POLARIZATION PROFILES OF ELECTRON-BEAM POLARIZED VDF-TrFE COPOLYMER FILMS

Doris Schilling, Joachim Glatz-Reichenbach, Klaus Dransfeld, Eckardt Bihler*, and Wolfgang Eisenmenger*

Fakultät für Physik, Universität Konstanz, D-7750 Konstanz
*1. Physikalisches Institut der Universität Stuttgart, D-7000 Stuttgart

Introduction

In order to generate a polarization in polyvinylidenefluoride (PVDF) the method of electron-beam poling offers some special features [1, 2]. With the aid of a *focused* electron beam, poling patterns of small lateral extension can be written and afterwards can be read out using the method of potential contrast imaging in the scanning electron microscope (SEM) [3]. Furthermore due to the finite penetration depth of the electrons into the polymer, piezoelectric monomorphs of *large area* can be produced using a *defocused* monoenergetic electron beam [4], whereas irradiating prepolarized samples of PVDF with a focussed electron beam creates piezoelectric bimorphs over the scanned area of a few mm^2 [2]. The electron beam poling of PVDF leads to a nonuniform distribution of the polarization across the sample thickness [1, 2] leaving an unpoled or in some cases a reverse poled layer of a few microns near the beam exposed surface.

Experimentally we are able to detect the polarization profiles using the method of piezoelectrically generated pressure pulses (PPS) developed by Haardt and Eisenmenger [5]. This technique not only allows a high resolution estimate of the polarization distribution across the film thickness, but also gives information on the absolute value of the remanent polarization with an accuracy of 5%.

In order to understand more clearly the poling mechanism in ferroelectric polymers, we applied the PPS-technique to copolymer films of vinylidenefluoride with trifluoroethylene: P(VDF-TrFE), poled by a focused monoenergetic electron beam. In this method charges are injected in a well defined way into the polymer films and therefore may provide information on the influence of externally introduced electrical charges on the poling process in ferroelectric polymers.

Experimental Methods

Granules (Atochem, France) or plates of VDF-TrFE copolymers in the composition range between 60-40 and 80-20 have been dissolved in ethyl-methylketone. Films having a thickness of 25 $\mu m \pm 2\ \mu m$ were prepared by spinning the solution on flat glass substrates. After removing them from the substrate, most of these copolymer foils were annealed at 130 °C for two hours. Later on they were bonded onto a polished aluminum substrate and inserted into a scanning electron microscope (Cambridge Mk 2A).

For poling a slow single scan across an area of 6.5 mm^2 (lasting 1000 s) was performed by a well focused monoenergetic electron beam at energies varying between 5 and 30 keV for a beam current of 1 nA.

After finishing this poling procedure the copolymer films were removed from the substrates and shorted for a few days. In order to measure the polarization

profiles for copolymers of different composition irradiated with electrons of different energies, we used a PPS-equipment described elsewhere [5]

Results and Discussion

In order to study the influence of electron beams at various energies on profile and absolute magnitude of polarization, annealed samples of P(VDF-TrFE) of four compositions (60-40, 70-30, 75-25, and 80-20) were irradiated with electrons at energies between 5 keV and 30 keV. Figures 1a - 1d show the resulting different polarization profiles for identical copolymer material but for growing energy E_o of the incident electron beam of 5, 10, 20, and 30 keV, respectively. The PPS signals refer to the case that the acoustic step enters the copolymer film from the same side from which the film surface had been irradiated before by the polarizing electron beam.

