# Field-Induced Crystallization in Highly Plasticized Poly(vinylidene fluoride) Films

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ABSTRACT: Highly plasticized films of poly(vinylidene fluoride) ($PVF_2$) containing approximately 18% by weight of tricresyl phosphate (TCP) and with initial crystallinities (phase II) of approximately 15% were poled under high vacuum. The poling temperatures were 75 and 90 °C, and the poling field was 250 kV/cm. The poling time was varied from 15 to 240 min. Weight measurements and X-ray diffraction data of poled films showed that with increasing poling time (up to 4 h) the plasticizer content decreased (to a minimum of ~11%) and the crystallinity of the $PVF_2$ films increased (to a maximum of 45%). The field-induced crystallization occurred as highly oriented phase I crystals. After the films were poled for 1 h (at 90 °C), a significant percent of the crystalline material was observed to be in the polar phase I form. At longer times, a measure of the relative percent of phase I with respect to the total crystallinity decreased. As expected, the piezoelectric strain constant $d_{31}$, piezoelectric stress constant $e_{31}$, and pyroelectric coefficient $P_y$ increased with increasing phase I content, reaching maximum values after a 1-h poling time at 90 °C of $d_{31} \approx 10$ pC/N, $e_{31} \approx 11$ mC/m$^2$, and $P_y \approx 17$ $\mu$C m$^{-2}$ K$^{-1}$. The dynamic mechanical modulus and dielectric constant (measured at 3 Hz) were found to be ~1.3 GN/m$^2$ and ~14.7, respectively, under these poling conditions.

## Introduction

Previous studies[1-3] have shown that when phase II $PVF_2$ films are subjected to poling fields, field-induced crystal transitions occur by way of several stages. At relatively low fields, the nonpolar phase II converts to polar phase II (phase IV), and this is reflected in an increase in piezoelectric and pyroelectric response. At higher fields, phase I is formed. Furthermore, if the films are initially unoriented, the threshold fields for transitions depend on the initial orientation of the crystals.[4] Preliminary studies in our laboratories have shown that addition of plasticizer to the films before poling has a strong influence on the piezoelectric and pyroelectric properties.[5] Both $d_{31}$ and $e_{31}$ were higher for plasticized films compared to unplasticized films poled under identical conditions. We have also shown that crystal-phase transitions in the plasticized $PVF_2$ films take place at lower poling fields as compared to the unplasticized films under identical poling conditions.[6] At higher poling fields, the amount of phase I formed is also much greater and more highly oriented in the case of plasticized films.

An early study by Scheinbeim et al.[7] found that the effects of field on isothermal crystallization from the melt were limited, owing to the small fields which could be applied, the dielectric strength at high temperatures being very low. Recently, Stein et al.[8] stated that on the basis of experimental studies of isothermal crystallization of $PVF_2$ cooled from the melt in an electric field, the effect of the field is to lower the free energy of nucleation of phase III. They showed that at certain undercoolings and applied fields crystallization in the polar phase III crystalline form is favored and that the phase III spherulites produced exhibit an angularly dependent radial growth rate. An infrared spectroscopic study of the crystallization behavior of $PVF_2$ from the melt by Hsu et al.[9] also showed that more phase III occurs in samples crystallized in the presence of an electric field.

In the case of highly plasticized $PVF_2$ films with low initial crystallinity, it should be possible to crystallize at lower temperatures and hence at much higher fields than those that can be applied to the melt. If we start with highly plasticized $PVF_2$ and apply an electric field as plasticizer is removed, then the field should bias the cold crystallization process. For the phase II TGTG′ conformation, the dipole moment normal to the chain axis is $4.0 \times 10^{-28}$ C/cm, while that along the chain is $3.4 \times 10^{-28}$ C/cm. For the all-trans phase I conformation, the dipole moment is $7.0 \times 10^{-28}$ C/cm and lies essentially normal to the chain direction.[10] The potential energy associated with a TGTG′ conformation is ~−23 kcal/mol, while for an all-trans conformation the potential energy is ~−17 kcal/mol.[11,12] This large difference in conformational energy implies that the presence of an electric field in the amorphous regions should have little effect on biasing chain conformations toward those found in the polar crystal forms; however, if we compare the total crystal energy of the phase I and phase II crystals obtained by using the crystal structures determined by Hasegawa[13] and Doll and Lando[14] and calculated by Hopfinger[11] and Bachmann and Lando,[15] the energy values are very close. So in the presence of an electric field, even a small biasing effect arising from the interaction energy might result in oriented growth of the phase I form, as it would then correspond to the lowest free energy state, depending on the magnitude of the local electric field. On the basis of this idea, we decided to conduct a series of experiments where heavily plasticized $PVF_2$ films with very low initial crystallinities are subjected to an electric field while plasticizer is allowed to evaporate and crystallization occurs.

