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THE ROLE OF ORDER IN PYROELECTRICITY OF PVF_2

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A series of studies of the pyroelectric effect in polyvinylidene fluoride indicates that reversible changes in the amount of order in the polymer films plays an important role in the pyroelectric effect. Experiments were conducted which showed that only one-half to two-thirds of the total pyroelectric effect can be accounted for on the basis of the usual primary and secondary effects. This observation led to the hypothesis that reversible changes with temperature of the crystallinity of the semicrystalline polymer might account for the rest. This hypothesis predicted that the crystallinity of the polymer should depend on the magnitude of an applied electric field. Experiments have been conducted in which this effect was observed.

INTRODUCTION

It is now well established that the polymer poly(vinylidene fluoride) is ferroelectric.[1] Poly(vinylidene fluoride) is composed of monomer units which have a high dipole moment ($-CH_2-CF_2-$) and in the planar zig-zag configuration, the dipole moments of the monomer units are all aligned. In the crystal structure associated with the planar zig-zag configuration there are two molecules per unit cell and the dipole moments of the two molecules are aligned. A ferroelectric crystal is one which is polar and in which it is possible to change the direction of polarization by the application of an electric field. It is clear from the crystal structure that poly(vinylidene fluoride) is polar so the only question remaining is whether the direction of polarization of crystalline regions can be changed by the application of an electric field. Kepler and Anderson[2] were the first to demonstrate that it can. They did

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this by measuring the intensity of x rays diffracted from a sample as a function of orientation of the sample both before and after poling (applying a high electric field).

Studies of poly(vinylidene fluoride) were originally initiated by the observation by Kawai[3] in 1969 that it exhibited a higher piezoelectric coefficient than any of the many polymers he had studied and the subsequent observation of a large pyroelectric coefficient by Bergman, et al.[4] Considerable effort has been expended in the last decade to determine the origin of the large piezoelectric and pyroelectric effects in polyvinylidene fluoride. Broadhurst and coworkers[5] were the first to attempt to develop a theory which could predict quantities which could be measured experimentally. The physical effects included in their model which could contribute to the pyroelectric coefficient included the number of dipoles per unit volume, amplitude of libration of the dipoles and magnitude of the local field.

Since the pyroelectric coefficient is simply the change in polarization with a change in temperature, it is clear that any change in the number of dipoles per unit volume such as that which would occur when a sample changes its volume as a result of thermal expansion or contraction would contribute to the pyroelectric coefficient. The amplitude of libration of the monomer units in the polymer chains contributes to the pyroelectric effect because the time average of the dipole moment of the molecules depends on the amplitude of libration. Finally, the local field contributes because the dipoles are polarizable and therefore the magnitude of the dipole moment of the dipoles changes with changes in the local field.

Broadhurst and coworkers[5] found that they were able to account for the magnitude of the experimentally determined pyroelectric effect by using reasonable values for the various parameters used in their theory. However, there was considerable latitude in the value of the parameters.

Kepler and Anderson[6,7] carried out a series of experiments which were designed to shed light on the origin of pyroelectricity in poly(vinylidene fluoride). It is possible to define two types of pyroelectricity, primary and secondary. Primary pyroelectricity is the change in polarization observed when the temperature of a sample is changed while holding its dimensions constant. Secondary pyroelectricity is the additional change in polarization observed when the sample dimensions are allowed to change.

After carrying out the experiments to determine the magnitude of the primary and secondary contributions to

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the pyroelectric effect, it was found that only one-half to two-thirds of the total pyroelectric effect could be accounted for by these measurements.

This observation led us to consider the hypothesis that reversible changes in the amount of order in the polymer were contributing to the pyroelectric effect. It had been pointed out to us by R. R. Lagasse that the crystallinity (defined as the percent of the polymer molecules that are in the ordered phase) of polyethylene is a reversible function of temperature and that such a phenomenon, if it occurred in polyvinylidene fluoride, would contribute to the pyroelectric effect.

In the next section of this paper, the experimental program designed to determine the magnitude of the primary and secondary pyroelectric effects will be described briefly. The third section will describe the reversible crystallinity hypothesis more completely and the theory derived from this hypothesis, which predicts that the application of an electric field should change the amount of order in poled polymers, will be developed. The experimental investigation of the electric field dependence of crystallinity will be described in the fourth section and the significance of the results will be discussed in the final section.

