Second-Order Dielectric Constant of a Copolymer of Vinylidene Fluoride and Trifluoroethylene (52:48 Mole Ratio)

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ABSTRACT: The second-order dielectric constant ε_2 of a copolymer of vinylidene fluoride and trifluoroethylene (52:48 in mole) was measured by means of the difference frequency method. ε_2 is related to spontaneous polarization P_s and the linear dielectric constant ε_1 through a thermodynamic representation of free energy. The relation explains the observed temperature dependence of ε_2. ε_2 was found to be proportional to the remanent polarization P_r. This is interpreted by the model that the ferroelectric crystal is composed of parallel and antiparallel domains. ε_2 in the crystal was deduced from that of the whole polymer on the assumption of the ellipsoidal crystal model.

KEY WORDS Nonlinear Dielectric Constant / Second-Order Dielectric Constant / Ferroelectric Polymer / Vinylidene Fluoride–Trifluoroethylene Copolymer /

Poly(vinylidene fluoride) (PVDF) and copolymers of vinylidene fluoride (VDF) and trifluoroethylene (TrFE) possess piezoelectric, pyroelectric and ferroelectric properties. The ferroelectricity and the ferroelectric-to-paraelectric phase transition of the copolymers have been studied by D–E (electric displacement-electric field) hysteresis,[1,2] polarization reversal switching current[3,4] and anomalies of various quantities at the transition.[5] Molecular conformations and crystal structures of the copolymers in the vicinity of the transition have been investigated by X-ray diffraction and IR absorption.[6,7] Since the ferroelectric polarization is deduced thermodynamically from the free energy as a function of polarization P including higher order terms as P^4 and P^6, higher order dielectric constants with an appreciable magnitude are expected to appear in the ferroelectric polymers. These constants should be closely related to the coefficients of P^4 and P^6 terms in the free energy.

In the first part of this paper, an experimental system to obtain the second-order dielectric constant is described. The system is essentially similar to that reported by Hayakawa and his coworkers.[8]

Secondly we measured the temperature dependence of second-order dielectric constant of a VDF–TrFE copolymer with VDF fraction of 52 mol% which exhibits a ferroelectric phase transition at *ca.* 70°C. Since the second order dielectric constant of the copolymer vanishes in the paraelectric state with a symmetry center, we could determine the transition temperature from its temperature dependence.

Thirdly, the dependence of the second order dielectric constant on the remanent polarization P_r of samples was observed to be discussed on the assumption that the system has a multi-domain structure. Since the ferroelectric polymer includes paraelectric non-crystalline regions, we must employ a com-

posite model for deducing the intrinsic properties of a crystal from the results observed for the whole polymer. The relation between the observed ferroelectricity and the intrinsic property of the crystal is discussed on the basis of a simple ellipsoid model. The second order dielectric constant of crystal is evaluated by this model.

EXPERIMENTAL

Materials

Samples were cut out from a sheet of VDF–TrFE copolymer (52% VDF content) manufactured by Daikin Kogyo Co. The thickness of samples ranged around 45 μm. Prior to measurements, the samples were annealed at 130°C for 30 min and then poled under an electric field of 90 MVm^{-1} at 20°C for 30 min. The linear dielectric constant and thermally stimulated current were measured with a Rheolograph-Solid (Toyo Seiki Co). The remanent polarization at each temperature was calculated by integrating the thermally stimulated current with respect to time.

Measurement of Second-Order Dielectric Constant

The electric displacement D of a ferroelectric material is expanded in a power series of electric field E as

$$D = P_s + \varepsilon_1 E + \varepsilon_2 E^2 + \varepsilon_3 E^3 + \cdots \quad (1)$$

where ε_n is the n-th order dielectric constant.

