

OBSERVATION OF CHARGE COMPENSATED POLARIZATION ZONES IN POLYVINYLIDENFLUORIDE (PVDF) FILMS BY PIEZOELECTRIC ACOUSTIC STEP-WAVE RESPONSE

W Eisenmenger and M Haardt

Physikalisches Institut der Universität Stuttgart, D 7000 Stuttgart 80, Pfaffenwaldring 57, Germany

(Received 27 September 1981 by M Cardona)

A high resolution (2 μm) acoustic step-wave probing techniques has been developed to investigate the inhomogeneous distribution of the piezoelectric response of incompletely corona poled 85 μm thick PVDF films. We observe persistent polarization zones or layers of 20-40 μm width within the films which are electrostatically compensated by charge accumulation at the polarization zone boundaries. The zone development is explained by charge-trapping in proportion to polarization.

POLYMERS with molecular chains carrying a transverse dipole moment as PVDF (polyvinylidenfluoride) are strongly piezoelectric and pyroelectric [1-11] after poling by corona discharge or by high electric fields. Whereas most experiments concerning the basic nature of piezoelectricity and pyroelectricity in this system indicate the importance of dipole orientation in crystallites of the polymer (cf [2]), there is a lack of knowledge with respect to the detailed nature of the polarization process, especially since inhomogeneous polarization distributions [10, 11] by incomplete poling have been observed.

In this communication we report the observation of charge compensated finite width polarization zones within film generated during incomplete poling. This gives evidence for the coupling of charge-injection, -transport and -accumulation to dipole orientation in the poling process [12] of PVDF.

For the experimental analysis of inhomogeneous charge, polarization or piezoelectric distributions in dielectric films, an acoustic pressure or velocity step (AVS) method, as first described by Laurenceau *et al* [16], has been applied. We achieved resolution improvement of two orders of magnitude by generating the pressure or velocity step function, instead of using a shock tube [16], by the transient response of a piezoelectric crystal [17] (e.g. X-quartz) to a short risetime voltage pulse. The PVDF-film is directly coupled to the generating crystal by a thin silicon oil film ($d < 2000 \text{ \AA}$). As depicted in Fig 1, rectangular electrical pulses are applied to the X-quartz crystal (diameter = 25 mm, thickness = 3 mm). With the detector electrode coupled to a B & H, Model AC 3011 low noise wide band pre-amplifier, the signal is either displayed on a Tektronix 7104 scope or x-y recorded, using a Philips PM 3400 sampling scope.

By the piezoelectric transient response [17] of the

quartz disk, rectangular acoustic pulses propagate from both surfaces into the crystal and are transmitted into the PVDF sample. The particle velocity in the transmitted wave for the pulse starting from the sound soft crystal backside according to acoustic transient response and boundary conditions is given by, cf [17],

$$v = \frac{2Z_1}{Z_1 + Z_2} k \sqrt{\left(\frac{\epsilon_0 \epsilon_1}{\rho_1}\right)} \frac{V}{d} \quad (1)$$

v is the step-wave particle velocity in the film, Z_1 and Z_2 are the acoustic longitudinal wave impedance in quartz and in the film, respectively, k , ϵ_1 , ρ_1 and d are the piezoelectric coupling constant for longitudinal waves, high frequency dielectric constant, density and thickness of the X-quartz plate, respectively, ϵ_0 is the vacuum dielectric constant and V is the pulse voltage amplitude.