PRIMARY AND SECONDARY PYROELECTRICITY EXPERIMENTS

Since secondary pyroelectricity results from piezoelectricity, it is possible to calculate the secondary pyroelectric coefficient, p_3^s, from the piezoelectric coefficients, the thermal expansion coefficients and the stiffness coefficients. The relationship is

$$p_3^s = {}_j c_{jk} d_{3k} \tag{1}$$

where α_j, c_{jk} and d_{3k} are the coefficients of thermal expansion, coefficients of stiffness and piezoelectric coefficients, respectively, in matrix notation where j and k equal one through six. The polymer films are not single crystals, but on a macroscopic scale they exhibit orthorhombic symmetry since three mutually perpendicular axes can be identified. It has become customary in studies of polyvinylidene fluoride films to identify the 1, 2 and 3 axes as parallel to the draw direction, perpendicular to the draw direction in the plane of the film, and perpendicular to the plane of the film, respectively.

In order to determine if the observed pyroelectric effect in poly(vinylidene fluoride) could be explained on

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the basis of secondary pyroelectricity, two different types of samples were studied in reference 6, biaxially and uniaxially oriented films.

The coefficients of thermal expansion were obtained by suspending long samples in a temperature-controlled oven and measuring the length of a sample as a function of temperature with a cathetometer. For the biaxially oriented films, the axes 1 and 2 were defined as parallel and perpendicular to length of the roll from which the samples were cut. The thermal expansion coefficients could only be measured in the plane of the films and it was assumed for the calculations that the coefficient of expansion in the 3 direction is equal to the coefficient in the 2 direction.

The piezoelectric coefficients d_{31} and d_{32}, which determine the amount of charge per unit area induced in the 3 direction by a uniaxial stress in the 1 and 2 directions, respectively, were obtained by attaching a small weight to one end of a long strip while the other end was attached to a rigid mount. An electrometer was connected between the electrodes on the two sides of the strip and the amount of charge induced on the electrodes by the addition of weight to the bottom end of the film was measured.

Determining d_{33} was much more difficult, but two different methods were used and the results were found to agree. One method involved using the converse piezoelectric effect. The thickness of a very small sample was measured as a function of applied electric field using a laser interferometer. Sharp needle contacts had to be used to minimize constraints on the sample. In the second method, d_{33} was measured indirectly by measuring the piezoelectric coefficient which results from the application of hydrostatic pressure and using its value and the value of d_{31} and d_{32} to calculate d_{33}.

Young's modulus, E, of each sample was measured using a Rheovibron mechanical spectrometer. The measurements of the elastic moduli in the 1 and 2 directions showed that the mechanical properties of these samples were essentially the same and isotropic. In order to calculate the secondary pryoelectric coefficient, it was assumed that the mechanical properties were isotropic and that Young's modulus for both materials was 2.5×10^9 Pa. Using this assumption and the value of the volume compressibility, K, of poly(vinylidene fluoride) determined from data reported by Weir[8], the terms of the stiffness matrix were calculated.

The results of these measurements and calculations are summarized in Table 1. Using these values and Eq. 1, the secondary pyroelectric coefficients were determined to be -0.44×10^{-5} and -1.48×10^{-5} C/m^{2}K for the biaxially and the uniaxially oriented films, respectively. These numbers are to be compared with the experimental values of the total pyroelectric coefficient of -1.25×10^{-5} and -2.74×10^{-5} C/m^{2}K.

TABLE I. SUMMARY.

