

Field Induced Gas Emission of Polymer Films

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Abstract

Poling PVDF under vacuum conditions causes strong gas emission which is analyzed with a quadrupole mass spectrometer. The dominant peak in the mass spectrum is HF which is produced by electro chemical reactions at the sample surface. Surprisingly after switching off the electric field the gas emission even increases to a value higher than under field. This can be explained by ionic charge detrapping and charge migration.

1 Introduction

The piezo- and pyroelectricity in PVDF is caused by the formation of a remanent polarization in the crystallites of the polar β -phase under field strengths greater than 50MV/m. The crystallite dipoles are oriented under field in steps of 60° in the quasi hexagonal lattice of β -phase PVDF [1]. But measurements of the polarization after voltage pulses shorter than 100ms at different field strengths [2, 3] showed that the built up of the remanent polarization in pure PVDF is delayed by a factor 0.3 to 1 compared to the time of orientation of the dipoles under field. To explain the delay in addition to the dipole orientation under field a second mechanism is necessary for making the polarization remanent. Experiments with blocking electrodes [4] indicate that charge injection is responsible for the development of the remanent polarization. The charge trapping model [5] describes this by the trapping of charge carriers at the surface of the polarized crystallites. The polarization is stabilized by the Coulomb interaction between these trapped charges and the polarization charges.

Yet so far the origin and nature of these trapped charges are unknown. The pressure dependent conductivity [6, 7] indicate charge transport by ions in PVDF. As earlier proposed these ions are formed by electro chemical reactions at the surface of the PVDF films under field [8]: Electrons are injected from the electrode material into a monomer unit of a PVDF chain splitting off F^- ions and H atoms by secondary radical reactions. On the other electrode holes are injected into a polymer chain splitting off H^+ and also H atoms by secondary reactions. With porous electrodes the gas atoms and recombined ions can be emitted from the PVDF film in the form of H, F, and HF. We find a strong emission of HF during the poling process of PVDF. This gas emission was

already detected and analyzed with a quadrupole mass spectrometer in earlier experiments [8] but the authors could not exclude the possible contribution of electrical surface discharge phenomena. By increasing the sensitivity of the apparatus and improving the process of porous electrode preparation we now can present results in which surface discharge processes are avoided.

2 Experimental

Samples used were $25\mu\text{m}$ thick biaxial stretched PVDF films with ca. 70% β content. These films were evaporated on one side with 200nm Al and on the other side with 20nm Au. The gold layers were porous which was checked with an electron microscope after the poling experiments. The diameter of the sample area was about 60mm. The quadrupole mass spectrometer ionisation chamber was mounted opposite to the porous gold electrode. The samples were poled in an UHV system at about 10^{-9} mbar. The voltage applied to the sample was increased in steps of 50V. After each voltage step a complete mass spectrum between 1amu and 50amu was measured. Recorded was the mass signal as ion current transmitted through the bar system of the quadrupole mass spectrometer. The time necessary to measure this complete spectrum was 0.5s. When the electric field reached 100MV/m the voltage was kept constant for 40s. Afterwards the samples were kept under short circuit conditions. During this time the gas emission analysis was continued for further 200s after the voltage was switched off.

3 Results

3.1 PVDF

Fig. 1 shows the mass spectrum of a $25\mu\text{m}$ thick PVDF film at the time when the applied voltage reached its maximum. The highest peak in fig. 1 is the one with mass no. 20 which corresponds to HF. Next intense peaks are mass no's. 18, 28 and 44. These peaks are attributed to H_2O , N_2 and CO_2 . These gases are adsorbed in the polymer and in the UHV system. The other peaks between mass no. 12 and no. 14 and between mass no. 25 and no. 29 are attributed to CH_4 and C_2H_6 . The peak at mass no. 47 is attributed to C_2FH_5 . The signal of mass no. 1 and no. 2 which correspond to H and H_2 are less precise because mass no. 1 is not resolved and the calibration of the mass spectrometer for mass no. 2 is very difficult. The relative composition of the mass spectra does not depend on the sign and value of the applied field strength. Merely the intensity of the measured ion current increases with increasing field strength and varies for one order of magnitude as function of the porosity of the gold layer.

