F 10 Electrical Poling of Polymers

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1. Introduction

Piezo-, pyro- or ferroelectric polymers receive a lot of attention because of their potential use in sensor and actuator applications [Nalwa 95]. These electrical properties can only be found in non-centrosymmetric materials. To break the centrosymmetry, the polymers usually have to be polarized. The resulting polarization can be caused by the orientation of dipoles and/or domains, the build-up of charge layers in heterogeneous polymer materials, as well as a combination of both effects. In order to achieve dipole orientation in the material, a sufficiently high electric field must be applied between the surfaces of a polymer film or layer. There are various possibilities for generating the electric field across the sample thickness. Often the internal electric field is generated by charging the polymer in a corona discharge, by poling two-side metallized samples in direct electrode contact, by depositing charge layers with an electron beam or by charging the surface with a liquid contact. Several methods are available to investigate the polarization distribution in the poled polymer across the thickness or the surface of the polymer film. Sophisticated techniques such as the piezoelectrically generated pressure-step method (PPS), the laser-induced pressure-pulse method (LIPP), the laser-intensity modulation method (LIMM) were employed after electric poling for non-destructive probing.

This lab experiment is focused on the investigation of the polarization build-up in ferroelectric polymers during the poling process. For comparison poling of in a non-ferroelectric polymer is also carried out.

It is necessary to study this manual in detail before starting the experiment.

For testing of your basic understanding there are a few checkpoints in the text. You should be prepared to answer the questions in the discussion with the tutor prior the experiment.

Physical concepts

- electric polarization
- theory of ferroelectricity
- polar and non polar polymers

Equipment

- different polymer films (free standing films)
- different HV-devices
- function generator
- oscilloscope, electrometer

Safety instruction

Be careful when using high voltage. Turn off the high-voltage when building up the electrical circuits. The tutor will connect the HV-power supply with the sample holder.
2. Tasks

Poling of a ferroelectric polymer sample with constant electric fields
Measure the poling currents during poling with constant electric field. Record the poling currents during switching using positive and negative electric fields. Calculate the polarization and compare the result with the theoretical values.

Poling of a ferroelectric polymer sample with varying electric fields using different field shapes
Measure the poling currents during poling with varying electric fields. Use different shapes of the electric field, i.e. bipolar poling cycles as well as a combination of bipolar and unipolar poling cycles, respectively. Calculate the different current contributions in the measured poling current. Discuss the calculated polarization values.

Poling of a ferroelectric polymer sample with varying electric fields using different frequencies of the poling field
Measure the poling currents during poling with varying electric fields with bipolar cycles. Use five different frequencies for the applied electric field in the range from 50 mHz to 1 mHz. Calculate the different current contributions in the measured poling current. Discuss the calculated polarization values and the dependence on the frequency of the poling field.

Poling of a ferroelectric polymer sample with varying electric fields using different poling voltages
Measure the poling currents during poling with varying electric fields with bipolar cycles. Use different electric fields in the range from 30 MV/m up to 100 MV/m. Calculate the polarization for each poling field and discuss the polarization as a function of the poling field.

Poling of a non-polar sample
Measure the poling currents during poling with constant as well as varying electric field (bipolar poling cycles and a combination of bipolar and unipolar poling cycles). Discuss the measured dependencies of the poling current.
3 Theoretical background

3.1 Polarization phenomena

There are different origins of polarity in polymers, like orientated molecular dipoles, orientated domains, separated and trapped charges, or a combination of these effects. Usually an electric poling process is used to polarize the polymers (Fig. 1).

![Figure 1: Schematic view of possible orientation phenomena in a poled sample.](image)

One group of polar polymers, the ferroelectric polymers, become special interest related to applications and to basic research. In the literature there exist different definitions for ferroelectricity. In summary, a ferroelectric material is described as a material that can contain two (or more) different orientations, which are based on the same structure. Only the polarization vector of this remanent polarization without an electric field should distinguish both orientations. The orientation can be switched by application of an electric field and the polarization is stable at temperatures below the so-called Curie temperature $T_C$, at which the phase transition to the paraelectric phase occurs. If the application of high enough fields is possible, ferroelectric polymers show a characteristic coercive field and a saturation of the polarization, which yields to a hysteresis of the polarization as a function of the electric poling field.