## Experimental Procedures

**A. Sample Preparation.** Kureha capacitor grade poly(vinylidene fluoride) film was dissolved in plasticizer (tricresyl phosphate) at 185 °C to obtain solution-cast films with very high plasticizer content (≈70%) and with no crystallinity as detected by wide-angle diffractometer scans (reflection mode). These films were very difficult to handle due to the high level of plasticizer. The solution-cast films were then placed in a vacuum oven at 100 °C for 10 h, subsequently, melt pressed at 200 °C between aluminum foils, and quenched in ice water. $PVF_2$ films containing approximately 19% by weight of tricresyl phosphate and with initial (phase II) crystallinities of approximately 13% were obtained. The film thickness was measured to be ≈25 $\mu$m.

**B. Poling.** Plasticized films were placed in the poling apparatus between two polished copper plates, connected to a high-voltage dc supply, and then placed under high vacuum (~$10^{-6}$ torr). Samples were poled at 250 kV/cm at 75 and 90 °C. The poling time was varied from 15 min to 4 h. At 90 °C, however, the samples could not be poled longer than 2 h due to the excessive occurrence of dielectric breakdown. The film surface was coated with silver paint to provide sample electrodes. Figure 1 shows a schematic diagram of the poling apparatus.

**C. Electrical and Mechanical Measurements.** The piezoelectric strain constant ($d_{31}$), piezoelectric stress constant, ($e_{31}$), dielectric constant, and modulus were measured at 3 Hz. The silver paint was first removed from the film surfaces, which were

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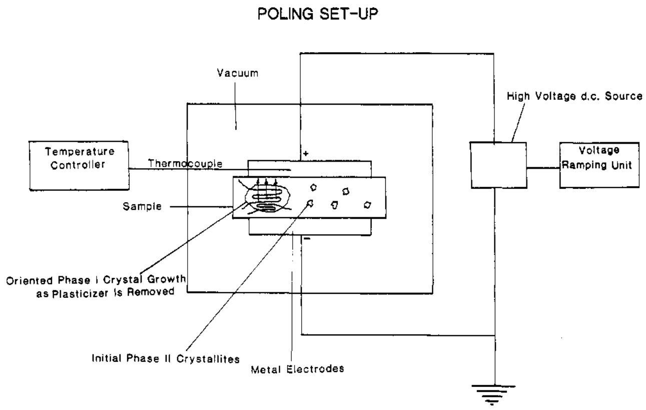

**Figure 1.** Schematic representation of field-induced crystallization of highly plasticized PVF$_2$ film.

then coated with a thin layer of soft silver paste to serve as electrodes for the electrical and mechanical measurements. The pyroelectric coefficient ($P_y$) was measured by placing a sample between two copper plates connected to an electrometer. The sample was then placed in a temperature-controlled chamber. Currents were measured for both heating and cooling cycles at a constant controlled rate of 3 °C/min. The pyroelectric coefficient at room temperature was obtained by using

$$P_y = (1/A)[(i^+ - i^-)/2\beta]$$

where $i^+$ and $i^-$ are the currents at room temperature during heating and cooling cycles, respectively, $A$ is the electrode area, and $\beta$ is the heating and cooling rate in °C/s. By taking the difference in the measured currents, $i^+$ and $i^-$, the small but significant contribution of the background current is removed.