		BIAXIALLY ORIENTED FILM	UNIAXIALLY ORIENTED FILM
THERMAL EXPANSION COEFFICIENTS (10^{-4} K^{-1})	α_1	1.24	0.13
	α_2	1.00	1.45
PIEZOELECTRIC COEFFICIENTS (10^{-12} C/N)	d_{31}	4.34	21.4
	d_{32}	4.36	2.3
	d_{33}	-12.4	-31.5
	d (HYDROSTATIC)	-4.8	-9.6
	$d_{33}{}^{a}$	-13.5	-33.3
MECHANICAL PROPERTIES	E (10^9 Pa)	2.5	2.5
	K(10^{-10} Pa^{-1})	2.6	2.6
	ν	0.392	0.392
	s_{11}(10^{-10} Pa^{-1})	4.0	4.0
	s_{12}(10^{-10} Pa^{-1})	-1.57	-1.57
	c_{11}(10^9 Pa)	5.04	5.04
	c_{12}(10^9 Pa)	3.25	3.25
PYROELECTRIC COEFFICIENT (10^{-5} C/m^2 K)	p_3	-1.25	-2.74
	p_3^s (CALCULATED)	-0.44	-1.48

[a] CALCULATED FROM HYDROSTATIC PIEZOELECTRIC COEFFICIENT, d_{31} AND d_{32}.

These results imply that secondary pyroelectricity accounts for only about one-half of the total pyroelectric effect in poly(vinylidene fluoride).

Our assumption at that point in our program was that the rest of the effect was primary pyroelectricity. In order to test this hypothesis, we heated samples suddenly using a 200 ps laser pulse and measured the time dependence of the appearance of the pyroelectric charge.[7] Charge resulting from primary pyroelectricity would appear as fast as the sample is heated, but charge resulting from

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secondary pyroelectricity would appear only as rapidly as the sample can relax to the new higher temperature dimensions.

In order to heat the samples uniformly on a very short time scale, the films were lightly dyed with a molecule which had a very short excited state lifetime (~ 1 ns). Figure 1 shows typical results that we have obtained in experiments subsequent to those published in Ref. 7. We have seen no evidence for primary pyroelectricity, but because of experimental uncertainties caused by such considerations as the frequency dependence of the dielectric

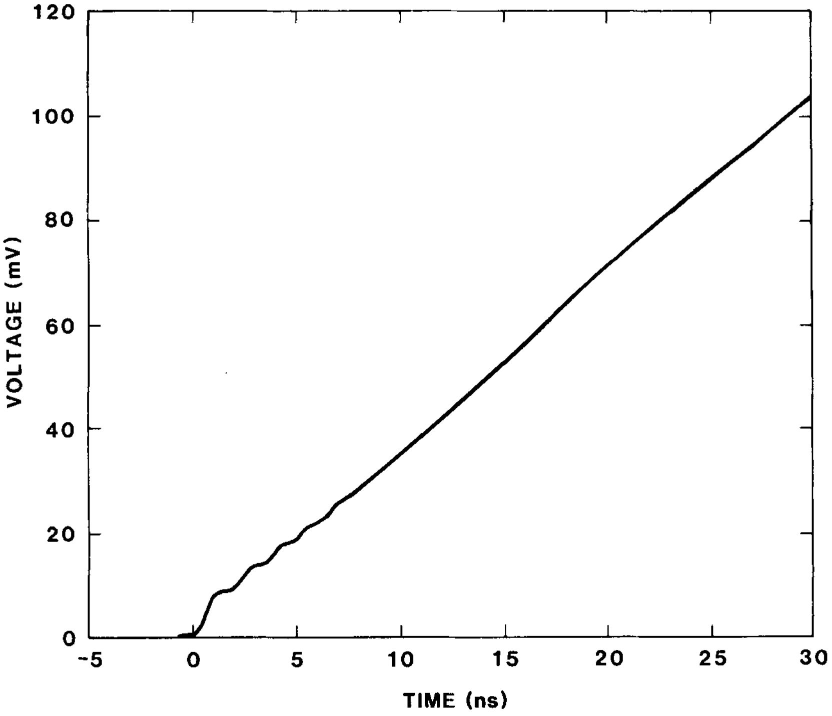

Figure 1. Voltage across a sample versus time at very short times after a 200 ps laser pulse. The total pyroelectric voltage at long times after this heat pulse is on the order 80 mV.

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constant, variations from sample to sample that may be caused by inhomogeneous doping, the need to precisely define t_0, the time the laser fired, and the need to know the precise time dependence of heating, we have concluded that we can say only that the primary pyroelectricity contribution to the total pyroelectric effect can be no larger than 15%.

