# Anomal Recovery of the Remanent Polarization after Heating Polarized PVDF Films up to 180°C

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## 1 Introduction

It is well known that the remanent polarization in PVDF which causes the strong piezo- and pyroelectricity of this polymer is stable for some years at room temperature. To make the polarization in PVDF remanent two mechanisms are necessary:

- The crystallite dipoles are oriented under field strengths greater than 50MV/m in steps of 60° in the quasihexagonal lattice of $\beta$-phase PVDF [1].
- Coulomb traps are formed by the dipol orientation at the surface of the crystallites. Therefore charges which are injected into the polymer film during the poling process [2] are trapped at the surface of the crystallites [3]. The coulomb interaction of these real charges with the dipolar charges causes the strong stability of the remanent polarization.

This was experimentally checked by the fact that the dipol orientation under field and the remanent polarization have different time constants by poling new PVDF and P(VDF/TrFE) samples with short (< 100ms) HV pulses [4, 5] and that no remanent polarization arises by poling with blocking electrodes [6]. The trapped charges are ions for example $F^-$ and $H^+$ as indirectly shown by measuring the field induced gas emission of PVDF [7].
In this work we want to measure the temperature dependent stability of the remanent polarization. To distinguish between an irreversible and reversible polarization loss by heating up polarized PVDF films we measured the polarization at elevated temperatures and after cooling down to room temperature again. The reversible polarization loss causes the pyroelectricity of PVDF.

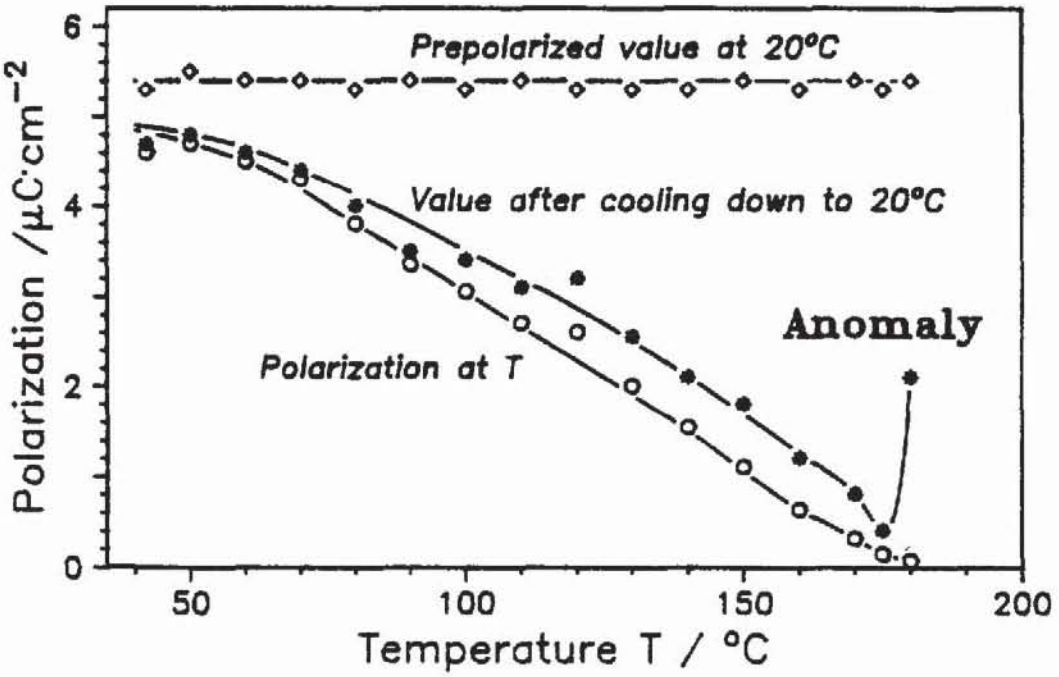


Figure 1: *Thermal depolarisation of PVDF. The ◇ represent the remanent polarization of each sample after poling at 20°C, the ○ the polarization at high and the ⋆ after cooling down to room temperature.*

## 2 Experimental

Biaxial stretched 38$\mu$m thick PVDF samples with about 80% $\beta$ content are poled at room temperature at E = 200MV/m for 5s. The remanent polarization was measured with the PPS methode [8] first at 20°C then after heating up to an elevated temperature and a third time after cooling down the sample to room temperature again. The piston electrode of the PPS apparatus prevents the sample from shrinking as otherwise observed in heating biaxial stretched polymer films.

