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Origin of the strong temperature effect on the piezoelectric response of the ferroelectric (co-)polymer P(VDF$_{70}$-TrFE$_{30}$)

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HIGHLIGHTS

- The strong impact of temperature on the piezoelectric response of the electroactive polymer P(VDF$_{70}$-TrFE$_{30}$) is explained.
- A straightforward measurement methodology is presented to measure the piezoelectric constant d_{33} of piezoelectric polymers.
- A CMOS-compatible process is presented for the fabrication of capacitors in which the polymer P(VDF$_{70}$-TrFE$_{30}$) is integrated.
- Different measurements methodologies are compared for the determination of the piezoelectric response.

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ABSTRACT

The electroactive (co-)polymer poly(vinylidene fluoride$_{70}$-trifluorethyline$_{30}$) is predestined for applications in flexible and soft electronic devices. However, the piezoelectric properties are highly temperature sensitive and so far, reported results cannot provide an explanation for their strong temperature dependence. For this purpose, we investigate the impact of temperature on important electrical, mechanical and electromechanical properties. For instance, both the electric-field- and the load-induced piezoelectric response characteristics were determined using micromachined capacitor-type test structures. Our results show that the piezoelectric performance of the polymer is strongly temperature-dependent even before the phase transition from the ferroelectric to the paraelectric regime. Starting from 25 °C, we measured an increase in the piezoelectric constant d_{33} up to 150% with increasing temperature up to 80 °C. We show that the highly increasing piezoelectric response of the polymer is directly linked to the temperature dependence of its elastic modulus and polarization.

1. Introduction

Poly(vinylidene fluoride) (P(VDF)) and its copolymers are electroactive (fluor-)polymers. This family of functional materials is well-known for their remarkable ferroelectric and piezoelectric properties. Their ability to convert mechanical strain to electrical charge and *vice versa* offers numerous application possibilities, especially in the field of flexible and soft electronics [1–4]. The unique mechanical flexibility of these polymers compared to other typically used piezoelectric materials such as lead zirconate titanate (PZT) [5] or aluminium nitride (AlN) [6,7] paves the way for a new generation of stretchable electronic devices. Nowadays, they are already used as electromechanical transducers in sensors [3,4], actuators [8] and energy harvesters [1]. For the fabrication of micromachined devices, these polymers can also be integrated into a CMOS-compatible process, thus increasing the potential for high volume production.

P(VDF) is a semi-crystalline material that primarily crystallizes in five different phases or orientations, i.e. α-, β-, γ-, δ- and ε-phase [9]. Here, the β-phase exhibits especially high piezoelectric properties, because the polymer chains consisting of the monomer units (CH_2-CF_2) are aligned as all-trans (planar zigzag) conformation. Due to the large difference in the electronegativity between the fluorine atoms and the hydrogen as well as the carbon atoms, a strong electric dipole moment occurs, leading to a macroscopic polarization in the material. Basically, P(VDF) is present in the non-polar α-phase after synthetization. However, it can be transformed into the β-phase by various complex treatments such as mechanical deformation or crystallization under high pressure [9]. To avoid such cumbersome procedures, the (co-)polymer poly(vinylidene fluoride-trifluorethylene) (P(VDF-TrFE)) is often utilized. P(VDF-TrFE) preferably crystallizes into a crystal structure similar to that of the β-phase of P(VDF), which tremendously facilitates the fabrication of electroactive polymer thin films. Nevertheless, the

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polymers must be polarized by an electric field so that all domains get aligned to achieve maximum macroscopic polarization.