When an electric field given by eq 2 is applied to a sample, nonlinear responses at $2f_1, 2f_2, f_1 - f_2, f_1 + f_2, \cdots$ etc. arise from the higher order terms in eq 1 in addition to linear responses at f_1 and f_2.

$$E = E_0(\cos 2\pi f_1 t + \cos 2\pi f_2 t) \quad (2)$$

where f_1 and f_2 are the frequencies of two wave fields.

In the present case, we employed $f_1 = 87$ Hz and $f_2 = 78$ Hz. In this study we extracted the difference frequency response at $(f_1 - f_2) =$

9 Hz because this component is located far apart from the responses at f_1, f_2 and their harmonics which the signal generator might include. Substituting eq 2 into eq 1, we obtain the response at $f_1 - f_2$ as

$$D(f_1 - f_2) = [\varepsilon_2 E_0{}^2 + 3\varepsilon_4 E_0{}^4 + \cdots]$$
$$\times \cos 2\pi(f_1 - f_2)t \quad (3)$$

The amplitude of $D(f_1 - f_2)$ includes all the even order dielectric constants. We assumed that the higher order terms ε_4 etc. are negligibly small. This assumption was confirmed from the experimental fact that the amplitude of $D(f_1 - f_2)$ is proportional to the square of the input amplitude $E_0{}^2$.

The block diagram of measuring system is shown in Figure 1, which is essentially similar to that by Hayakawa *et al.*[8] The system enables us to stimulate the sample by the sum of
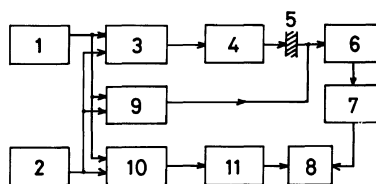
Figure 1. Block diagram of apparatus for second order dielectric constant measurements. 1, oscillator (f_1); 2, oscillator (f_2); 3, summing amplifier; 4, high voltage amplifier; 5, sample; 6, charge amplifier; 7, band pass filter; 8, osciloscope; 9, compensator; 10, multiplier; 11, band pass filter.
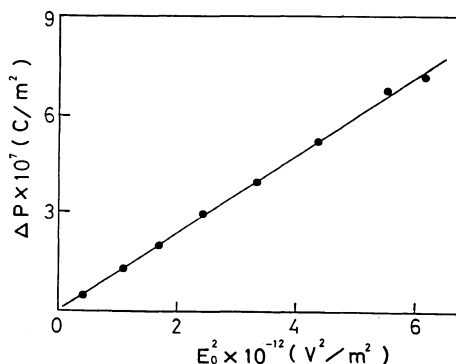
Figure 2. Relation between difference frequency response at 9 Hz and squared amplitude of input sine waves in poled VDF–TrFE (52:48) copolymer.

two waves and extract the difference frequency response from the responses.

The poled sample of the copolymer gives the $(f_1 - f_2)$ response as illustrated in Figure 2, where we find that the response is proportional to E_0^2 at least in the range of $E_0 < 2.5\,\mathrm{MVm^{-1}}$. Accordingly, we can obtain ε_2 from this response.

RESULTS AND DISCUSSION

Temperature Dependence of Second Order Dielectric Constant of VDF–TrFE (52:48) Copolymer

In this section, the temperature dependence of ε_2 of VDF–TrFE (52:48) copolymer is discussed.

A simple description of elastic Gibbs energy for a ferroelectric material per unit volume is usually written as a function of P as[9]

$$G - G_0 = (1/2)\beta(T - T_0)P^2 + (1/4)\gamma P^4 + (1/6)\delta P^6 \quad (4)$$

where G_0 stands for the free energy at $P = 0$, β, γ, δ, and T_0 are constants. For the first order phase transition, $\beta > 0$, $\gamma < 0$, and $\delta > 0$, whereas for the second order phase transition, $\beta > 0$, $\gamma > 0$, and $\delta > 0$.