## 3 Measurements

Figure 1 shows the result for 16 samples. The rhombic points show the remanent polarization after poling at 20°C, the cicles the polarization at high temperature and the stars the polarization after cooling down the samples to room temperature. For each temperature a new sample has been used. The difference of the polarization between high temperature and after cooling down to 20°C describes the reversible polarization loss, the difference between the prepolarized value and the polarization left after cooling down to 20°C describes the irreversible polarization

loss. Figure 1 shows that until 175°C the reversible polarisation loss is small compared to the irreversible loss. But by cooling from 180°C the polarization unexspectedly increases from $0.07\mu C/cm^2$ to $2.1\mu C/cm^2$ which is about 40% of the prepolarized value. In contrast to this by cooling from 175°C the polarization recovers only from $0.14\mu C/cm^2$ to $0.4\mu C/cm^2$. The temperature dependent measurements of the polarization by cooling polarized samples from 180°C showed a strong increase of the polarization between 170°C and 150°C and a slower increase until 20°C [9]. By cooling from 175°C the strong increase between 170°C and 150°C is missing [9].
If nonpoled films are heated up to 180°C and cooled down to 20°C no polarization arises. But in contrast to poled samples the nonpoled samples are deformed by the pressure of the piston of the PPS apparatus at temperatures exceeding 179°C. For example at 180°C the rubber electrode of the PPS apparatus is pressed through the melting nonpoled PVDF films in contrast to the poled material. Also an electrical breakdown occurs if a voltage is applied to nonpoled samples at temperatures higer than 179°C. By applying a voltage to nonpoled samples at 179°C and cooling down to 20°C remanent polarization rises again. But its value is with $0.8\mu C/cm^2$ at 300V distinctly smaller than the recovery by cooling polarized samples as described above.

## 4 Discussion

The recovery of the remanent polarization by cooling from temperatures until 175°C down to 20°C can be attributed to the pyroelectricity of PVDF. But by cooling from 180°C down to 20°C the anomalous recovery can not be described by the pyroelectricity alone. The strong deformation and the electrical breakdown of nonpoled films at 180°C indicate that the melting point of nonpoled samples is at about 180°C. But polarized films are not molten completely at 180°C because 1% of the prepolarized value of the polarization is still remanent. The trapped charges which stabilize the remanent polarization increase the thermal stability of the crystallites, too, and their melting temperature. Therefore in polarized samples some crystallites are still present at 180°C. These crystallites are crystallisation nuclei with a preference direction by cooling down polarized samples from 180°C to room temperature. The PVDF chains are oriented into this preference direction if the film recrystallizes. The strong increase of the polarization between 170°C and 150°C [9] indicate that PVDF recrystalizes in this temperature region.

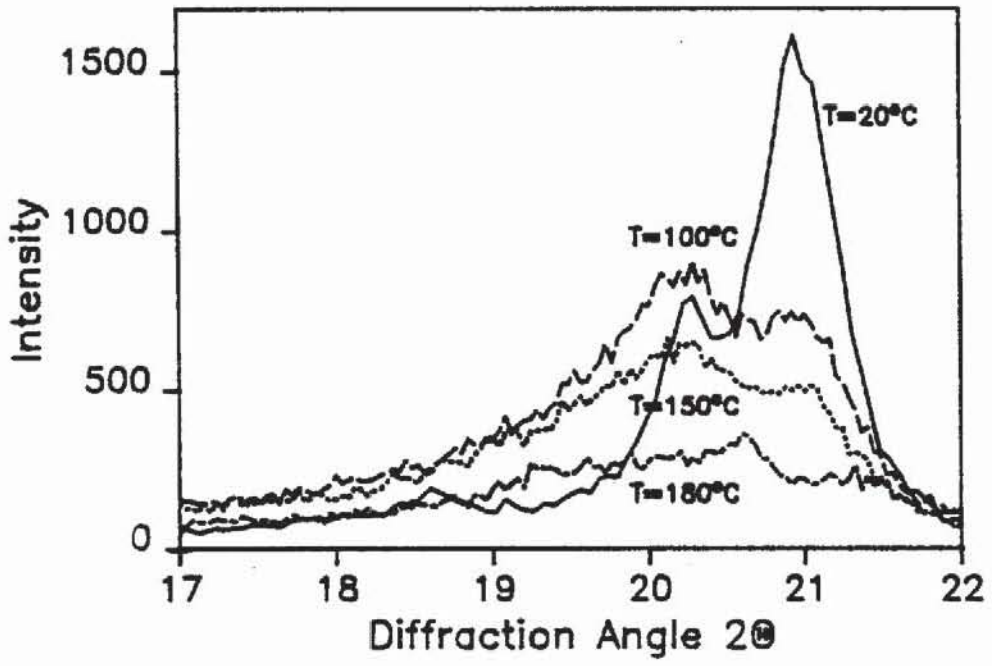


Figure 2: *X-ray diffraction at different temperatures by heating up a poled PVDF sample. The peak at angle* $2\Theta = 21$ *degrees is attributed to* $\beta$*-phase the peak at the angle* $2\Theta = 20$ *degrees to the* $\alpha$*-phase.*