Fig. 2 shows the time dependence of the HF mass signal. All measured masses between 1amu and 50amu show the same time behaviour but with different intensities. The gas emission increases with increasing field strength (*HVon*

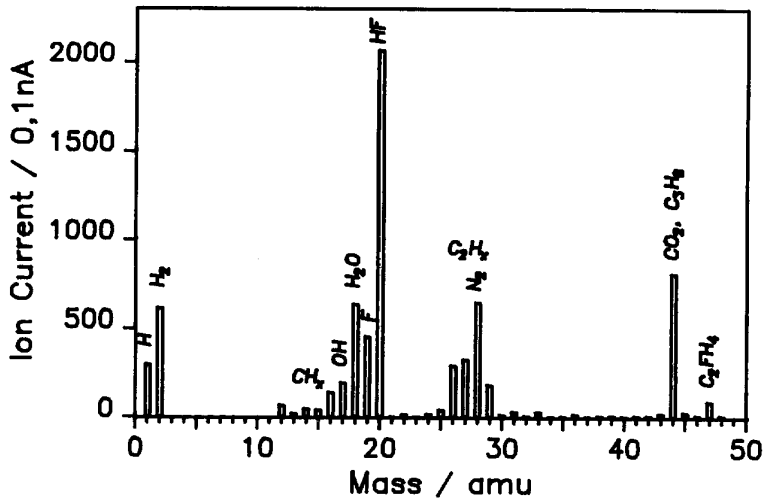


Figure 1: Mass spectrum by poling a $25\mu\text{m}$ thick PVDF film. The spectrum was recorded when the voltage reached its maximum of 100MV/m . A few molecule symbols are added to the mass numbers.

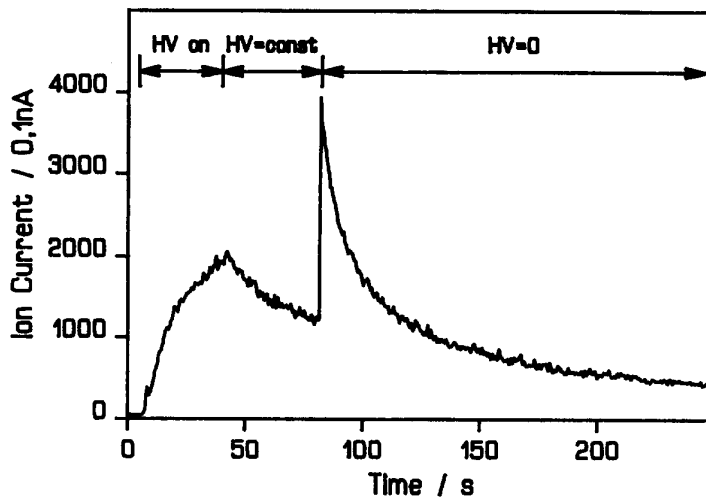


Figure 2: Time dependent ion current of HF by poling a $25\mu\text{m}$ thick PVDF film with $E = 100\text{MV/m}$.

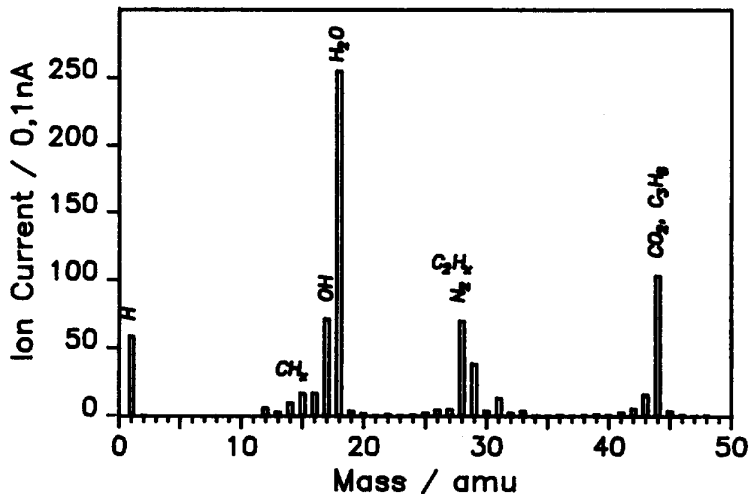


Figure 3: Mass spectrum by poling a $25\mu\text{m}$ thick PET film. The spectrum was recorded when the voltage reached its maximum of 100MV/m . A few molecule symbols are added to the mass numbers.

in fig. 2). During the time period with constant voltage ($HV = \text{const}$) the gas emission decreases to a steady state value. This indicates space charge limited charge transport in PVDF. If the sample is shorted ($HV = 0$) the gas emission rises surprisingly to a value higher than under field. It was checked with several experiments that this increase of the signal is real and not produced by electronic artefacts. The gas emission under short circuit decays with two time constants: A fast decay with a time constant of about 10s which depends on short circuit conditions and a slow decay with a time constant of about 100s. The time constant of 100s corresponds to the Maxwell relaxation time of free charges in PVDF at room temperature. The mass spectra under short circuit are of the same shape as illustrated in fig. 1 but with different intensities. The gas emission under zero field is further evidence that surface discharge processes can be excluded.