The calibration of the piezoelectric response according to equations (1) and (2), see below, by using a thin X-quartz crystal ($d = 0.19 \text{ mm}$) instead of the PVDF film, cf Fig 1 (insert), reveals a rectangular response signal (risetime = 1 ns) within 5% of the calculated signal amplitude. For a film sound velocity [18] of $(2.2 \pm 0.07) \times 10^5 \text{ cm sec}^{-1}$, the overall risetime of 1 nsec corresponds to 2 μm resolution of the electrical active film structures. These can be layered distributions of polarization, space charge or intrinsic piezoelectricity which are revealed by single or multiple signal current maxima, cf Figs 2 and 3, during step wave propagation in the film. The detailed analysis [19] of the corresponding total signal results in the following relation

$$I_s(t) = \frac{A}{l} v \left| (1 + \gamma) \left\{ \sigma_1 + \int_0^{x_s} \rho(x) dx \right\} - e(x_s) - \gamma P_0(x_s) \right| \quad (2)$$

with $I_s(t)$ = short circuit signal current, cf Fig 1,

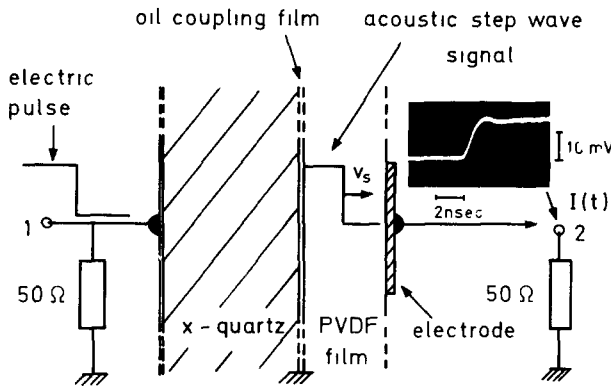


Fig 1 Schematic representation of the experimental technique (1) Connection to voltage pulse generator, 400 V, 150 psec risetime, 100 nsec pulse duration, 100 Hz repetition rate (2) Connection to wide-band preamplifier and oscilloscope Insert current response signal $I_s(t)$ of a 0.19 thick x -quartz plate, effective electrode diameter 4.6 mm, pre-amplification factor = 10

$x_s = v_s t$ step from position after propagation time t , A = sample area, l = sample thickness, v = velocity amplitude in the step-wave, v_s = step propagation velocity, $\gamma = -(1/\xi)(\partial\epsilon/\partial s)$ relative electrostriction coefficient

$$\sigma_1 = \frac{1}{l} \int_0^l P_0(x) dx - \int_0^l \left(1 - \frac{x}{l}\right) \rho(x) dx$$

static counter charge per area on the grounding electrode of the sample under short circuit condition, $\rho(x)$ space-charge density in the sample volume coupled to the particle velocity of the step wave, $e(x_s)$ = intrinsic piezoelectric constant, $P_0(x_s)$ = persistent polarization in the unstrained film Note Changes of oriented elementary dipole moments by strain (direct contribution to be considered small for PVDF [2]) or by local strain induced electrostriction [2] are contained in $e(x_s)$, whereas the elementary dipole moments of $p_0(x)$ by definition do not change under strain In deriving equation (2), Maxwell's equation, and the strain $s = -v/v_s$ in the step wave have been used

Since in our experiments σ_1 in general turns out to be zero, we discuss the situation of complete field neutralization by the condition $\rho(x) = \partial P_0(x)/\partial x$, i.e. the space charge distribution is in electrostatic equilibrium with the persistent polarization In this case equation (2), even with finite electrostriction γ , reduces to

$$I_s(t) = \frac{A}{l} v |P_0(x_s) - e(x_s)|, \tag{3}$$

where $P_0(x_s)$ can be replaced by $\int_0^{x_s} \rho(x) dx$, since $I_s(t)$ is due to the movement of charges and not to the movement of elementary dipoles with constant dipole moment

