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THE DEPENDENCE OF THE PIEZOELECTRIC RESPONSE OF POLY(VINYLDENE--ETC(U)

APR 79 J I SCHEINBEIM, K T CHUNG, K D PAE

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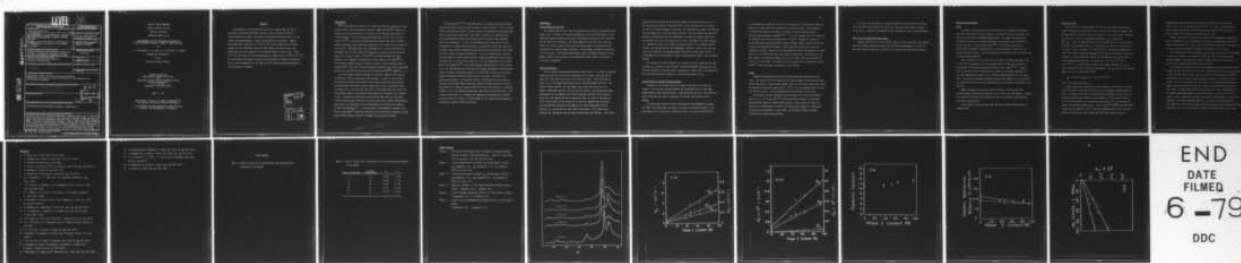
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THE DEPENDENCE OF THE PIEZOELECTRIC RESPONSE OF
POLY(VINYLIDENE FLUORIDE) ON PHASE I VOLUME FRACTION

by

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ABSTRACT

Investigations of the dynamic piezoelectric response (d_{31}^* and e_{31}^*) of unoriented, poled poly(vinylidene fluoride) films containing different volume fractions of phase I and phase II crystalline materials shows a linear relationship between phase I content and piezoelectric response. Samples were poled under conditions (10^6 V/cm at 23°C) which produced no observable changes in x-ray diffraction patterns taken before and after poling. The piezoelectric strain constant of the unoriented phase II film is $d_{31}' = 0.48 \times 10^{-12}$ C/N, while that of the unoriented phase I sample is $d_{31}' = 6.68 \times 10^{-12}$ C/N. The data supports the model⁷ in which the piezoelectric response is primarily due to a bulk polarization of the PVF_2 by a 180° dipole switching mechanism in the polar phase I crystals.

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INTRODUCTION

Since the initial discovery of the large piezoelectric response of poled, oriented films of poly(vinylidene fluoride) (PVF_2) by Kawai⁽¹⁾, several subsequent studies have attempted to elucidate the mechanisms responsible for this phenomenon. Since the greatest piezoelectric activity (by at least a factor of 3)⁽²⁾ is found for poly(vinylidene fluoride) films with the phase I crystal structure, any satisfactory explanation of the effect must account for this feature. Mechanisms most often discussed are: a bulk polarization of the sample due to field induced reorientation or switching of the molecular dipoles in the polar, phase I crystals⁽³⁾; non-uniform charge injection leading to an asymmetric distribution of real charge in the sample⁽⁴⁾; a field induced charge-trapping of injected charge or ionic charges present as impurities⁽⁵⁾; some type of surface phenomenon caused by the strong interaction between the positive electrode and the film during poling⁽⁶⁾.

The first model proposed, presented in the most complete form recently by Broadhurst et al.⁽⁷⁾ is accepted by many workers. It has the virtue that it has implications which would apply to PVF_2 films crystallized and oriented in various ways, and even to other polymers and so can be rigorously tested. One objection to this model has been that it would imply that PVF_2 films with the non-polar phase II crystalline form should not be piezoelectric, whereas in fact a substantial piezoelectric activity has been found in such films. A field induced phase transition to a polar phase with a lattice dimensionally equivalent to the phase II lattice (polar phase II structure) was proposed by Davis and Broadhurst⁽⁸⁾. A recent detailed investigation by Newman, Yoon, Pae and Scheinbeim⁽⁹⁾ confirmed that indeed the piezoelectric response of poled phase II PVF_2 films is related to changes in the crystal structure.