Like all ferroelectrics, this class of polymers also shows a phase transition from a ferroelectric (electroactive) to a paraelectric (non-electroactive) phase at the so-called Curie temperature T_C. Above this temperature, they are not useable as electromechanical transducers, since the macroscopic polarization and thus the piezoelectricity is lost. The Curie temperature is quite low for most polymers. For example, P(VDF_{70}-$TrFE_{30}$) has a Curie temperature of around 100 °C. But even below this temperature, the piezoelectric as well as the electrical and mechanical properties are highly temperature sensitive. Some measurements of the piezoelectric performance of P(VDF-TrFE) at room temperature can be found in literature. However, there are only few studies on the temperature dependence of the piezoelectric constants. For example, scanning near-field acoustic microscopy (SNAM) was used to investigate the electric-field-induced (inverse) piezoelectric effect, but not the load-induced (direct) piezoelectric effect [10]. In addition, the reported results cannot explain the strong impact of temperature on the piezoelectric response of this polymer. It was assumed that the temperature dependence of the piezoelectric response is related to the temperature dependence of the mechanical properties. To the best of the authors' knowledge, a rigorous justification of this assumption is, however, still missing.

In this study, we show how the impact of temperature changes the piezoelectric response of the polymer P(VDF_{70}-$TrFE_{30}$) up to 110 °C, and reveal the origin of the strong temperature dependence. For this purpose, we present a straightforward method to measure the temperature dependence of the direct piezoelectric effect without the use of complex measuring equipment and compare these results with those of other measurement approaches based on e.g. atomic force microscopy providing the inverse piezoelectric constant.

2. Experimental details

Sample fabrication and characterization of the polymer. To investigate the impact of temperature on the electrical and electromechanical properties micromachined P(VDF_{70}-$TrFE_{30}$) capacitor-type test structures were fabricated. For this purpose, we used a 4" 100 mm (100) silicon (Si) wafer coated with 150 nm LPCVD silicon dioxide (SiO_2) as substrate for the following fabrication procedure.

The bottom electrodes were formed by a conventional lift-off process. We deposited 50 nm of titanium (Ti) by electron-beam evaporation as an adhesion promoter for a 200 nm thermally evaporated gold (Au) layer. The Au film helped to increase the electrical conductivity of the bi-layered metallization. We used a polymer powder P(VDF_{70}-$TrFE_{30}$) with a ratio VDF:TrFE of 70:30 mol%, which was purchased from the Piezotech/Arkema Group. This powder was dissolved at a weight ratio of 8% in the solvent methyl ethyl ketone (MEK). Subsequently, the solution was spin-coated onto the wafer and the solvent MEK was carefully evaporated at 80 °C in air. This is followed by an annealing process at 130 °C for 2 h in a vacuum furnace to enhance the degree of crystallinity. Finally, we obtained a thin polymer film with a thickness of $t = 1$ µm.

To analyse the present phase and the molecular conformation of the material, we used a Fourier transform infrared (FTIR) spectrometer Tensor 27 by Bruker and an X-ray diffractometer (XRD) X'Pert Pro from Molvern Panalytic. Both FTIR and XRD measurements show that the polymer P(VDF_{70}-$TrFE_{30}$) crystallized into the highly polar β-phase. In the FTIR spectrum in Fig. 1 (a), the absorption bands at 1288 cm^{-1} and 850 cm^{-1} are associated with the β-phase possessing all-trans sequences. As shown in the inset of Fig. 1 (a), the diffraction peak is found at $2\Theta = 19.7°$, which is attributed to the reflections of the (110) and (200) crystallographic planes associated with the β-phase of P(VDF_{70}-$TrFE_{30}$) [11]. The ferroelectric domain size is investigated by applying atomic force microscope (AFM) (Dimension Edge from Bruker). Fig. 1 (b) shows the surface characteristics of the thin polymer film, which was annealed at 130 °C in vacuum. At this annealing temperature, we obtained a ferroelectric domain size of around 100 nm. In general, the piezoelectric response as well as the Curie temperature of this class of polymers depend on the ferroelectric domain size and the comonomer content [12,13]. However, both the FTIR and XRD measurements as well as the AFM image indicate ferroelectric properties of the polymer P(VDF_{70}-$TrFE_{30}$) being comparable to those reported in literature. Thus, a solid basis is given to study the impact of temperature on the electromechanical film properties in detail.

