

# Polarization Distributions in Isotropic, Stretched or Annealed PVDF Films

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## ABSTRACT

The time development of the polarization distribution across the film thickness in Polyvinylidene Fluoride (PVDF) was observed using the pressure step response technique. The crystallite phase composition of the samples was changed by annealing and stretching at elevated temperatures. It is shown that the crystallite phase composition, *e.g.* the  $\beta$  crystallite content, determines the spatial distribution of the permanent polarization in PVDF.

## INTRODUCTION

POLYVINYLIDENEFLUORIDE (PVDF) is a semi-crystalline polymer, of which the crystallinity varies in a typical range of 40 to 60%. Three crystal phases are important:

1. The  $\alpha$  phase is not polar and thermodynamically is the most stable. Samples which are extruded and cooled from the melt mainly contain  $\alpha$  crystallites.
2. The  $\beta$  phase is polar and exhibits a spontaneous polarization of  $22 \mu\text{C}/\text{cm}^2$ . This crystal phase is responsible for the high piezoelectric activity of the PVDF films. Phase transitions from the  $\alpha$  to the  $\beta$  phase are obtained by stretching the films or subjecting them to high electric fields ( $> 3.5 \text{ MV}/\text{cm}$ ).
3. The  $\delta$  phase is obtained from the  $\alpha$  phase by applying an electric field  $> 1.2 \text{ MV}/\text{cm}$ . It is polar and exhibits a polarization of  $12 \mu\text{C}/\text{cm}^2$ .

The spatial distribution of the piezoelectric coefficient in polarized PVDF has been investigated by several authors using different methods [1-6]. In addition, also the time development of the polarization distribution in PVDF under external electric fields was studied for a variety of commercially available PVDF films from

different suppliers using the piezoelectric pressure step (PPS) technique [7,13]. For lower field strengths ranging from 0.5 to 1 MV/cm, samples from different suppliers developed either (1) a central polarization zone with no piezoeffect in the boundary regions close to the film surface or (2) a polarization maximum close to the positive charging electrode (anode) without polarization from the approximate center of the film to the negative electrode. Since sample inhomogeneities can be excluded, the development of polarization zones are to be explained by charge injection and trapping [3,9]. In principle, the different behavior (1) and (2) must be attributed either to possible differences in the general chemical composition of the films of different suppliers, or to differences in the morphology of the samples. So far it was found [7,13] that the central polarization zone (1) appeared in films with a finite content of  $\beta$ -form crystallites, whereas the polarization maximum at the positive electrode (2) appeared for pure  $\alpha$  material. In order to check the possible influence of the crystallite structure independently from the chemical sample composition, we investigated the polarization distributions for the same material as received first with dominant  $\alpha$ -crystallite content, then after biaxially stretching in order to increase the  $\beta$ -crystallite content and finally after annealing again in order to reduce the  $\beta$ -crystallite content.

## EXPERIMENTAL TECHNIQUE

THE spatial distribution of the polarization in PVDF films was measured at room temperature with the PPS method [3,7]. The pressure steps are generated by applying a HV pulse with a rise time of less than 1 ns to a quartz disk. The pressure step is coupled into the polymer samples through a thin (200 nm) oil film. The propagating pressure step displaces charges and deforms the polarization. The corresponding displacement current in the short-circuited sample is measured with a wide-band amplifier and displayed on a fast real-time oscilloscope. In order to investigate the time development under external fields a thin insulating PET film covered by an evaporated aluminum electrode was inserted between sample and the measuring electrode. This additional polymer acts as a wide band coupling capacitor to the measured displacement current. It does not influence the shape of the signal. The crystallite phase composition of the PVDF films was determined by IR absorption. The ratio between the relative absorption at  $530\text{ cm}^{-1}$  ( $\alpha$  crystallites) and  $510\text{ cm}^{-1}$ , ( $\beta$  crystallites) is taken as a standard for the  $\alpha/\beta$  phase content (according to [8]).