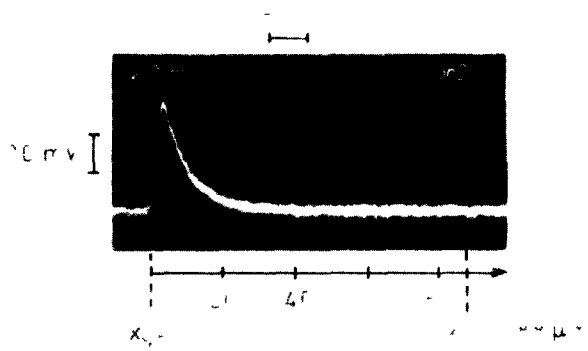


Fig 2 Acoustic step response signal $I_s(t)$ of a thermally poled 88 μ m thick PVDF film with high content of α -form crystallites, poling conditions Voltage 18 kV, time 1 hr, temperature 120°C, evaporated Al-electrodes Pre-amplification factor = 83, effective electrode diameter = 5 mm x_s = step position in the PVDF film The step wave enters the positive poled side of the film, $x_s = 0$, with positive particle velocity in propagation direction

Our measurements of $I_s(t)$ show the following results For a thermally poled film (thickness 88 μ m) we observe (Fig 2) a positive $I_s(t)$ signal at the plus-polarity-poling electrode with the sharp onset corresponding to the instrumental resolution of 2 μ m The signal decays to the zero baseline indicating the absence of polarization and space charges in the sample volume towards the negative poling electrode in agreement with the results of Phelan *et al* [10] and Sussner and Dransfeld [11] for incomplete poling

For films (thickness 85 μ m) incompletely poled at room temperature by a positive 18 kV corona point discharge, the $I_s(t)$ signals for different poling times are shown in Figs 3(a-d) These results reveal for the first time polarization zones or layers completely confined to the film interior without signal contributions at the film boundaries The single zones in Figs 3(a-c) show the same halfwidth of approx 30 μ m and increase in amplitude roughly linear with poling time until a maximum is reached after about 20 sec For longer poling times the amplitude of the single zone decreases to zero, followed by the development of double zone structures, as shown in Fig 3(d)

The absence of signal contributions, Figs 3(a-d), at the film boundaries indicates zero charge density $\sigma_1 = 0$ on the grounding electrode (as also $\sigma_2 = 0$, charge density on the detecting electrode) and consequently complete field neutralization [22] by compensating space charge accumulation at the polarization zone boundaries, as consistent with the finite electrical conductance in PVDF (dielectric relaxation time [1] 10^2 sec) From this follows that the signal current is described by equation (3) By corresponding