On top of the polymer, 200 nm Au electrode pads were patterned by a wet-chemical etching process. An adhesion promoter was not necessary, since the adhesion between Au and P(VDF_{70}-$TrFE_{30}$) is sufficient. We did not use a lift-off process, since standard solvents for photoresists, such as propylene glycol monomethyl acetate (PGMEA), attack the polymer, which results in large cracks all over the polymer layer. Finally, the capacitor-type test structure was finalized applying a dry etching process in O_2 plasma with the top electrode as hard mask, thus excluding from the residual chip surface any parasitic effects from the P(VDF_{70}-$TrFE_{30}$) film during electromechanical characterization. Fig. 2 (a) summarizes schematically the process flow of the capacitor-type test structures. The diameter of the circular capacitors is 0.8 mm, whereas a cross-sectional SEM image is shown in Fig. 2 (b). Finally, the polymer films were poled at room temperature only once at an electric field of 100 V/µm by applying a DC voltage.

Electrical and mechanical characterization of the polymer thin films. The macroscopic polarization P of the material can be measured via a Sawyer-Tower bridge. By applying an AC electric field of $E = \pm 80$ V/µm above the coercive field $E_c = \pm 50$ V/µm to the capacitor at 10 Hz, it is possible to determine the switching behaviour of the polarization. As a result, the typical P-E hysteresis common in ferroelectrics is measured. However, the permittivity ε_r must be known in order to achieve the polarization via the relation $P = \varepsilon_0 (\varepsilon_r - 1) E$. We measured the permittivity ε_r using the LCR meter IM3533-01 purchased from Hioki.

The elastic modulus Y (Young's modulus) of P(VDF_{70}-$TrFE_{30}$) was measured using a dynamic mechanical analysis (DMA Q800) by TA Instruments. For this purpose, 10 µm thin polymer films were fabricated. The polymer solution was spin-coated on a 4″ 100 mm (100) silicon wafer and treated under the same conditions as for the capacitors process. Finally, the polymer film was peeled off the wafer and cut into an appropriate size.

Electromechanical characterization of the polymer thin films. We used the AFM to determine the electric-field-induced piezoelectric response of the polymer films [14,15]. Here, the AFM was only used to measure the displacement of the capacitor-type test structure at one single point. The measurement procedure is illustrated in Fig. 3. A silicon nitride cantilever (non-conductive, with a spring constant of 0.32 N/m) was placed on the top electrode at the center of the fabricated capacitor-type test structure. By applying an external 10 Hz triangular waveform signal to the capacitor, the cantilever was deflected, so that it was possible to measure the piezoelectric response of the electroactive polymer P(VDF_{70}-$TrFE_{30}$). The vertical displacement Δt and hence the strain $S = \Delta t/t$ of the polymer was measured as a function of the electric field E. The result is the typical butterfly curve of ferroelectric materials. In parallel, we measured its polarization hysteresis with a Sawyer-Tower bridge. Before each measurement, force-distance curves were obtained in order to calibrate the conversion factor between optical output and displacement of the cantilever. The capacitor was rigidly fixed to the sample holder by vacuum, as shown in Fig. 4. Since the top- and bottom-electrode have the same size and the lateral dimension of the capacitor ($d = 0.8$ mm) is substantially larger than the thickness of the polymer film ($t = 1$ µm), clamping effects can be neglected if we measure at the centre of the capacitor-type test structures (i.e. far away from the edges) [16]. In addition, Wang et al. showed that clamping effects are reduced if the difference of the elastic properties of polymer to electrode material is large [16].