## RESULTS

A commercial PVDF film (Dyflor™ 2000, Dynamit-Nobel, Troisdorf, Germany) with almost all crystallites of the  $\alpha$  type was poled at room temperature. The film was poled 1 h at a field strength of 0.5 MV/cm and afterwards kept under zero voltage conditions for another hour. The piezo profile in Figure 1 shows a sharp peak located closely to the anode. The same material then was stretched at a temperature of  $150^\circ\text{C}$  with a thickness reduction to about 20% of its original value. The  $\alpha/\beta$  phase ratio of the stretched film was 3.9. The time development of the polarization profiles of the stretched film is shown in Figure 2a for a field strength of 0.6 MV/cm. The development always starts with a homogeneous profile caused by the external field. The signal then begins to change its shape, indicating homo charge injection from both electrodes. An almost central polarization zone is built up. The boundaries of the film are free of polarization. The injected charges are evidently trapped at the boundaries of the polarization zone. (The same polarization development was already observed in stretched films as received with a finite  $\beta$  crystallite content [7,13].) At medium field strength (0.8 MV/cm), see Figure 2b, the profile shows a nearly rectangular shape. The zone near the cathode, which

is free from polarization, is smaller than at lower field strengths. A polarization free zone near the anode cannot be resolved within the experimental resolution. At both electrodes again homo charge injection is observed.

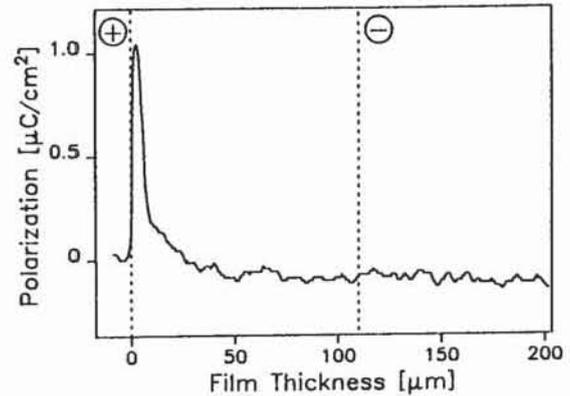


Figure 1.

Polarization distribution of an isotropic PVDF film, after poling 1 h at 1.5 MV/cm. The film thickness is 110  $\mu\text{m}$ .

For higher field strength (1.8 MV/cm) homogeneous profiles are observed as depicted in Figure 2c. In this case the transition from zero to maximum polarization at the film boundaries is within the experimental resolution.

Now the previously stretched films were finally annealed at  $180^\circ\text{C}$  for 3 h. The film thickness increased by a factor of 2.5. The  $\alpha/\beta$  phase ratio increased to 17.

As shown in Figure 3 the polarization develops again only in a small region close to the anode. The polarization step at the cathode gets smoothed out with time indicating homo charge injection. The plateau between the cathode and the anode polarization peak is decreasing with increasing polarization in the peak, indicating an increasing internal field in the polarization zone and charge trapping at the boundaries of this zone.

For comparison we investigated also a stretched material supplied from the Kureha company, Japan. The  $\alpha/\beta$  ratio was 1.25. Figure 4a shows the time evolution of the polarization for this sample under an external field of 0.6 MV/cm. Again a central polarization zone develops for this  $\beta$  material. Now this film material was annealed at  $160^\circ\text{C}$  for 3 h. The  $\alpha/\beta$  ratio increased to only 1.5. The thickness increased by 10% to 55  $\mu\text{m}$ . The polarization development in Figure 4b shows a polarization