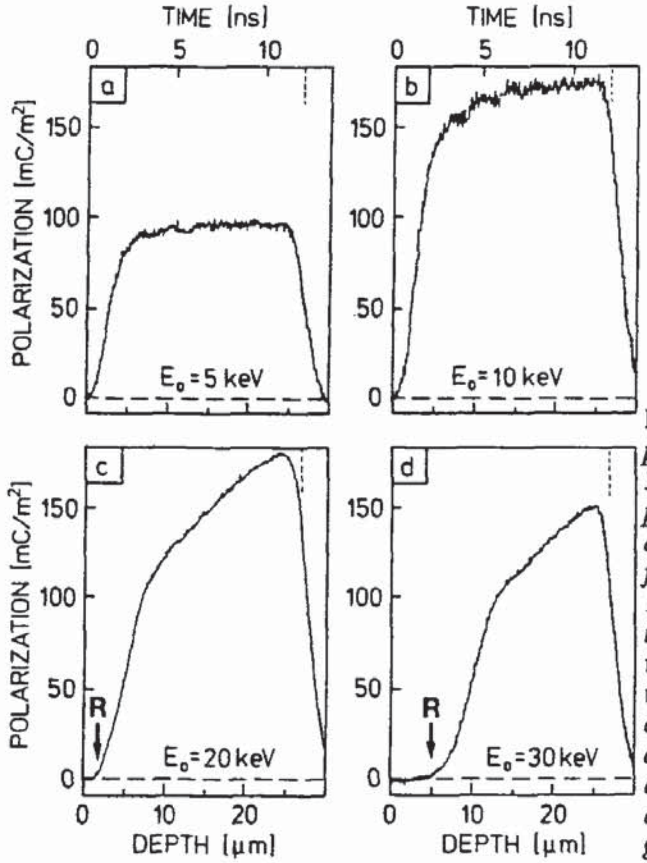

Fig. 1: *Polarization profiles of 27 μm thick 70-30 P(VDF-TrFE) films poled by electrons of different energies E_o. The foils irradiated with 5 and 10 keV electrons are seen to be relatively symmetric whereas the samples poled with 20 and 30 keV electrons show a rather asymmetric polarization distribution. The vertical dashed lines mark the grounded rear electrode.*

As already observed for electron-beam polarized samples of pure ß-PVDF [2], the polarization builds up a few microns away from the irradiated surface inside the sample at a characteristic depth R, which increases with rising electron energy, in a way rather similar to the penetration depth of the electrons. For foils irradiated with 5 and 10 keV electrons the shape of the polarization profiles is nearly the same as reported for ß-PVDF. Increasing electron energy (i.e. 20 and 30 keV), however, leads to rather more asymmetric profiles exhibiting a steep

rise of the polarization at the depth R followed by a slower but steady growth towards the grounded rear electrode.

A deviation from this behaviour is only observed for annealed films of 60-40 P(VDF-TrFE) irradiated with 30 keV electrons (Fig. 2b). These samples show a very asymmetric profile having a relativly small amount of polarization the very sharp maximum of which is located close to the grounded rear electrode. In Figure 2a, for comparison, the profile of an identical film, but irradiated with 20 keV electrons, can be seen more similar to the other copolymer compositions (c.f. Fig 1c). Apparently in the case of the 60-40 P(VDF-TrFE) films it is the energy of the incident electron beam which mainly determines the shape of the polarization profile contrary to the observation on PVDF, where clearly the amount of α-phase content has the dominant influence on the polarization profile.

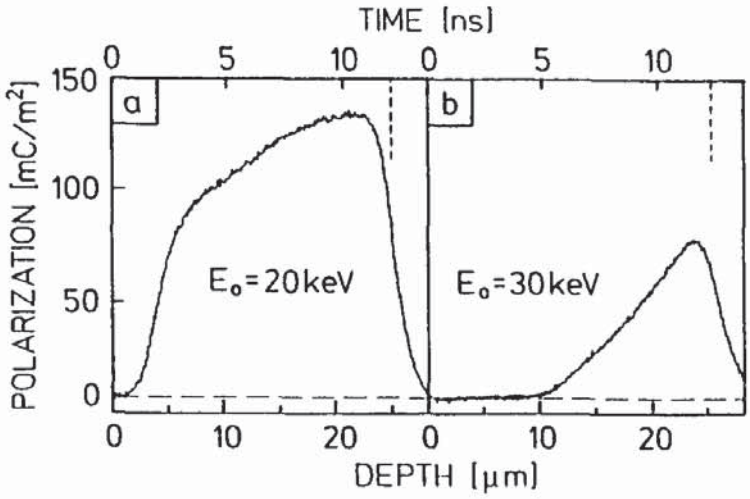

Fig. 2: *The irradiation of identical samples of 60-40 P(VDF-TrFE) with 20 and 30 keV electrons, respectively, leads to quite different polarization profiles.*

One of us (E.B.) observed that VDF-TrFE copolymer films polarized between evaporated metal electrodes after annealing, always exhibit a homogenious polarization distribution across the whole sample thickness. Consequently the method of electron-beam polarization is a useful technique for the production of very asymmetric profiles in annealed P(VDF-TrFE) foils.

In Figure 3 the maximum polarization $P_{max.}$ as a function of electron energy is drawn for the compositions 60-40 and 80-20 respectively. To our surprise for the 80-20 P(VDF-TrFE) film we found very high values of polarization exceeding those measured for electron-beam polarized ß-PVDF by a factor of three. Within an experimental error of about 15 % samples of composition 70-30 and 75-25 reach the same high value of P_{max} as the 80-20 sample. The error is mainly attributed to the lacking reproduceability of the polarization generated by a focused electron beam. Such high polarization values, up to 180 mC/m², have to our knowledge, never been reported before. The 60-40 composition, however, shows somewhat smaller values of P_{max}. Interestingly, for the films irradiated with 30 keV electrons the maximum polarization is reduced for all copolymer compositions investigated so far.

