OFFICE OF NAVAL RESEARCH

Contract N00014-91-J-1078

R&T Code 4132046

Technical Report No. 37

# EFFECTS OF PLASTICIZER ON THE MECHANICAL AND FERROELECTRIC PROPERTIES OF UNIAXIALLY ORIENTED β-PHASE $PVF_2$

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Submitted
to
*Special Edition of the Journal of Polymer Science, Polymer Physics Edition*

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April 1996

# EFFECTS OF PLASTICIZER ON THE MECHANICAL AND FERROELECTRIC PROPERTIES OF UNIAXIALLY ORIENTED $\beta$-PHASE $PVF_2$

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## SYNOPSIS

The ferroelectric, piezoelectric, and dynamic mechanical properties of uniaxially oriented films of poly(vinylidene fluoride) $PVF_2$, undoped and doped with a plasticizer, tricresyl phosphate (TCP), were investigated. X-ray diffraction studies were carried out and show that for uniaxially oriented films, as dopant concentration increased, the percentage of non-polar $\alpha$-phase increased. These results also confirmed previous studies which indicate that the dopant resides in the amorphous regions. The piezoelectric coefficients ($d_{31}$ and $e_{31}$), pyroelectric coefficient ($p_y$), and remanent polarization ($P_r$) were observed to be enhanced by doping with TCP. Measurements of the pyroelectric coefficient, $p_y$, showed that the dopant produced a large increase in $p_y$ from 19.6 to 28.5 $\mu C/m^2/K$, suggesting an increase in the thermal expansion coefficient, $\alpha_3$. The data also suggest that a small amount of dopant in the noncrystalline regions greatly enhanced the high-temperature stability of the remanent polarization.

**Keywords:** $PVF_2$, ferroelectric polarization, piezoelectricity, pyroelectricity, plasticizer, dopant, depolarization.

## INTRODUCTION

It is well known that Poly(vinylidene fluoride), $PVF_2$, can exist in at least four polymorphic crystal forms[1] and other crystal forms have also been suggested[2]. Of the four well documented polymorphs, three are polar while the fourth is non-polar. There is much research published concerning the properties of each polymorph[3]. Of the known polymorphs, the all trans β-phase is the most polar. The β-phase can be obtained by mechanical drawing of the α-phase[4], annealing under pressure[5], pressure quenching[6], application of high electric fields[7], and electric field-induced crystallization from highly plasticized films[8]. Up to the present time, uniaxially oriented β-phase $PVF_2$ films yield the largest piezoelectric response of any homopolymer film. In these films, the main chain axis (c-axis) is parallel to the plane of the film in the direction of draw, and the dipole axis (b-axis) is randomly oriented (cylindrical symmetry) about the c-axis. Application of an external electric field to these films induces changes in orientation and gives a preferred dipole orientation perpendicular to the film surface, by rotation about the molecular stems, thereby yielding the greatest spontaneous polarization. The dipole moment is due primarily to the combined vector moment of the two C-F bonds[9].

Previous work in the area of plasticized, uniaxially oriented $PVF_2$ films was reported by Sen[10] and Takase[11]. This work involved doping uniaxially oriented $PVF_2$ films by dipping them into Tricresyl Phosphate (TCP) at elevated temperatures. This produced final plasticizer concentrations of 5% and 1% by weight respectively. It was found that doping with TCP enhanced the piezoelectric activity, the pyroelectric coefficient, and the remanent polarization, while stabilizing the remanent polarization to higher temperatures. X-ray diffraction studies showed smaller d-spacings and half-widths, indicating that polarization of the doped films produced tighter packing and greater crystal perfection[11]. Moreover, it was shown that the coercive field, $E_c$, was lowered by the presence of dopant. Their results suggest that a small amount of dopant in the noncrystalline regions greatly improve ferroelectric switching. It is commonly accepted that ferroelectric phenomena in $PVF_2$ originates from the field induced reorientation of molecular dipoles in the crystalline regions. The method previously described for doping had a limiting upper dopant level of about ≈5% by weight[12]. Mathur *et al.* carried out similar studies with plasticized uniaxially oriented nylon 11 films[13].

In this study, a different method of introducing plasticizer into the polymer films was utilized. Here, the dopant was initially mixed with the $PVF_2$ powder (forming a slurry) prior to pressing. Using this doping technique, higher plasticizer concentrations can be obtained than previously possible with the dipping method. Most importantly, this fabrication method eliminates any annealing effects due to the higher temperatures used in previous studies to facilitate diffusion of the dopant into the polymer. This new fabrication technique also allows a precisely measured concentration of plasticizer to be introduced into the films, with a more even distribution of dopant in the amorphous phase. Since the plasticizer is added prior to uniaxial orientation, it was possible to assess the role dopant plays in the orientation procedure. Furthermore, orientation decreased film conductivity and avoided the dielectric breakdown problems encountered with poling doped-unoriented films[14]. In addition, the mechanical and ferroelectric properties of these doped films as a function of plasticizer content was studied in order to gain further insight into the role of dopant in uniaxially oriented $PVF_2$ homopolymer films.

## EXPERIMENTAL

### 1. Film Preparation

The $PVF_2$ polymer used in this study was provided by Kureha Chemical Industries, Co.

Ltd. (KF-1000). The polymer was received in pellet form and ground to a fine powder using a Spex liquid nitrogen cryogenic mill. The plasticizer, Tricresyl Phosphate, (TCP) was added to the homopolymer (forming a slurry) prior to pressing, with the percentages of plasticizer chosen as 0%, 5%, and 10% by weight. Films were prepared by melting the plasticized powder between aluminum foils in a hot press at 210°C, followed by quenching into ice water. Residual moisture from the quenching process was removed from the films by placing them in a vacuum oven at room temperature for one hour. The final plasticizer content was determined by weight measurements.

For orientation, undoped and doped samples were placed in a heated oven at 55°C and stretched at a rate of 0.05 in/min to a final draw ratio of 3.9:1. This temperature was chosen because it was the lowest temperature that allowed easy stretching of the undoped samples without film fracture. Furthermore, the transformation of oriented $\beta$-phase back to the non-polar $\alpha$-phase upon release of tension is minimized at lower temperatures[15]. Doped films could be drawn to identical ratios at lower temperatures. The final film thickness was $\approx$25 microns. Aluminum electrodes, each about 40 mm$^2$, were deposited on opposing sides of the films by vacuum evaporation.

## 2. Apparatus

All electrical measurements were carried out by placing the samples in an electrically shielded copper cell equipped with a heater and temperature sensor. X-ray diffraction profiles were obtained at room temperature with a Philips XRG 3100 X-ray generator using nickel-filtered CuK$\alpha$ radiation. Piezoelectric, dielectric, and dynamic mechanical modulus measurements were performed using a Rheolograph Solid® (Toyo Seiki) at a measurement frequency of 10 Hz. at room temperature, and over the temperature range of -100°C to 125°C.

J-E hysteresis characteristics were measured at 20°C using a high-voltage power supply and a picoammeter connected in series with the sample. The sample was studied using a 500 second period saw-tooth shaped electric field waveform, as previously described[11]. Data used for determining the depolarization current and pyroelectric coefficient were obtained from poled samples by placing then in series with the picoammeter in an electrically shielded copper cell filled with silicone oil, while the sample was subjected to heating and cooling cycles of 2°C/min. The operation of data collection, data processing, and equipment control were consigned to a microcomputer (IBM).

## RESULTS

### 1. Wide Angle X-ray Diffraction Profiles

Wide angle X-ray diffraction profiles were measured in both reflection and transmission modes in a Philips vertical diffractometer at room temperature to analyze the crystal structure and orientation of the melt-quenched and drawn films. Figure 1a (reflection mode) and 1b (transmission mode) show the initial diffractometer scans of the uniaxially oriented samples at 0%, 5%, and 10% T.C.P. dopant concentration. In figure 1a (reflection mode) there are two observable reflections with Bragg angles at $2\theta \approx 20.7°$ and $2\theta \approx 36.4°$. These reflections are consistent with the β-phase oriented with the c-axis in the direction of draw. The β-phase unit cell dimensions used are: a = 8.58Å, b = 4.91Å, c = 2.56Å in an orthorhombic unit cell with space group Cm2m[4][16]. The first peak at $2\theta \approx 20.7°$ corresponds to the (200) ($2\theta$ = 20.71°) and the (110) ($2\theta$ = 20.85°) reflections, while the second peak corresponds to the (310) ($2\theta$ = 36.36°) and (020) ($2\theta$ = 36.61°) reflections. It should be noted that no change in $2\theta$ for these reflections can be observed with increasing dopant concentrations and this confirms the previous result that the plasticizer must be located in the amorphous regions or at the crystal-amorphous interface[11]. In figure 1b (transmission mode), only a single strong reflection with Bragg angle $2\theta \approx 35.6°$ is observed. This is consistent with the β-phase (001) reflection with a d-spacing of 2.56Å.