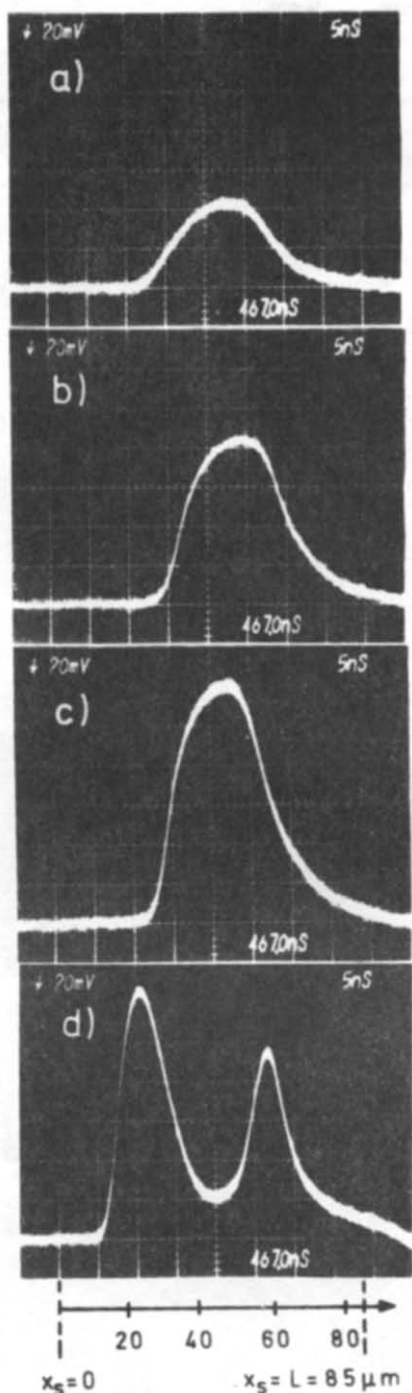


Fig 3 Acoustic step response signal $I_s(t)$ of plus corona point discharge poled PVDF films with high content of α -form crystallites for different poling times. Poling condition Voltage plus 18 kV, point electrode distance 1.3 cm, films in contact with grounded copper electrode, no evaporated electrodes, room temperature. Poling times (a) 7 sec, (b) 13 sec, (c) 17 sec, (d) 4 min. The step wave enters the positive poled side of the film, $x_s = 0$, with positive particle velocity in propagation direction. Pre-amplification factor = 83, effective electrode diameter = 5 mm. The $x_s = 0$ and $x_s = l$ positions were determined by delay time calibration.

quantitative evaluation of our measurement we obtain maximum [21] persistent $P_0(x)$ values of $8 \mu\text{C cm}^{-2}$ comparable with literature data [2] and with the estimated value of $10 \mu\text{C cm}^{-2}$, based on our poling conditions injection current density $1 \mu\text{A cm}^{-2}$, poling time 20 sec, and persistent (zero field-remnant) polarization amounting to approx 50% of the total polarization at maximum field.

From this follows that the roughly time-proportional polarization zone development, Figs 3(a–c), can be described as a charging process of an intrinsic capacitive layer with reduced conductance. The decrease of conductance must be directly caused by polarization, since the unpolarized material appears to be homogeneous. Corresponding to this model, we solved the non-linear differential equation of charge-injection, -transport and -polarization with charge trapping [15] in proportion to polarization, obtaining internal polarization [23] in agreement with our observations. Polarization-proportional trapping, therefore, provides the necessary feedback mechanism causing internal field enhancement by reducing the effective charge mobility, i.e. the conductance decrease of an internal zone. Our calculation shows that the width of the polarization free boundary zone increases with the logarithm of the ratio of charge mobility and injection current density, indicating also the conditions for homogeneous poling. Microscopically, charge trapping in proportion to polarization may be due to trapping at oriented dipoles at the crystallite surface [23].

In explaining the transition from a single zone [Figs 3(a–c)] to a double zone [Fig 3(d)], we expect that after reaching the saturation polarization of the crystallites, a further field increase leads to charge detrapping by the Poole-Frenkel [24] effect. With “soft” intrinsic ferroelectricity [25, 26] of the crystallites, charge detrapping causes the decay of polarization in the first zone [Fig 3(c)] by “discharge”, which is consistent with our observations. The detrapped charges, together with the charges injected from the film surface, then initiate the development of the double zone structure [Fig 3(d)] by the same mechanisms, discussed with respect to the development of the first polarization zone. We believe that the strongly asymmetric polarization in Fig 2 can also be described [27] by our model.

Since our observation of internal polarization zones is consistent with charge injection and polarization-proportional charge trapping, we believe that this mechanism is also responsible for the high electrical and thermal stability [25] of polarization in PVDF or other polar polymers.

The AVS-technique appears also useful for investigations of polarization and charge distributions in real charge electrets [28] and possibly for charge

distributions at metal-insulator or metal-semiconductor interfaces [29]

Acknowledgements – The authors gratefully acknowledge helpful discussions with H-J Bauer, S Dottinger, K Dransfeld, R Gerhard, N Karl, K Lassmann, H Kreuzinger, G M Sessler, M Sussner and M Walter. We wish to thank Mrs G Mayerhoffer for technical assistance. Financial support for this work was granted by the Deutsche Forschungsgemeinschaft. The PVDF samples were kindly provided by K Dransfeld and H Sussner.