**D. X-ray Studies.** A measure of the amount of phase I material produced by field-induced crystallization of highly plasticized PVF$_2$ films was obtained from wide-angle diffractometer scans using Cu K$\alpha$ radiation. A measure of the total crystallinity (phase I + phase II) was determined from the reflection-mode diffractometer scans by taking the ratio of the area under the phase I and phase II peaks to the area under all the crystalline diffraction peaks and the amorphous scattering. The assignment of diffraction peaks to phase I or phase II crystal forms was based on previous crystallographic studies.[14,16] A measure of the amorphous contribution to the diffracted intensity was determined by subtracting the crystalline and base-line intensities from the total diffracted intensity, assuming that the amorphous peak is symmetric. A measure of phase I crystallinity was determined by taking the ratio of the area under the phase I peak to the total area (crystalline + amorphous). Relative phase I crystallinity was calculated by taking the ratio of the area under the phase I peak to the area under all crystalline diffraction peaks (phase I + phase II).

The areas under the phase I "shoulders" [phase I (110) reflection] were obtained from the diffractometer data. The shoulder area was determined by first assuming that the phase II (110) reflection was symmetric (which is the case for an all phase II sample). After the amorphous scattering was subtracted, the total area under the composite peak (phase II with its phase I shoulder) was measured. The area just under the phase II peak was then measured and subtracted from the area under the composite peak. Each measurement was performed five times. The areas obtained differed by less than ±5% in all cases. The numerical average of the five values was used. X-ray photographs were also taken on flat film with the X-ray beam perpendicular to and parallel to the plane of the PVF$_2$ films both before and after poling. Although none of these measures of crystallinity or relative crystallinity are accurate in any absolute sense, they allow for some basis of comparison for films subjected to similar poling histories.