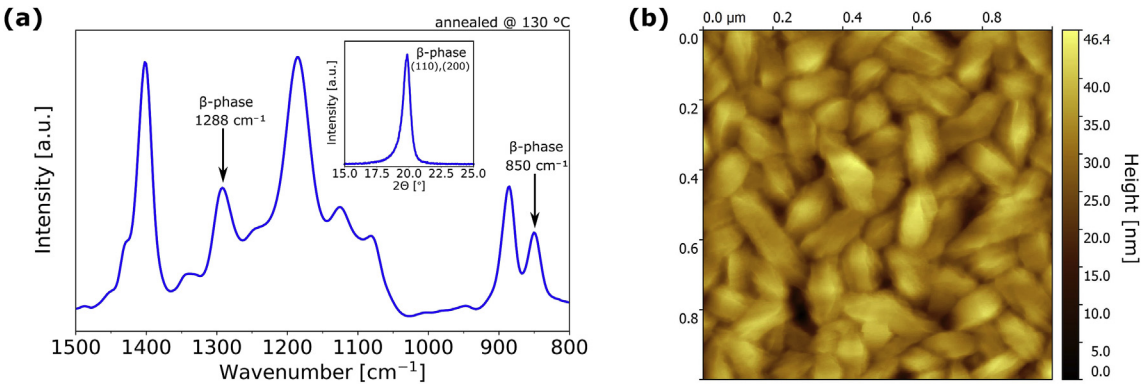

Fig. 1. (a) FTIR spectrum of P(VDF_{70}-$TrFE_{30}$). The dominant peaks at 1288 cm^{-1} and 850 cm^{-1} verify that the polymer film crystallized into the high polar (ferroelectric) β-phase. The inset shows XRD data, which in addition confirm the presence of β-phase in the polymer film. **(b)** Surface topography of the polymer P(VDF_{70}-$TrFE_{30}$) annealed at 130 °C and measured with AFM. The ferroelectric domain size is around 100 nm.

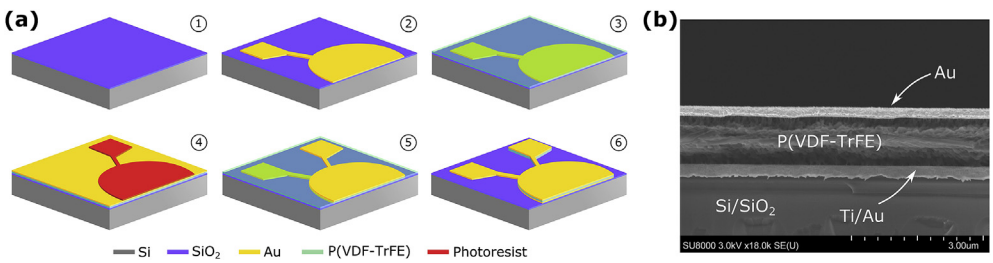

Fig. 2. (a) Process steps for the fabrication of the capacitor-type test structures: (1) Starting with a 4" (100) Si wafer coated with 150 nm LPCVD SiO_2. (2) Bottom electrode patterning through a lift-off process. (3) Spin-coating of the P(VDF_{70}-$TrFE_{30}$) polymer film. (4), (5) Top electrode patterning through a wet-chemical etching process. (6) Etching of P(VDF_{70}-$TrFE_{30}$) in O_2 plasma. **(b)** Cross-sectional SEM image of the P(VDF_{70}-$TrFE_{30}$) capacitor-type test structure.

For the temperature-dependent measurements, we used a small hot plate (Linkam, PR600) and controlled the temperature on the sample with a thermo element.

