have the ratios, $e_{31}^a/P_r = 0.9$ and $e_{32}^a/P_r = 0.2$. If the dimensional effect is dominant, these ratios should be comparable to corresponding Poisson's ratios. It has been shown that ν_{31} of drawn semicrystalline polymers can exceed 0.5, e.g., Tasaka and Miyata reported a value of 0.7 for ν_{31} of PVDF.²⁵ Thus the value of 0.9 for e_{31}^a/P_r in the VDF/TeFE copolymer may be broadly consistent with the prediction from the dimensional effect. Although ν_{32} for the VDF/TeFE copolymer is not available so far, the value of 0.2 for e_{32}^a/P_r may also be consistent with the corresponding Poisson's ratio.²⁶

Stefanou measured the longitudinal piezoelectric constants d_{33} for VDF/TeFE copolymers of composition ranging from 61/39 to 96/4 molar ratio.¹⁵ He used an experimental set-up similar to ours, where a sample was sandwiched between a pair of brass electrodes. In such a configuration, we consider the in-plane deformation of a sample to be restricted and hence, the piezoelectric constant obtained to be d_{33}^a rather than the true d_{33} . He reported a value of -6.2 pC N^{-1} for d_{33} in his notation with respect to the 78/22 copolymer. This value corresponds to d_{33}^a of our sample with $P_r = 20 \text{ mC m}^{-2}$.

In Figures 9 and 10, we show the temperature dependence of the piezoelectric constants. Both d_{31} and d_{32} increase with temperature except above 60°C where the disordering of aligned dipoles takes place. The temperature dependence of e_{31}^a and e_{32}^a is less than that of the d constant. If the dimensional effect is dominant, the curves in Figure 10 should reflect a temperature dependence of e_{31}^a in the VDF/TeFE copolymer similar to that in PVDF.²⁰

Sussner²⁷ has discussed the temperature dependence of Poisson's ratios using Ohigashi's data for the temperature dependence of the electromechanical coupling factor k_{31} and k_{33} .²⁸ Going a simple assumption that only the longitudinal piezoelectric constant e_{33} is essential and independent of temperature while e_{31} and e_{32} are zero, Sussner derived the change in Poisson's ratio ν_{31} with temperature, that is, ν_{31} increases from 0.2 (-100°C) to 0.6 (50°C). His assumption is equivalent to the prediction from the dimensional effect in terms of the anisotropy of the true e constant. We found in the VDF/TeFE copolymer that e_{31}^a at a room temperature is three times that at -150°C . As shown in Figure 10, this can be interpreted in terms of an increase in ν_{31} by a factor of three which is same as the prediction by Sussner in PVDF.

The e_{32}^a value remains constant up to -40°C and then gradually decreases with increasing temperature. Such behavior may reflect the temperature dependence of ν_{32} .

From these considerations, we can conclude that the piezoelectric activity in an 80/20 copolymer of VDF/TeFE primarily arises from macroscopic dimensional changes in a similar manner as in PVDF and VDF-rich copolymers with TrFE. However, the observed ratio of e_{31}^a/P_r is too large and that of e_{32}^a , slightly small compared to the corresponding Poisson's ratio. There must be certain other effects, although they are minor. The electrostrictive coupling proposed in VDF/TrFE copolymers may be one factor responsible for the remain-

ing contributions.

The pyroelectric constant p_3 for a mechanically free sample generally consists of two terms:¹⁸

$$p_3 = \left(\frac{\partial P_3}{\partial T} \right)_{x_i=0} + \sum_{i=1}^3 e_{3i} \alpha_i \quad (16)$$

where T is the temperature and α_i , the thermal expansion coefficient. The first term, called the primary effect, expresses the intrinsic pyroelectricity which appears in a clamped sample. The second term indicates coupling of the piezoelectricity and thermal expansion, and is called the secondary effect. We can calculate the secondary effect using true e_{31} and e_{33} , if the thermal expansion coefficient α_i is known. Since the dimensional effect is dominant in the piezoelectricity of the VDF/TeFE copolymer, e_{31} and e_{32} are negligible and e_{33} is nearly equal to $-P_r$. From Figure 6, we obtain the values of $-4.7 \times 10^{-4} \text{ K}^{-1}$ and $-5.4 \times 10^{-4} \text{ K}^{-1}$ for p_3/P_r in undrawn and drawn copolymers, respectively. These values were compared to the thermal expansion coefficient α_3 in the thickness direction in order to evaluate the contribution from the secondary effect. Koizumi and coworkers reported the value of $1.10 \times 10^{-4} \text{ K}^{-1}$ for the thermal expansion coefficient of VDF/TeFE copolymer of composition 79/21.²¹ We can take $1.10 \times 10^{-4} \text{ K}^{-1}$ as the thermal expansion of the copolymer. The result indicates that the secondary effect contributes only 1/4 the total pyroelectric activity in the undrawn 80/20 VDF/TeFE copolymer. The remaining is attributed to the primary effect which may be due to the reversible disordering of the dipoles.

CONCLUSIONS

The d_{31} , d_{32} , d_{33}^a and pyroelectric constant p_3 were measured for undrawn and uniaxially drawn VDF/TeFE copolymers of molar composition 80/20 as a function of the remanent polarization P_r . The ratio of the activity to P_r indicates that the dimensional effect is the

primary contribution to piezoelectric activity in this copolymer. The secondary pyroelectric effect contributes 1/4 the total activity.

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