These results led us to conclude that we could account for only one-half to two-thirds of the total pyroelectric effect on the basis of the sum of the primary and secondary pyroelectric effects and led us to speculate that reversible changes in crystallinity (changes in order) might account for the rest.[7]

REVERSIBLE CRYSTALLINITY HYPOTHESIS AND THEORY

Poly(vinylidene fluoride) is a crystalline polymer with a crystallinity, χ_c, of about 0.5. If the crystalline regions in a poled sample are all aligned in the same direction and the polarization of a crystal is P_c, the polarization P of the sample is $\chi_c P_c$. Therefore, changes in the polarization of the sample can arise not only from the temperature dependence of the polarization of the crystalline phase, but also from the temperature dependence of the crystallinity.

Support for this hypothesis is given by investigations of the temperature dependence of the crystallinity of polyethylene. Kavesh and Schultz[9] found that the crystallinity changed from 67% at 25°C to 57% at 100°C. If the changes in polyvinylidene fluoride are of a similar size, this effect could easily account for a large fraction of the pyroelectric effect.

Experimental evidence for this hypothesis was found in our measurement of time dependence of the appearance of pyroelectric charge after a sudden change of temperature.[10] We dyed samples, as in the experiments to observe primary pyroelectricity, so that they would absorb light from a frequency-doubled neodymium laser and sputtered transparent indium-tin oxide electrodes on both sides. These samples were freely suspended in a vacuum and irradiated with 200 ps laser pulses. The pyroelectric charge was measured for several seconds after the laser pulse. A typical result is shown in Fig. 2. In addition to dimensional oscillations in the thickness, width and length modes, it is easy to see that there is a slow but continual increase in the pyroelectric charge up to the time thermal radiation and conduction effects cool the sample. We attribute this slow increase to reversible changes in crystallinity with temperature.

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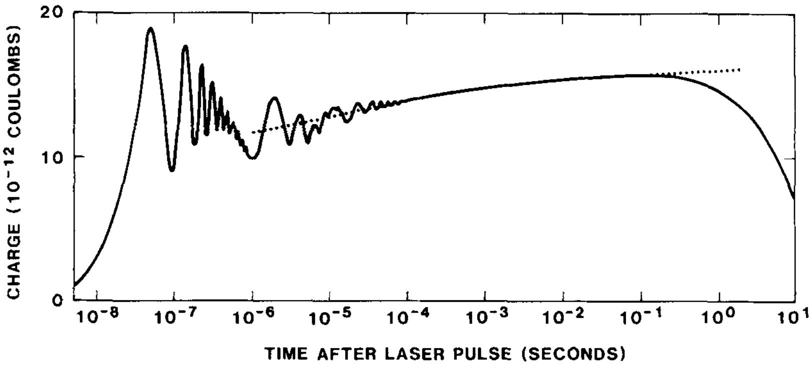

Figure 2. Pyroelectric charge versus time after a very short heating pulse at room temperature.

If crystallinity changes reversibly with temperature, thermodynamic relations indicate it should also change with an applied electric field.[11] Since the Gibbs free energy, G,

$$G = U - \underline{p}V - ST - \underset{\sim}{P}\cdot\underset{\sim}{E},$$

does not change on crossing a phase boundary, changes in G along the boundary are equal in the two phases. If we consider the amorphous-crystalline phase boundary, then $dG_a = dG_c$ and

$$S_a dT + P_a dE = S_c dT + P_c dE$$

where the subscripts a and c denote the amorphous and crystalline phases respectively, and for simplicity the electric field is applied parallel to the polarization. The term involving pressure, $\underline{p}$, is dropped since the pressure is maintained constant. Therefore,

$$(S_a - S_c)dT = (P_c - P_a)dE$$

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and since $P_a = 0$ and $(S_a - S_c)T = \ell$, where ℓ is the latent heat of melting, the change in the melting temperature dT_m resulting from a change in the electric field applied dE is

$$dT_m = \frac{TP_c dE}{\ell} \quad . \tag{2}$$

In order to calculate the magnitude of the change in crystallinity caused by an electric field, we assume that a fraction, κ, of the pyroelectric coefficient, p, results from reversible changes in crystallinity with temperature, $d\chi_c/dT$. Therefore, with the approximation of perfect alignment of the crystallites,

$$\frac{d\chi_c}{dT} P_c = \kappa p$$

or

$$\frac{d\chi_c}{dT} = \frac{\kappa p}{P_c} \quad . \tag{3}$$

Since we are interested in the change in crystallinity resulting from a change in the electric field, we can combine equations (2) and (3) to determine

$$\frac{d\chi_c}{dE} = - \frac{d\chi_c}{dT}\frac{dT_m}{dE} = - \frac{\kappa p T}{\ell} \quad . \tag{4}$$