3.2 PET

Fig. 3 shows the mass spectrum by poling a $25\mu\text{m}$ thick Hostaphane PET film when the high voltage reached its maximum of 2500V. The highest peak in fig. 3 corresponds to H_2O followed by peaks which are attributed to H, N_2 and CO_2 . Again the CH_4 , C_2H_6 and C_3H_8 groups are seen in fig. 3. The intensity of the gas emission is about two orders of magnitude smaller as compared to PVDF (fig. 2).

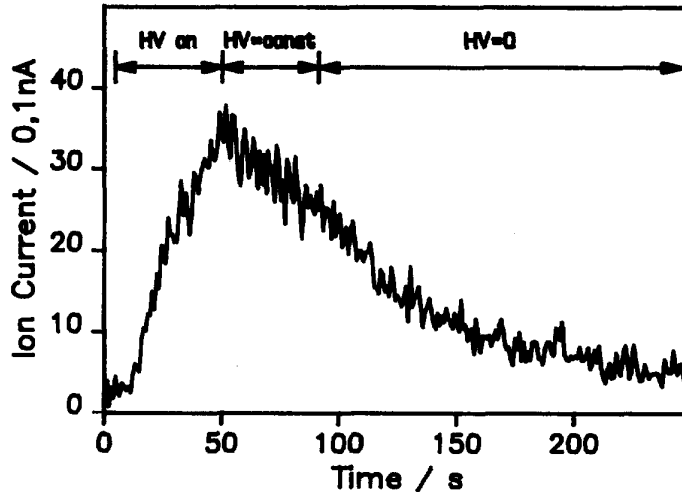


Figure 4: Time dependent ion current of C_2H_5 by poling a $25\mu m$ thick PET film with $E = 100MV/m$.

Representative for all other masses fig. 4 shows the time dependent ion current of mass 29 which is attributed to C_2H_5 . As in PVDF the gas emission increases with increasing voltage and decreases at constant voltage. But in contrast to PVDF no increase of the gas emission in PET is seen after switching off the high voltage.

4 Discussion

The strong emission of HF and other chain fragments during the poling process of PVDF indicate that electro chemical reactions occur at the electrodes as proposed by Bihler et al. [8]. After creation at the surface the ions migrate into the PVDF film and contribute to the charge transport in this polymer. Some of these ions are trapped at crystallites and stabilize the remanent polarization. The observed gas emission under field can be explained by the recombination of the ions with electrons or holes or with each other. Also secondary reactions of free radicals generated by the direct electro chemical production of F^- and H^+ ions can lead to F, H and HF emission from the electrodes. Under short circuit the free ions which are not trapped recombine with their counter charges. Therefore a gas emission with a time constant similar to the relaxation time of free charges in PVDF is observed. The strong increase of the gas emission by shorting the PVDF samples can be due to a

high concentration of ions near the film surface which is known for the case of space charge limited electrical transport. These ions recombine with a shorter time constant compared to the Maxwell relaxation time dependent from short circuit conditions. Yet so far it is unclear why the adsorbed gases H_2O , N_2 and CO_2 show the same time behaviour as HF.

The electro chemical reactions depend on the dipole moment of the polymer chain. The higher the dipole moment the lower the activation energie for splitting off an ion from a polymer chain [8]. Therefore in the mass spectrum of PVDF (fig. 1) HF is the peak with the highest intensity. The $C - F$ and $C - H$ bonds are the most polar bonds in the PVDF chain. Because the dipole moments in PET are much smaller than in PVDF the observed gas emission of this polymer is some orders of magnitude lower than in PVDF. An experiment with a Teflon FEP film showed no gas emission.

The internal production of HF by poling a P(VDF/TrFE) copolymer film was reported by Tsutsumi et al. [9]. The observed colour change from a dye doped copolymer film during poling was attributed to the production of HF under field.

References

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