REFERENCES

- 1 For a general review see *Electrics* (Edited by G M Sessler) *Topics in Applied Physics*, Vol 33 Springer Verlag, Berlin (1980)
- 2 M G Broadhurst *et al*, *J Appl Phys* **49**, 4992 (1978)
- 3 T Furukawa *et al*, *J Appl Phys* **51**, 1135 (1980)
- 4 M Date *et al*, *J Appl Phys* **51**, 3830 (1980)
- 5 D K Das-Gupta & K Doughty, *J Phys D Appl Phys* **13**, 95 (1980)
- 6 J E McKinney *et al*, *J Appl Phys* **51**, 1676 (1980)
- 7 B A Newman *et al*, *J Appl Phys* **50**, 6095 (1979)
- 8 D K Das-Gupta & K Doughty, *J Appl Phys* **51**, 1733 (1980)
- 9 D Naegelé & D Y Yoon, *Appl Phys Lett* **33**, 132 (1978)
- 10 R J Phelan *et al*, *Ferroelectrics* **7**, 375 (1974), The authors, in addition, observed complete poling of 6 μm thick PVDF films. We also observed in long-time-corona poling complete polarization of 50 μm films, in agreement with other Laboratories' results
- 11 H Sussner & K Dransfeld, *J Polymer Sci Polymer Physics Ed*, Vol 16, 529–543 (1978)
- 12 The possible influence of charge injection, charge compensation and countercharges have been discussed by several authors, [1, 2, 4, 6, 8, 11, 13–15]
- 13 G Pfister *et al*, *J Appl Phys* **44**, 2064 (1973)
- 14 N Murayama *et al*, *J Polymer Sci Polymer Physics Ed*, Vol 13, 1033–1017 (1975), Vol 14, 989–1003 (1976)
- 15 N Murayama *J Polymer Sci Polymer Physics Ed*, Vol 13, 929–916 (1975)
- 16 P Laurenceau *et al*, *Phys Rev Lett* **38**, 46 (1977)
- 17 W Eisenmenger, *Acustica* **12**, 165 (1962)
- 18 This value of v_s results from our $I_s(t)$ measurements with a 25 μm homogeneously poled film, and with inhomogeneously poled 85 μm films, using the sound soft reflection signals from the sample rear-side for evaluation.
- 19 W Eisenmenger, To be published (1981), similar results including also electrostriction, yet restricted to space charges and fields, were published by Laurenceau *et al* [16] and Migliori and Thompson [20]
- 20 A Migliori & J D Thompson, *J Appl Phys* **51**, 479 (1980)
- 21 In this evaluation $e(x_s)$, contributing [2] roughly 30% of the signal, has been neglected
- 22 Figure 3(d) can be alternatively described by *non-equilibrium* charge accumulation in the *unpolarized* regions between the edges of the unchanged polarization zone of Fig 3(c) and the film surfaces. This yet results in internal fields of 1 MV cm^{-1} , which is in contradiction to, the finite conductance in PVDF, the signal stability in Fig 3(d) observed over several months, and the time development from Fig 3(c) to Fig 3(d)
- 23 W Eisenmenger, To be published (1981)
- 24 Cf Ref [1] and K C Kao & W Hwang, *Electrical Transport in Solids* Pergamon Press, New York (1981)
- 25 M G Broadhurst & G T Davis in [1] The cooperative *2-site* model of these authors, explaining the high coercive field strength, implicitly rests on stability against cooperative dipole rotation. The "hard" ferroelectric behavior experimentally observed, cf [3] and [26], therefore may be due to charge trapping at oriented surface dipole ends of the crystallites providing orientation stability, even for non-ferroelectric crystallites
- 26 P Herchenroder *et al*, *Phys Rev Lett* **45**, 2135 (1980)
- 27 This distribution, obtained by low poling voltage at elevated temperature, indicates that positive charges are either not injected or have a strongly reduced mobility. Further results to be published
- 28 First successful experiments were performed together with G M Sessler and R Gerhard (1981), unpublished
- 29 Suggested by K Dransfeld (1981)