Equation (4) relies on the assumption that a field-induced change in the melting temperature results in the same amount of melting or crystallization at constant temperature as an actual change in temperature of the same amount but of the opposite sign.

ELECTRIC FIELD DEPENDENCE EXPERIMENT

As a test of this prediction, we have measured the changes observed in the intensity of x rays (Cu Kα) diffracted from 30-μm-thick poled poly(vinylidene fluoride) β-phase films (Piezofilm from Kureha) when an electric field is applied.[11]

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The diffracted x-ray peak was that corresponding to diffraction from the 200 and 110 planes. The films were glued to an aluminum plate which served as one electrode. A thin evaporated aluminum film served as the other electrode and the incident and diffracted x-ray beam passed through this electrode.

In our arrangement, the observed x rays were diffracting from planes perpendicular to the electric field. Under the assumption of good alignment between the poling field and the dipole moment of each crystallite, the diffracted x rays arose predominantly from 110 planes in crystallites where the dipole moments were inclined 30° with respect to the electric field. It is reasonable to assume that the behavior of such crystallites in an applied electric field is representative of all the crystallites.

The intensity of the diffracted x-ray beam was obtained by integrating the total number of x-ray photons counted during an automatic scan of 2θ at 0.5° min^{-1} from 19.25° to 21.75°. A typical count rate versus angle is shown in Fig. 3. The total count during a scan was on the order of 2×10^6. No attempt was made to subtract the background counts since they contributed only a small fraction of the total count.

In order to obtain adequate statistics and to minimize the effects of a slow drift in the x-ray intensity, the change in intensity induced by a given electric field was determined by taking the average of twelve measurements of the change resulting from the application or removal of the electric field. The intensity was first measured with no voltage applied. Subsequent measurements of intensity were obtained at voltages applied according to the following sequence: positive, zero, negative, zero. This sequence was repeated until thirteen measurements of intensity were acquired. The twelve intensity changes were then obtained by taking the difference between each intensity measurement and the intensity measurement made just prior to it. The percentage change in intensity observed in one sample as a function of applied voltage is shown in Fig. 4. Each data point shown is the average of twelve measurements of the change in intensity as described above.

The average change in intensity with applied electric field for a given sample was found by fitting a least-squares line, which was constrained to pass through the origin, to data like that in Fig. 4. Three samples were measured and the average field dependence of the crystallinity was found to be $(1.8 \pm 0.2) \times 10^{-10}$ $(\mathrm{V/m})^{-1}$ where the error quoted is the estimated error in the mean obtained from the experimental data.