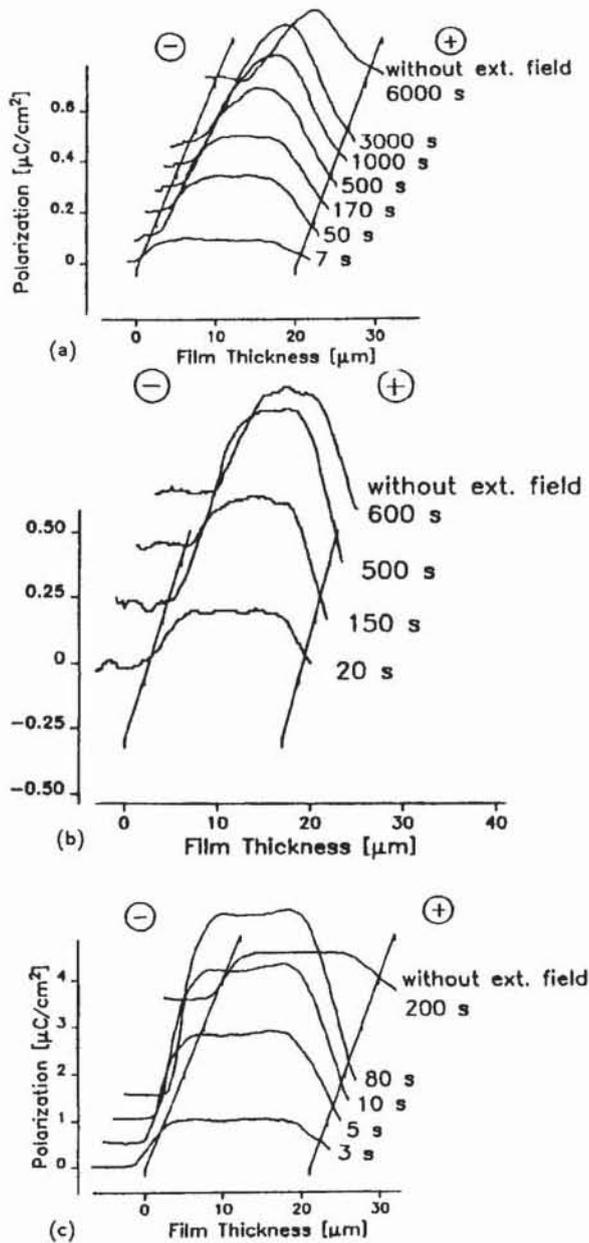


Figure 2.

(a): Time development of the polarization distribution in a stretched PVDF film of 20  $\mu\text{m}$  thickness. The  $\alpha/\beta$  phase ratio is 3.9. The poling field strength is 0.6 MV/cm. (b): Time development of the polarization distribution in a stretched PVDF film of 17  $\mu\text{m}$  thickness. The  $\alpha/\beta$  phase ratio is 3.9. The poling field strength is 0.8 MV/cm. (c): Time development of the polarization distribution in a stretched PVDF film of 20  $\mu\text{m}$  thickness. The  $\alpha/\beta$  phase ratio is 3.9. The poling field strength is 1.8 MV/cm.

zone shifted towards the anode. First the step at the

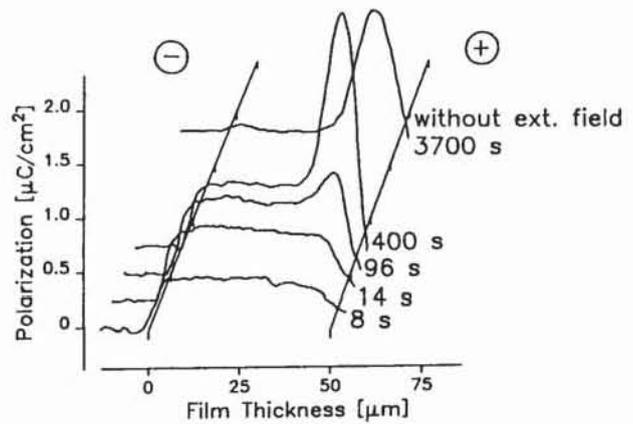


Figure 3.

Time development of the polarization distribution in an annealed PVDF film of 55  $\mu\text{m}$  thickness. The  $\alpha/\beta$  phase ratio is 17. The poling field strength is 0.6 MV/cm.

cathode becomes smoothed indicating charge injection. The same occurs later at the anode. The position of the resulting internal permanent polarization apparently is determined by the differences in the charge mobility and injection from the electrodes.