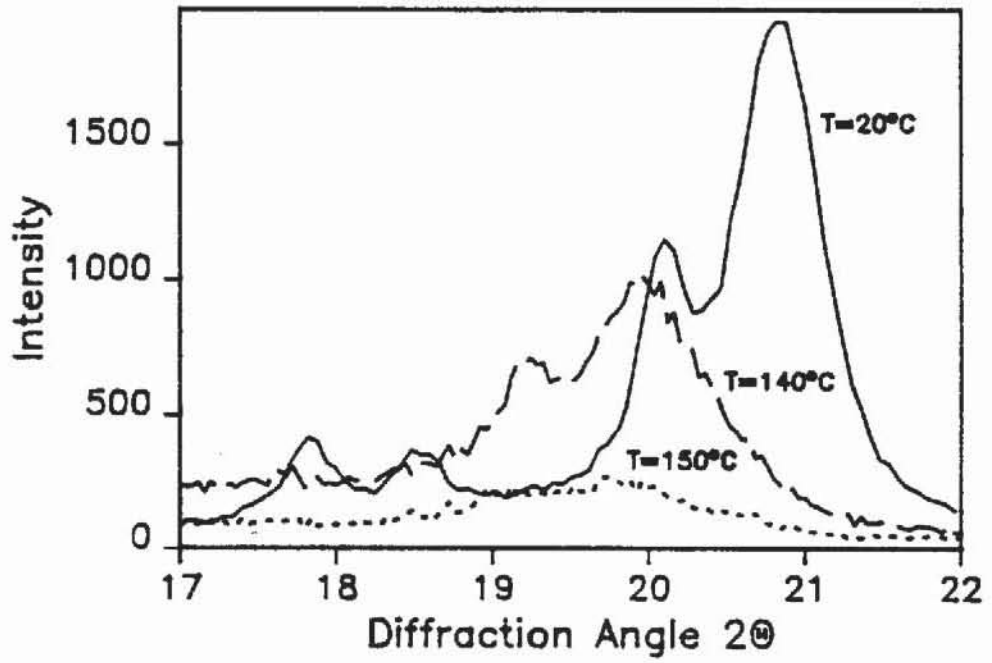


Figure 3: *X-ray diffraction at different temperatures by heating up a nonpoled PVDF sample.*

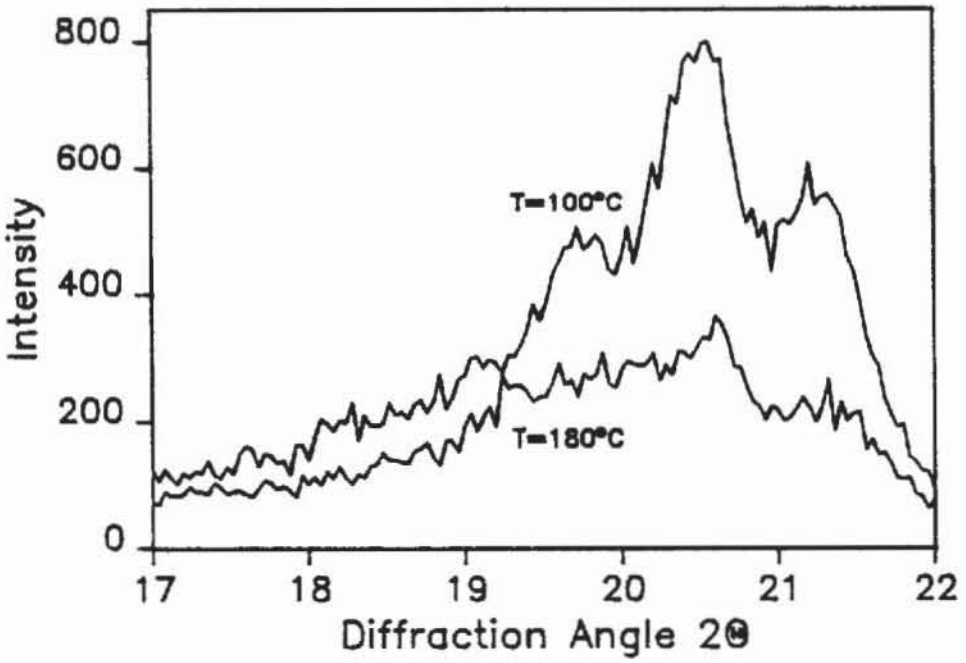


Figure 4: *X–ray diffraction at different temperatures by cooling down a poled PVDF sample.*