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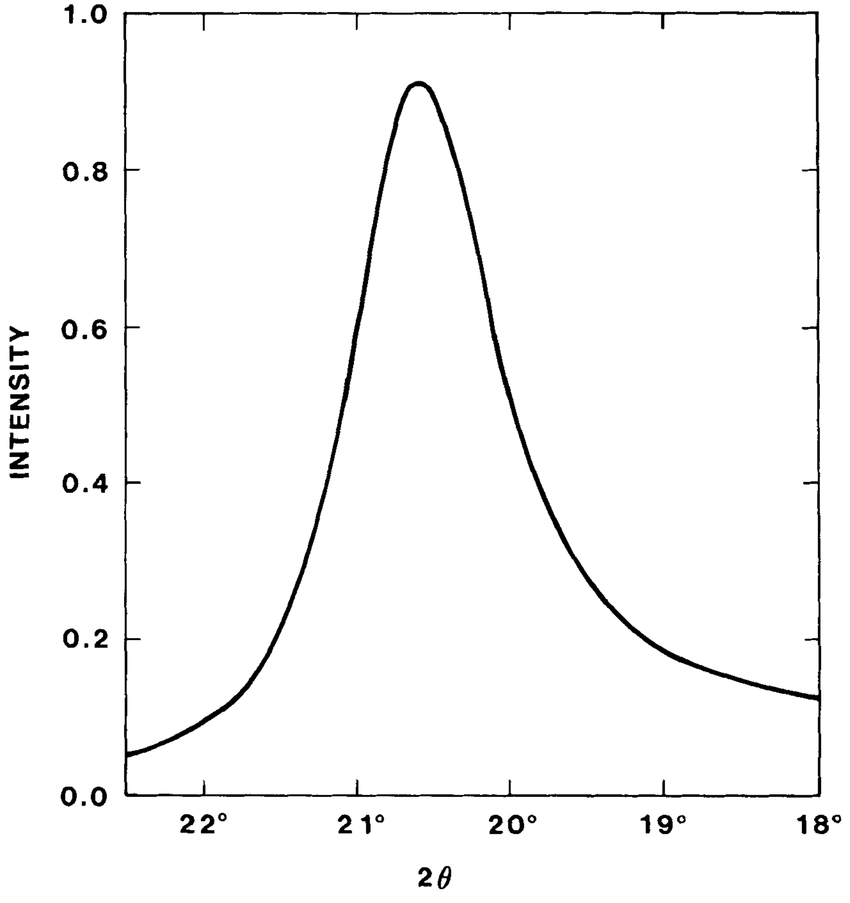

Figure 3. Diffracted x-ray intensity versus diffraction angle (arbitrary intensity scale).

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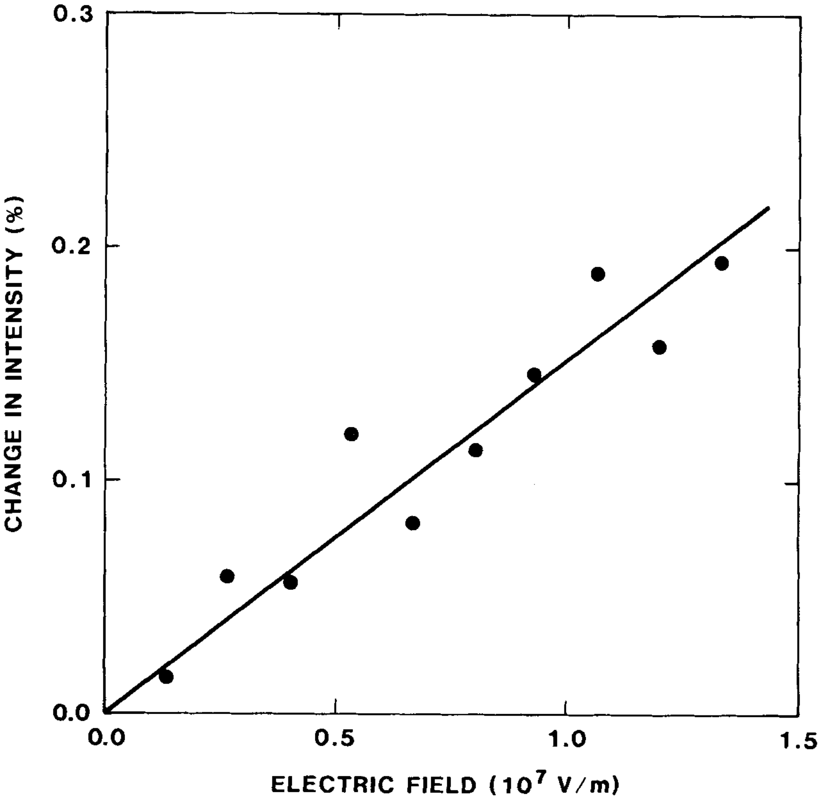

Figure 4. The change in intensity of the diffracted x-ray beam as a function of the applied electric field as observed for one sample. The solid line is the least-squares line defined by the data and constrained to pass through the origin.

If our hypothesis is correct, no change in intensity of the diffracted x-ray beam should occur when an electric field is applied to an unpoled sample. In an unpoled sample the crystallite axes are oriented at random with respect to the applied electric field; when the electric field is applied, those with a component of their dipole moment parallel to the electric field will increase in size while those with a component of their dipole moment antiparallel will decrease in size leading to no net change in crystallinity.