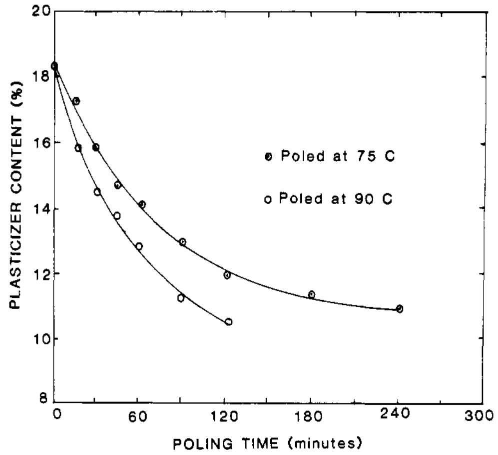

**Figure 2.** Plasticizer content in poled PVF$_2$ films for various poling conditions.

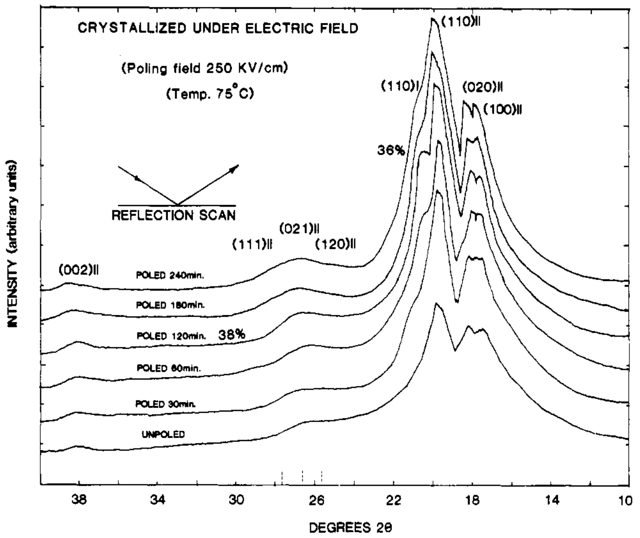

**Figure 3.** Diffractometer scan (reflection mode) of PVF$_2$ films poled at 75 °C.

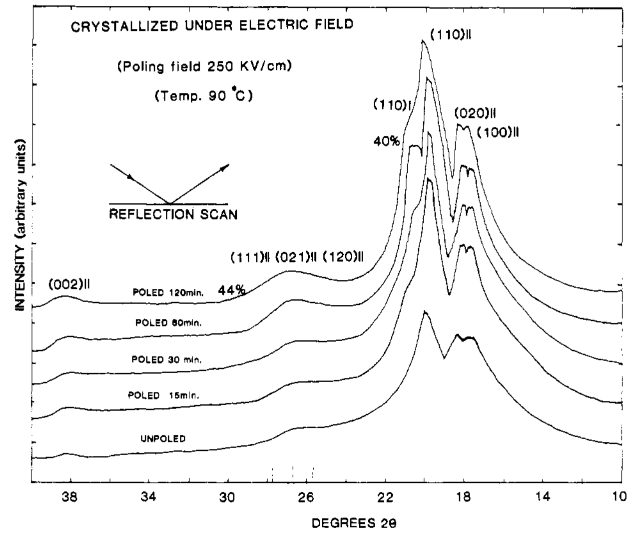

**Figure 4.** Diffractometer scan (reflection mode) of PVF$_2$ films poled at 90 °C.

## Results and Discussion

Figure 2 shows the plasticizer content as a function of time while poling at 75 and 90 °C. As expected, with increased poling temperature the plasticizer evaporated faster. After a poling time of 2 h, the amount of plasticizer left in the PVF$_2$ films is 12.1% at 75 °C and 10.5% at 90 °C (by weight). It is also observed that the amount of plasticizer evaporated at 90 °C after 2 h is higher than the amount of plasticizer which evaporates at 75 °C after 4 h. The diffractometer scans (reflection mode) of the PVF$_2$

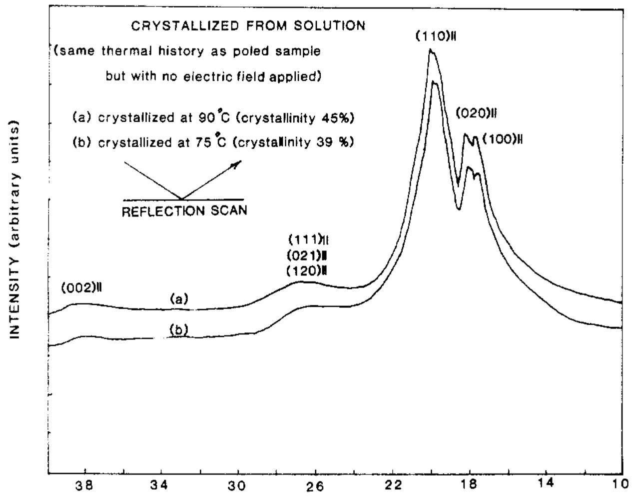

**Figure 5.** Diffractometer scan (reflection mode) of $PVF_2$ films (unpoled) under similar thermal history as poled sample.

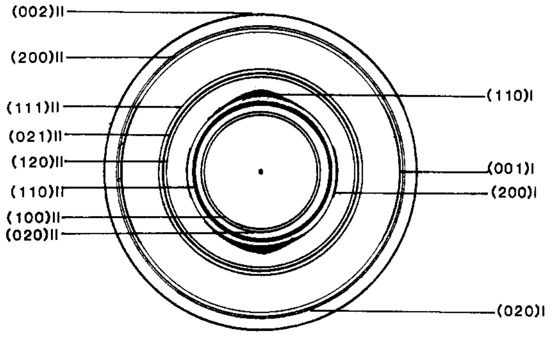

**Figure 6.** Representation of the X-ray diffraction patterns from poled $PVF_2$ film taken with X-ray beam in the plane of the film (poled at 90 °C).