3. Results and discussion

The *S-E* butterfly curve of the ferroelectric polymer. To ensure a high piezoelectricity of our fabricated P(VDF_{70}-$TrFE_{30}$) thin films, we measured the piezoelectric response at a temperature of 25 °C using the AFM measurement procedure. The obtained strain S as a function of the applied electric field E is shown in Fig. 5 (a). The result is a pronounced S-E butterfly curve, which is typical for ferroelectric materials. Using the equation

$$d_{33} = \frac{\partial S}{\partial E}|_{E=0} \ , \tag{1}$$

it is possible to deduce from the data of the S-E butterfly curve the piezoelectric constant d_{33}. We determined for d_{33} a value of −32 pm/V ± 1 pm/V by a linear approximation around E = 0 V/µm within an interval of −5 V/µm to +5 V/µm, thus confirming a strong piezoelectric activity of our fabricated polymer films. We choose this interval, as in this range the Pearson correlation coefficient is larger than 95% in all measurements. Temperature-dependent measurements with the AFM could not be performed, since it has no heatable sample

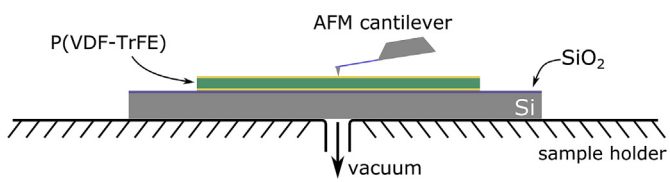

Fig. 4. Clamping of the capacitor-type test structures. At the center of the capacitor, we measure the piezoelectric response of the polymer P(VDF_{70}-$TrFE_{30}$) with an AFM setup. Since the polymer film is very thin compared to its lateral dimension, clamping effects can be neglected [16].

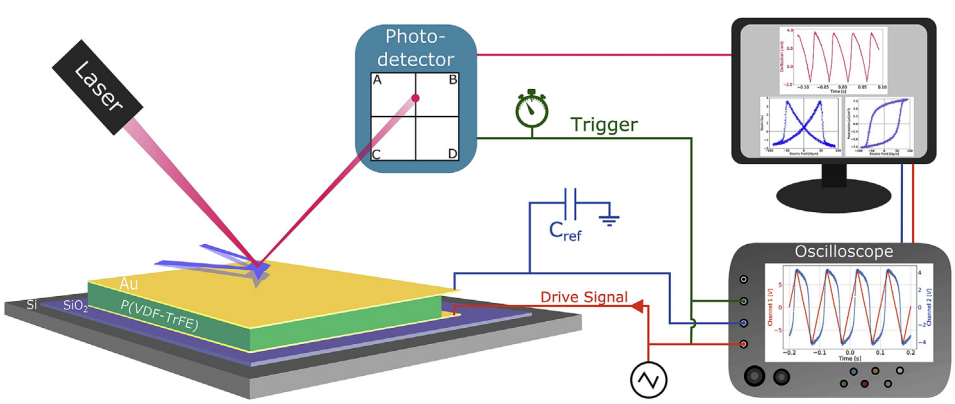

Fig. 3. Measurement setup to determine the electric-field-induced piezoelectric response of the polymer P(VDF_{70}-$TrFE_{30}$) using the fabricated capacitor-type test structures. Using the AFM setup and the Sawyer-Tower bridge, the deflection of the electroactive polymer as well as its polarization are measured simultaneously.

