# CHARGE AND POLARIZATION DYNAMICS IN POLYMER FILMS

Karl HOLDIK and Wolfgang EISENMENGER
Physikalisches Institut, Universität Stuttgart
Pfaffenwaldring 57, D-7000 Stuttgart-80, Federal Republic of Germany

## 1. Introduction

Recently nondestructive methods have been developed which make it possible to investigate layered charge and dipolar distributions in dielectric materials within an order of $1\mu m$ resolution. These direct methods which do not use mathematical deconvolution techniques are the LIPP-[1] and the PPS-method [2]. The PPS-method operating with an almost ideal acoustic step excitation results in getting an 1:1-image of the longitudinal piezoelectric distribution within a thin film as demonstrated for PVDF by Haardt [3]. The results are consistent with charge compensated polarization layers within incompletely poled films. In order to obtain more informations on the possible reasons for these distributions we investigated the time dependence of the step response signal during poling. The nature of the compensation charges appears to be ionic as consistent with the pressure dependence of conductance.

## 2. Measuring method

Figure 1 shows the assembly of the used apparatus. A high voltage pulse of a cable discharge generator (length 100ns, rise time <300ps, amplitude 800V) induces steplike mechanical release waves in a piezolectric single crystal (X-cut quartz, $LiNbO_3$). These pressure steps are coupled into the polymer film under investigation by a thin (200nm) oil film. Charge displacement and polarization deformation result in a typical short circuit current in the probe loop. Because the risetime of the temporal signal is less or equal than 1ns we can achieve a spatial resolution of the dielectric distribution of about $2\mu m$ for organic polymers. The actual sensitivity of the method in real time is about $20nC/cm^2$ given by the pressure amplitude of $<10^5 Pa$ and the noise limit of the broadband amplifiers.

The short circuit current signal I(t) can be used to calculate [2] the absolute values of the polarization P(x) as follows:
$$I(t) = W \cdot K \cdot G \cdot P(x=ct)$$
W is the exitation constant:
$$W = c' \cdot d' \cdot u / l'$$
K is the acoustic coupling constant
$$K = 2 \cdot Z' / (Z + Z')$$
and G is a factor of the sample capacitor geometry
$$G = A / l$$
(c',d',l' are the sound velocity, the piezoelectric constant and the thickness of the generator crystal repectively; u is the electric exitation pulse amplitude; Z, Z' are acoustic impedances of sample and generator; A, l stand for electrode area and thickness of the sample).

In order to apply a variable electric poling field across the sample during poling it is necessary to decouple the sample circuit by the sandwichlike structure shown in Fig.1. A thin insolating film is inserted between the sample film and the conductive rubber electrode of the measuring circuit. This film carries a thin (100nm) circular metal electrode connected to a high voltage source. Dynamically this layer is a broadband coupling capacitor reducing the signal amplitude but with no in-

