Broadband dielectric relaxation spectra of PVDF copolymer films

Bjoern Martin, Manfang Mai, and Herbert Kliem
Institute of Electrical Engineering Physics, Saarland University, Campus A5 1, D-66123 Saarbruecken, Germany
E-mail: b.martin@mx.uni-saarland.de

Abstract. The dielectric permittivity of polyvinylidene fluoride (PVDF) and its copolymer containing trifluoroethylene (TrFE) is investigated in the frequency domain with variation of the temperature. A pronounced relaxational behavior is observed in the films at high frequencies. In thick commercial PVDF films a Vogel-Tammann-Fulcher (VTF) dependence of the relaxation time versus the temperature is found yielding a thermally activated process. In thin Langmuir-Blodgett P(VDF-TrFE) films the relaxation times determined from the dielectric permittivity in the frequency range are not consistent with the relaxation times determined from the temperature range. The data extracted from the temperature domain also here show a VTF behavior. Nevertheless, the relaxation times calculated from the frequency domain cannot be fitted with the VTF formula. Thus, the time-temperature superposition principle is not valid in the thin films.

1. Introduction
Polyvinylidene fluoride (PVDF) and also its copolymers containing trifluoroethylene (TrFE) have gained much interest during the past years (see references in [1]). Due to the possibility to produce ultra-thin films down to 1 nm with a Langmuir-Blodgett deposition technique the material is a promising candidate for use in integrated electronic circuits. Since the polarization can be switched between two stable states with an external applied field it should be possible to employ P(VDF-TrFE) as nonvolatile ferroelectric access memory device. In former experiments it was demonstrated that also the thin films show ferroelectric properties like hysteresis loops with a remanent polarization of about 10 \( \mu C/cm^2 \) [2].

Small signal broadband dielectric spectroscopy measurements of PVDF and its copolymer in the frequency domain reveal a pronounced relaxational behavior at frequencies of about 10 MHz close to room temperature [1,3-6]. The temperature dependent behavior of the relaxation time is investigated here for different samples.

2. Samples preparation and experimental procedure
At first commercially available foils of pure PVDF with thicknesses of 9 \( \mu m \) and 22 \( \mu m \) are investigated. Aluminum electrodes are evaporated to both sides of the samples. With this sample geometry a simple measurement of the broadband dielectric relaxation spectra is possible. Also, thin films of P(VDF-TrFE) copolymer are prepared by a horizontal Langmuir-Blodgett (LB) technique. This method allows the transfer of copolymer monolayers [7]. On the top
of a glass substrate Al stripes with a width of 200 µm are evaporated (Fig. 1). Afterwards, the copolymer is transferred to the substrate. Al electrodes perpendicular to the first ones are evaporated to the copolymer film then. The crossing area of the Al stripes determines the active sample area.

The measurements in the frequency range are performed with an Agilent 4294A impedance analyzer for frequencies ranging from 40 Hz to 110 MHz and with an Agilent 4291A impedance analyzer from 1 MHz to 1.8 GHz. In the low frequency range below 1 kHz a self made analyzer system is used. All measurements are carried out in dry atmosphere in shielded measurement cells which can be cooled down to 200 K and heated up to 400 K. The thick commercial samples are placed in a coaxial line adjusted to the characteristic impedance of the measurement system which allows measurements up to 400 MHz. For the LB films onto the Al stripes Cu pads are evaporated (Fig. 1). The inner conductor of a coaxial line is directly soldered to the Cu pads. It should be noted that the use of contacting needles or silver paste yields measurement errors and unreproducible results when the temperature is varied.

During the heating and cooling cycle each 10 K a measurement of the complete frequency range is performed to find the data in the frequency range with a variation of the temperature, \( \varepsilon''(\omega) \). In the same run the temperature and the dielectric permittivity at selected frequencies are measured each 30 s to get the data in the temperature range with variation of the frequency, i.e. \( \varepsilon''(T) \). The relaxation time is identified by the maximum of the imaginary part of the dielectric permittivity either in the frequency or in the temperature range.

3. Experiments

3.1. Measurements performed with thick samples

Broadband dielectric spectroscopy measurements are performed using the commercial available PVDF foils. A pronounced relaxation is found in the high frequency range [6]. The relaxation time is shifted to shorter values with increasing temperature. The relaxation spectra is not Debye like but broadened especially at lower temperatures. An Arrhenius representation of the relaxation times for two different sample thicknesses (9 µm and 22 µm) is shown in figure 2. As can be seen the data for the two different sample thicknesses are nearly identical. The data determined from \( \varepsilon''(\omega) \) and from \( \varepsilon''(T) \) respectively are consistent. The data can be fitted with the well-known Vogel-Tamman-Fulcher (VTF) equation

\[
\tau = \tau_0 \cdot \exp\left(\frac{B}{T - T_0}\right)
\]

with the VTF temperature \( T_0 = 184 \) K and the constants \( B = 1170 \) K and \( \tau_0 = 2.6 \cdot 10^{-12} \) s. The time-temperature superposition principle is fulfilled for these samples.
3.2. Measurements performed with thin samples

In the next step three LB samples with different thicknesses (28 nm, 45 nm, and 69 nm) are investigated. The dielectric relaxation spectra in the frequency range with variation of the temperature during the heating process for the 28 nm sample are shown in figures 3(a) and 3(b). Also for these samples a dielectric relaxation is found in the high frequency range [1,3-5].