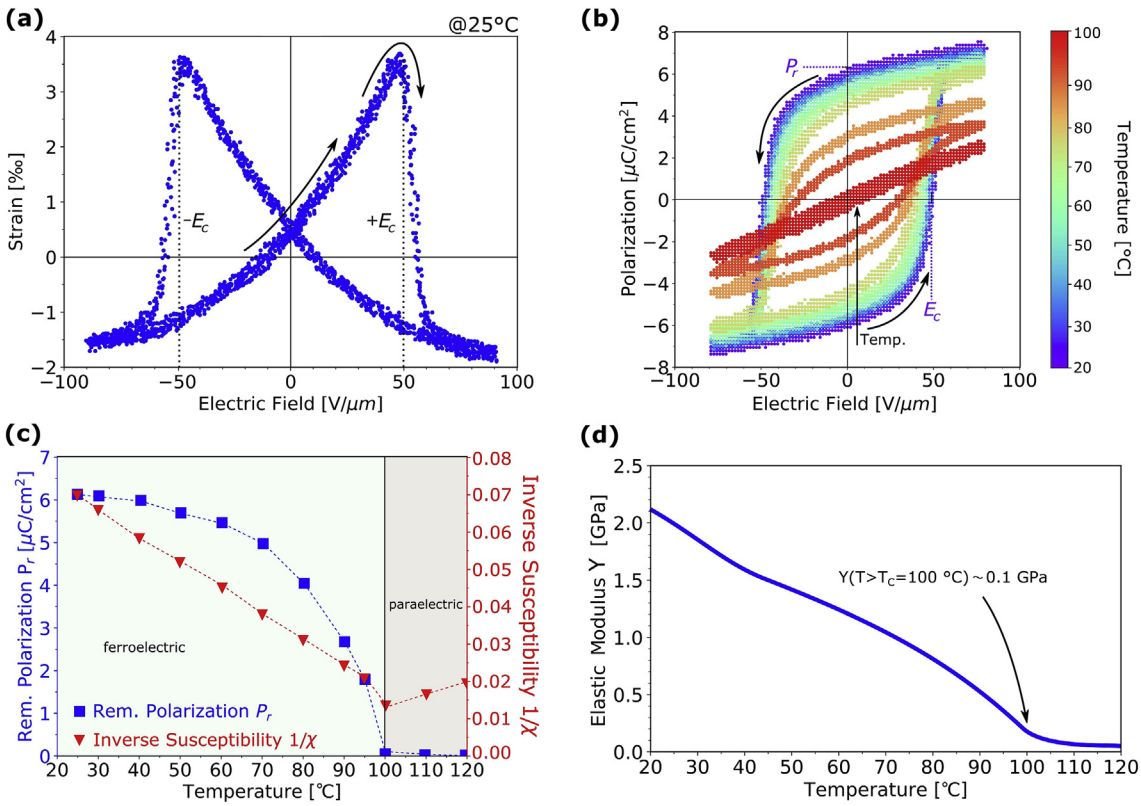

Fig. 5. (a) Strain as a function of the applied electric field measured with an AFM at 25 °C and at 10 Hz (*S-E* butterfly curve). **(b)** *P-E* hysteresis obtained using 10 Hz bipolar triangular waveforms for different temperatures. **(c)** Temperature dependence of the remanent polarization P_r and the inverse susceptibility $1/\chi$, which show the phase transition from the ferroelectric to the paraelectric regime at the Curie temperature $T_C = 100$ °C. (d) Impact of temperature on the elastic modulus Y (Young's modulus) of P(VDF$_{70}$-TrFE$_{30}$) films.

holder. However, the AFM measurement provides a useful reference for all further results at 25 °C.

From electrical and mechanical material parameters to the piezoelectric coefficient. Another approach to determine the thermal influence on the piezoelectric constant d_{33} is to measure the temperature dependence of the remanent polarization P_r and the Young's modulus Y. From the electrical and mechanical properties of P(VDF$_{70}$-TrFE$_{30}$), we can determine according to

$$d_{33} \approx -\frac{P_r}{Y} \tag{2}$$

the electromechanical parameter d_{33} [17–19]. Fig. 5 (b) shows the *P-E* hysteresis at different temperatures. The remanent polarization P_r is the polarization that is maintained in the material even when no electric field is applied, i.e. $P_r = P(E = 0)$. For example, we obtain for P_r a value of 6.2 μC/cm^2 at a temperature of 25 °C. All other temperature-dependent values of P_r are depicted in Fig. 5 (c). Generally, the impact of temperature on P_r is at low temperatures only moderate, but close to the Curie temperature $T_C = 100$ °C P_r decreases rapidly and even vanishes. In addition, Fig. 5 (c) shows the inverse susceptibility $1/\chi = (\varepsilon_r - 1)^{-1}$. The change of the slope in the $1/\chi$ characteristics confirms the Curie temperature at $T_C = 100$ °C. The temperature dependence of the elastic modulus Y is presented in Fig. 5 (d). In the given temperature range, Y decreases almost linearly until this parameter remains constant at a value of about 0.1 GPa at T_C or above. At a temperature of 25 °C, an elastic modulus of $Y = 2$ GPa and a remanent polarization $P_r = 6.2$ μC/cm^2 results in a piezoelectric constant $d_{33} = -31$ pm/V using equation (2). This result agrees very well with the AFM-based measured value of $d_{33} = -32$ pm/V.

