# Dynamics of Polarization Growth and Polarization Reversal in PVDF Films

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## 1.Introduction

The risetime of the polarization response to electrical field steps in form I PVDF (high $\beta$-crystallite content) was investigated by several authors /1,2/. In these fast rise time switching experiments yet the amount of persistent polarization after field removal has not been determined. In this contribution we present measurements of the maximum displacement at the end of a rectangular high voltage pulse together with the remanent polarization after the pulse under short circuit condition as a function of the polarizing pulse end length. The pulse length varied from 10 $\mu$s to 100 s, the field strength ranged from 0.8 MV/cm to 2 MV/cm. The original samples were reversely polarized or unpolarized 12 $\mu$m thick films from Kureha Chem. Ltd containing 37% $\beta$-material /3/.

## 2. Experimental

Fig.1 shows the high voltage pulse generator. High voltage is applied to the sample by closing switch S1 and opening S2, shorting the sample is provided by reverse operation. The switches S1 and S2 consist of field-effect power transistors and are triggered by external pulse generators.

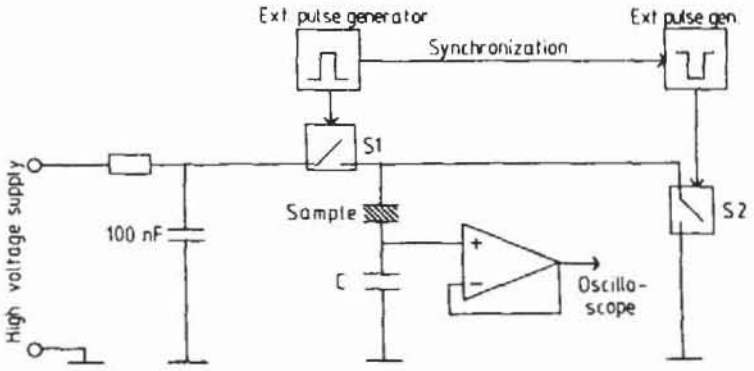


*Fig.1: Block diagram of the high voltage pulse generator used for polarizing the samples.*

The dielectric displacement D at the end of the field pulse is calculated from the charge on capacitor C. The remanent polarization P caused by the pulse is measured after several minutes under short circuit conditions with the PPS-method (piezoelectrically generated pressure step) /4,5/. The result of this measurement is called the remanent polarization P in the further context.

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3. Results

a) unpolarized films:

The dielectric displacement D and the remanent polarization P were measured for the electric field of 2 MV/cm as function of the pulse duration (fig.2).

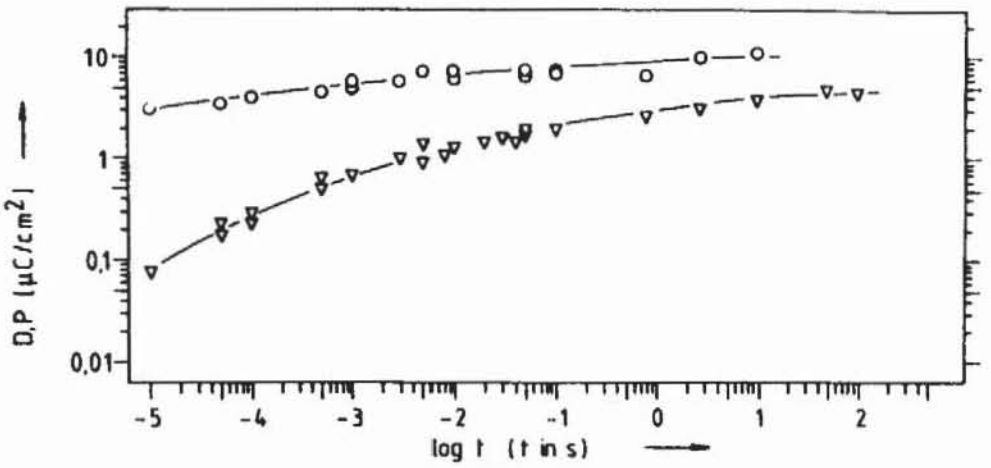


*Fig.2: Development of the displacement D (o) and the remanent polarization P ( ∇ ), unpolarized samples, E = 2MV/cm.*

The development of the remanent polarization is significantly delayed against the fast build up of the dielectric displacement under the applied electric field. This shows a comparison of the times after which half of the long time (10 s) values have been reached:

| | after 10 s | the half of this value is reached after |
|---|---|---|
| displacement D | 10 $\mu C/cm^2$ | 200 $\mu s$ |
| remanent polarization P | 4 $\mu C/cm^2$ | 100 ms |

Between 200 $\mu s$ and 10s the displacement doubles its value, while during the same time intervall the remanent polarization increases by a factor of 10.

