Thermal Depolarization of PVDF
Anomaly at 180°C

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ABSTRACT
PVDF samples with high β content (80%), prepolarized at room temperature, are heated to higher temperatures. The preparation is measured first under open circuit conditions at the high temperature and then after cooling down again to room temperature. For elevated temperatures up to 175°C the polarization is reduced to 2% of the original value, yet recovers roughly to 8% of the original value after cooling down to room temperature. In contrast to this when heating the film to 180°C, a significantly different behavior is observed. In cooling down to room temperature again the polarization returns from ~1% at 180°C to ~40% of the original prepolarized value.

INTRODUCTION
Compared to other polymers, polyvinylidene fluoride (PVDF) shows high piezo- and pyroelectricity [1,2] which is caused by the formation of a remanent polarization in the crystallites of the polar β phase by applying electric fields exceeding 50 MV/m. This is theoretically described by the rotation of the polymer chains in steps of 60° caused by the pseudo hexagonal structure of the β crystallites [3–5]. The times which are necessary for dipole orientation in an external electric field calculated by the 60° model [6] agree well with the measured times [7]. Yet so far no prediction about the stability of the remanent polarization after switching off the electric field has been made. Instead it has been assumed that the polarization remains constant after removing the external electric field as consequence of the anisotropy of the crystal field and of the cooperative interaction of the dipoles [5,8]. More recent measurements indicated that the alignment of the dipoles in field direction and the stability of the remanent polarization have different time constants in pure PVDF [9] and in the P(VDF/TrFE) copolymer [10]. This implies that the 60° model has to be supplemented by mechanisms which describe the stability of the remanent polarization. Measurements with blocking electrodes showed that the polarization is only stabilized if charges are injected and trapped at the surface of the crystallites [11]. From this it has been conjectured that the stability of polarization in PVDF at room temperature is caused by the Coulomb interaction of the dipoles with these trapped charges. In order to investigate the binding energies of the charges we measured the temperature-dependent decay of the remanent polarization. This thermal depolarization is studied by measuring the polarization at the elevated temperature and also after cooling down to room temperature.

EXPERIMENTAL
Our samples were biaxial stretched, 38 µm thick PVDF films with high β content (80%). The samples were poled at room temperature at $E = 200$ MV/m for 5 s. After poling they were kept under short circuit conditions for several minutes. The remanent polarization at room temperature was measured with the piezoelectric induced pressure step (PPS) method [12,13]. Then the
temperature was increased and the polarization was measured again at high temperature. The PPS apparatus was placed into an oven. Immediately after measuring the remanent polarization at high temperature the door of the oven was opened and the sample was cooled down to room temperature. At room temperature the remanent polarization was measured for the third time, without removing the sample from the PPS apparatus. The surfaces of the sample were under dc high-resistance open circuit conditions during the measurements described above.

The pressure caused by the piston which presses the polymer film against the piezo crystal of the PPS apparatus prevents the samples from shrinking. Shrinking was expected because the polar $\beta$ phase which results from stretching is changed to the nonpolar $\alpha$ phase if the films are annealed to high temperature. Thus the thickness of the samples remains almost constant even until 180°C if they remain in the PPS apparatus during heating.

With increased heating temperature the polarization decreases slowly from 5.4 $\mu$C/cm$^2$ at 20°C to 4.3 $\mu$C/cm$^2$ at 70°C. The difference in polarization at high temperature and after cooling down to 20°C is small compared to the polarization reduction above 70°C. Between 120 and 170°C the absolute difference of these two values remains almost constant, whereas the high temperature polarization tends to zero at 180°C. The ratio of the polarization after cooling down to room temperature compared to the polarization at high temperatures increases from 1.05 at 80°C to 1.23 at 120°C and finally to 2.85 at 175°C.

When the temperature is increased to 180°C a significant change of the behavior is observed when the sample is cooled down to room temperature. The measured polarization at 180°C amounts to 0.07 $\mu$C/cm$^2$. This is $\sim 1\%$ of the prepolarized value. Yet if the sample is cooled down to room temperature again, the polarization unexpectedly increases to 2.1 $\mu$C/cm$^2$ which is $\sim 40\%$ of the prepolarized value. In contrast to this by cooling down from 175°C to room temperatures the polarization recovers from 0.14 to only 0.4 $\mu$C/cm$^2$. The anomalous increase of the polarization by cooling down from 180°C means that polarization which has almost disappeared before arises again. The ratio of the polarization after cooling down from 180°C to 20°C is 301. This is significantly larger than the ratio of 2.85 by cooling down from 175°C.