Previous workers^(10,11) have shown that at low poling voltages the piezoelectric properties increase with the phase I crystal content. Since, in these studies, the extent of phase I crystal content was increased by increasing draw ratio (or molecular orientation) this result is open to the objection that the increased piezoelectric activity may only be related to the increased molecular orientation. In fact, if piezoelectricity is the result of bulk polarization of samples containing phase I crystallites, then there should be a strong linear relation between the piezoelectric coefficients and the volume fraction of phase I crystalline material. Up to the present time it has not proved possible to obtain unoriented PVF₂ containing different volume fractions of phase I and it has not been possible to test this implication of the model. Recent investigations⁽¹²⁾ of the high pressure crystallization of PVF₂ carried out in our laboratories have shown that the pressure quenching (crystallization caused by rapidly increasing pressure) of molten PVF₂ can produce unoriented samples containing different volume fractions of phase I (and phase II) crystalline material. We therefore decided to investigate the piezoelectric response of unoriented films containing different volume fractions of phase I, but subjected to identical poling conditions, which would produce no observable changes in the x-ray diffraction patterns taken before and after poling. This, we hoped, would allow us to examine the dependence of piezoelectric response on volume fraction of phase I, without regard to the complications produced by orientation or phase transition effects.

EXPERIMENTAL

Initial Sample Preparation

The samples used in this work were prepared from 25 micron, capacitor grade, Kureha film. To remove the biaxial orientation of the as-received film, it was sandwiched between aluminum foil sheets and melted in a press at 210°C and then held at 130°C for 15 minutes. The stress applied by the press was ~2000 psi; however, 25 micron (steel) shim stock was placed between the pressure plates to maintain the original sample thickness. Actual sample thickness varied from 23 to 25 microns. Wide angle diffractometer scans (of samples prepared in this manner) taken in both reflection and transmission modes showed no evidence of crystallite orientation.

Pressure Quenching

For the pressure quenching experiments, thin strips (~1 cm wide) of aluminum sandwiched film were cut from the unoriented, melt pressed, films and the exposed film edges were coated with a thin layer of epoxy. After allowing the epoxy to set, the samples were placed inside the high pressure DTA cell. The pressure medium (silicon oil) was added, some sample was melted onto the sample thermocouple junction, and the cell was sealed. The aluminum and epoxy surrounding the film samples effectively prevented diffusion of the pressure medium into the samples and had a negligible effect in terms of altering the state of hydrostatic stress (pressure) to which the samples were subjected. The high pressure system was then pumped up to some predetermined initial pressure, P_i , and the DTA cell was heated (externally). The steady state heating rate, determined from the sample thermocouple was $\approx 8^\circ\text{C}/\text{min}$. Just before

sample melting occurred, the DTA pressure vessel was isolated from the rest of the high pressure system by closing a valve in the high pressure line between the DTA cell and the pressure intensifier. The high pressure system (intensifier) was then pumped up to some much higher pressure. When the sample had completely melted (as indicated by the DTA thermogram), the valve was quickly opened and the pressure in the DTA cell rapidly (≤ 0.1 sec.) increased to a final pressure, P_f . Immediately after the increase in pressure from P_i to P_f , sample crystallization (as indicated by the DTA thermogram) occurred. The DTA cell was then cooled (by replacing the external heaters with water cooled copper coils) to approximately 40°C , the pressure reduced to atmospheric pressure, and the samples removed.

By varying the initial pressure, P_i , between 1.6 and 2.0 Kbar and the final pressure, P_f , between 2.7 and 6.6 Kbar, we produced samples containing 0%, 37%, 47%, 64%, and 94% of the polar phase I polymorphic crystal form; the remainder of the crystalline material consisted of the non-polar phase II form.

X-Ray Studies of Pressure Quenched Samples

A measure of the volume fraction of phase I and phase II crystallites present in the pressure quenched samples was determined from the wide angle diffractometer scans shown in Figure 1; $\text{CuK}\alpha$ radiation was used. The diffractometer scans were also used to determine the percent crystallinity of the samples.

The fractional content of phase I and phase II was determined by taking the ratio of the area under the phase I or phase II diffraction peaks, to the area under all the crystalline diffraction peaks. The percent crystallinity

was determined by taking the ratio of the area under the crystalline diffraction peaks to the area under the crystalline and amorphous peaks. The assignment of diffraction peaks to the phase I or phase II crystal form was based on previous crystallographic studies⁽¹³⁻¹⁵⁾. It is not supposed that the crystalline to amorphous ratios and the volume ratios of phase I to phase II obtained by these measurements provide accurate absolute values; however, they do provide an accurate and reproducible measure of these quantities which can be used for comparative studies. Because of the approximations used in determining the volume ratios of the crystalline phases and percent crystallinity, and because of the small amount of diffracted intensity at high 2θ values, only those reflections with $2\theta < 43^\circ$ were used. No evidence for the presence of any additional crystal forms^{8,16} other than phase I and phase II was observed.