The n-th order non-linear dielectric constant ε_n is defined as

$$\varepsilon_1 = \mathrm{d}P/\mathrm{d}E\big|_{E=0} + \varepsilon_0,$$

$$\varepsilon_n = (1/n!)\,\mathrm{d}^nP/\mathrm{d}E^n\big|_{E=0} \quad (n > 2) \quad (5)$$

where ε_0 is the permittivity of free space. The second order dielectric constant ε_2 is derived from eq 4 as

$$\varepsilon_2 = -(3\gamma + 10\delta P_s^2)P_s(\varepsilon_1 - \varepsilon_0)^3 \quad (6)$$

where P_s is the spontaneous polarization. ε_1 and P_s are respectively given by the equations:

$$\varepsilon_1 - \varepsilon_0 = [\beta(T - T_0) + 3\gamma P_s^2 + 5\delta P_s^4]^{-1} \quad (7)$$

and

$$P_s^2 = (1/2\delta)[-\gamma + [\gamma^2 - 4\beta\delta(T - T_0)]^{1/2}] \quad (8)$$

When the coefficients γ and δ in eq 4 are independent of temperature, the second order dielectric constant ε_2 should depend on temperature through P_s and ε_1.

The solid line in Figure 3 shows the temperature dependence of P_s in poled VDF–TrFE copolymer. P_s gradually decreases with
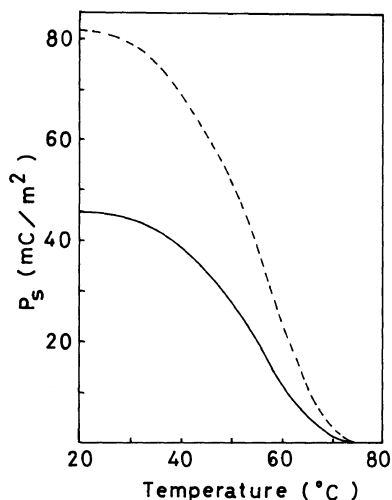

Figure 3. Temperature dependence of spontaneous polarization P_s of poled VDF–TrFE (52:48) copolymer. Solid line shows P_s of the whole polymer and broken line that of crystal estimated by eq 11.
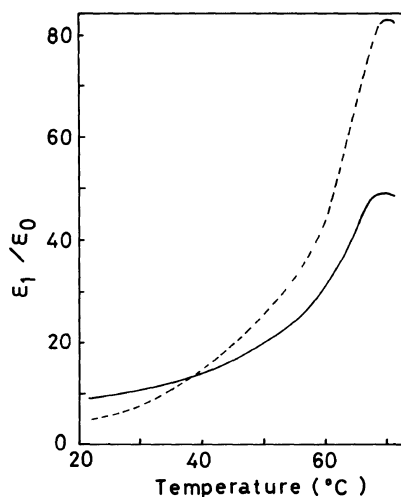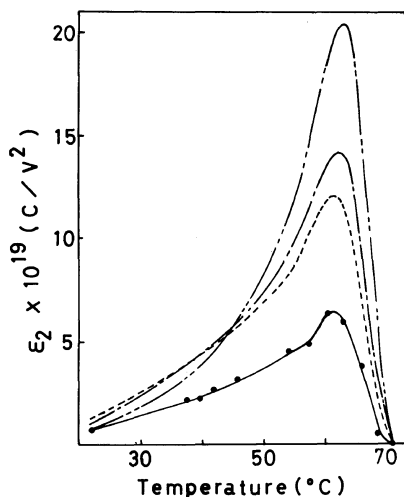

Figure 4. Temperature dependence of linear dielectric constant ε_1 of VDF–TrFE (52:48) copolymer. Solid line shows ε_1 of the whole polymer and broken line that of crystal estimated by eq 19.

Figure 5. Temperature dependence of second order dielectric constant ε_2 of VDF–TrFE (52 : 48) copolymer. Solid line shows ε_2 of the whole polymer. Broken lines a, b, and c show ε_2 of a crystal at $L = 0.01$, 0.1, and 1/3, respectively.