films taken before and after poling at 75 and 90 °C for various poling times are presented in Figures 3 and 4 and show the development of (phase I and phase II) crystallinity with poling time. The unpoled samples had an initial crystallinity of ≈13%, and after a poling time of 2 h at 75 and 90 °C, the crystallinity was measured to be ≈38% and 43%, respectively. It is also observed that initially no phase I was present, but with time, the phase I shoulder becomes more and more prominent. At a poling time of 2 h at 75 °C, the relative phase I crystallinity was found to peak at ~36%, and at a poling time of 1 h at 90 °C, it peaked at ~40%. At longer times, the phase I shoulder diminished in relative intensity, indicating that little additional phase I was being formed. Reflection scans for the unpoled films with the same thermal history (1 h at 75 and 90 °C) as that of the poled sample are shown in Figure 5. It is seen that the films crystallized under identical conditions but with no poling field contain only the nonpolar phase II form. Figure 6 shows a representation of the flat-film X-ray diffraction pattern obtained with the X-ray beam parallel to the plane of the $PVF_2$ film after being poled at 90 °C for 1 h. It can be seen that the phase I formed on field-induced crystallization is highly oriented. The (110) phase I reflection appears as an arc centered on the meridional position. Figure 6 also shows that the intensity of the phase I (110) reflection occurs over an arc of ~30° to either side of the meridian, suggesting that phase I crystals within this angular range of orientation with respect to the applied field form on field-induced crystallization. Since the dipole direction of phase I is along the crystallographic *b* axis, the observed phase I diffracted intensity in the reflection-mode diffractometer scans, Figures 3 and 4, should result only from the (110) reflection and not from the (200) reflection.

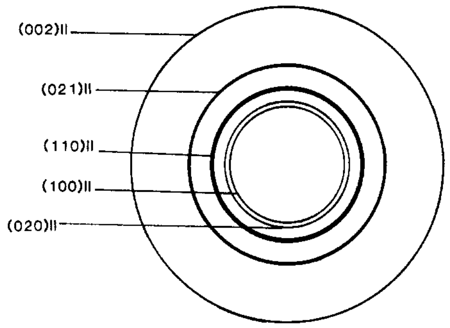

**Figure 7.** Representation of the X-ray diffraction patterns from the unpoled film having similar thermal history as poled $PVF_2$ film with X-ray beam in the plane of the film (at 90 °C).

The phase I (200) and (001) reflections appear as arcs in the equatorial position, which indicates the orientation of the phase I crystals as *a* axis and *c* axis in or close to the plane of the film and *b* axis (dipole direction) close to normal to the film surface. The diffractometer scans also showed that no phase IV (polar phase II) was formed during poling since no change in the relative intensities of the (100) and (200) phase II reflections was observed.[6] This would support an assumption that phase I forms directly by field-induced crystallization and not from a poling field induced phase transformation from phase II or IV. The fact that the Debye–Scherrer rings from phase II are complete also supports this assumption.[4] Figure 7 schematically represents a flat-film X-ray photograph taken with the X-ray beam parallel to the plane of a $PVF_2$ film with the same history as a poled sample but with no poling field applied. It is clearly seen that in the absence of an electric field no phase I formation takes place and only phase II is formed. The phase II crystallites are unoriented as is clear from Figure 7: all crystal orientations are equally present as the Debye–Scherrer rings are complete.

Figures 8 and 9 show a measure of total crystallinity (phase I + phase II) and a measure of phase I crystallinity produced on poling the highly plasticized films at 75 and 90 °C. After a poling time of 2 h, the amount of phase I formed at 90 °C (17%) is higher than the amount of phase I formed at 75 °C (13%). The total crystallinity (phase I + phase II) is approximately 40% after poling, as shown in Figure 8. If the phase I crystals are highly oriented, the actual amount of phase I formed will be significantly lower than that determined from the diffractometer scans (reflection mode) as these scans record diffracted intensities only from the crystallographic planes parallel to the film surface. The phase I produced by crystallization during poling is clearly oriented, as it is seen that the most intense reflection for phase I (110) is an arc centered on the meridional position. This is shown in the X-ray photograph represented in Figure 6. Comparing Figures 8 and 9 shows that the total crystallinity (phase I + phase II) and the phase I crystallinity developed faster at a higher poling temperature. This is due to the faster rate of plasticizer evaporation at higher temperature, as shown previously in Figure 2. The total crystallinity (phase I + phase II) after a poling time of 1 h is 41% and 32% at 90 and 75 °C, respectively. A measure of relative phase I crystallinity (ratio of area under phase I peaks to area under phase I + phase II peaks) with poling time is shown in Figure 10. It is seen that after a certain poling time (1 h at 90 °C and 2 h at 75 °C) the percent of phase I relative crystallinity decreases, which indicates that during poling both phases