3.2 Theory of ferroelectricity

According to Landau’s phenomenological model for phase transitions, it is possible to describe the structure change using order parameters. The polarization is the order parameter in case of the ferroelectric phase transition. The order of the phase transition was described by the manner of the change. A volatile decrease of the polarization described a first order phase transition. At the second order phase transition the polarization decreases continuously during increasing of the temperature until the Curie-temperature $T_C$ is reached. To describe the
ferroelectric phase transition the free energy density $F$ (or the Gibbs function $G$) is expanded in terms of the polarization $P$ as shown in equation (1) ([Devonshire 54], [Smolenskij 84]).

$$F(T, P) = F_0(T) + \frac{1}{2} \alpha(T)P^2 + \frac{1}{4} \gamma(T)P^4 + \frac{1}{6} \delta(T)P^6$$ (1)

In equation (1) it was assumed that $F$ is symmetrical with respect to $P$. $F_0$ is the free energy density of the paraelectric phase. $F$, $\alpha$, $\gamma$ and $\delta$ are functions of temperature $T$.

The consideration was limited by the expansion up to the sixth term of the order parameter, furthermore mechanical deformations are negligible and to simplify only one-dimensional ferroelectrics are described.

The free energy density has a minimum in thermodynamic equilibrium, therefore the equations (2) must be fulfilled.

$$\frac{\partial F}{\partial P} = 0, \quad \frac{\partial^2 F}{\partial P^2} > 0$$ (2)

Differentiating $F$ with respect to $P$ yields

$$\frac{\partial F}{\partial P} = \alpha(T)P + \gamma(T)P^3 + \delta(T)P^5, \quad \frac{\partial^2 F}{\partial P^2} = \alpha(T) + 3\gamma(T)P^2 + 5\delta(T)P^4.$$ (3)

From (2) and (3) it follows for the non-polar case ($P = 0$) that $\alpha$ must be greater than zero. To solve the condition (2) also in the polar case ($P \neq 0$), $\alpha$ must change its sign at the transition temperature $T_C$. This can be mathematically achieved using the assumption (4) (Devonshire approximation).

$$\alpha = \alpha_0(T - T_C)$$ (4)

Therefore equation (5) follows to describe $F$ as a function of $P$.

$$F(P) = F_0 + \frac{1}{2} \alpha_0(T - T_C)P^2 + \frac{1}{4} \gamma P^4 + \frac{1}{6} \delta P^6$$ (5)

Different possibilities for first-order or second-order phase transitions according to the parameter $\alpha$, $\gamma$, $\delta$, $T$ and $T_C$ follow from equation (5), which are discussed in the literature (e.g. [Furukawa 89]).

The free energy density $F$ as a function of polarization $P$ for the second-order phase transition ($\alpha_0 > 0$, $\gamma \geq 0$ and $\delta > 0$) is shown in Figure 2 for different values of the parameter $\alpha$. According to equation (4) the different cases $\alpha < 0$, $\alpha = 0$ and $\alpha > 0$, respectively, are describing the behavior below, at and above the Curie temperature $T_C$.

Differentiating $F$ with respect to $P$ yields the dependence of the polarization as a function of the electric field (6).

$$E = \alpha_0(T - T_C)P + \gamma P^3 + \delta P^5$$ (6)
Figure 2: Free energy density as a function of polarization and of temperature.