Figure 6. Relation between second order dielectric constant ε_2 and residual polarization P_r VDF–TrFE (52 : 48) copolymers.
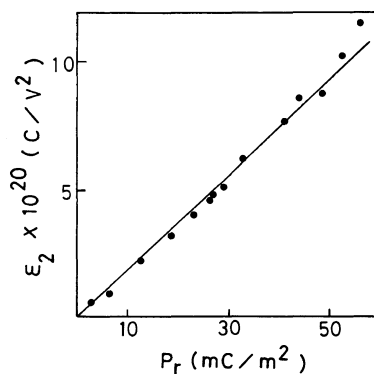
increasing temperature and vanishes at the transition temperature T_c. The temperature dependence of the linear dielectric constant ε_1 is illustrated by the solid line in Figure 4. ε_1 increases with increasing temperature up to T_c. Figure 5 shows the temperature dependence of ε_2. ε_2 has a maximum at 61°C and vanishes at *ca.* 70°C which corresponds to T_c. Vanishment of ε_2 at T_c together with P_s can be predicted by eq 6. The increase of ε_2 below 61°C is ascribed to the increase of ε_1 whereas the decrease of ε_2 above 61°C to the decrease of P_s.

Relation between ε_2 and P_r

Consider a system consisting of domains whose spontaneous polarizations are either parallel $(+P_s)$ or antiparallel $(-P_s)$ to the electric field. Since the total dipole moment of the system is the sum of dipole moments in each domain, the remanent polarization of the system is written as

$$P_r = v_+ P^+ + v_- P^- \quad (P^+ = -P^- = P_s) \quad (9)$$

where v_+ and v_- stand respectively for the volume fractions of parallel and antiparallel

domains. In the range of E_0 much lower than the coercive field, changes of v_+ and v_- due to the applied electric field may be neglected. Then ε_2 for the composite system is obtained from eq 5 and 9 as

$$\varepsilon_2 = (1/2)(v_+ - v_-)\, \mathrm{d}^2 P^+ / \mathrm{d}E^2 \big|_{E=0}$$
$$= -(3\gamma + 10\delta P_s^{\,2})P_r(\varepsilon_1 - \varepsilon_0)^3 \quad (10)$$

which indicates that ε_2 is proportional to the remanent polarization.

Samples with different values of P_r were prepared by decreasing the electric field to zero from intermediate points of the hysteresis curve. Figure 6 shows the P_r dependence of ε_2. We can see in Figure 6 that ε_2 is proportional to P_r as predicted by eq 10.

Intrinsic Ferroelectric properties of Polymer Crystal

The ferroelectric polymer is composed of ferroelectric crystals and paraelectric amorphous region. In order to elucidate the ferroelectric nature of the polymer crystal, the values of ε_1, ε_2, and P_s observed for the whole polymer must be converted to those of the crystal by an appropriate model. In the following, $\bar{x}$ stands for a quantity of crystal and x that of the whole polymer.

We adopted the model proposed previously in which the crystal is a prolate ellipsoid with

the major axis directed along E and is embedded in the polymer matrix of a smeared-out mixture of crystals and amorphous region.[10,11]

In this model, the spontaneous polarization and the electric field in the crystal are related to those in the whole polymer by

$$\bar{P}_s = P_s/B\phi \qquad (11)$$

and

$$\bar{E} = BE \qquad (12)$$

Here, ϕ is the volume fraction of crystals and B is

$$B = \varepsilon_1/[\varepsilon_1 + L(\bar{\varepsilon}_1 - \varepsilon_1)] \qquad (13)$$

where L is the depolarization field coefficient of the crystal.