fluence on the signal shape. The repetition rate of the cable discharge generator is about 200Hz, so temporal changes of the polarization within a dielectric can principally be detected with a resolution of 5ms. The registration is performed by a real time oscilloscope (Tektronics 7104) and a video system coupled to it.
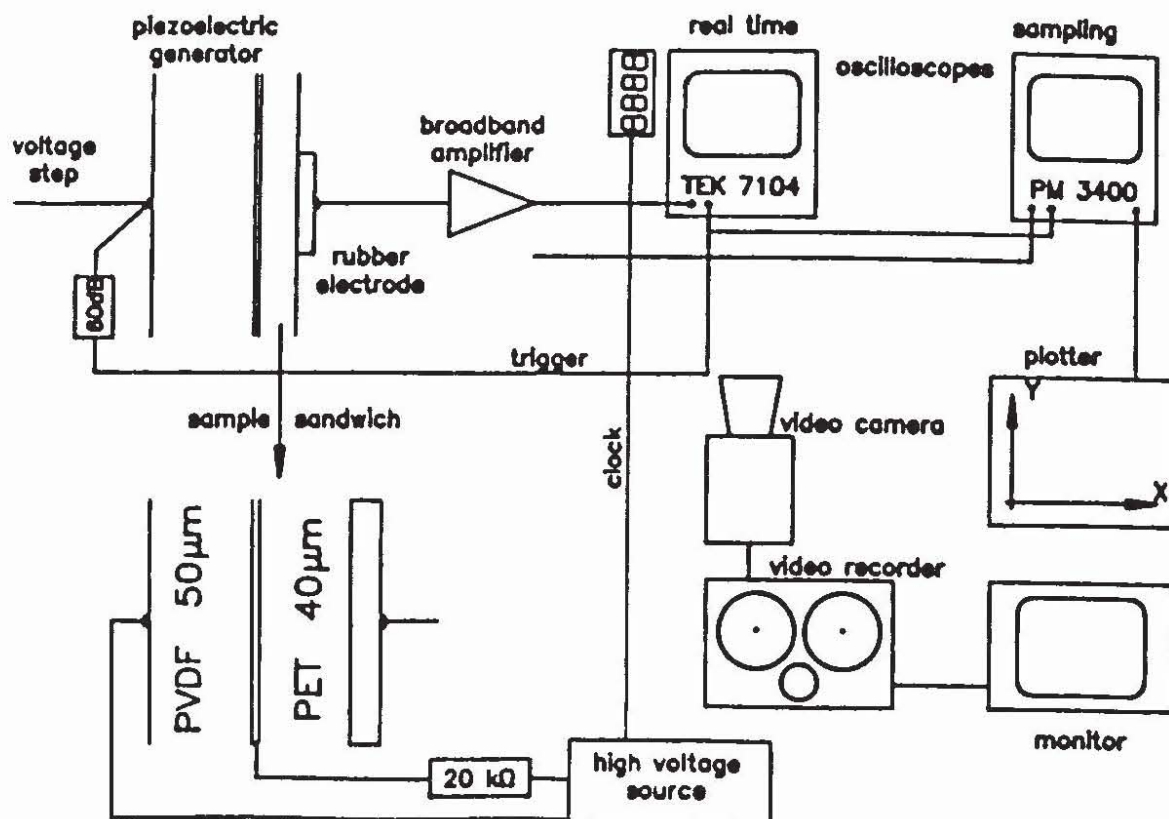


Fig.1: Schematic assembly of the "In-situ-PPS" apparatus.(The sampling oscilloscope is optional).

## 3. Sample material

We investigated buildup and decay of the polarization in films of polar polymers exhibiting a piezo- and pyroelectric effect like poly(vinylidene fluoride), PVDF, and the polyamides, PA-6: poly($\epsilon$-caprolactame) and PA-11: poly(undecaneaminoacid). The schematic chemical structure formulae of these materials are given in Fig.2. Morphologically these polymers are semicrystalline and the molecules are carrying permanent elementary dipoles.

PVDF shows two important molecular chain conformations: the strongly polar extended zigzag type-I and the weakly polar helical type-II. Mechanical pretreatment of PVDF films determines the proportion of the crystallites ($\beta$-form and $\alpha$-form respectively) of these coformeres. Electrical transformation of unpolar $\alpha$- into polar $\beta$-crystallites via a polar $\epsilon$-form is also reported [4].

PA-n of an odd number of carbon atoms in a monomer can in a way like PVDF become pizoelectric. Its pizoelectric constant, however, is about an order of magnitude lower. This might be due to the lower content of molecular dipols per unit volume [5]. Chains of even-n-PA in the all-trans conformation are not expected to exhibit a permanent macroscopic polarization because adjoining dipols point in opposite direction. PA-chains are coupled by hydrogen bonds. The conductivity (for temperatures exceeding the glass transition) is caused by protons [6].
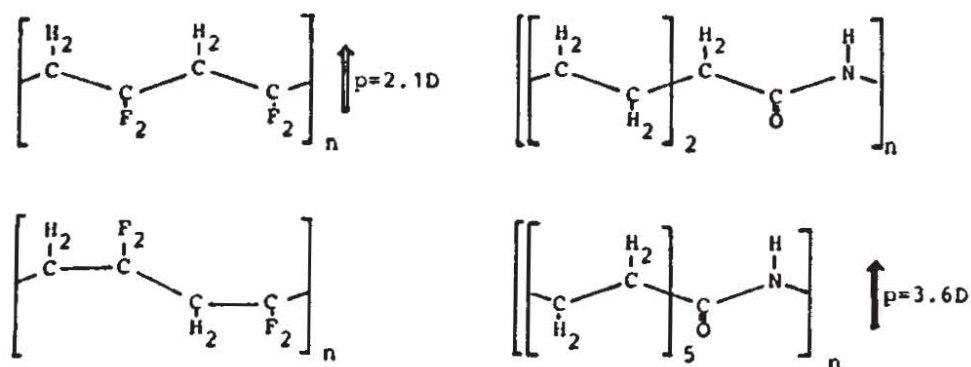
$p=2.1D$