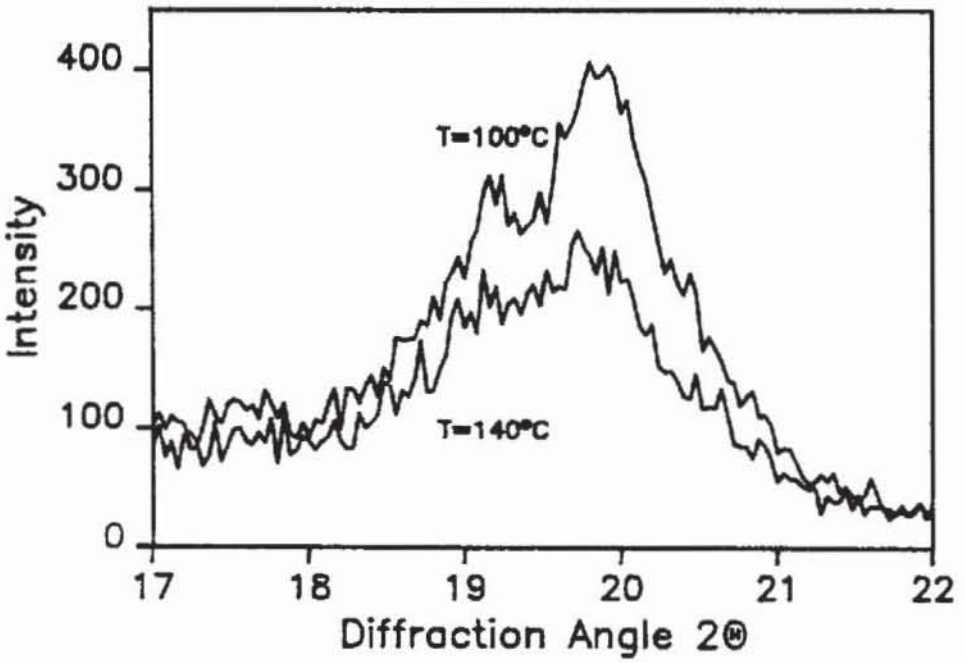


Figure 5: *X–ray diffraction at different temperatures by cooling down a nonpoled PVDF sample.*

We checked this with X–ray diffraction measurements at poled and nonpoled PVDF films during heating and cooling. Figure 2 shows the result by heating a poled PVDF sample up to 180°C and figure 3 for a nonpoled sample which was heated up to 150°C. At 20°C we can see two peaks. One at the angle $2\Theta = 21$ degree which is attributed to the (110) and (200) planes of the $\beta$–phase and one at the angle $2\Theta = 20$ degree which corresponds to (110) plane of the $\alpha$–phase [10]. In figure 2 we can see a structured diffraction signal of the poled film up to 180°C while for nonpoled films (figure 3) the diffraction signal vanishes at 150°C. In cooling down poled films (figure 4) almost the same diffraction intensity results as before. In contrast to this nonpoled films show reduced diffraction intensities (figure 5). The X–ray diffraction measurements confirm that poled PVDF films are melting at higher temperatures than nonpoled films.

# References


[1] R. G. Keppler, R. A. Anderson, J. Appl. Phys., Vol 49, pp. 1232–1235, 1978

[2] K. Holdik, W. Eisenmenger, Proc. 5th Int. IEEE Symp. Electrets, pp.553–558, Piscataway 1985

[3] W. Eisenmenger, M. Haardt, K. Holdik, IEEE 1990 Annual Conf. Elect. Insul. and Dielect. Phen., pp. 52–57, Piscataway 1982

[4] M. Womes, E. Bihler, E. Eisenmenger, IEEE Trans. on El. Insul., Vol. 24, pp.461–468, 1989

[5] G.Eberle, E. Bihler, W. Eisenmenger, IEEE Trans. Electr. Ins., Vol. 26, pp. 69–77, 1991

[6] E. Bihler, G. Neumann, G. Eberle, W. Eisenmenger, IEEE 1990 Annual Conf. Elect. Insul. and Dielect. Phen., pp140–145, Piscataway 1990

[7] M. Selle, G. Eberle, B. Gompf, W. Eisenmenger, "Field Induced Gas Emission of Polymers", this proceedings

[8] W. Eisenmenger, M. Haardt, Solid State Comm., Vol. 41, pp. 971–920, 1982

[9] G. Eberle, W. Eisenmenger, Proc. 7th Int. IEEE Symp. Electrets, pp. 477–482, Piscataway 1991

[10] G. T. Davies, J. E. McKinney, M. G. Broadhurst, S. C. Roth, J. Appl. Phys., Vol. 49, pp 4998–5002, 1978