Poling

Samples were prepared for poling by evaporating gold electrodes on both sides. The samples were then placed in the poling apparatus, (two polished copper plates connected to a high voltage supply) which was then placed under high vacuum. The chamber pressure was pumped down to $\sim 10^{-5}$ Torr and the samples poled for one hour at 10^6 volts/cm. Poling temperatures varied between 21°C and 23°C .

The fairly low value of poling field was chosen to be below the threshold value of $\sim 1.2 \times 10^6$ volts/cm^(8,9) at which significant changes in wide angle diffractometer scans are observed after poling. This allowed us to avoid the difficulty of determining the effects of field induced changes in crystallite orientation and polymorphic crystal form. No measurable change in sample crystallinity occurred during poling.

Of course, we were unable to determine whether or not crystallite reorientation by 180° rotation about the chain axis occurred in the phase I crystals as this type of change in orientation is not detectable in our x-ray measurements.

Electrical and Mechanical Measurements

Dynamic piezoelectric strain constant (d_{31}^*) and stress constant (e_{31}^*) measurements and dynamic mechanical modulus and dielectric measurements (at 3Hz) were performed using a Toyo Seiki, Piezotron "U", Dynamic Piezo-Electricity Analyzer.

RESULTS AND DISCUSSIONS

X-Ray

The phase I content and percent crystallinity of the samples determined from the x-ray data are shown in Figure 1 and listed in Table 1, together with the initial and final quenching pressures used. The sample containing only the phase II form was not pressure quenched, but was melted and crystallized by slow cooling. As previously reported⁽¹²⁾, the pressure quenching of molten PVF₂ can produce crystallization in the polar phase I form, with the volume fraction of phase I crystalline material dependent on both the initial and final quenching pressures.

PVF₂ crystallizes by slow cooling in the phase II form at pressures below ~3 Kbar and in the phase I form at pressures above ~4 Kbar, and mixtures of both phases are obtained at pressures between 3 and 4 Kbar⁽¹⁷⁻²⁰⁾. Because PVF₂ is unstable at high temperatures, it exhibits very marked degradation at the high temperatures required for isothermal crystallization into the phase I form. The pressure quenching technique subjected the samples to high pressures and temperatures only for short time periods, and no evidence of degradation was observed.

Sample crystallinity, as can be seen in Table 1, varies little with crystallization (quenching) conditions and is ~50% for all the samples. Nakagawa and Ishida⁽²¹⁾ discussed this behavior in terms of secondary crystallization occurring during cooling.

X-ray scans of the poled films were the same as those obtained from the unpoled films.

Piezoelectricity

The results of our measurements (at 25°C) of the dynamic piezoelectric strain constant (d_{31}^*), measured at 3 Hz, of poled (10^6 volts/cm) samples with different phase I content are shown in Figure 2. Both the in phase component, d_{31}' , and out of phase (or quadrature) component, d_{31}'' , of d_{31}^* (where $d_{31}^* = d_{31}' - i d_{31}''$) increase linearly with increasing percent or volume fraction of phase I, crystalline material. The data for d_{31}' was fit to the straight line $d_{31}' = [0.062 \times (\% \text{ phase I}) + 0.48] \times 10^{-12} \text{ C/N}$. Annealing the samples at 125°C (100°C above the poling temperature) for one hour produced a significant decrease in the piezoelectric response of the samples, with the 94% phase I content sample decreasing from an initial value of $6.3 \times 10^{-12} \text{ C/N}$ to $3.6 \times 10^{-12} \text{ C/N}$, a 40% decrease, however, the linear dependence of d_{31}' on volume fraction of phase I was still maintained. The d_{31}' data for the annealed samples was fit to the straight line:

$$d_{31}' = [0.036 \times (\% \text{ phase I}) + 0.30] \times 10^{-12} \text{ C/N}$$

and is also shown in Figure 2.

These results are striking for several reasons. For the first time the linear increase in piezoelectric activity with increasing volume fraction of phase I is shown. This type of linear dependence supports the view that the persistent polarization induced in poled samples of PVF_2 depends primarily on the bulk polarization of the sample and probably on the reorientation of dipoles in the polar crystal phase. Other studies^(10,21-24) have not shown these results for two reasons: First, they were comparing samples with different degrees of orientation, and second, they were using poling fields and

temperatures which, most probably, produced a change from the non-polar phase II form to the polar phase II form^(8,9). The samples we investigated were randomly oriented and poled just below the threshold field (at 23°C) where changes in the phase II structure begin to occur.