MEASUREMENTS

Figure 1 shows the results for a series of 16 samples heated to different temperatures up to 180°C. The rhombic points show the polarization of each sample after prepolarization. Selected were samples with a polarization of (5.4 ± 0.1) $\mu$C/cm$^2$ to eliminate sample fluctuations. The circles show the measured polarization at high temperatures and the stars the polarization of the same sample after cooling down to room temperature. At each temperature a new sample was used. The 'Remanent polarization' in Figure 1 corresponds to the maximum value of the polarization within the film thickness.

The anomaly described above was observed for several samples. The measurements described were made with PVDF films supplied in 1988 by Solvay Cie, (film A). Newer films with higher crystallinity supplied in 1990 by
If the same depolarization experiments are made under short circuit conditions, i.e. the sample surfaces are connected with a resistance of 3.3 kΩ, no different behavior to the high-resistance termination case is observed during heating and cooling from 180°C to room temperature. At samples from film B the polarization recovers from 0.34 μC/cm² at 180°C to 4.0 μC/cm² at 20°C. These experiments indicate that no macroscopic field is necessary for the recovery of the polarization during cooling.

**STRUCTURAL CHANGES**

If prepolared PVDF films are heated up in the temperature range from 40 to 180°C the remanent polarization decreases by thermal depolarization. If the films are cooled down to room temperature again before the heating temperature reaches 180°C, the difference of the remanent polarization at high temperature and at room temperature can be due to the higher thermal agitation of the crystallite dipoles which causes a lower dipole moment \( \rho_i \) in polarization direction and to the volume expansion \( dV \) at increasing temperature.

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dP = \frac{\sum \delta \rho_i}{V} - \frac{\sum \rho_i}{V^2} dV
\]

\( \delta \rho_i \) and \( dV \) are of opposite sign and we cannot decide which of both gives a greater contribution to \( dP \). \( dP/dT \) describes the pyroelectricity. For heating temperatures of 180°C an anomalous increase of the polarization is observed after cooling which cannot be explained by the pyro effect. The also observed change in film thickness and the electric breakdown of nonpolarized films under low voltage indicate that the melting point of the crystallites in the films is reached at \( \sim 180°C \). But at this temperature the polarization in prepolared films does not disappear completely. The charges which are trapped at the surface of the crystallites stabilize the polarization and increase the thermal stability of these crystallites. The melting temperature is increased and the crystallites do not melt at 180°C. Therefore in cooling crystallization nuclei are present with preference direction in which the crystallite dipoles are oriented when the films recrystallize. The recrystallization occurs apparently between 170 and 150°C [14], leading to the strong increase of the remanent polarization as observed in this temperature region.

To check this behavior we made X-ray diffraction measurements at poled and nonpolarized PVDF samples by heating and cooling. Figure (4) shows the result by heating nonpolarized PVDF to 150°C. At 20°C we can see two peaks, one at \( 2\theta = 21° \) which can be attributed to the reflection at the (110) and (200) planes of the \( \beta \) phase [15]. The second peak at \( 2\theta = 19° \) is caused by the diffraction at the (110) plane of the \( \alpha \) phase. The X-ray signal
Nonpoled PVDF films are melting between 179 and 180°C. In contrast to this, PVDF films which are poled at room temperature and heated up to 180°C are not melted completely at 180°C. They are still containing 1% of the remnant polarisation at room temperature. The crystallites of poled PVDF films are stabilized by trapped charges at the surface of the crystallites. In cooling down to room temperature again these crystallites are crystallisation nuclei with a preferential direction in which the chains are oriented. The remnant polarisation which was destroyed by heating raises again. Therefore an anomalous increase of the polarisation to about 40% of the prepolarised value can be observed after cooling poled PVDF films from 180 down to 20°C.

REFERENCES


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