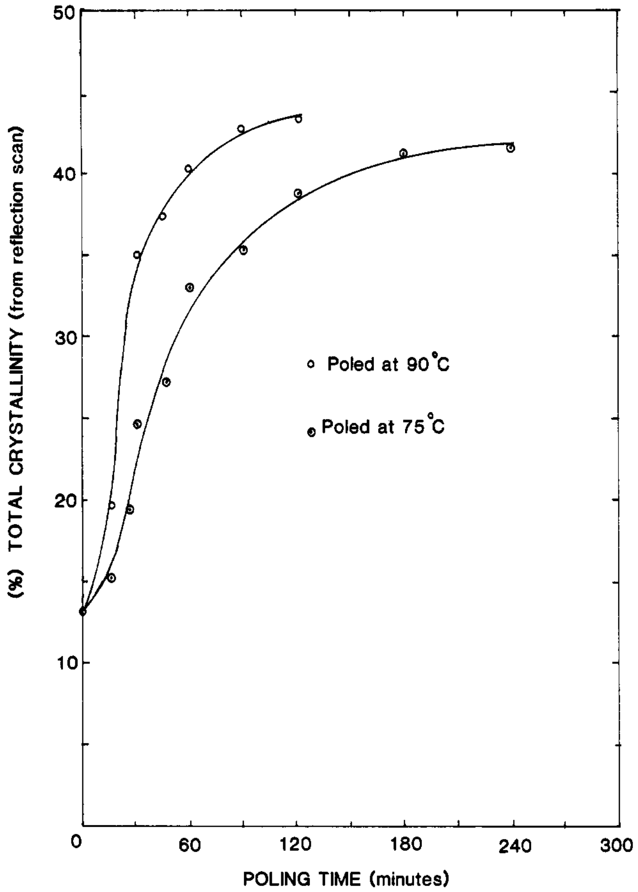

**Figure 8.** Measure of total crystallinity of poled films.

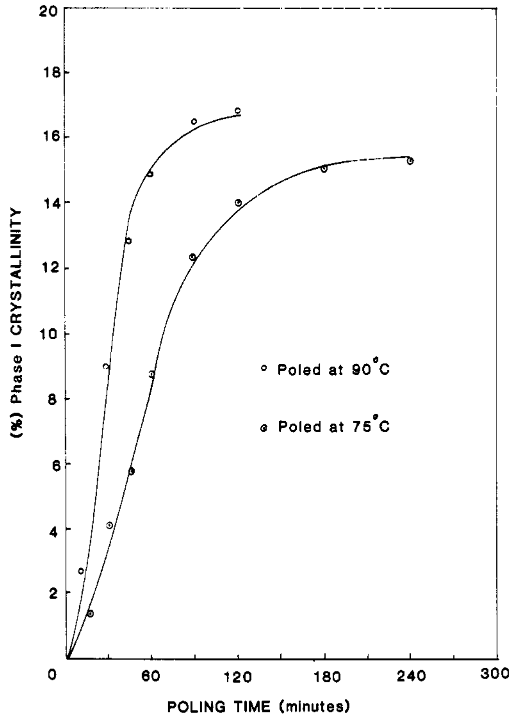

**Figure 9.** Measure of phase I crystallinity produced on poling.

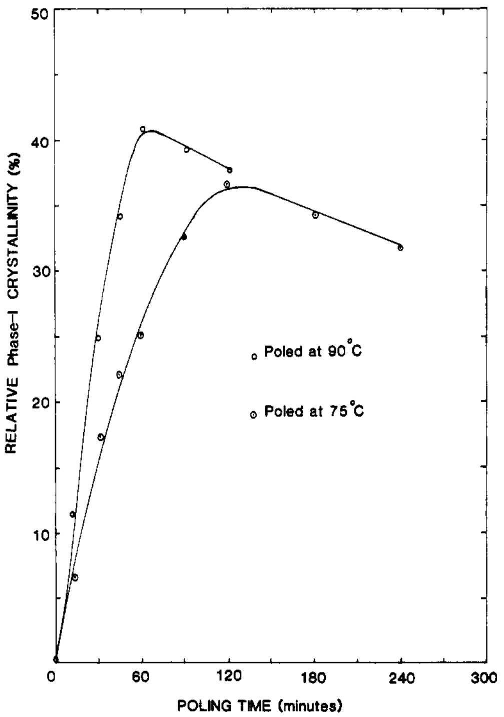

**Figure 10.** Measure of relative percent phase I crystallinity produced on poling.

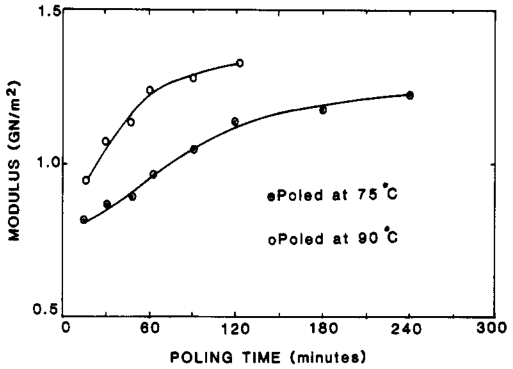

**Figure 11.** Modulus of the PVF$_2$ films poled at 75 and 90 °C.

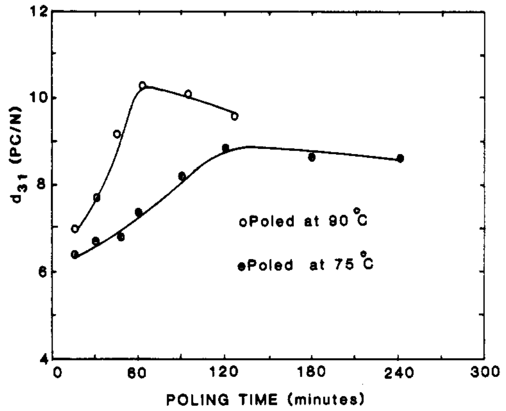

**Figure 12.** Piezoelectric strain constant for PVF$_2$ films poled at 75 and 90 °C.

I and II are being formed but that after some time the formation of the nonpolar phase II crystals predominates.

The moduli of the poled films (poled at 75 and 90 °C) are shown in Figure 11. As expected, the modulus increased with loss of plasticizer and increased crystallinity. The increase is of course more rapid for films poled at 90 °C compared to those poled at 75 °C. The modulus of a film poled at 90 °C (for 60 min) is 1.3 GN/m$^2$, whereas it is 0.9 GN/m$^2$ when poled at 75 °C for the same time. The poling time dependence of the piezoelectric strain constant ($d_{31}$), piezoelectric stress constant ($e_{31}$), and pyroelectric coefficient ($P_y$) is shown in Figures 12–14, respectively. The piezoelectric and pyroelectric response increased with increasing phase I content. At 90 °C, $d_{31}$, $e_{31}$, and $P_y$ reached their maximum values of $d_{31} \approx 10$ pC/N, $e_{31} = 9.8$ mC/m$^2$, and $P_y = 17$ $\mu$C m$^{-2}$ K$^{-1}$ at a 1-h poling time. At