These results will, of course, not explain the inhomogeneous polarization and the dependence of the polarization on electrode configuration reported by other investigators^(5,6), but it does conform to the model used by Broadhurst et al.⁽⁷⁾ to calculate the piezoelectric response of the phase I form of PVF₂.

The piezoelectric stress constants, e'_{31} and e''_{31} as a function of the phase I content of the samples, are shown in Figure 3 for both the unannealed and annealed samples. This data also shows a linear increase in piezoelectric activity with increasing volume fraction of phase I.

The dielectric constants (ϵ') of the unannealed and annealed films (after poling) are shown in Figure 4 and indicate a small increase with increasing phase I content for both sets of data. This may be due to small decreases in sample crystallinity at the higher quenching pressure needed to increase the phase I content. This is not reflected in the results of the x-ray determinations of sample crystallinity given in Table 1; however, the method used to determine the percent of sample crystallinity is accurate only to $\pm 5\%$. Measurements of the dynamic mechanical modulus of the poled films at 3 Hz (25°C), shown in Figure 5, show a significant (linear) drop with increasing phase I content and, therefore, increasing quenching pressure. At first, it was supposed that this might be a cause for the linear increase in piezoelectric response previously discussed, but it was not possible to explain a 1400% increase in d'_{31} on the

basis of a 22% decrease in sample modulus. The annealed samples showed a much smaller dependence of modulus on phase I content.

The observed increase in dielectric constant and decrease in modulus for the unannealed samples may be due to decreases in sample crystallinity or possibly differences in sample morphology.

The fact that the variations in sample modulus and dielectric constant decrease significantly when the samples are annealed points towards differences in crystallinity, but at the present time we are unable to verify this possibility. Investigations of sample morphology are incomplete and will be reported in a separate publication.

From the piezoelectric, dielectric, and mechanical data, we calculated the electromechanical coupling factor, K , ($K = \frac{4\pi G'd_{31}^2}{\epsilon}$) for unannealed and annealed films. Their values are shown in Figure 6, and show more than a tenfold increase for the all-phase I sample compared to the all-phase II sample.

CONCLUSIONS

From measurements of the piezoelectric activities of unoriented PVF₂ films:

1. Containing different volume fractions of the phase I and phase II polymorphic crystals forms.
2. Poled below the threshold value of electric field strength above which changes in the x-ray diffraction patterns occur which have been shown to be consistent with a field induced transformation from phase II to polar phase II^(8,9).
3. Poled below the value of electric field necessary to produce any observable changes in the x-ray diffraction patterns of the films corresponding to crystallite reorientation.

We have found a linear dependence of piezoelectric activity on the volume fraction of phase I crystalline material present in these films. These results support the view that the persistent polarization observed in poled samples of PVF₂ is primarily a result of the bulk polarization of the samples and is probably dependent on the field induced 180° re-orientation of molecules dipoles in the polar phase I crystal form.

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TABLE HEADINGS

Table 1 - Phase I Content (%), % Crystallinity, and Crystallization
Pressures of the Samples

TABLE 1 - Phase I Content (%), % Crystallinity, and Crystallization Pressures of the Samples.

Phase I Content (%)	Percent Crystallinity	P_i	P_f
0	53	1 atm.	1 atm.
37	51	1.6 Kb	2.7 Kb
47	54	1.6 Kb	6.4 Kb
64	52	1.7 Kb	6.5 Kb
94	51	2.0 Kb	6.6 Kb

FIGURE CAPTIONS

- Figure 1 - Wide angle diffractometer scans of samples containing different percents of phase I crystalline material. % phase I, from bottom scan to top scan is: 0%, 37%, 47%, 64%, 94%.
- Figure 2 - A plot of piezoelectric response (d_{31}) versus phase I content: d'_{31} unannealed (●), d''_{31} unannealed (■), d'_{31} annealed at 125°C for 1 hour (▲).
- Figure 3 - A plot of piezoelectric response (e_{31}) versus phase I content: e'_{31} unannealed (●), e''_{31} unannealed (■), e'_{31} annealed at 125°C for 1 hour (▲).
- Figure 4 - Dielectric constant (ϵ') for sample containing different phase I content: unannealed (●), annealed (▲).
- Figure 5 - A plot of dynamic mechanical modulus (G') versus phase I content: G' unannealed (●), G' annealed (▲).
- Figure 6 - A plot of the electromechanical coupling factor, K, versus phase I content: K unannealed (●), K annealed (▲).