If there is no external poling field, equation (7) with solution (8) follows. Using the described prerequisite \((\alpha_0 > 0, \gamma \geq 0, \delta > 0)\) yields the solution \(P_{Sp} = 0\) (case \(T > T_C\)) and \(P_{Sp} = \pm P_{Sp0}\) (case \(T < T_C\)).

\[
\begin{align*}
0 &= \alpha_0(T-T_C) + \gamma P^2 + \delta P^4 \\
|P_{Sp0}| &= \sqrt{\frac{1}{2\delta} \left( -\gamma \pm \sqrt{\gamma^2 - 4\alpha_0 \delta} \right)}
\end{align*}
\]

Therefore a spontaneous polarization \(P_{Sp}\) can occur without an applied external electric field, if the ferroelectric material is in a thermodynamic equilibrium at a temperature below \(T_C\).

If an external electric field is applied the calculated polarization (using the same parameter \(\alpha_0 > 0, \gamma \geq 0, \delta > 0\)) is shown for different temperatures around \(T_C\) in Figure 3.

Figure 3: Calculated polarization as a function of an external electric field at different temperatures around the curie temperature \(T_C\).
In the case $T < T_c$ the polarization dependence corresponds to an unstable condition between the points B and D. Therefore during poling of an idealized ferroelectric material with increasing absolute values of the electric field a jump occurs, i.e. a discontinuity place, in the polarization at positive and negative electric field, respectively. These are symbolized in Figure 3 by dotted lines between A and D as well as B and C. Such a behavior results in a hysteresis of the polarization as a function of the electric field, with significant values for the remanent polarization $P_R$ and the coercive field $E_C$.

Therefore a ferroelectric polymer shows a $P(E)$-hysteresis under special conditions, i.e. during application of a high enough poling field at a temperature below $T_C$. However, it has been shown ([Lines 77]), that no ferroelectric properties can be concluded from a measured hysteresis during poling of a material. The hysteresis behavior is a necessary but not sufficient condition.

### 3.3 Electric poling of ferroelectric polymers

As explained before, different processes, e.g. dipole orientation, orientation of domains, movement and trapping of charges, aging effects, etc. can occur during electrical poling. To investigate and to separate these effects different procedures have been developed for the electrical poling of polymers or other polar materials. Special procedures also exist for poling of ferroelectric polymers, based on the build up of a remanent polarization after a first application of an electric field.

Usually to characterize the orientation phenomena the poling current or the charge build up are measured during the electrical poling process. Here we focus on the description of the poling current, according to the experimental setup in the lab experiment.

The poling current can contain different origins (eq. (9)), e.g. a possible polarization build up $I_p$, a capacitive charging $I_c$ as well as a current based on the conductivity $I_{con}$ of the sample. $A$ is the sample area, $C$ the sample capacitance, $V_p$ the poling voltage and $R$ the resistance.

$$I(t) = I_p(t) + I_c(t) + I_{con}(t) = \frac{A dP}{dt} + \frac{C dV_p}{dt} + \frac{V_p}{R}$$ (9)

If we neglect aging effects, it is possible to separate the contributions to the poling current using special measurement procedures. Useful also for the interpretation of microscopic sample properties are poling procedures with constant and (e.g. sinusoidally) varying electric fields.

**Poling with constant electric fields**

Poling of a polar material with a suitable electric field (field-time dependence in Fig. 8) yields a poling current $I_p$, which is based partly on an orientation process of dipoles of domains (Fig. 4). If the orientation process saturates and if no immediate relaxation occurs, a second poling with the same polarity of the electric field yields the poling current $I_b$ also shown in Figure 4. With these assumptions the origin of the poling current $I_p$ are only capacitive charging and conductivity effects, but not an orientation process. Therefore the polarization current $I_p$ and the polarization $P$ can be easily calculated from equations (10) and (11),
respectively. For the calculation (11) it was assumed that the sample was previously poled with opposite field polarity.

\[
I_s(t) = I_d(t) - I_b(t)
\]

\[
P = \frac{1}{2A} \int I_p(t) dt
\]

**Figure 4:** Theoretical currents during poling of polar materials with constant electric fields of the same polarity (assuming the saturation of the orientation process).

The advantage of such switching experiments is that the switching time of the orientation process can be determined, if the time resolution of the experimental equipment is high enough.