## SUMMARY AND CONCLUSIONS

THE development of inhomogeneous and internal polarization zones can be attributed to charge injection and charge trapping at the polarization zone boundaries [3,9]. The polarization zone develops at a position where the critical field strength for dipole orientation in the crystallites is exceeded by the approach of injected homo charges (or without injection by the depletion of internal homo charges and the excess of hetero charges). The critical field for  $\alpha$  crystallites corresponds to an electric field phase transition at 1.2 MV/cm [10]. (For  $\beta$  material a thin film permanent polarization threshold of 0.5 MV/cm is reported [11].)

Since we observe for  $\alpha$  material a polarization zone at the anode for a total field strength of 0.6 MV/cm, this indicates strong negative charge injection at the cathode with high charge mobility and little positive charge injection from the anode. There may be also an additional field enhancement in the anode regime by intrinsic positive charges in the film which are depleted at the anode by extraction to the cathode leaving excess hetero charges in the anode regime [7,13].

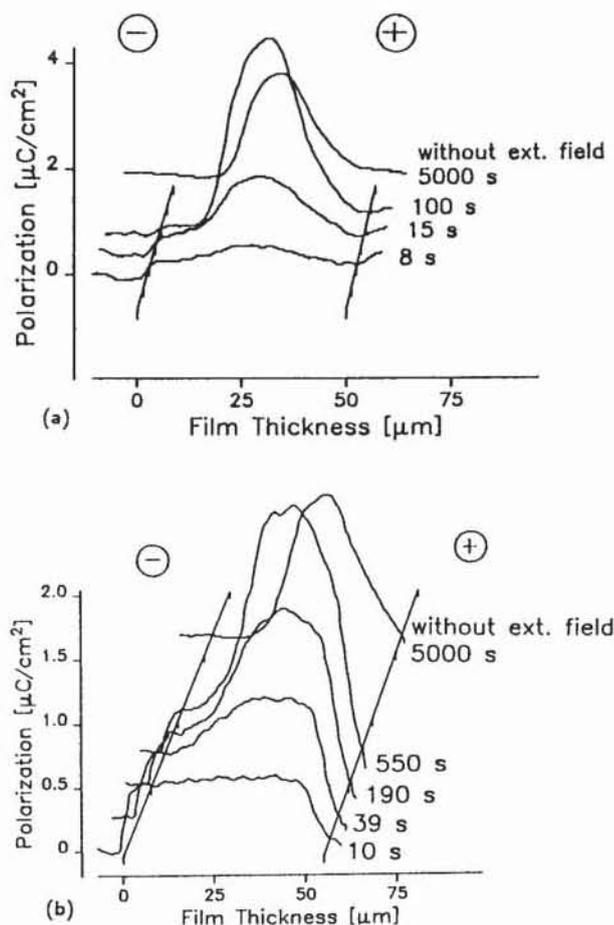


Figure 4.

- (a): Time development of the polarization distribution in a Kureha Film, as received. The film thickness is 50  $\mu\text{m}$ . The  $\alpha/\beta$  phase ratio is 1.25. The poling field strength is 0.6 MV/cm.
- (b): Time development of the polarization distribution in a Kureha Film, as received. The film thickness is 55  $\mu\text{m}$ . The  $\alpha/\beta$  phase ratio is 1.5. The poling field strength is 0.6 MV/cm.

The development of central polarization zones in PVDF containing  $\beta$  crystallites indicates injection of charges with both signs and almost equal mobility. Since the difference in the position of the polarization zone between pure  $\alpha$ -material and films containing  $\beta$  crystallites evidently is caused by the  $\beta$  crystallite content, the  $\beta$  crystallites either determine the charge injection rate or the mobility or both. A strong reduction of the mobility of negative (and positive) charges can be explained by the model of polarized crystallites as traps [3,9]. The trap properties of  $\beta$  crystallites can be explained by the same mechanism of charge trapping by oriented dipole ends at the crystallite surface. Thus the transition from

the polarization zone at the anode in  $\alpha$ -material to the central polarization in  $\beta$ -material can be explained by the reduction of the mobility of negative charges by  $\beta$  crystallites. The influence on the mobility of positive charges is expected to be comparatively small, because this mobility appears to be already low in the pure  $\alpha$  material.

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