We have introduced two methods to determine the piezoelectric constant d_{33} of P(VDF$_{70}$-TrFE$_{30}$). On the one hand the electric-field-induced piezoelectric response of the polymer was measured using the AFM setup leading to the *S-E* butterfly curve and on the other hand the d_{33} was deduced via the remanent polarization P_r and the elastic modulus Y according to equation (2). But, a quantitative determination of the load-induced piezoelectric response of a soft material like P(VDF$_{70}$-TrFE$_{30}$) is still missing.

Measurement procedure for the direct piezoelectric response. The load-induced piezoelectric performance of the polymer thin film is investigated using the measurement procedure as shown in Fig. 6 (a). We connected the P(VDF$_{70}$-TrFE$_{30}$) based capacitor-type test structure to an oscilloscope in combination with a charge amplifier. A test mass m was placed on the capacitor and the generated charge Q was measured with an accuracy of ± 0.2 pC. If the test mass is removed, an opposite charge is generated. The raw data of such a measurement cycle are displayed in Fig. 6 (a). The signal is disturbed by the 50 Hz signal present in the European electricity net, which can be removed through a Notch filter (see Fig. 6 (b)). The deceleration-related force component that is transferred when placing the test mass on the capacitor cannot be determined quantitatively, since each test mass is put on the capacitor differently. However, when the test mass is removed from the capacitor, a charge is generated which is only caused by the corresponding change in weight force of the test mass. Thus, it is possible to quantitatively determine the piezoelectric constant d_{33} using the relation

$$d_{33} = \frac{\partial Q}{\partial F}\Big|_{F=0}. \tag{3}$$

The inset of Fig. 6 (b) shows the absolute value of the generated charge for various test masses (i.e. forces). As only small forces in the range of 3–17 cN act on the piezoelectric film, the output characteristics is linear. We used a linear fit of the data to determine a $|d_{33}| = 30.4$ pC/N via equation (3). We repeated this procedure at different temperatures up to 110 °C. Before we put a mass on the test structure, we waited