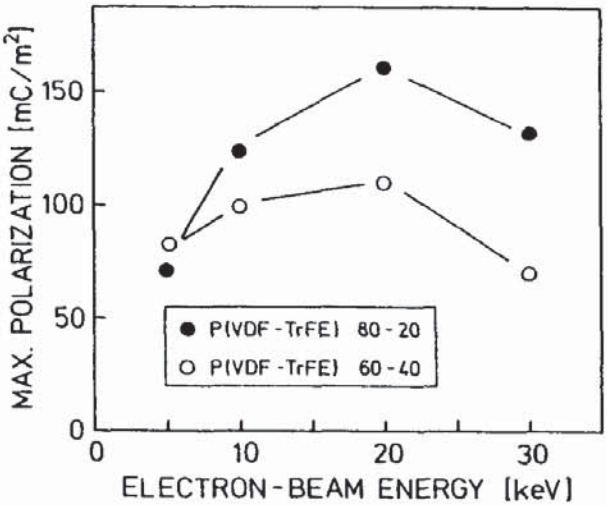

Fig. 3: *The maximum polarization P_{max} as a function of the electron energy E_0 observed for two different VDF-TrFE copolymer samples for constant electron dose.*

Consequently, the qualitative model we developed for the electron beam poling of pure PVDF, described in more detail elsewhere [2], is also applicable for the electron-beam poling in VDF-TrFE copolymers: The electrons penetrating into the copolymer film form a virtual negative electrode at the penetration depth followed by a build up of an electric field towards the grounded rear electrode. Under the influence of this electric field, which is modified by conductivity effects, the orientation of the CF_2-dipoles takes place, probably stabilized by compensation charges. The growing asymmetry of the polarization profiles with increasing electron energy (i.e. 20 and 30 keV) which is more pronounced in the copolymers than in pure ß-PVDF indicate a strong drift of charge carriers towards the grounded rear electrode. As a consequence the local electric field may rise resulting in an increase of polarization having its maximum near the rear electrode.

Furthermore, externally introduced charges may also be responsible for the stabilisation of the generated polarization by compensation [9]. Possibly for P(VDF-TrFE) foils irradiated with 30 keV electrons, showing for all copolymer compositions lowered P_{max}-values compared to the films irradiated with 20 keV electrons of the same intensity, the number of charges may not be sufficiently high to compensate such high values of polarization, which are observed to be generated by the method of electron-beam poling in VDF-TrFE copolymers. This assumption is supported by the observed current collected from the rear electrode which grows for increasing electron energy and which, besides the poling current for the dipole orientation, contains also ohmic contibutions. This hypothesis should be clarified by irradiating identical P(VDF-TrFE) films with electrons of constant energy but at varying intensities.

The 60-40 VDF-TrFE copolymer may, in addition, show defects in the crystalline phase, i.e. the all-trans ferroelectric structure may be broken by few paraelectric sequences as reported for 52-48 P(VDF-TrFE) films [6]. Furthermore, this disorder is possibly increased by the electron irradiation, specially for high energy electrons, as was observed by Lovinger [7], at intensities two orders of magnitude above ours. This fact may be responsible for the observed reduction of P_{max} and the strong asymmetric profile for the films irradiated with 30 keV electrons (c.f. Fig. 2 a).

Annealing Effects From X-ray diffraction experiments it is known that the annealing of copolymer films of VDF with TrFE at temperatures well above T_C enhances their degree of crystallinity from 30 % to more than 80 % as is reported by Tajitsu et al. [8]. As the remanent polarization is originated from the crystalline regions, it increases with rising degree of crystallinity [8].

In the case of electron beam polarized (20 keV) copolymer films of composition 60-40 we observed a systematic increase of the maximum remanent polarization P_{max} with the annealing temperature T_a as can be seen in Figure 4. P_{max} rises strongly near T_C and increases further but more slightly at higher temperatures.

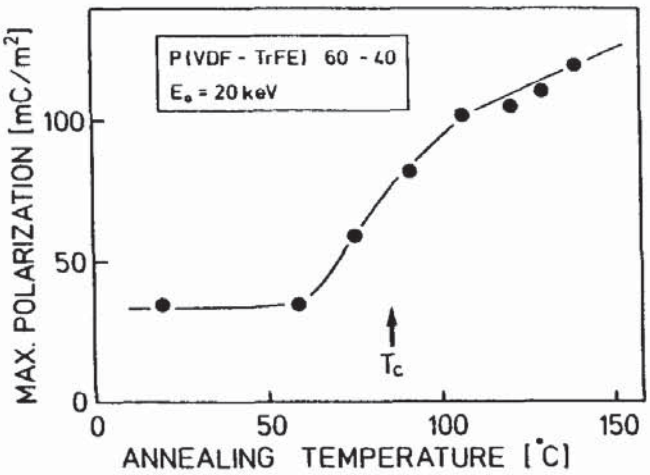

Fig. 4: *The maximum remanent polarization P_{max} as a function of the annealing temperature T_a for 60-40 P(VDF-TrFE) films irradiated by 20 keV electrons of identical intensity.*

In Figure 5 the profile of an annealed film of 80-20 P(VDF-TrFE) poled by 20 keV electrons is compared to that of an identical but unnanealed film iradiated in the same way.