$p=3.6D$

Fig.2: Simplified chemical structure representation of the investigated electret polymers. On the left PVDF in conformation of the β- and α-type; on the right the polyamides, PA-6 (top) and pa-11 (bottom).

## 4. Experimental results

We investigated the polymers at constant voltage, in the way that a steep electric field step of given heigth was applied to the samples and held for times between some seconds and several hours. The charged surfaces of the dielectric in the beginning of the polarization process (t = 0) result in a rectangular signal of the charge layer $\sigma = \epsilon\epsilon_0 E$; real charges are located in signal gradients $\rho \sim \nabla P$.

PVDF

Experiments were carried out on 50μm-films of different provenience. Field strength exceeding approximately 1.5MV/cm polarise oriented films instantly and entirely (Fig.3a). Applying lower field levels of a few 100kV/cm the temporal development of the signals indicate charge injection into the films. Thereby the local field strength is enhanced to a level so that orientation of dipols occurs which can be seen as an increase of the signals. Two typical shapes of signals are found. The first one is a symmetrical central form of polarization which we found in oriented films of Kureha KF (Fig 3b,c) and obviously caused by symmetrical charge injection from both electrodes. The other form is a very sharp anodic border polarization developing at room tempeature in isotropic material no matter what source (Fig.3d). This form of imperfect polarization was often reported to occur in thermal (>100 C) polarised films [7,8]. Here the evolution diagramms suggest rather additional migration of internal -already in the material contained- charges (charge seperation and extraction). The polarization in either case can concentrate within approximately 10 to 30% of the film thickness as a function of the applied voltage. The local maximum polarization depends upon the polarization time and the content of phase-I crystallites. Injected charge carriers forming an inner virtual electrode discussed above are also clearly revealed when shortening the sample. The excess charges are compensated by surface countercharge layers, which lead to a partially negative signal. This is shown experimentally and schematically in Fig. 4. Obviously this arrangement relaxes to equilibrium with a time constant of 100s which is closely to the Maxwell relaxation time $\tau = \rho\epsilon\epsilon_0$ of PVDF.