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In order to show that this was the case and to check for spurious effects, we ran an experiment on an unpoled, 50-μm-thick, β-phase film. No effect was observed even though fields up to 4 x 10^7 V/m were applied. A least-squares fit to the experimental data yielded a coefficient of $(-0.43 \pm 1.5) \times 10^{-11}$ $(V/m)^{-1}$. This is 40 times smaller and opposite in sign to that obtained with the poled film.

In order to eliminate other possible effects of the electric field that might lead to changes in the diffracted x-ray intensity, with particular emphasis on possible changes in the amplitude of libration of the polymer molecules,[12] we have measured the temperature dependence of the electric-field-induced changes in the intensity of the diffracted x rays. In Ref. 11 it was shown that if the change in intensity of the diffracted x rays arises from a change in amplitude of libration upon the application of an electric field, the change in intensity should depend linearly on the temperature since B_0 depends linearly on temperature. On the other hand, if a change in crystallinity is involved as we have proposed, changes in intensity should disappear below the glass transition temperature, about -40°C, and probably would increase more rapidly than linearly with temperature.

At -50°C the electric field had no appreciable effect on the diffracted x-ray intensity. We studied only one sample at low temperature, but for that sample, the change in diffracted x-ray intensity for 400 V at room temperature was found to be (0.15 ± 0.03)%. At -50°C the change was (-0.01 ± 0.03)%, where the minus sign indicates a change opposite to the direction expected. At +50°C the change in intensity of the diffracted x rays caused by the application of an electric field was found to be 50% larger than at room temperature for the three samples mentioned earlier.

These results are clearly inconsistent with the hypothesis that the effect results from an electric-field-induced change in the amplitude of libration, but they are consistent with the hypothesis of an electric-field-induced change in crystallinity.

In order to compare the experimental results with the prediction of equation (4), the latent heat of melting for the temperature at which the electric field was applied is required. A value for ℓ at room temperature was estimated from the standard relation

$$\ell(T_2) = \ell(T_1) - \int_{T_2}^{T_1} (C_a - C_c)dT, \qquad (5)$$

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where C_a and C_c are heat capacities of the liquid and crystal. The heat absorbed in melting the partially crystalline film was found to be 53 J per gram of sample. This measurement plus an assumed weight fraction crystallinity of 0.5 yielded $\ell(375K) = 110$ J per gram of crystal. Heat-capacity measurements above the melting point were fitted by a linear function to determine C_a. C_c was computed by combining heat-capacity measurements below the melting point, the assumed $X_c = 0.5$ and the C_a function. With these input data, equation (5) yielded $\ell(298\ K) = 55\ J\ g^{-1}$.

With 55 J g^{-1} as the latent heat for the melting at room temperature and with the assumption than one-third of the pyroelectric effect at room temperature results from reversible changes in crystallinity,[6,7] equation (4) predicts that the field dependence of crystallinity should be $2.8 \times 10^{-11}\ (V/m)^{-1}$ for a pyroelectric coefficient of $-2.7 \times 10^{-5}\ C\ m^{-2}\ K^{-1}$.[6] The experimentally observed value reported earlier in this paper was $1.8 \times 10^{-10}\ (V/m)^{-1}$, about six times larger than predicted. We speculate that this large discrepancy results from a large difference between the actual latent heat for melting and our estimate. Crystalline regions which melt at temperatures far from the melting point are probably highly strained and may melt with a considerably lower latent heat. Some discrepancy might also be accounted for by the fact that the polymer films are heterogeneous, and the dielectric constant (and perhaps the conductivity) of the amorphous phase is much larger than that of the crystalline phase. Depending on the morphology, the resulting field enhancement in the crystalline phase could account for up to a factor of two in the discrepancy.

CONCLUSION

The magnitude of the order-disorder effects discribed in this paper probably vary widely from sample to sample because they should be strongly dependent on how the samples are prepared as well as their thermal history. But there seems to be little doubt about the existence of the effect. The observations discussed here are the first to show that reversible changes in order can play an important role in pyroelectricity.

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