Figure 1b (transmission mode) provides some evidence that as more plasticizer is added to the polymer, the α-β phase transition is not complete. There is a small peak at $2\theta \approx 39°$ developing on the right side of the (001) β-phase reflection for the doped films. This peak indexes as the (002) ($2\theta = 38.99°$) reflection of the α-phase and corresponds to the c-axis repeat distance, where the unit cell dimensions of the α-phase are: a = 5.02Å, b = 9.63Å, c = 4.62Å[17]. The (001) reflection ($2\theta = 19.2°$) is systematically absent in the α-phase which has a monoclinic $P2_1/c$ space group[18]. This (002) reflection grows in intensity as more plasticizer is added to the system but is not visible in the pure $PVF_2$ homopolymer sample, indicating that the phase transition is complete without the presence of plasticizer. X-ray diffraction scans on several of the plasticized samples were also carried out on films held under tension, to determine if the α-phase appeared from the release of tension after the drawing procedure, or simply due to incomplete orientation. It was observed that the α-phase was present, even under tension, so the phase was not attributed to the release of tension, but was present at the final draw ratio. Obviously, the addition of plasticizer to the system reduces the efficiency of the α-β phase transformation, yet the resultant α-phase is oriented. From the transmission mode scans, it was determined that the percentage of α-phase in the three samples was negligible for undoped films but was ≈7% and ≈12% respectively, for samples with 5% and 10% dopant levels. In order to achieve the same degree of transformation in doped samples, higher draw ratios are required.

The ferroelectric switching mechanism in $PVF_2$ is ascribed to 180° and 60° dipole switching due to the pseudo-hexagonal nature of the β-phase crystal structure[2][19]. Figures 2a and 2b show the X-ray diffractions profiles of the poled films in both reflection and transmission modes respectively. The first peak in the reflection mode at $2\theta \approx 20.7°$ [composite (200)/(110) reflection] shifts to a slightly higher $2\theta$, ascribed primarily to the (110) reflection, indicating that following polarization the b-axis (dipole axis) is now aligned in the field direction within ± 30° from the normal to the film surface. The second peak corresponding to the composite (310)/(020) reflection also shifted to slightly higher $2\theta$, and this reflection can now be ascribed primarily to the (020) reflection which has a smaller d-spacing than the (310) reflection.

Figure 2b, (transmission mode after poling) now shows the absence of the (002) α-phase shoulder on the (001) β-phase c-axis reflection for the doped films, indicating that the oriented α-phase present in the plasticized samples has transformed to β-phase. This suggests that electric field poling converted the gauche bonds of the α-phase to the all trans bonds characteristic of the β-phase. The Bragg angle measured for the (001) β-phase reflection in the unpoled films was $2\theta \approx 35.6°$, and shifted to slightly lower $2\theta$, indicating that the poled sample had a more expanded c-axis repeat distance. This small shift suggests an increase in the d-spacing for the (001) reflection as a result of poling.

## 2. Dynamic Mechanical Modulus and Dielectric Constant

The process of drawing $PVF_2$ films should give increases in both the dynamic mechanical modulus and dielectric constant with respect to an unoriented $PVF_2$ sample. The dielectric constant should increase because there are now a larger percentage of chains in the amorphous regions which are preferentially oriented in the draw direction. In an unoriented sample, the chains in the amorphous region are completely random, and a larger fraction of dipoles are unable to respond to the applied electric field. In a polymer film above the glass transition temperature, $T_g$, the chains in the amorphous regions make the largest contribution to the dielectric constant.

The value of the dynamic mechanical modulus for the unplasticized films was determined to be 3.24 $X10^9$ ($N/m^2$). As plasticizer was added to the system, the modulus dropped 22% to 2.52 $X10^9$ ($N/m^2$) for the sample doped with 10% TCP. This decrease in modulus may be attributed to a more mobile amorphous phase due to higher plasticizer content and also perhaps, that the amorphous phase may be less oriented. A less oriented amorphous phase results in less main chains (primary bonds) carrying the applied load. This may result from an "internal lubrication" effect (i.e. increased mobility) from the plasticizer allowing the internal microstructure to slip, reducing shear during orientation, resulting in a less oriented amorphous phase. During orientation, the entanglements can more easily slip, thereby reducing shear so the $\alpha$ to $\beta$ crystal phase transformation is not as complete. In addition, the theoretically calculated crystalline modulus of the $\alpha$-phase is less than the $\beta$-phase. It was also shown in the X-ray diffraction data that the concentration of $\alpha$-phase increases with increasing dopant concentration.

The dielectric constant, measured at 10Hz., increases in value from those previously reported for unoriented $PVF_2$ films[14]. The value for the melt quenched oriented-unplasticized sample was 14.0, which is a 52% increase over that of an unoriented sample ($\varepsilon = 9.2$). With addition of plasticizer, the dielectric constant was observed to decrease, (13.5 @ 5% and 13.1 @ 10% T.C.P.), a decrease of 7% for the 10% plasticized sample. The reason for this is probably the lower dielectric constant ($\varepsilon = 7$) of the TCP plasticizer mixed in with the amorphous phase ($\varepsilon = 30$)[20], and based on a rule of mixtures analysis, the bulk amorphous dielectric constant would be reduced. Also the orientation of the amorphous regions may be less for the doped samples.

Temperature dependent measurements for both dynamic mechanical modulus and dielectric constant containing three different plasticizer levels are shown in figures 3a and 3b respectively. Both sets of data show marked changes in property as the samples pass from the low temperature region through the glass transition temperature. The values for $T_g$, as determined from the peak temperature of the loss curves in the modulus data, are reported as -38, -43, and -42°C respectively. This decrease in value is indicative of the addition of plasticizer which is known to lower the relaxation temperature. The results for $T_g$ from the dielectric data do not show the same trend. Values are reported as -28, -25, -25°C for the three samples. This phenomena is opposite to the expected result, and the Tg determined from the dynamic mechanical modulus data. The mechanical and electrical relaxation mechanisms differ and apparently are also effected differently by the doping process. One possible explanation may involve swelling of the amorphous phase due to the presence of dopant. As the orientation process occurs, the percent crystallinity increases, with the increased crystallinity usually in the form of fibrils. A direct consequence of this procedure is a larger concentration of TCP in the non-crystalline phase. Since the dopant level is fixed, and lies outside the crystalline regions, there is less amorphous phase available, resulting in a higher dopant concentration. An increased concentration of dopant may cause swelling of the amorphous phase resulting in it being under tension and necessitating a higher temperature for the onset of the relaxation. Data collected for these properties are summarized in table 1.

### 3. J-E and D-E Hysteresis

Parts a and b of figure 4 show current density, J, and electric displacement, D, respectively, as a function of applied electric field, E, when the three films are subjected to several cycles of a triangular electric field pulse with a maximum field strength of 150 MV/m. Graphs for D-E (which is equal to the time integrated current density) give a measure of remanent polarization, $P_r$, the value of D at E=0, and coercive field, $E_c$, the value of E at D=0. The coercive field and remanent polarization are defined as the averaged intercept values. All hysteresis curves are corrected for conduction, as previously described[21]. Figures 4a and 4b are obtained after subtracting the conduction components from the raw data. The ferroelectric response obtained for the three samples are listed in table 2.

Results presented here for the J-E data show some differences between switching peak characteristics as a function of TCP content. The curve for 5% plasticizer content shows a well defined switching peak which has a larger amplitude, when compared with the others (0% and 10% TCP), and the switching occurs over a much narrower range of electric field. This result is similar to the results obtained by Takase *et al.*[11] at 1% dopant, where the dopant was shown to enhance the shape of the J-E switching curves. However, the plasticizer raised the value of the coercive field (72.5, 78.5, and 77.5 MV/m for 0, 5, and 10% dopant) with increasing dopant concentrations, instead of lowering it as evidenced by Takase. Despite the higher switching field, the 5% sample displays a much sharper switching curve than the other two samples, so a small amount of TCP in the non-crystalline regions, or the crystal-amorphous interface (crystal surface) does indeed improve the switching behavior. In figure 4b, the remanent polarization is also seen to be changed by the presence of plasticizer. The values obtained for $P_r$ were 50.1, 51.2, and 47.3 mC/m$^2$ respectively. Again for the 5% sample, the remanent polarization is slightly enhanced over the unplasticized films, but for plasticizer level of 10% the $P_r$ value decreases, most likely due to a decrease in crystallinity. Takase reported a value of 66 mC/m$^2$ for their 1% doped samples, but these values were for annealed films.

It should be noted that at the highest doping level, 10% of the weight of this sample is plasticizer. When the results are analyzed on a polymer mass basis[14] (excluding the mass of TCP), then the decrease in $P_r$ does not appear as significant. $P_r$ values adjusted to be the same mass of polymer are 50.1, 53.7, and 52.0 mC/m$^2$ respectively for the three dopant levels. In fact, the 10% sample now yields a slightly better response than the undoped films when analyzed on a per-mass of polymer basis. Even though the crystallinity is probably decreased by the presence of dopant, it is clear that the dopant enhances the resultant remanent polarization.

## 4. Piezoelectric Response of Poled Films with Dopant

Figures 5a and 5b show the temperature dependence of the piezoelectric strain coefficient, $d_{31}$, and the piezoelectric stress coefficient, $e_{31}$, for the three samples after poling and the room temperature values are listed in table 2. Values for the $d_{31}$ coefficient are reported as 34.0, 35.0, and 32.5 pC/N for plasticizer levels of 0, 5, and 10%, respectively, at room temperature. Previous studies have shown that the remanent polarization and the resultant piezoelectric activity in these films arises from electric field induced crystal phase and dipole orientation changes[2]. The figure shows that there is an increase in $d_{31}$ at all temperatures greater that than 25°C with the addition of 5% plasticizer, but the value for 10% plasticizer was the lowest at all temperatures. These results directly correspond with those observed in figure 4b for $P_r$ from the D-E hysteresis data. Sen *et al.* reported $d_{31}$ values of 25.1 pC/N for 5% dopant using the dipping method at a draw ratio of 4.4:1[12], while Su *et al.*[22] reported a value of 40.9 for a uniaxially oriented PVF$_2$/Nylon 11 bilaminate film. When adjusted for the mass of crystals per mass of polymer basis, the $d_{31}$ values are now 34.0, 36.8, and 35.8 pC/N respectively for the three dopant levels, differences more significant than first realized. Again, the 10% doped samples show an enhanced value over the undoped samples when analyzed on a polymer mass basis.