We conclude from our experiments that the polarization patterns are
not caused by mechanical or chemical inhomogeneities of the films.
The arguments are: 1)The shapes were locally and temporally reproducible in
a great amount of samples. 2)The pattern orientation depends on the field
direction, not on the sample direction. 3)This is also found upon field re-
versal (hysteresis experiments). 4)Form and location of the patterns are
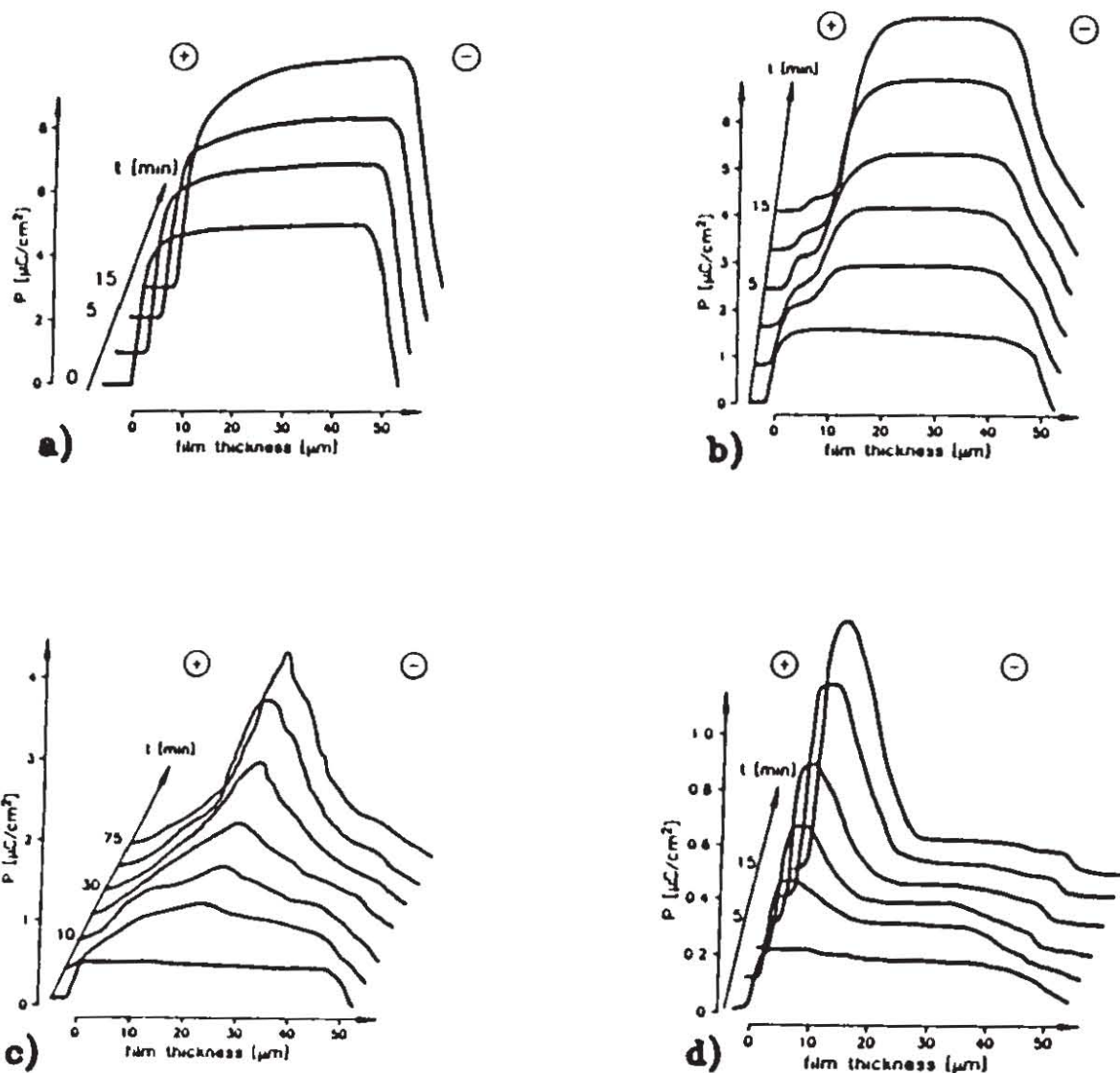readily influenced by electrolytes (acid or basic doping).



Fig.3: Polarization evolution in PVDF-films of 50μm thickness at different
electrical field strength: a) 1.6MV/cm, b) 0.8MV/cm, c) 0.4MV/cm,
d) 0.6MV/cm (different material).