Since the component at $(f_1 - f_2)$ in the response arises from the term proportional to E^2 in eq 1, the polarization changes at $(f_1 - f_2)$ in the crystal and the whole polymer are respectively written as

$$\Delta\bar{P}_{f_1-f_2} = \bar{\varepsilon}_2 \bar{E}_0{}^2 \cos 2\pi(f_1 - f_2)t \qquad (14)$$

and

$$\Delta P_{f_1-f_2} = \varepsilon_2 E_0{}^2 \cos 2\pi(f_1 - f_2)t \qquad (15)$$

On the other hand, since the polarization change at $(f_1 - f_2)$ belongs to the crystal alone, the relation between the polarization changes of the crystal and the whole polymer should be given by the same way as P_s:

$$\Delta\bar{P}_{f_1-f_2} = \Delta P_{f_1-f_2}/B\phi \qquad (16)$$

Equations 12—16 yield

$$\bar{\varepsilon}_2 = \varepsilon_2/B^3\phi \qquad (17)$$

Similarly, we have in general

$$\bar{\varepsilon}_n = \varepsilon_n/B^{n+1}\phi \quad (n > 2) \qquad (18)$$

In order to evaluate B, the values of L_1, $\bar{\varepsilon}_1$, and ε_1 are required. Since the contribution of amorphous region to ε_1 cannot be neglected, $\bar{\varepsilon}_1$ is not obtained by eq 18. The relation between $\bar{\varepsilon}_1$ and ε_1 is obtained by following pro-

cedures.[12] Consider hypothetical system in which the crystal ellipsoid is replaced by the amorphous phase. Since the sum of this system and our (real) model at volume fractions of $1 - \phi$ and ϕ should yield a homogeneous whole polymer system, we have

$$\phi\frac{\bar{\varepsilon}_1 - \varepsilon_1}{\varepsilon_1 + L(\bar{\varepsilon}_1 - \varepsilon_1)} + (1 - \phi)\frac{\varepsilon_{1a} - \varepsilon_1}{\varepsilon_1 + L(\varepsilon_{1a} - \varepsilon_1)} = 0$$

$$(19)$$

where ε_{1a} is ε_1 of the amorphous region.

Thus we can estimate $\bar{\varepsilon}_1$, $\bar{\varepsilon}_2$, and $\bar{P}_s$ from those of the sample. In this estimation, we assume as the following:

1) ε_{1a} is constant over the temperature range covered in this study.

2) $\bar{\varepsilon}_1$ at 20°C is equal to $5\varepsilon_0$.

3) The electronic part of ε_1, $\varepsilon_{1\infty}$, is equal to $4\varepsilon_0$.[3]

4) $\phi = 0.55$, $L = 0.01$ and $T_c = 68$°C.

First ε_{1a} is evaluated by eq 19 from $\bar{\varepsilon}_1$ and ε_1 at 20°C. Then the value of $\bar{\varepsilon}_1$ at any temperature is obtained by eq 19 from ε_{1a} and ε_1 at the same temperature.

The temperature dependence of $\bar{P}_s$, $\bar{\varepsilon}_1$, and $\bar{\varepsilon}_2$ is illustrated by broken lines in Figures 3—5. In this case, the differences between crystal and whole polymer in the spontaneous polarization and the second order dielectric constant come dominantly from the volume fraction of the crystal because L is small and B is equal almost to unity.

The value of L, however, should change with the change in crystal shape, which depends on thermal history or other sample treatments. The present authors found L of poly(vinylidene fluoride) (PVDF) not to be larger than 0.08 from the profile of its D–E hysteresis curve.[11] Values of L over the range from 0.001 to 0.1 is possible for PVDF and VDF–TrFE copolymers. In Figure 6, $\bar{\varepsilon}_2$-temperature curves at $L = 0.01$, 0.1, and 0.33 are illustrated. $\bar{\varepsilon}_2$ at $L = 0.1$ is approximately 15% larger than that at $L = 0.01$, the latter corresponding to the case of B nearly equal to unity. At $L = 0.33$ (spherical crystal model) the

curve is deformed dominantly by B. Since $\bar{\varepsilon}_n$ in eq 18 is inversely proportional to B^{n+1}, the correction factor by the crystal shape increases with increasing n.

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