**Poling with varying electric fields**

Usually poling with varying electric fields is performed using a sinusoidal or triangular time-shape of the electric field. Performing of orientation processes in the polymer using different combinations of poling cycles with positive or negative polarities (e.g. Figures 10 and 11) gives the possibility to analyze hysteresis phenomena in the polymer.

For poling with varying fields the same physical consideration can be carried out to separate the contributions in the poling current.

**Checkpoint:** Discuss the proposed separation of the different current contributions to the poling current during poling with bipolar electric fields according to the reference [Dickens 92].
4 Experiment

4.1 Polymer samples

Thin films of polyvinylidene fluoride (PVDF) are used for the investigation of the poling behavior. Since the discovery of its piezoelectric properties in 1971, PVDF is of interest for basic research as well as for sensor and actuator applications. PVDF has the repeat unit –[CH₂–CF₂]–. It is a semicrystalline polymer, consisting of crystallites embedded in an amorphous matrix. In PVDF different crystal classes exist, which are based on three chain conformations: a planar form (all-trans form, called TTTT or I), a helical form (trans-gauche-trans-gauche form, called TGT or II) as well as a “combination” of both chain conformations (called TTTGT or III) (Fig. 5).

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Figure 5: Different chain conformations and resulting phases of PVDF (upper part from reference [Tashiro 81]).

Five crystal phases are observed in PVDF, according to the order of the polymer chains in the unit cell (Fig. 5). The chain orientations for the two most important phases, the non-polar $\alpha$ and the polar $\beta$ phase, are shown in Figure 6.
In PVDF the CF$_2$ groups create a strong dipole moment. The monomer unit of β-PVDF shows a permanent dipole moment of $\mu = 2.1$ D ($\equiv 7 \times 10^{-30}$ Cm); the typical dipole density is $N = 1.9 \times 10^{28}$ m$^{-3}$. Usually films of β-PVDF have a crystallinity of around 50%. In α-PVDF the dipole moment of the monomer unit is compensated. Macroscopically a α-PVDF film looks like a non-polar polymer. The glass transition of PVDF was observed at a temperature of around –40°C, the melting temperature around 170°C and the Curie temperature was calculated to 207°C.

![Image](image.png)

**Figure 6:** Chain orientation in unit cells of polar β-PVDF and non-polar α-PVDF, respectively ([Tashiro 81]).

**Checkpoint:** Should the orientation of ferroelectric domains in films of β-PVDF be possible at room temperature?

**Checkpoint:** Calculate the expected maximum polarization in β-PVDF for a complete orientation of all dipoles in one macro domain.

**Checkpoint:** Which dependencies of the measured poling current as well as the calculated polarization as a function of a varying poling field or a constant poling field would be expected, related to the microscopic properties of β- and α-PVDF.

### 4.2 Poling and measurement setup

**Poling with constant electric fields**

The setup for poling with constant electric fields consists of a high voltage power supply which is connected in series with the sample and with an oscilloscope for measuring the poling current using an additional resistor in the electrical circuit (Figure 7). The voltage selection as well as the voltage application is carried out by hand. The measured poling signal as well as a signal which represents the poling voltage are stored in the oscilloscope. Only after the measurement these values can be transmitted to the computer using the program “poling_s.tst” (Testpoint). Unfortunately, the available HV power supply in combination with the electrical circuit yields a rise time of the voltage pulse in the range of microseconds. Therefore the real switching time of the molecular dipoles in the ferroelectric β-PVDF cannot be measured with the
available equipment. However, because of the fast rise-time the measured poling current represents the orientation in the material, but not on the correct time scale. According to the discussion of the different current contributions, it is useful to carry out two switching experiments with the same field polarity (Figure 8). For each poling cycle a poling time of 5 s should be used.