The relaxation time depends on the temperature and decreases with increasing temperature. From the same set of data the dielectric permittivity in the temperature range is determined with variation of the frequency. The real part of the dielectric permittivity shows a typical ferroelectric behavior (Fig. 3(c)). During heating $\epsilon'$ increases up to the Curie temperature $T_{C1} \approx 380$ K in the ferroelectric phase. In the paraelectric region $\epsilon'$ decreases. If the sample is cooled afterwards the dielectric permittivity increases again down to a temperature $T_{C2} \approx 340$ K. Below $T_{C2}$ the dielectric permittivity decreases with decreasing temperature. Thus, $\epsilon'$ shows a temperature hysteresis as expected for type I ferroelectrics. The hysteresis and the dielectric relaxation are also found in the imaginary part of the dielectric permittivity (Fig. 3(d)). All further data are extracted during the heating process. However, the high frequency dielectric relaxation time is not influenced by the direction of the temperature variation. This is a first indication that the dielectric relaxation is not directly caused by the ferroelectric system.

In figure 3(e) the relaxation times for different sample thicknesses calculated from the maximum of $\epsilon''(T)$ in the temperature range are presented. The values for all samples coincide and a fit of the data with the VTF formula ($\tau_0 = 2 \cdot 10^{-10}$ s, $T_0 = 195$ K, and $B = 750$ K) is possible. On the other hand the relaxation times observed from the maximum of $\epsilon''(\omega)$ in the frequency range for the 69 nm and the 28 nm sample show a curvature which cannot be fitted by VTF (Fig. 3(f)). Here, a fit with a simple Arrhenius formula seems to be possible if the temperatures below 240 K are neglected where the P(VDF-TrFE) undergoes the glass transition in thick samples [6]. Furthermore, the relaxation times presented in figure 3(e) differ from the values determined from $\epsilon''(T)$ shown in figure 3(f). Thus, the time-temperature superposition principle is not valid in the thin films.

Now, the question about the physical origin of the dielectric relaxation arises. In measurements performed on ferroelectric BaTiO$_3$ a comparable relaxational behavior is observed at frequencies of about 1 GHz at room temperature [8]. This behavior is attributed to a motion of domain walls. Because the relaxation in P(VDF-TrFE) is also present in the paraelectric phase a vibration of the domain walls can be excluded. Additionally, the relaxation time is independent of the polarization state, i.e. the unpolarized sample shows the same relaxation time as a completely polarized sample where no domains and thus no domain walls are present.
Figure 3. (a) Real and (b) imaginary part of the dielectric permittivity for the 28 nm thick LB sample in the frequency domain with variation of the temperature during the heating process. (c) Real and (d) imaginary part of the dielectric permittivity for the same data set in the temperature range with variation of the frequency. Next figures: Arrhenius plot of the relaxation times for three different LB samples calculated (e) from the maximum of $\varepsilon''(T)$ in the temperature range and (f) from the maximum of $\varepsilon''(\omega)$ in the frequency range. Different relaxation times are found and a fit with the VTF formula is not possible for the data calculated from $\varepsilon''(\omega)$. 
in the ideal case.

Thus, the physical origin of the relaxation and the explanation of the temperature dependence of the relaxation time in the LB films still remains an open question.

4. Conclusion
It is shown that a thermally activated relaxational behavior is found in thick PVDF as well as in thin LB P(VDF-TrFE) films. In the thick samples the relaxation times do not depend on the sample thickness and follow a VFT law in the temperature range. The thin samples show different behavior for the relaxation times versus the temperature determined from the maximum of $\varepsilon''(\omega)$ compared to the data determined from the maximum of $\varepsilon''(T)$. Thus, the time-temperature superposition principle is not valid in the thin films whereas it does hold for the thick films. Additionally, a domain wall motion can be excluded as the physical origin of the dielectric relaxation.

References
[1] Martin B, Kuehn M and Kliem H 2010 J. Appl. Phys. 108 084109
[2] Kliem H and Tadros-Morgane R 2005 J. Phys. D: Appl. Phys. 38 1860
[3] Jogad M S and Ducharme S 2002 Curr. Sci. 83 472
[4] Verkhovskaya K A, Plakseev A A, Lotonov A M and Gavriloa N D 2009 Ferroelectrics 379 144
[5] Martin B, Vizdrik G and Kliem H 2009 J. Appl. Phys. 105 084114
[6] Solnyshkin A V and Kislova I L 2010 Ferroelectrics 398 77
[7] Palto S, Blinov L, Bune A, Dubovik E, Fridkin V, Petukhova N, Verskovskaya K and Yudin S 1995 Ferroelectr., Lett. Sect. 19 65
[8] Poplavko Y M, Tsykalov V G and Molchanov V I 1968 Soviet Physics - Solid State 10 2708