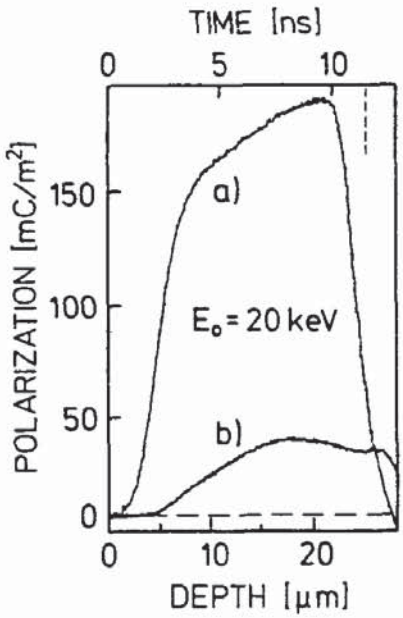

Fig. 5: *Comparison of the polarization profiles for two 80-20 P(VDF-TrFE) films irradiated by 20 keV electrons. a) The film was annealed at 130 °C before the poling. b) The film was irradiated as cast from solution.*

The polarization caused by the annealing is seen to be the fivefold of the value for a film poled directly after the production by spin coating. At the same time the onset of polarization is displaced towards the grounded rear electrode for the unannealed film. It must be emphasized that a rather asymmetric polarization distribution has already been observed for 60-40 P(VDF-TrFE) without any heat treatment, irradiated with 20 keV electrons (c.f. Fig. 6 in ref. 2).

Certainly these relatively low polarization values must be ascribed to the low degree of crystallinity in the copolymer films which have not been annealed. But the origin of the shape of their polarization profiles is not yet understood. To clarify this point more experiments must be done with respect to the degree of crystallinity of the samples which can be determined by X-ray diffraction-, differential calorimetry-, and NMR-experiments.

Summary

The electron-beam poling of P(VDF-TrFE) films creates very high values of polarization up to 180 mC/m^2 which exceeds those produced in ß-PVDF by electron irradiation by a factor of three. Such high values of remanent polarization, to our knowledge, have never been reported before.

The distribution of the polarization across the film thickness is rather asymmetric specially for samples irradiated with 20- and 30 keV electrons. This fact may be attributed to the rising electrical conductivity in our samples with increasing electron energy.

The annealing of the copolymer films before the poling procedure leads to a systematic increase of the polarizaton with T_a having its steepest rise around T_C.

References

[1] Gross B, Gerhard-Multhaupt R, Berraissoul A, and Sessler G M: Electron-Beam Poling of Piezoelectric Polymer Electrets, J. Appl. Phys. **62**, 1429 (1987)

[2] Schilling D, Dransfeld K, Bihler E, Holdik K, and Eisenmenger W: Polarization Profiles of Polyvinylidene Fluoride Films Polarized by a Focused Electron Beam, J. Appl. Phys. **65**, 269 (1989)

[3] Schilling D, and Dransfeld K,:Imaging of Polarized Regions in Ferroelectric Polymers, Ferroelectrics **81**, 377 (1988)

[4] Fukada E, Sessler G M, West J E, Berraissoul A, and Günther P: Bending Piezoelectricity in Monomorph Polymer Films, J. Appl. Phys. **62**, 3643 (1987)

[5] Haardt M, and Eisenmenger W: High Resolution Technique for Measuring Charge and Polarization Distributions in Dielectrics by Piezoelectrically Induced Pressure Step Waves (PPS), IEEE 1982 Annual Report CEIDP, 48 (1982)

[6] Furukawa T: Piezoelectricity and Pyroelectricty in Ferroelectric Polymers, Proc. 5th Intern Symp. Electrets, 883, Heidelberg (1985)

[7] Lovinger A J: Polymorphic Transformation in Ferroelectric Copolymers of Vinylidene Fluoride Induced by Electron Irradiation, Macrmolecules **18**, 910 (1985)

[8] Tajitsu Y, Ogura H, Chiba T, and Furukawa T:Investigation of Switching Characteristics of Vinylidene Fluoride/Trifluoroethylene Copolymers in Relation to their Structures, Jpn. J. Appl. Phys. **26**, 554 (1987).

[9] Bihler E, Neumann G, Eberle G, and Eisenmenger W: Influence of Charge Injection on Formation of Remanent Polarization in P(VDF-TrFE) Copolymers, This Conference.