![Diagram of setup for electrical poling in direct contact, using constant electric fields.](image)

**Figure 7: Setup for electrical poling in direct contact, using constant electric fields.**

![Graph showing time dependence of the electrical field used during switching experiments.](image)

**Figure 8: Time dependence of the electrical field used during switching experiments.**

**Poling with varying electric fields**

The setup for poling with varying electric fields consists of a high voltage power supply, which is connected in series with the sample, a resistor and an electrometer in current mode (Figure 9). A function generator is used to apply different wave forms to the high voltage device as basis for the high voltage, which is applied to the sample. The signal of the function generator is also used for monitoring the applied voltage by means of a voltmeter. The experimental setup is completely controlled by means of a computer program (“poling_h.tst”, Testpoint). The program allows to select the poling voltage, the frequency of the time-depending electric field as well as the shape of the electric field. Typically for poling with bipolar cycles a sinusoidal poling field (3 cycles) with zero values for the electric field before and after the poling cycles was used (Fig. 10). As combination of bipolar and unipolar poling cycles an electric field as shown in Figure 11 is used.
Figure 9: Setup for electrical poling in direct contact, using varying electric fields

Figure 10: Time dependence of the electrical field used during poling with bipolar poling cycles.

Figure 11: Time dependence of the electrical field used during poling with a combination of bipolar and unipolar poling cycles.
4.3 Running the Experiment

The samples are inserted in different sample holders; the sample surfaces are connected to an insulated BNC connector. These connections have to be prepared at least one day before the poling experiments, allowing the connecting glue to set.

Poling with constant electric fields

Measurement

1. Check the connections inside the sample holder.
2. Measure the sample capacitance and compare the result with the value calculated from the known sample properties. (The sample capacitance should be measured and recorded before and after every poling experiment.)
3. Connect all necessary devices and build up the electrical circuit according to Figure 7. After checking the electrical circuit, disconnect the sample holder from the HV power supply.
4. Select the first poling voltage using the potentiometer of the HV power supply.
5. Check the applied voltage using a measurement of the “1/1000” output of the HV power supply with the oscilloscope. Optimize the voltage selection.
6. Connect the sample to the HV power supply.
7. Set the correct trigger level and measurement level at the oscilloscope.
8. Apply the poling voltage; the oscilloscope will measure the current- as well as the voltage- time dependence.
9. Store the measured dependencies at the oscilloscope.
10. Stop the poling experiment after 5 seconds.
11. Use the program “poling_s.st” to read out the measured data from the oscilloscope.
12. Carry out more than one switching experiments for each sample at each voltage.
13. Carry out the next poling experiment following the steps 1. – 12.

Calculation

- Compare the measured currents during switching experiment for each sample / dependence.
- Calculate and set the new time basis.
- Calculate the polarization according to equation (11). (Use the second switching process, so that the assumptions of (11) are fulfilled.
- Discuss the calculated polarization values for the $\beta$-PVDF film and the result of the poling process on the $\alpha$-PVDF sample.
Poling with varying electric fields

Measurement

1. Check the connections inside the sample holder.
2. Measure the sample capacitance and compare the result with the value calculated from the know sample properties. (The sample capacitance should be measured and recorded before and after every poling experiment.)
3. Connect all necessary devices and build up the electrical circuit according to Figure 9.
4. Use the program “poling_h.tst” for applying and selecting the voltage, the frequency of repeating the poling cycles, and the shape of the electric field.
5. Apply the poling voltage. The electrometer will measure the poling current the computer will record the current - as well as the voltage-time dependencies.
6. Stop the poling experiments after 3 complete poling cycles.
7. Carry out the next poling experiment following the steps 1. – 6.

Calculation

• Show the measured poling currents for the investigated dependencies.
• Calculate the polarization according to the description in [Dickens 92]. (Use special computer programs for the calculation, cal_unip.tst for poling with a combination of bipolar and unipolar poling cycles, cal_bip.tst for poling with bipolar poling cycles.)
• Discuss the calculated polarization values, the field dependence and the value of the coercive field for the $\beta$-PVDF film.
• Discuss the result of the poling process of $\alpha$-PVDF film.

5 References