From figure 5b, the values for these piezoelectric $e_{31}$ coefficient at room temperature are determined as 74.4, 66.5, and 60.2 $mC/m^2$ with plasticizer levels of 0, 5, and 10% respectively. The measured values steadily decrease with increasing plasticizer content at all temperatures with a maximum loss of about 19% at room temperature between 0 and 10% dopant. This decrease corresponds to the decrease in elastic modulus. Sen reported an $e_{31}$ value of 59 $mC/m^2$ for films doped with 5% TCP (using a different film fabrication method), while the samples in this study yielded values of 66.5 $mC/m^2$ at the same plasticizer concentration. The $e_{31}$ coefficient for the samples show an increase up to about 52°C, then a sharp decline with increasing temperatures. The maximum value shown is 93.3 $mC/m^2$ @ 54°C for the undoped films.

## 5. Depolarization Current Densities and Pyroelectric Coefficient (py)

Measurements of depolarization currents (DPC) can yield information about the thermal stability of the remanent polarization, $P_r$, and also provide information about the depolarization mechanisms. These measurements are shown in figure 6a for the initial heating run after poling at a rate of 2°C/min for pure $PVF_2$ and the two plasticized films. The maximum temperature used was limited to 125°C, since temperatures higher than this gave rise to plasticizer exudation from the sample, introducing substantial error into the measurements. All three samples exhibit a well defined current density peak in the range of 45-55°C, and a broad maximum at higher temperatures (75-100°C). The peak appears in the undoped films at ≈55°C which shifts to lower temperatures, ≈50°C and ≈45°C for 5% and 10% respectively, as the plasticizer concentration is increased. The broad maximum in the range from 75-100°C is at approximately the same point for all three samples. These two peaks indicate that there are two different depolarization mechanisms.

In general, there are two contributions to the depolarization current densities: release of trapped charge and randomization of the field induced dipole orientation. Separating these two contributions is important to the understanding of the results. The first peak in figure 6a is believed to be attributed primarily to the release of the trapped charge. The variation in both dielectric and piezoelectric constants with temperature, shown in figures 3b and 5a in the temperature region of 45-55°C, is also suggestive of this behavior. The broad maxima at higher temperatures, in the range of 75-100°C, is attributed to randomization of the oriented dipoles. Takase *et al.* also reported a high temperature peak in the same temperature range[11].

Since $PVF_2$ does not show a ferroelectric to paraelectric crystal phase transition in the form of a defined Curie temperature, it is impossible to determine the total remanent polarization by integrating the area under the depolarization current (DPC) unless the sample is taken to the melting point. However, the total remanent polarization can be estimated from the magnitude of the pyroelectric coefficient. Figure 6b shows the data for $p_y$ for the three samples calculated from the DPC data on the cooling cycle after heating to 125°C at a rate of 2°C/min. This value of $p_y$ results from only the remanent polarization which is left after heating to 125°C. It is determined experimentally from the following equation:

$$p_{yi} = (J_i - J_{i-1})(t_i - t_{i-1}) / (T_i - T_{i-1}) \qquad (1)$$

where J is the current density (charge on the electrodes), t is the time, T is the temperature, and the subscript i defines the sampling number. Since the resultant polarization is in the 3 direction (normal to the film surface), the only non-zero component of the pyroelectric tensor is $\mathbf{P}_3$. $|\mathbf{P}_3| = p_y$, and is defined as the change in polarization with temperature,

$$p_y = dP / dT \tag{2}$$

and an increase in temperature produces an increase in volume (secondary pyroelectric effect) which results in a decrease in polarization yielding a negative $\mathbf{P}_3$.

The values obtained for $p_y$ at 40°C from the cooling curves for the three samples respectively are 19.6, 28.5 and 26.2 $\mu C/m^2/K$. The highest value reported here, 28.5 $\mu C/m^2/K$ for the 5% plasticized sample, is 225% higher than previously reported by Takase[11] when oriented $PVF_2$ films with 1% dopant were examined. Part of the reason for this discrepancy may be do to the fact that these samples were only heated to 125°C as compared to 140°C for the previous study. Apparently, some remanent polarization has not been removed due to the limited temperature range used here. Recall, it was stated earlier that higher temperatures caused the plasticizer to exude from the films. This causes a loosening of the electrode contact with the film surface.

The dopant significantly enhances the high temperature stable remanent polarization over that of the undoped sample. The sample containing 5% dopant showed a $p_y$ value 45% higher than the undoped sample and the 10% sample was 33% higher. These results are directly attributed to the enhancement of the thermal expansion coefficient with increased dopant concentrations. In both sets of doped films, the thermal expansion coefficient was larger resulting in a greater observed change in surface charge density at the electrodes as temperature was changed. The sample containing 10% dopant had a slightly lower value than the 5% sample due to the lower crystallinity; i.e., there is a competing relationship between the enhancement of the thermal expansion coefficient increasing $p_y$ and a decrease in crystallinity decreasing $p_y$ with increasing dopant concentrations. Changes in polarization resulting from the volume expansion with increasing temperature, which is enhanced by increases in the thermal expansion coefficient produced by the presence of dopant, are attributed to the secondary pyroelectric effect. Thus, the pyroelectric constant due to the dimensional effect[23] is given by:

$$p_3 = - P_r \alpha_3 \tag{3}$$

where $\alpha_3$ is the coefficient of thermal expansion in the thickness direction.

## DISCUSSION

Previous work by Takase[11] demonstrated that small levels (1%) of plasticizer added to a uniaxially oriented $PVF_2$ film enhances the high temperature stability of the resultant polarized material, and lowers the free energy barriers to reorientation of dipoles under the electric field. This phenomena was also confirmed in this study for samples up to 5% doping. During the course of this work, it became apparent that two competing processes occur in the films with increasing concentrations of dopant. On one hand, higher dopant levels gives rise to a decreased total crystallinity with decreased ferroelectric response, but on the other hand, the increased dopant levels act to increase dipole orientation under field and gives rise to a larger remanent polarization. Evidence of this trend was especially apparent with the enhancement of the high temperature stability, specifically the pyroelectric coefficient.

The wide angle X-ray diffractometer scans recorded in transmission mode (figure 1b) show that for the plasticized films oriented with a draw ratio of 3.9:1, there exists a substantial quantity of $\alpha$-phase crystals left in the oriented samples. During poling of these films, the $\alpha$-phase was converted to $\beta$-phase. It has also been demonstrated that the presence of dopant reduces the effectiveness of the mechanical orientation process in converting the $\alpha$-phase to the $\beta$-phase under the draw conditions used. For doped films, higher draw ratios may be needed to achieve the same degree of internal orientation as for the undoped films.

Data presented for the dynamic mechanical modulus shows that the modulus decreases, as expected, with increasing plasticizer content. However, the dielectric constant data also shows a decrease, whereas an increase was anticipated. The reason for this was attributed to the lower dielectric constant ($\varepsilon = 7$) of TCP compared to the value of 30 reported[20] for unoriented amorphous $PVF_2$. Based on a rule of mixtures analysis, the overall bulk dielectric constant of the amorphous phase should decrease when dopant is present, despite an increase in the amount of the amorphous phase. Plasticizer increases the percentage of amorphous material by dissolving out small crystallites. Usually, the resulting amorphous material has higher mobility and higher dielectric constant than either the crystalline phase or the plasticizer. This was true in our case, with the exception of the lower dielectric constant with additional quantities of plasticizer. In addition, it was shown that the orientation procedure was not as complete. A result of this is fewer dipoles in the amorphous phase being oriented to easily respond to the applied field.

The most significant result obtained from this investigation were the substantial increases in the pyroelectric coefficient of the doped films. While the dopant was reported to increase the value of the coercive field in the J-E measurements, the switching peak for the 5% samples was narrower and better defined, whereas the undoped and the 10% TCP samples exhibited switching characteristics spread over a wider range of electric field. The explanation for the higher coercive fields in the doped films involve the dielectric constant. It was shown that with increasing plasticizer levels, the dielectric constant decreases. With a lower dielectric constant, the voltage drop across the amorphous phase increases at the expense of the field across the crystals. In other words, the distribution of the electric field in the amorphous and the crystalline regions is different for the doped samples. In order to achieve the necessary voltage (electric field) across the crystals to cause ferroelectric polarization reversal, a higher overall voltage (electric field) is required for the bulk samples. Switching occurs over a more reduced range of electric fields since the plasticizer, which lies in the crystal-amorphous interfacial regions, may make the molecular chains on the surface of the crystallites more mobile and may melt out small and poorly formed crystals. The dopant at the crystal-amorphous interface may permit easier reorientation of chains in the crystals. This effect on the switching characteristics is also observed in the odd-numbered Nylon films which have been poled after absorption of water[24]. In addition, orientation in the doped samples is not as complete (as shown in figure 1b) and this may also contributes to a higher $E_c$.

The remanent polarization for the 5% sample was the largest reported for the three types of samples investigated. Again, the presence of dopant in the amorphous phase or the crystal-amorphous interface enhances the switching characteristics and therefore the remanent polarization in the 5% sample but not as much for 10% dopant. This result is in direct agreement with the results of Takase[11]. In addition, the data for depolarization current and $p_y$ measurements indicates the same trend. The DPC data (figure 6a) shows that the dopant stabilized the high temperature stability of the resultant polarization by exhibiting less depolarization at all dopant concentrations. A direct consequence of this enhancement of the high temperature stability, is a significantly higher pyroelectric coefficient in doped films. The reported value for $p_y$ reveals a 45% increase over that measured for the undoped films, an increase much higher than anticipated. This is also attributed to the enhancement of the thermal expansion coefficient in the thickness direction, $\alpha_3$.