The possible conduction mechanism involved was investigated by temperature
and pressure dependent I-V-measurements under constant current or voltage
conditions [9,10]. The charge transport in the studied material is ohmic
at low current densities and high temperature changing to space charge li-
mited at rising current or dropping temperature. It is connected with an
activation volume in the range of 25...100$A^3$, a typical value for an
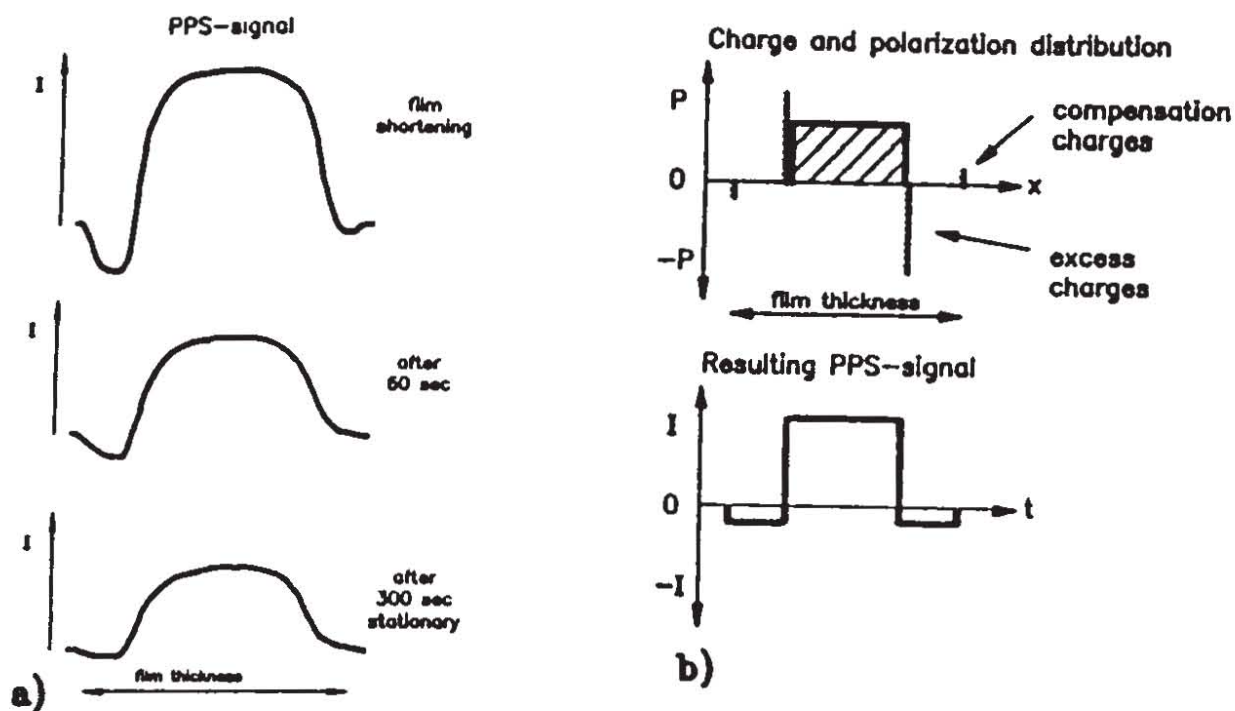ionic mechanism [11].

**Fig.4:** Polarization relaxation in PVDF: a)behaviour of sample Fig.3b) after shortening the external voltage, b)interpretating model of the cause by injected excess charges.
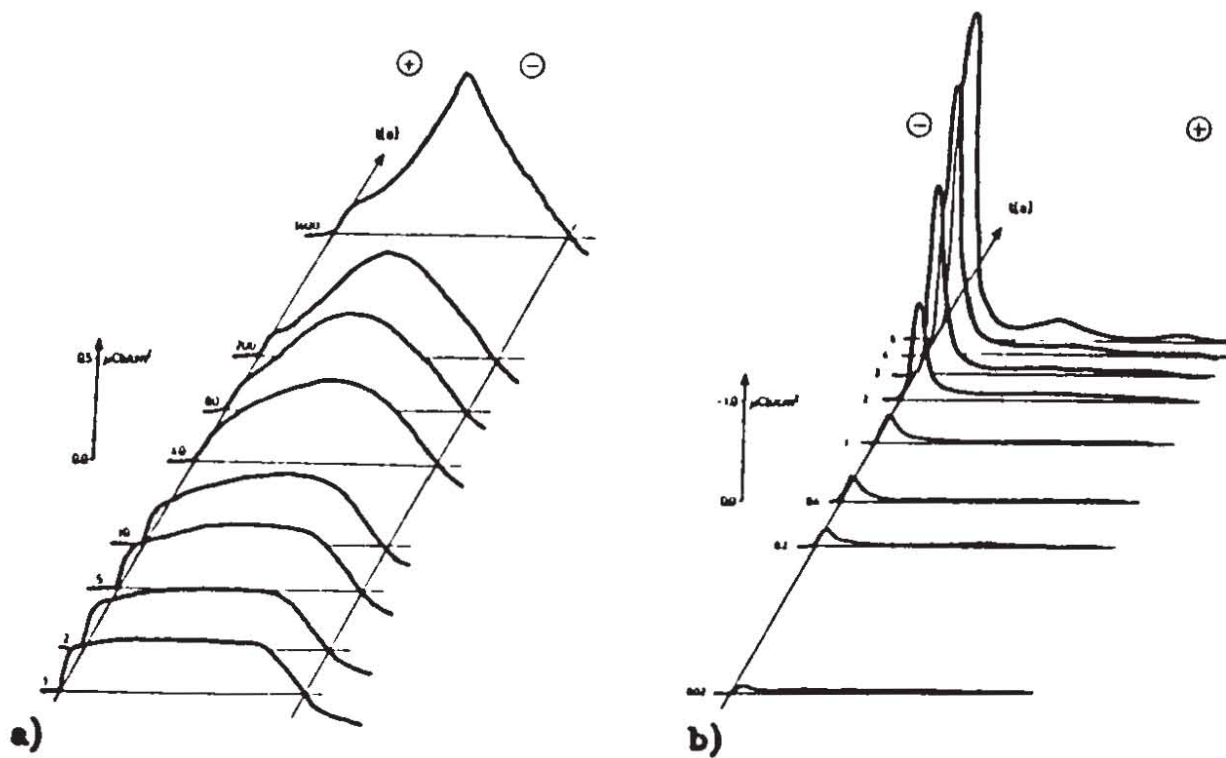