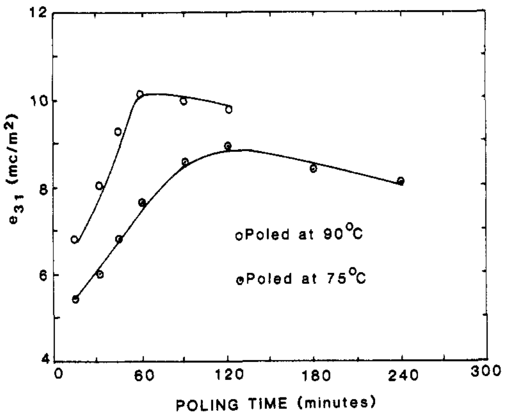

**Figure 13.** Piezoelectric stress constant for $PVF_2$ films poled at 75 and 90 °C.

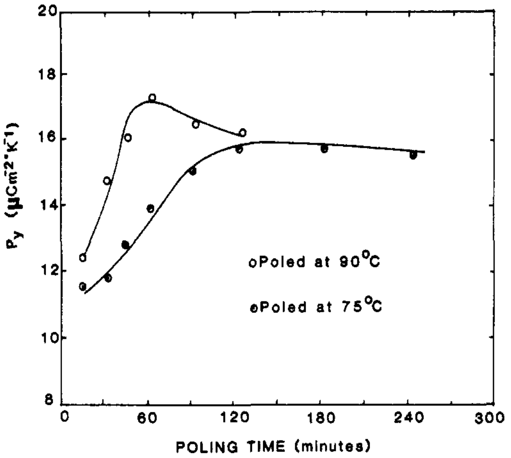

**Figure 14.** Pyroelectric coefficient for $PVF_2$ films poled at 75 and 90 °C.

75 °C, the maximum values of $d_{31}$ = 8.8 pC/N, $e_{31}$ = 8.6 mC/m², and $P_y$ = 15.8 μC m$^{-2}$ K$^{-1}$ were reached after a poling time of 2 h. The dielectric constants of the films poled at 75 and 90 °C are very close, ≈14.7, and decrease little with increasing poling time, as shown in Figure 15. The piezoelectric and pyroelectric coefficients follow the same trend as that of relative phase I crystallinity (see Figure 10), which indicates that the relative amount of polar phase present is directly related to the piezoelectric and pyroelectric response.[1,6] At longer poling times, the modulus increases, as shown in Figure 11, which accounts for the observed decrease in $d_{31}$. In addition, as the plasticizer content decreases and crystallinity increases, we might expect the increase in the modulus of the film to reduce the Poisson ratio and therefore the piezoelectric stress constant, $e_{31}$.[17,18] This would also produce a decrease in the coefficient of thermal expansion of the poled films and hence some decrease in the pyroelectric coefficient, as shown in Figure 14.

## Conclusions

In the present study, we observed that poling field induced crystallization of highly plasticized $PVF_2$ films (with low initial phase II crystallinity) results in the formation of highly oriented phase I crystals. At a poling field of 250 kV/cm, the amount of phase I formed increased with increasing poling temperature and initially with poling time. At a poling time of 1 h at 90 °C, a measure of relative phase I crystallinity indicates that approximately 45% of the crystalline material was in the phase I form. Since the phase I crystals are highly oriented, the actual amount of phase I is much less than 45%. At longer times, the relative percent of phase I decreased.

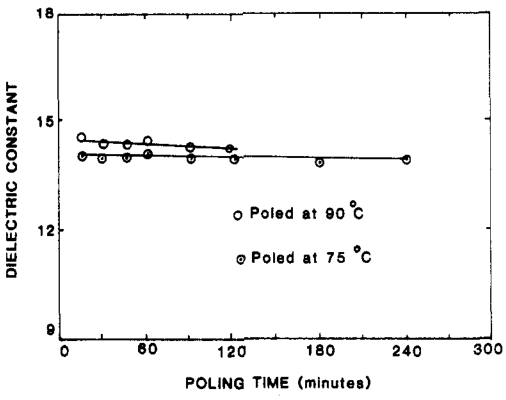

**Figure 15.** Dielectric constant for $PVF_2$ films poled at 75 and 90 °C.

This study has shown that the presence of a high electric field during crystallization of $PVF_2$ from solution can significantly bias the free energy of crystallization toward the formation of highly oriented, polar phase I crystals. However, as crystallinity increases with increasing poling time, this bias decreases and phase II crystallization predominates.

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**Registry No.** $PVF_2$, 24937-79-9; tricresyl phosphate, 1330-78-5.

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