Samples containing 10% plasticizer may have been "over-doped" for some applications.

In some cases, the properties show a reduced value over the pure homopolymer samples and those containing only 5% dopant. The 10% films show lower depolarization currents and higher pyroelectric coefficients than the undoped films. Most of the lower reported values are likely due to the lower crystallinity of these 10% doped films. With less crystallinity, there will be less net resultant polarization. Another problem encountered was the reduced orientation observed at the higher dopant level. It was clear from the transmission mode X-ray diffraction profiles (figure 1b) that a small, yet significant ($\approx$12%) quantity of $\alpha$-phase was present after orientation. Orienting the doped films to higher levels certainly would have improved the properties. Moreover, Poissons' ratio may be different for the doped films. No data is available with respect to this.

The piezoelectric data also shows some interesting results for $d_{31}$ and $e_{31}$. Even though the piezoelectric data for 0% and 10% TCP differ only slightly, it should be remembered that the presence of plasticizer introduces a decrease in the crystallinity. While the $d_{31}$ for the 10% plasticized film was 4% less than the pure homopolymer films, only 90% of the sample is polymer, with the remaining 10% being inactive plasticizer. The piezoelectric ($d_{31}$) response per unit mass of polymer was calculated and the results, on a mass basis of polymer, are 34.0, 36.8, and 35.8 pC/N for 0, 5, and 10% dopant respectively. While the overall bulk crystallinity is reduced by the dopant, the piezoelectric values on a mass basis show that the dopant has indeed improved the remanent polarization in the 10% doped films when compared with the undoped films.

## CONCLUSIONS

Based on the results of the present study of uniaxially oriented, doped $PVF_2$ films, the following conclusions can be drawn: The presence of dopant in $PVF_2$ films has the effect of lowering the crystallinity. A direct consequence of the lower crystallinity and the presence of dopant in the amorphous phase, is a lower dynamic mechanical modulus. The decreased dielectric constant is attributed to the substantially lower dielectric constant of the dopant offsetting the larger dielectric constant of the increasing quantities of amorphous phase. Electric field poling results show that the presence of small quantities of dopant can result in an enhancement of the ferroelectric properties. Further, the dopant can stabilize the polarization of these films to higher temperatures at all dopant concentrations. Both doped films (5% and 10%) exhibit less depolarization on heating, directly resulting in the larger pyroelectric coefficient observed during subsequent cooling. There was a 45% increase observed in $p_y$ for the 5% doped films compared with the undoped films. Another important result of this study was the increase observed in $p_y$ resulting from the increase in thermal expansion coefficient in the thickness direction, $\alpha_3$, with increasing dopant concentrations.

**Acknowledgements.**

This work was supported O.N.R.

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## Figure Captions

**Figure 1.** Diffractometer scans in (a) reflection mode and (b) transmission mode at room temperature of the three un-poled uniaxially oriented (3.9:1) $PVF_2$ films, doped prior to orientation at concentrations of 0%, 5%, and 10% T.C.P.

**Figure 2.** Diffractometer scans in (a) reflection mode and (b) transmission mode for samples poled under 150 MV/m at room temperature at three dopant concentrations for the oriented films.

**Figure 3.** The real components of the (a) temperature dependence of the dynamic mechanical modulus ($c_{11}$) along the draw direction and (b) temperature dependence of the dielectric constant ($\epsilon$). Samples were measured at 10 Hz. over the temperature range of -100°C to 125°C for the three oriented-doped $PVF_2$ films.

**Figure 4.** (a) Current densities, J, and (b) electric displacements D, versus electric field, E, characteristics during the poling procedure for the $PVF_2$ films at three dopant concentrations. Samples were subjected to a triangular electric field (150 MV/m) with a period of 500 sec at room temperature.

**Figure 5.** Real components for the temperature dependence of the (a) piezoelectric stain coefficient, $d_{31}$, and (b) piezoelectric stress coefficient, $e_{31}$, over the temperature range of -100°C to 125°C. The measurements were carried out at a frequency of 10 Hz.

**Figure 6.** (a) Depolarization current densities showing the polarization reversal process on the initial heating runs after poling and (b) Pyroelectric coefficients measured at 40°C showing high-temperature stable remanent polarization in the cooling half-cycle after heating to 125°C of the three doped-poled-oriented films. Heating and cooling rates were chosen at 2°C/min.

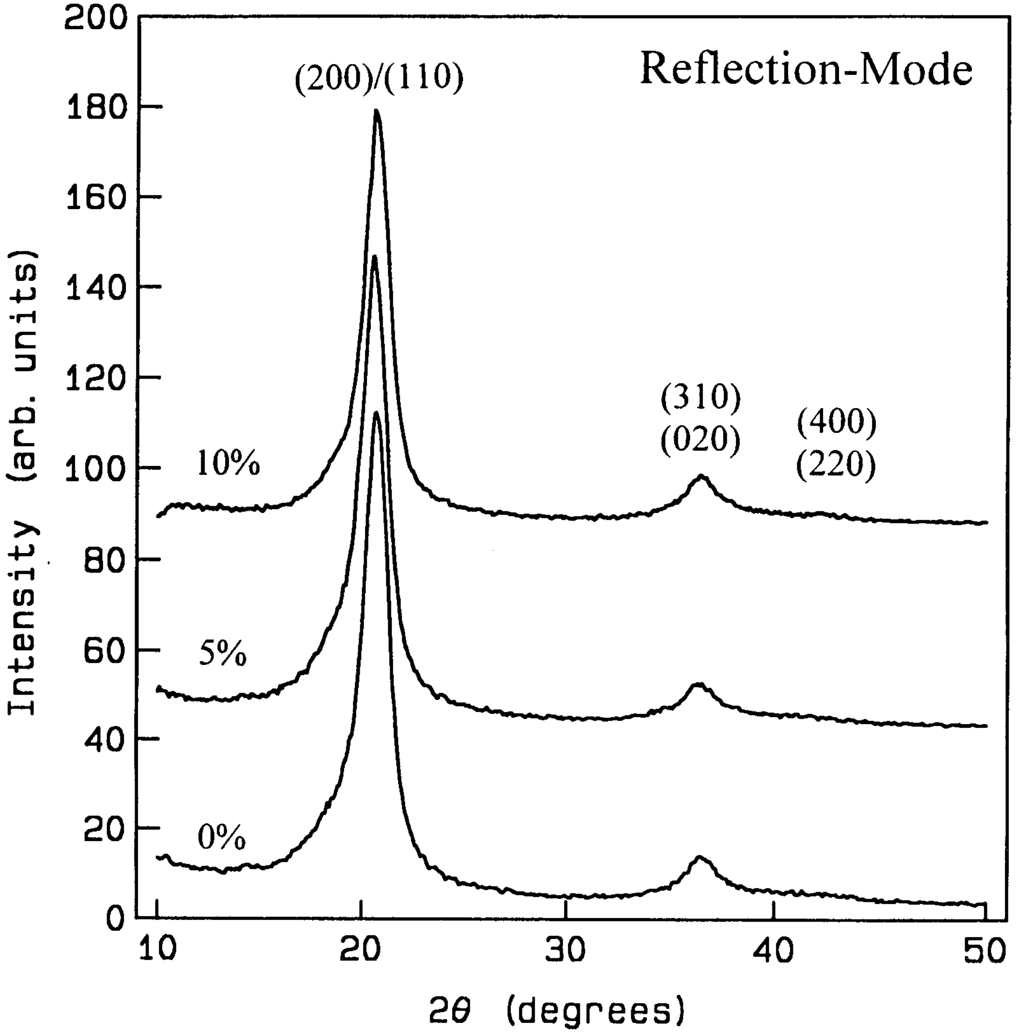

Reflection-Mode
(200)/(110)
(310)
(020)
(400)
(220)
10%
5%
0%
Intensity (arb. units)
200
180
160
140
120
100
80
60
40
20
0
10
20
30
40
50
2θ (degrees)

Figure 1a:

Figure 1b:

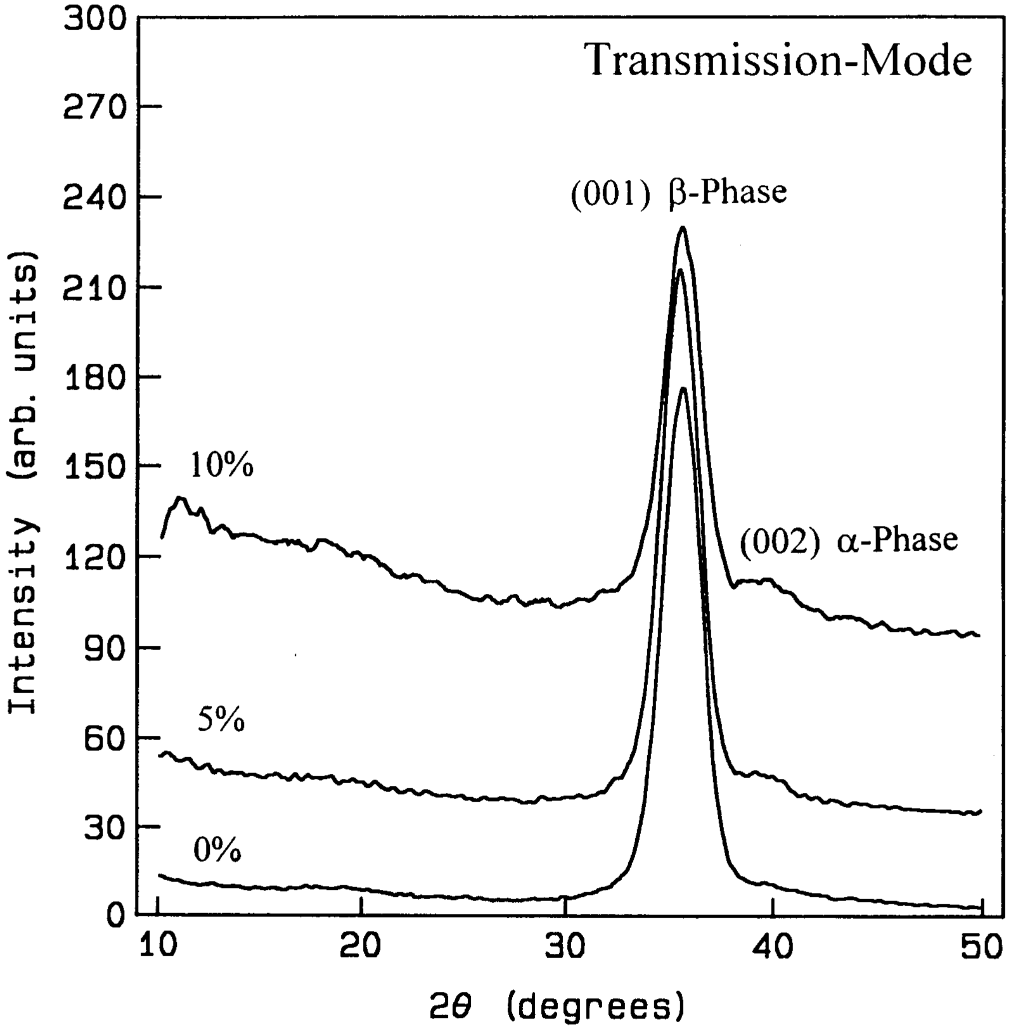
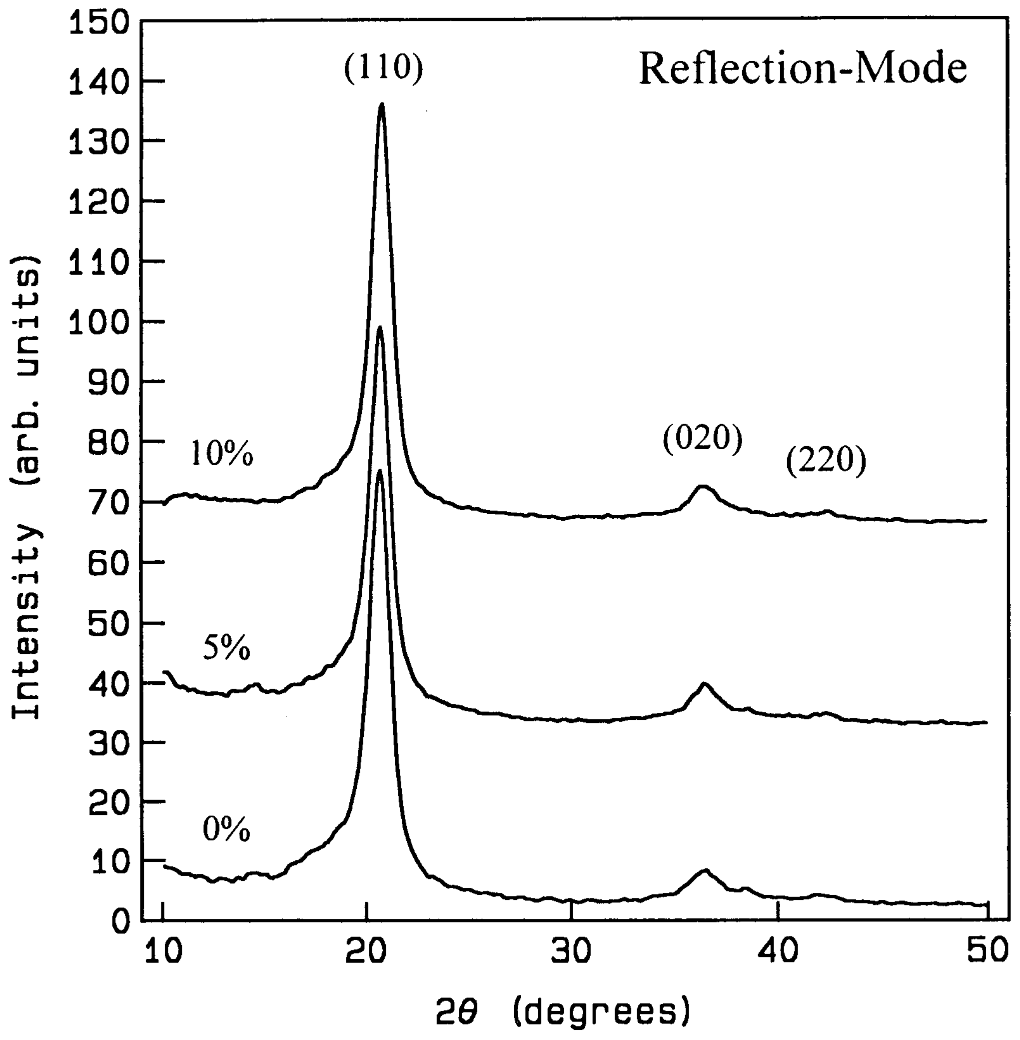

Transmission-Mode
(001) β-Phase
(002) α-Phase
10%
5%
0%
Intensity (arb. units)
0
30
60
90
120
150
180
210
240
270
300
2θ (degrees)
10
20
30
40
50

Figure 2a:


Reflection-Mode
(110)
(020)
(220)
10%
5%
0%
Intensity (arb. units)
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
10
20
30
40
50
2θ (degrees)

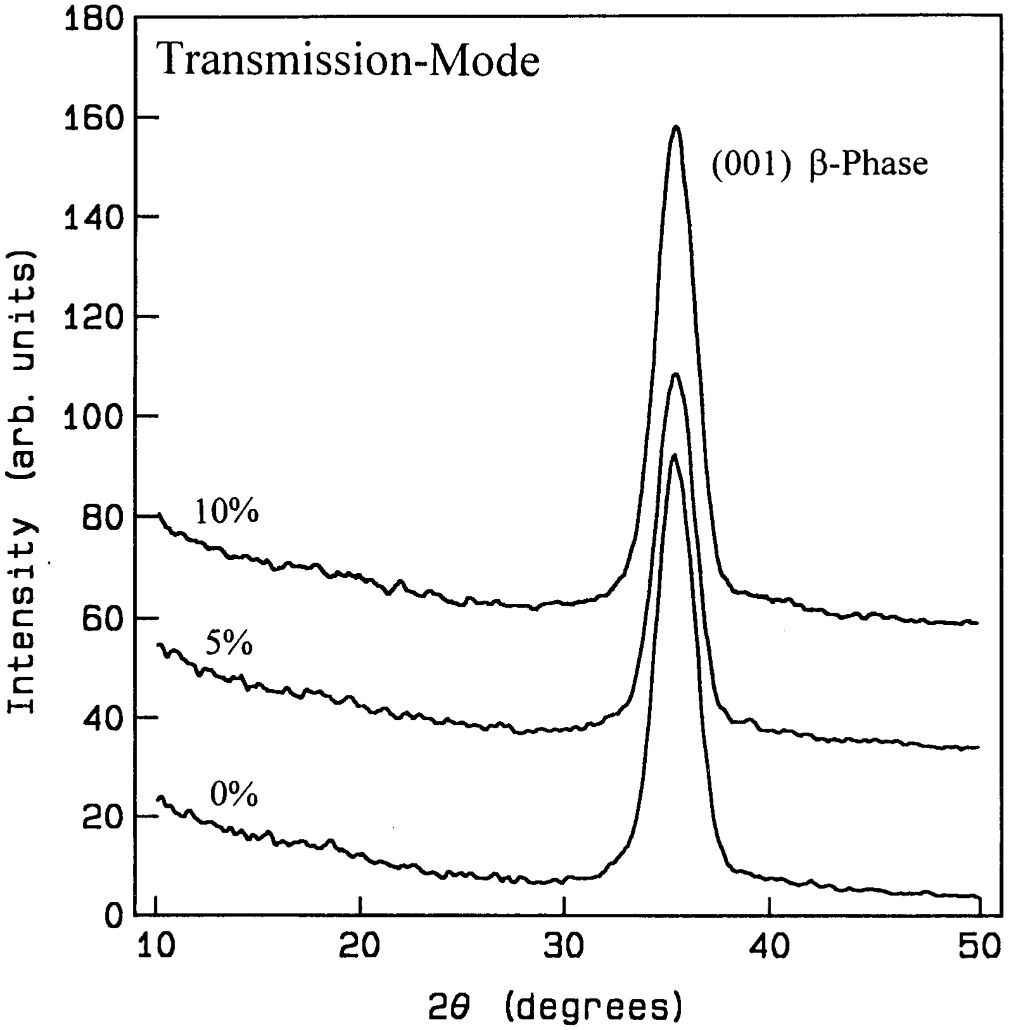

Transmission-Mode
(001) β-Phase
10%
5%
0%
Intensity (arb. units)
0
20
40
60
80
100
120
140
160
180
10
20
30
40
50
2θ (degrees)

Figure 2b:

Figure 3a:

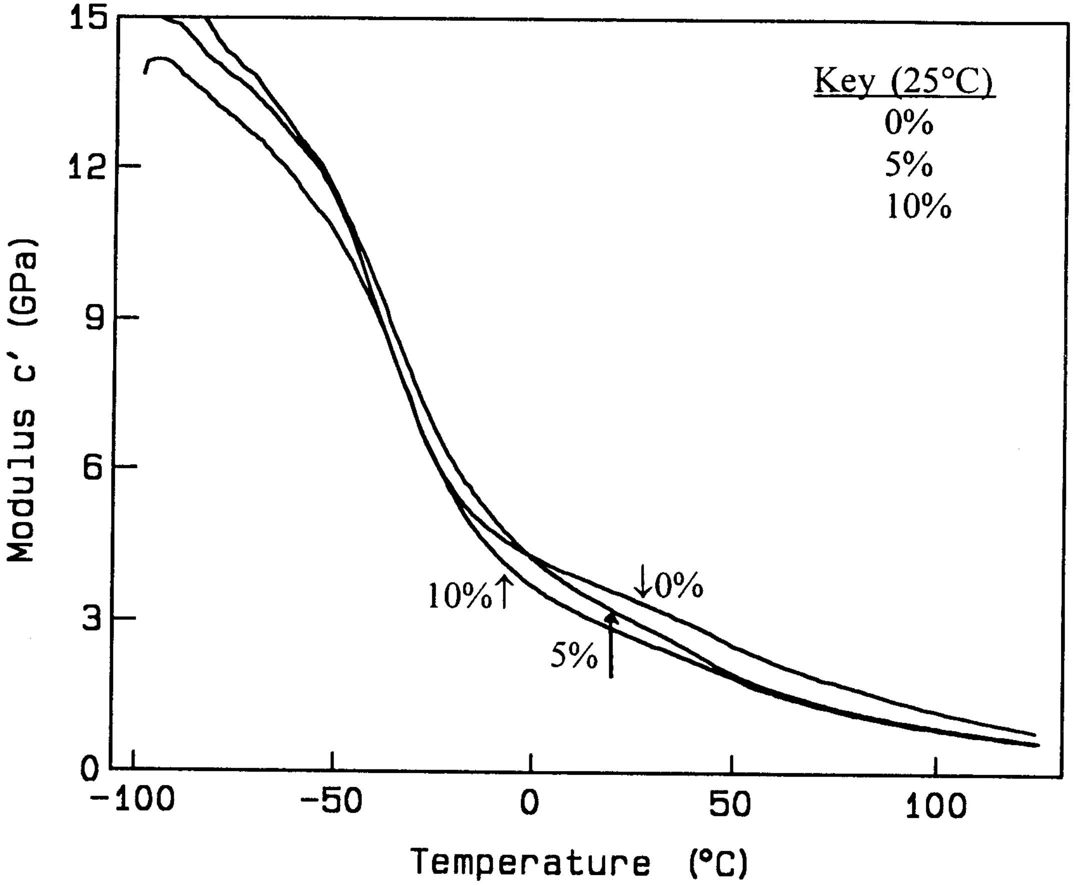
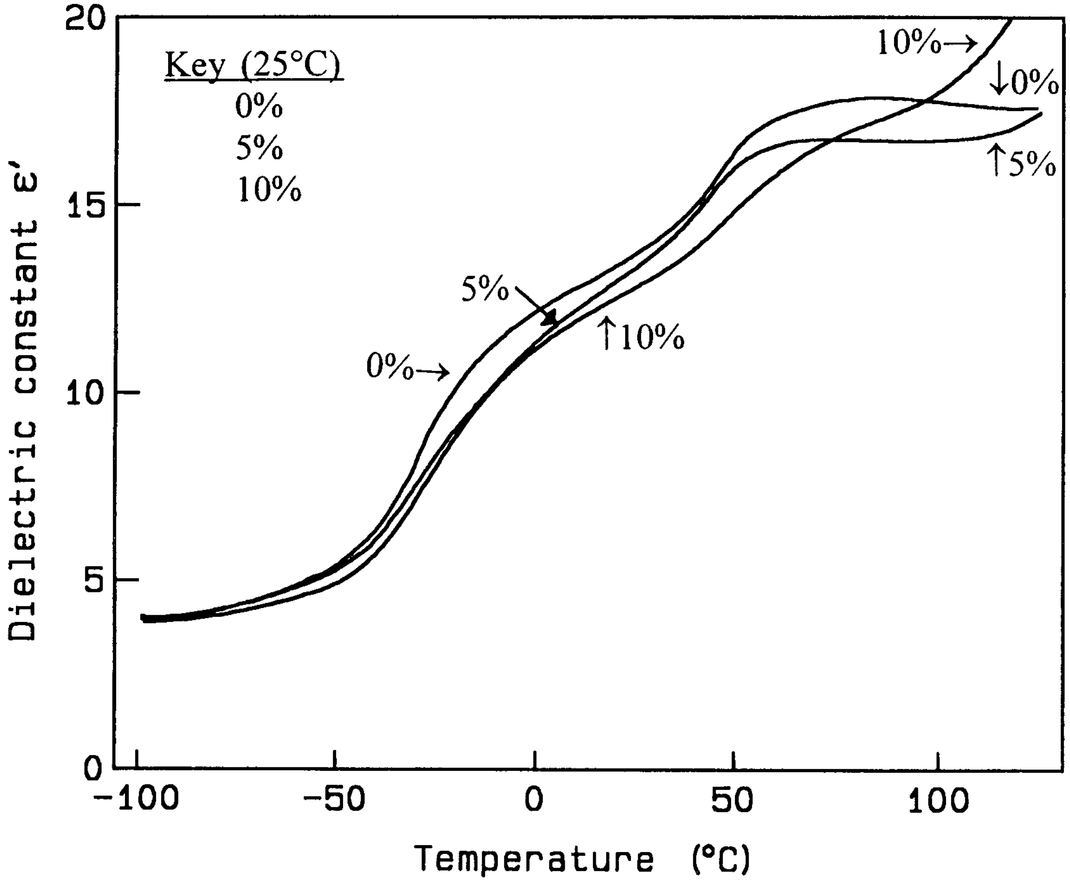

Modulus c' (GPa)
15
12
9
6
3
0
−100
−50
0
50
100
Temperature (°C)
Key (25°C)
0%
5%
10%
10%↑
↓0%
5%

Figure 3b:



Key (25°C)
0%
5%
10%
10%→
↓0%
↑5%
5%
↑10%
0%→
Dielectric constant ε′
20
15
10
5
0
−100
−50
0
50
100
Temperature (°C)