**Fig.5:** Polarization evolution in PA-6-films of 70μm thickness at 0.6MV/cm: a)vacuum-dryed film, b)damp film by saturated atmosphere moisture.

PA

Because Polyamide is a (partly) ion conducting piezoelectric and inhomogen-
ious piezoprofiles were also assumed [5], we looked for parallels in the
behaviour of the materials. High vacuum-dryed PA-6 exhibits a symmetric
central polarization like PVDF in Fig.3c with a factor 10 less in signal
amplitude. If the same material is stored in normal atmosphere, it will be-
come impure by a certain water content (1%) thus leeding to higher conduc-
tivity. The answer to the same applied field is a very rapid (seconds)
growing sharp polarization layer at the negative electrode [Fig.5].
In almost dry PA-11 during the first time a relatively homogenious polari-
zation is found, which tends to grow more near the positive electrode for
longer formation times. This behaviour resembles to PVDF .

## 5. Conclusions

The PPS-method has been shown to be a powerful instrument to reveal the
polarization evolution within a dielectric under a forming field. Because
the final polarization found in a material is not generally a monotonic
function of the formation time this can be used to control the polariza-
tion pattern by variation of external parameters during the process.
The reason for inhomogenious polarization patterns and thus the cause of
inhomogenious piezo- (and pyroelectric) reply of the examined dielectric
materials was found to be predominantly charge carrier transport.

## 6. Acknowledgement

## 7. References

[1] G.M.Sessler, J.E.West and R.Gerhard, Phys.Rev.Lett.**48**(8),563(1982)
[2] W.Eisenmenger and M.Haardt, Solid State Comm.**41**(12),917(1982)
[3] M.Haardt, PhD Thesis, Phys.Inst.YY281(1982), University of Stuttgart
[4] A.J.Lovinger in "Developments in Crystalline Polymers – 1",
                    D.C.Bassett, Ed., Applied Sciece Publishers, London 1982
[5] B.A.Newman, P.Chen, K.D.Pae and J.I.Scheinbeim, J.Appl.Phys,**51**(10),
[6] D.A.Seanor, J.Pol.Sci.A2,**6**,463(1968)                        5161(1980)
[7] H.Sussner und K.Dransfeld, Coll.Pol.Sci.**257**,591(1979)
[8] M.A.Marcus, Ferroelectrics **32**,149(1981)
[9] W.Burger, Diploma Thesis, Phys.Inst.Y1587(1982), Univ. of Stuttgart
[10]J.Kringler, Diploma Thesis, Phys.Inst.Y1677(1982), Univ. of Stuttgart
[11]S.Saito, H.Sasabe, T.Nakashima and K.Yada, J.Pol.Sci.A2,**6**,1297(1968)