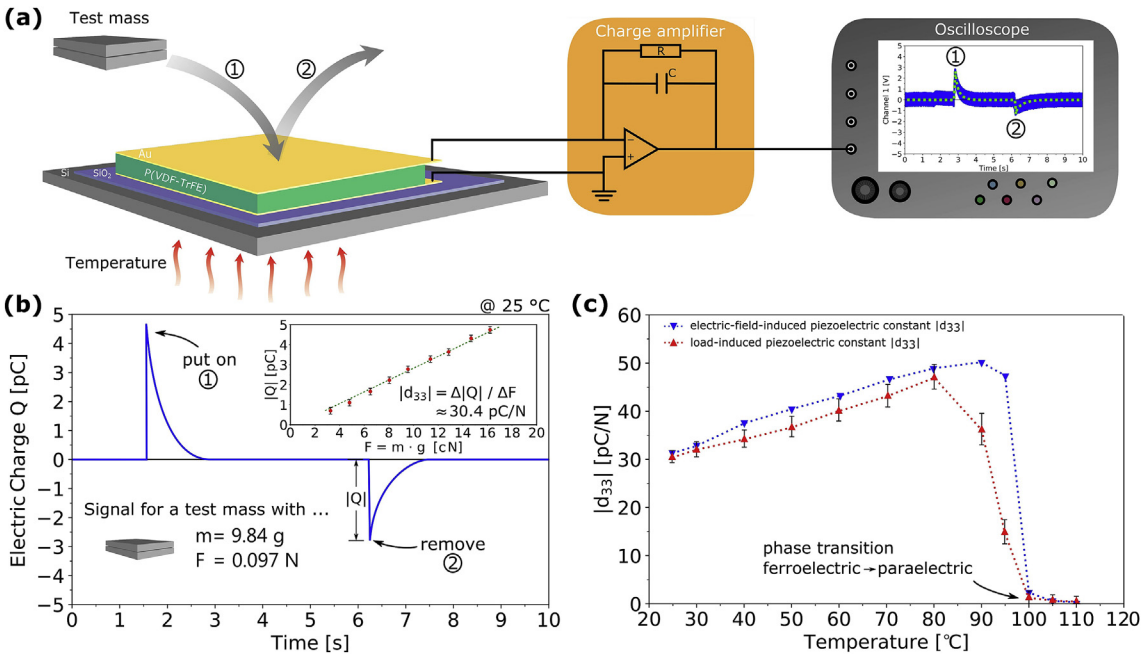

Fig. 6. (a) Measurement setup to determine the impact of temperature on the load-induced piezoelectric performance of P(VDF_{70}-$TrFE_{30}$) thin films. **(b)** FFT filtered signal of the generated charge for one test mass. The inset shows the absolute value of the generated charge for various test masses (forces). **(c)** Temperature dependence of the piezoelectric constant d_{33}.

until the sample reached the temperature. This was controlled with a thermo element on the sample. The results are plotted in Fig. 6 (c) and compared with the results from equation (2) for different temperatures. Independent of the measurement procedure, the piezoelectric constant d_{33} increases strongly with increasing temperature, up to 150% at 80 °C compared to that at 25 °C. As expected, there is a substantial decrease in d_{33} at the Curie temperature. The large increase of the piezoelectric constant d_{33} with temperature is due to the fact that the Young's modulus Y decreases linearly with temperature while the remanent Polarization P_r remains nearly constant and does not decreases significantly until just prior to T_C (see equation (2) and Fig. 5 (c) and (d)). Towards the phase transition, the remanent polarization P_r decreases rapidly until it completely vanishes at the Curie temperature. Consequently, the piezoelectricity is lost above T_C.

4. Conclusion

In summary, we have analyzed the impact of temperature on the electrical, mechanical and electromechanical properties of P(VDF_{70}-$TrFE_{30}$) thin films. For this purpose, we fabricated micromachined P(VDF_{70}-$TrFE_{30}$) capacitor-type test structures to measure the electric-field-induced and load-induced piezoelectric response. We have introduced a straightforward measurement procedure to obtain the load-induced piezoelectric constant d_{33}, which might also be useful for the characterization of other soft piezoelectric materials. In addition, we have shown that this setup is well suited to measure the temperature dependence of the d_{33} up to 110 °C. The results were evaluated against those gained from the electric-field-induced measurements showing excellent agreement. Furthermore, it could be demonstrated that the increase in the piezoelectric constant d_{33} is dominated by the strong decrease in temperature of the Young's modulus while the temperature-related decrease of the remanent polarization is up the Curie temperature substantially lower. Basically, the polymer becomes extremely soft and more flexible, so that the piezoelectric constant d_{33} increases strongly with increasing temperature, up to 150% at a temperature of 80 °C compared to the room temperature at 25 °C. Thus, the piezoelectric constant d_{33} is highly sensitive to any static or dynamic temperature loads. For applications as electromechanical transducer in sensors, actuators or energy harvesters, the temperature dependence of the electroactive properties of P(VDF_{70}-$TrFE_{30}$) must be taken into account, to exploit the full potential of this most promising soft material.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.polymer.2019.02.064.

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