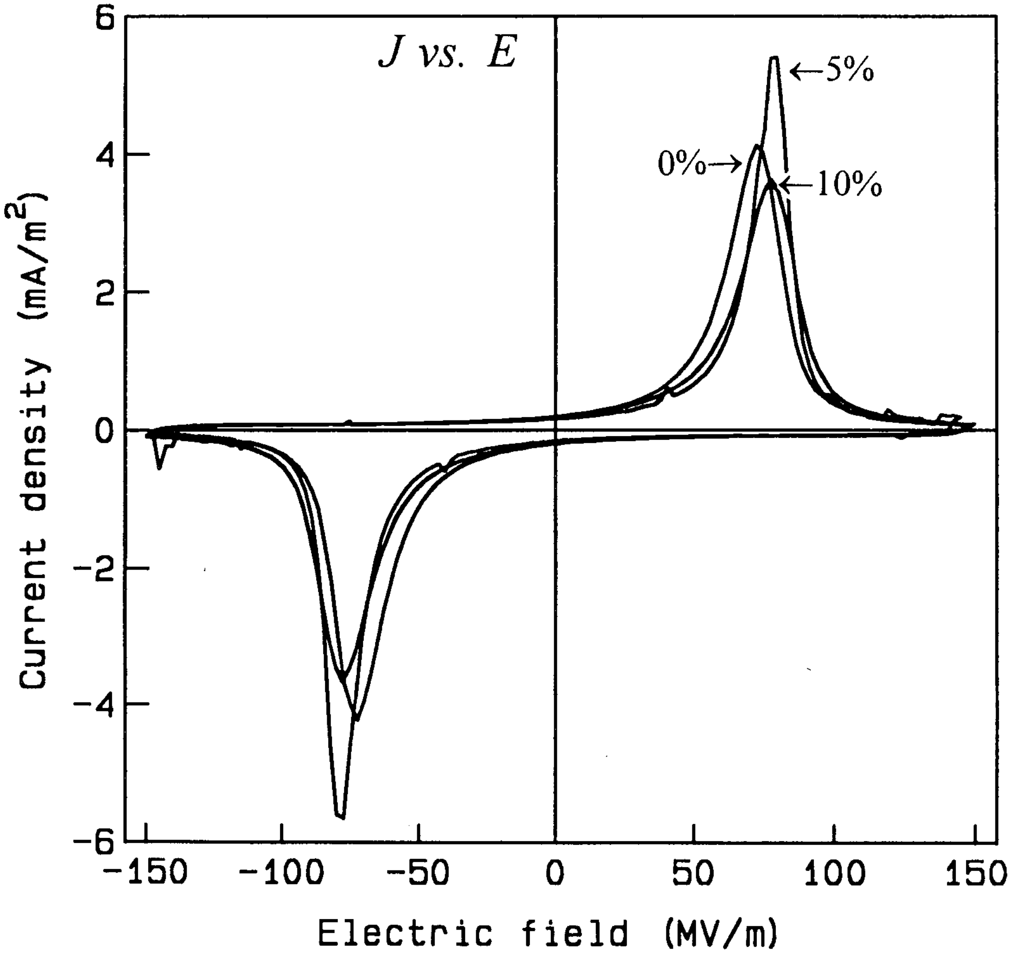
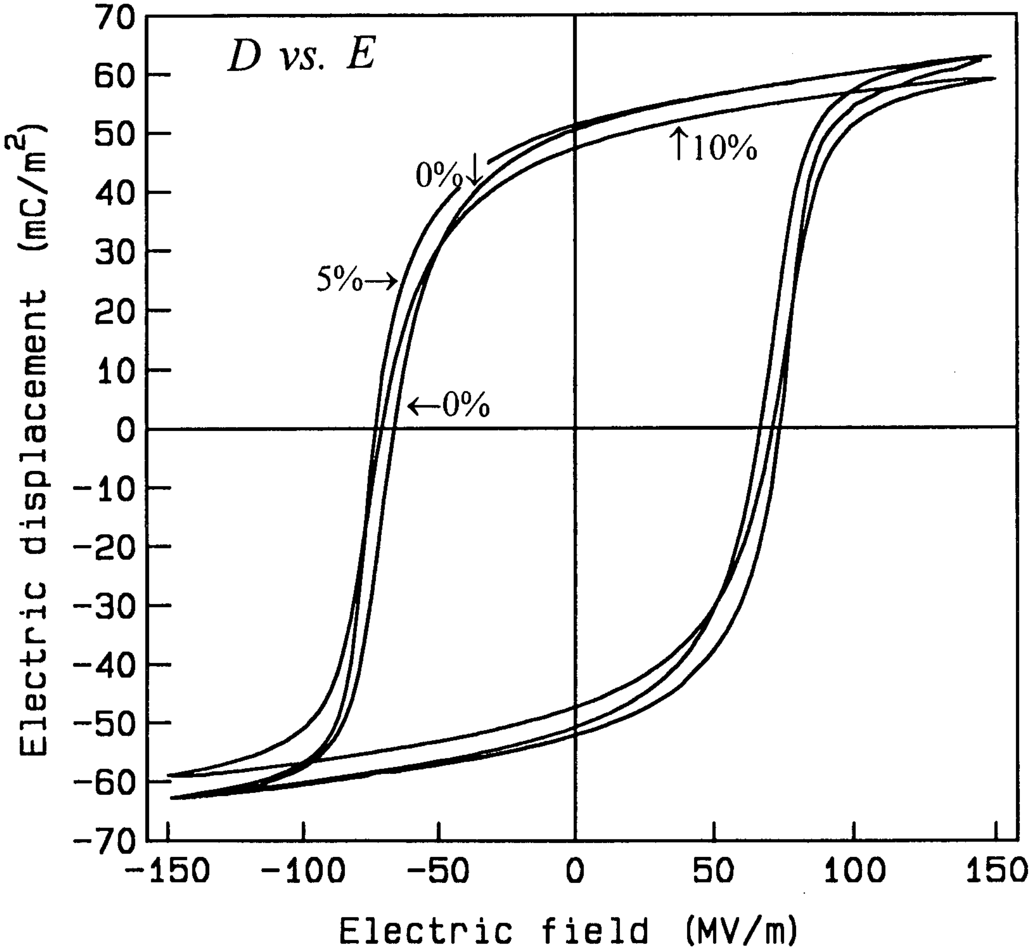

J vs. E
←5%
0%→
←10%
Current density (mA/m²)
6
4
2
0
-2
-4
-6
Electric field (MV/m)
-150
-100
-50
0
50
100
150

Figure 4a:

Figure 4b:


D vs. E
0%↓
↑10%
5%→
←0%
Electric displacement (mC/m²)
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−150
−100
−50
0
50
100
150
Electric field (MV/m)

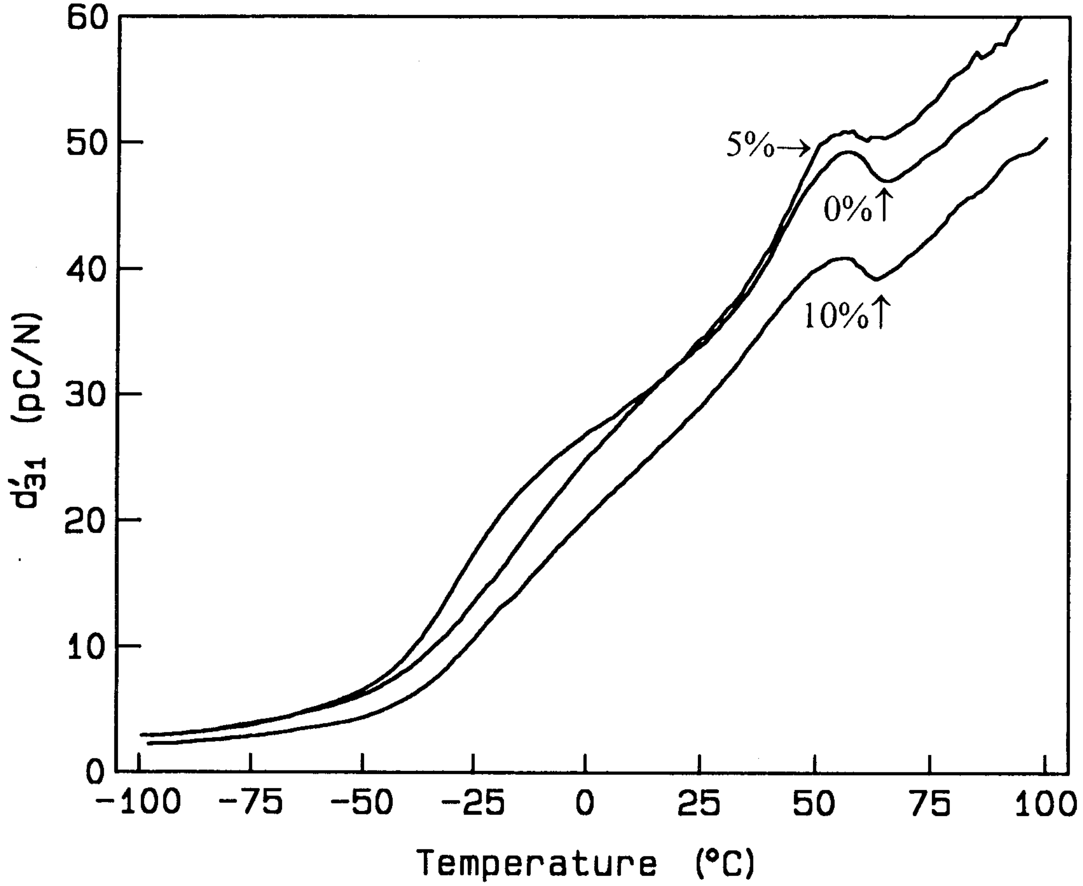

60
50
40
30
20
10
0
$d'_{31}$ (pC/N)
-100
-75
-50
-25
0
25
50
75
100
Temperature (°C)
5%→
0%↑
10%↑

Figure 5a:

Figure 5b:

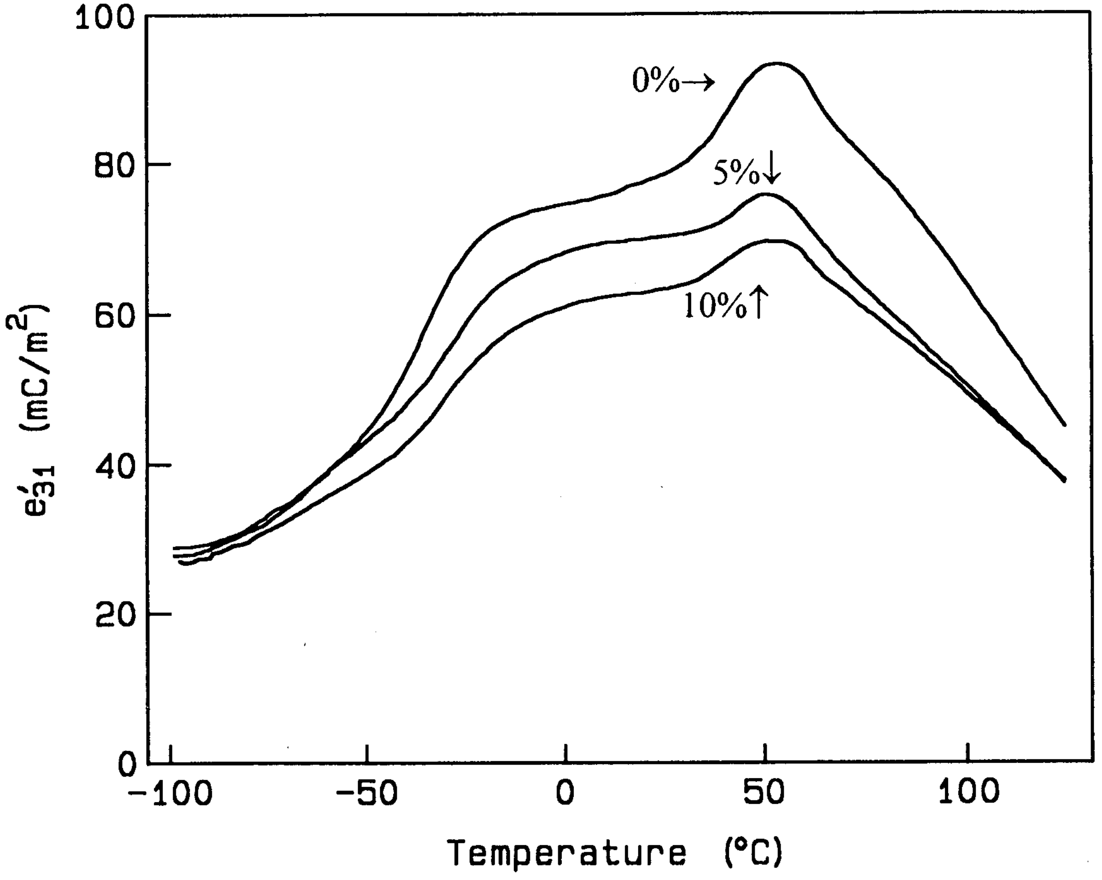


Figure 6a:

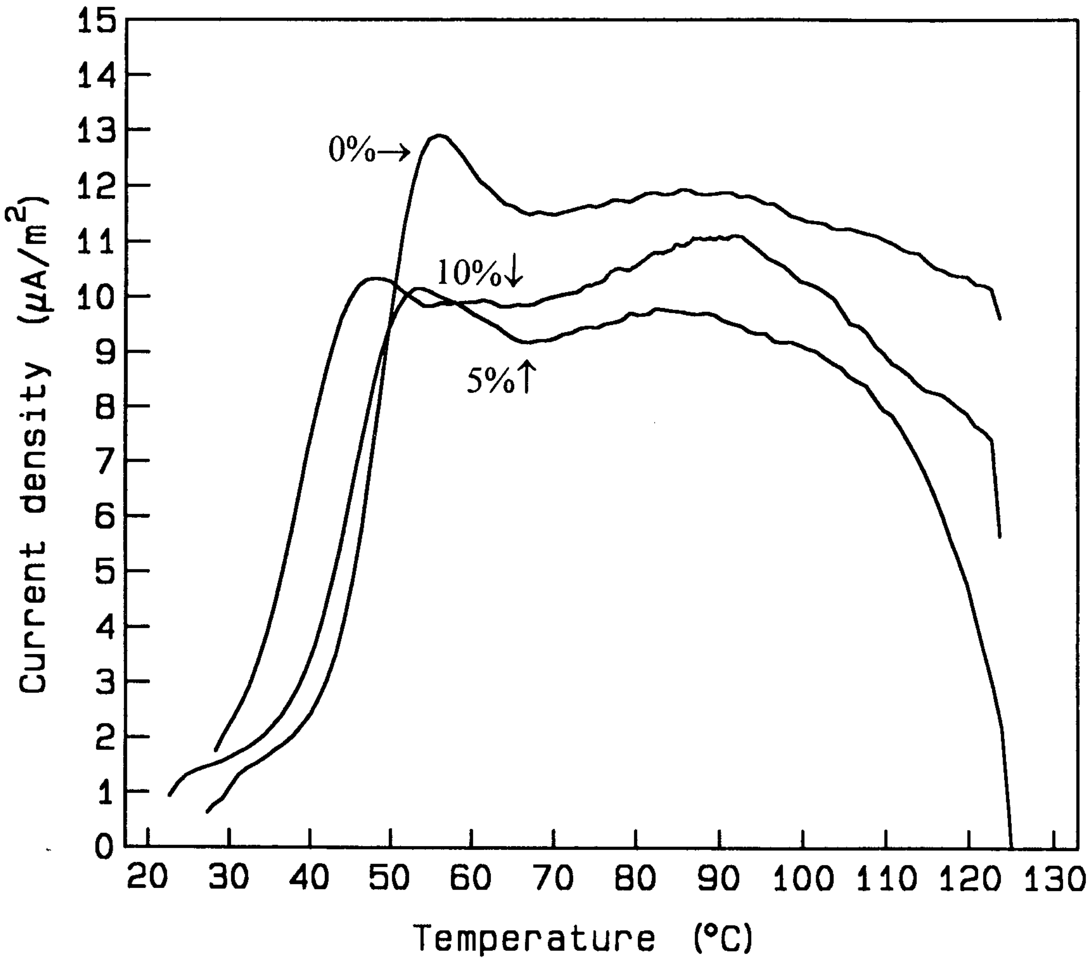
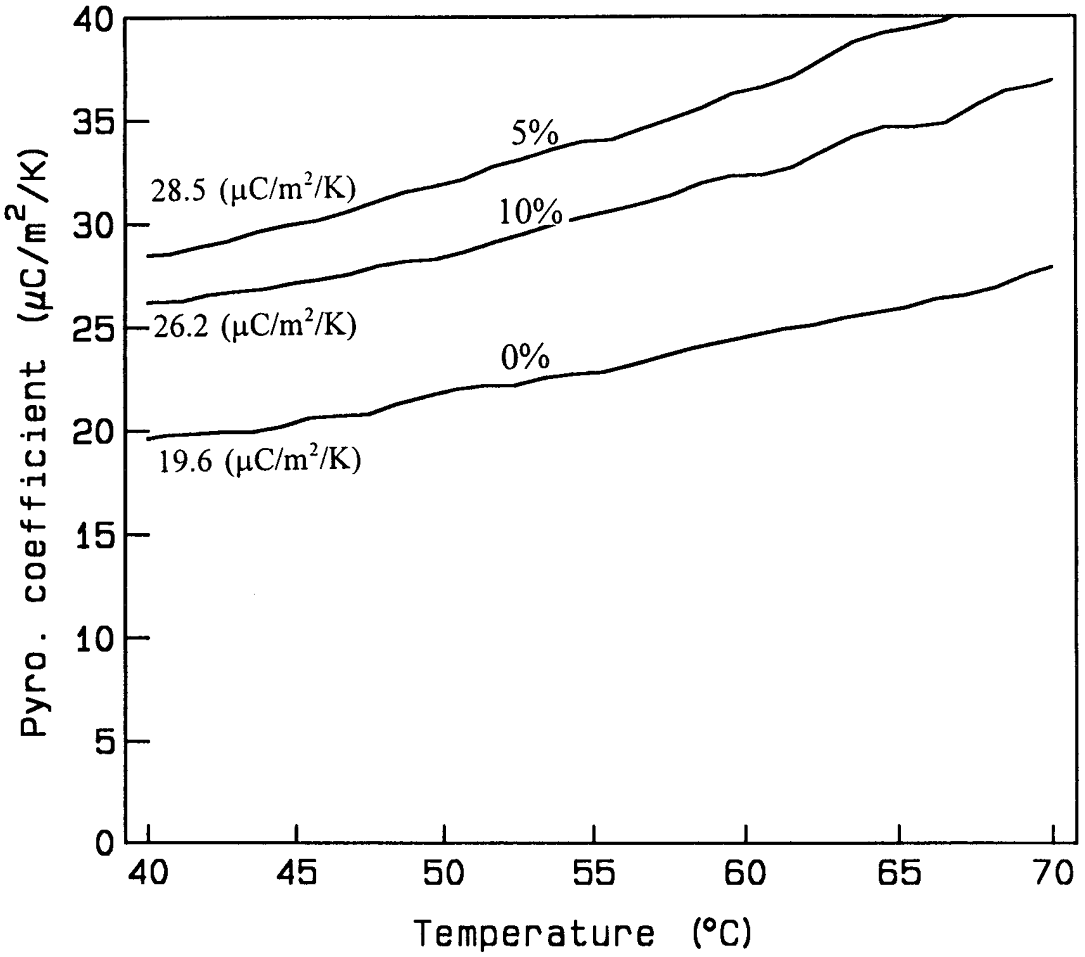

15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
Current density (μA/m²)
20
30
40
50
60
70
80
90
100
110
120
130
Temperature (°C)
0%→
10%↓
5%↑

Figure 6b:



Pyro. coefficient ($\mu C/m^2/K$)
Temperature (°C)
0
5
10
15
20
25
30
35
40
40
45
50
55
60
65
70
28.5 (μC/m²/K)
26.2 (μC/m²/K)
19.6 (μC/m²/K)
5%
10%
0%

## Table Captions

**Table 1.** Summary of data for uniaxially oriented (3.9:1) $PVF_2$ films doped at three concentrations measured at room temperature and 10 Hz. prior to electric poling.

**Table 2.** Comparison of data after poling doped $PVF_2$ films at 150 MV/m measured at room temperature and 10 Hz. for the three dopant concentrations.

**Table 1.** Summary of data for uniaxially oriented (3.9:1) $PVF_2$ films doped at three concentrations measured at room temperature and 10 Hz. prior to electric poling.

| **Property (10 Hz.)** | **0%** | **5%** | **10%** |
|---|---|---|---|
| C X $10^9$ ($N/m^2$) | 3.24 | 2.62 | 2.52 |
| $\epsilon$ | 14.0 | 13.5 | 13.1 |
| $T_g$ (°C) Modulus | -38 | -43 | -42 |
| $T_g$ (°C) Dielectric | -28 | -25 | -25 |

**Table 2.** Comparison of data after poling doped $PVF_2$ films at 150 MV/m measured at room temperature and 10 Hz. for the three dopant concentrations.

| **Property (10 Hz.)** | **0%** | **5%** | **10%** |
|---|---|---|---|
| $E_c$ (MV/m) | 72.5 | 78.5 | 77.5 |
| $P_r$ ($mC/m^2$) | 50.1 | 51.2 | 47.3 |
| $d_{31}$ (pC/N) | 34.0 | 35.0 | 32.5 |
| $e_{31}$ ($mC/m^2$) | 74.4 | 66.5 | 60.2 |
| $e_{31}$ max | 93.3 | 75.8 | 69.5 |
| $p_y$ ($\mu C/m^2/K$) @ 40°C | 19.6 | 28.5 | 26.2 |