A comparison of fig.2 with the results obtained under 1.2 MV/cm (fig.3) and 0.8 MV/cm (fig.4) shows, that the time delay of the beginning development of the remanent polarization depends critically on the field strength:

| field strength | development of the remanent polarization |
|---|---|
| 0.8 MV/cm | 1s |
| 1.2 MV/cm | 10 ms |
| 2.0 MV/cm | < 10 $\mu s$ |

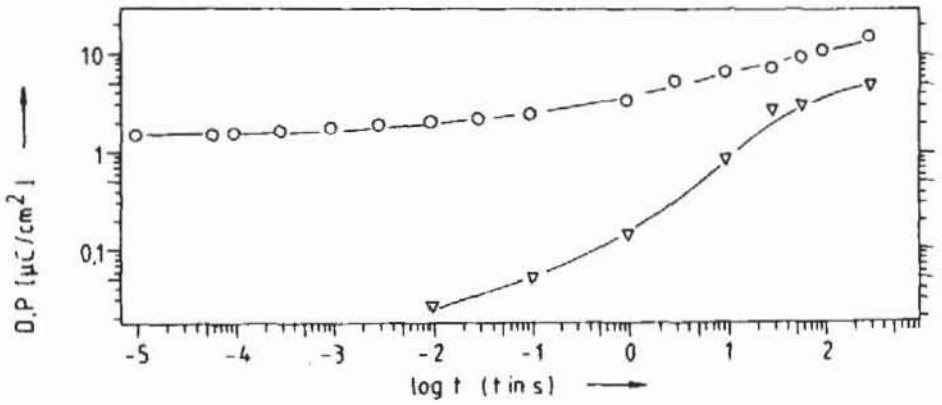


*Fig.3: Development of the displacement D (o) and the remanent polarization P ( ∇ ), unpolarized samples, E = 1.2 MV/cm.*

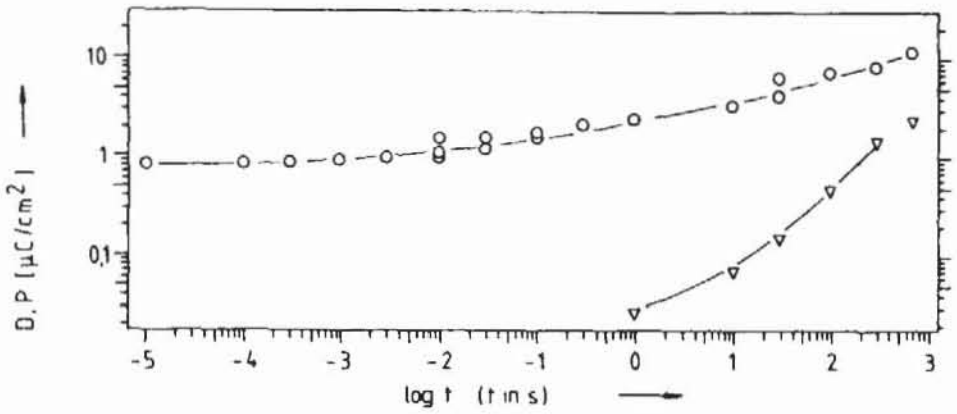


*Fig.4: Development of the displacement D (o) and the remanent polarization P ( ∇ ), unpolarized samples, E = 0.8 MV/cm.*

b) Polarized films:

The poling procedure was the same as Furukawa's and Johnson's /1/. The samples were polarized under 2 MV/cm for 100 s and then kept under short circuit conditions for another 100 s. After this procedure the samples had a remanent polarization of 4.8 $\mu C/cm^2$ ± 10%. Then a reversly directed field pulse of 2 MV/cm was applied and the displacement D and the remanent polarization P were measured as before. Fig.5 shows the result.

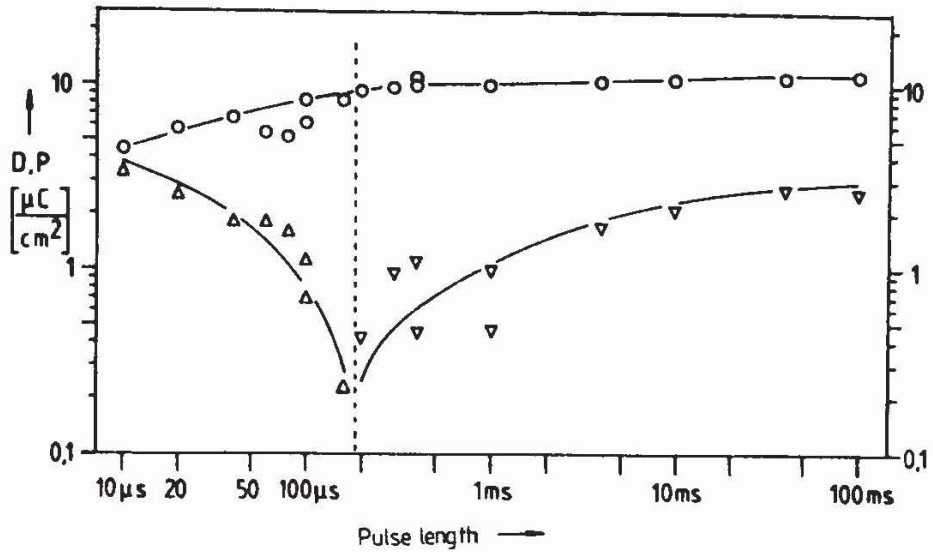


*Fig.5: Reversal of the remanent polarization in prepolarized samples, reversed field 2MV/cm, o: displacement D, Δ: remanent polarization, original direction, ∇: remanent polarization, reversed direction.*

After 200 μs the initially fast build up of the displacement is finished and is replaced by a slow ascent. This point marks the "switching time $t_S$" as defined by Furukawa /1/. We see that, with respect to the remanent polarization, this definition is not applicable, since at this time the remanent polarization first reduced to zero begins to change its sign. After 100 ms the polarization has reached only 60% of its initial value the opposite direction, a complete reversal takes more than 100 ms. After having changed its sign, the remanent polarization grows faster and reaches a higher value after 100 ms as compared to the unpolarized samples (cf.fig.2).

In comparison to Furukawa's and Johnson's results /1/ obtained with 7 μm thick films with possibly higher content of β-material, our samples show a somewhat different displacement increase. Under the same electrical field conditions in Furukawa's experiment the fast build up of the displacement is finished after 10 μs with no further increase following. In our experiment the corresponding times amount to 200 - 400 μs. At lower fields of 0.8 MV/cm...1.2 MV/cm, but after the same poling procedure, the times in our experiments necessary to change the sign of the remanent polarization became very long. So we were able to perform a time resolved poling experiment in the PPS-apparatus by connecting the sample with a high voltage source through an additional metallized PET-film /6/. The PPS-signals were recorded with a video system. Under a field of 1 MV/cm it takes 4.6 s for the apparent polarization to change its sign, but when we remove the field after 4.6 s, the polarization returns to its original direction and has still one third of its original value. Under fields of 0.8 MV/cm and 1MV/cm no complete reversal of the remanent polarization could be obtained after 40 and 15 minutes respectively. The development of the PPS-signal shows that under a field of 0.8 MV/cm no complete reversal of the remanent polarization is possible at all.

## 4. Discussion

The switching back of a large amount of the polarization after removal of the electric field and the significantly delay of the development of the remanent polarization compared to the displacement cannot be explained by a 6-site potential combined with cooperative behaviour alone, as suggested by Broadhurst and Davis /7/. The most simple explanation of our results gives a model of charge injection and trapping /4,8/. The number of deep traps is directly proportional to the polarization. The charges are trapped by dipole ends at the surfaces of the crystallites in PVDF.

In unpolarized films the dipoles become oriented under an external field, but switch back after removal of the field if not stabilized by trapped charges. This leads to a delay of the development of the remanent polarization (fig.2). The dynamics of the dipole orientation under field as well as the injection current depend on the field strength. This leads to a strong field dependence of the dynamics of the remanent polarization (fig.3,4).

In polarized films the dipoles align with the direction of the reversed electric field, but switch back after removal of the field, because trapped charges still stabilize the original direction. On the other hand the field induced chain rotation destroys the former trapping sites, the charges are able to move away and find new traps where they stabilize the reversed orientation. This leads to a slow and delayed reversal of the remanent polarization as compared to the faster displacement D (fig.5). The probability of field induced chain rotation and the mobility of the charges in the sample both depend on the field strength. Hence the times necessary to reverse the remanent polarization depend strongly on the field strength. This model also explains the faster development of the reversed remanent polarization in prepolarized films as compared to unpolarized films, since injected charges are already present in prepolarized films.

## 5. Conclusion

The cooperative model combined with a 6-site potential alone cannot explain the observed switching back of the remanent polarization, its delayed development, and the long times necessary for polarization reversal. The results are qualitatively consistent with a model of charge injection and charge trapping at polarized crystallites.

## 6. References

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