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# Electromechanical Coupling of Polymeric Films studied by using Piezoresponse Force Microscopy

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## Abstract

Electromechanical coupling is a fundamental mechanism underlying the functionality of many materials, including inorganic materials such as piezoelectric materials as well as many biological systems. The applications of electromechanical property cover many areas including sonar, medical imaging, sensors and energy harvesting technologies.

The aim of this project is to investigate the piezoelectric properties of two polymer films, polyvinylidene fluoride (PVDF) and polyvinylidene trifluoroethylene (P(VDF-TrFE)). Piezoresponse Force Microscope (PFM) is used to scan the film surface under different applied voltages, and to obtain the nanoscale structural images of height, frequency, amplitude and phase.

A proportionality constant ( $d_{33}$ ) was obtained for each sample. Local piezoelectric aging property was then studied by poling a certain area with negative bias followed by positive bias. Furthermore, hysteresis loop measurements were carried out on these two film samples. This project has demonstrated that both films show strong piezoelectric response. This can contribute towards future research of microelectronic devices, such as memory and data storage devices.

## Introduction

Materials with pyroelectric, piezoelectric, and ferroelectric properties are increasingly popular in making electromechanical devices, e.g., memory, thermal imagers, acoustic transducers, sensor and actuator and so on<sup>1</sup>. Many materials, such as single crystals, ceramics and polymers, have piezoelectric properties, i.e., the materials changes their dimensions with external applied voltage, or vice versa<sup>2</sup>. Among these materials, polyvinylidene fluoride (PVDF) and its trifluoroethylene copolymer P(VDF-TrFE) are the only polymeric materials exhibiting piezoelectric properties, PVDF and its copolymer are promising candidates for making non-volatile random-access data storage devices due to their low coercive voltage, small thickness, low cost and easy fabrication.

In this project, we therefore studied the nanoscale piezoelectric responses of the polymer films with different thicknesses, these are: PVDF films with 30nm and 400nm thickness, and P(VDF-TrFE) films with 50nm and 400nm thickness. Three main experiments were conducted to investigate the nanoscale piezoelectric properties of PVDF and P(VDF-TrFE) polymer films. Measurement of piezoelectric coefficient  $d_{33}$  is the basic experiment to characterize the degree of piezoelectric response from each sample upon the application of a dc voltage. Poling response and hysteresis loop measurement are important in identifying these polymers as potential candidates for being used in memory storage devices. Therefore, these three experiments are crucial in exploring the future uses of PVDF and its copolymer by examining their piezoelectric response at nanoscale.

## Materials and Methods

### Sample preparation

The PVDF 30 nm and P(VDF-TrFE) 50 nm film samples are prepared using Langmuir-Blodgett (LB) technique, whereas the PVDF 400 nm and P(VDF-TrFE) 400 nm film samples are prepared using spin-coating method, and these samples are provided by Institute of Materials Research and Engineering (IMRE) for this research work.

### Sample Structure

The chemical structures of the two films are schematically shown on Fig.1 and Fig.2<sup>3</sup>.

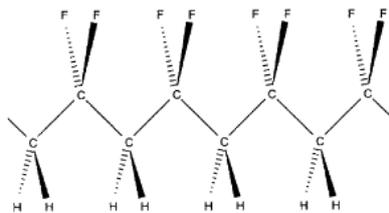


Fig.1. Molecular structure of PVDF

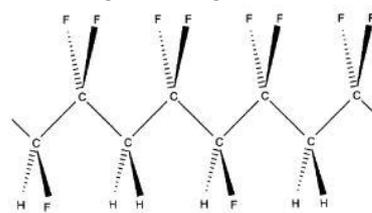


Fig. 2. Molecular structure of P(VDF-TrFE)

As shown in Fig.1, the polymer chain of the PVDF contains fluorine and hydrogen on opposite sides of the carbon. This makes PVDF a strong polar polymer. On the other hand, as shown in Fig.2, P(VDF-TrFE) has one fluorine and one hydrogen on the same side of the carbon. This neutralises some of the polar properties of P(VDF-TrFE), and this should make P(VDF-TrFE) a relatively weaker polar material than that of the PVDF.

## Experimental Setup

The PVDF and P(VDF-TrFE) thin films were studied using an Piezoresponse Force Microscopy<sup>4</sup>(PFM), as schematically shown in Fig. 3. PFM is a variation of the scanning probe microscopy (SPM) technique based on the converse piezoelectric effect, i.e., the material expands if the electric field is parallel to its polarization, and contracts if anti-parallel.

The tip of the cantilever used in PFM is made of a conductive material. It makes the electrical contact between the tip and the sample surface. When a bias (alternating voltage) is applied to the tip which is in contact with the sample surface, the sample will respond accordingly in terms of amplitude (expansion or contraction) and phase (polarization). Then the piezoelectric response can be measured from the deflection of the cantilever.

This measurement uses a lock-in amplifier (Fig.3). The frequency of the applied ac voltage is typically far from (below) the fundamental resonance frequency of the cantilever in order to avoid driving the cantilever into resonant oscillations.

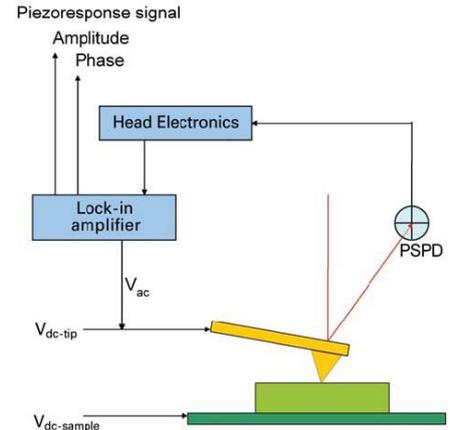


Fig. 3. The PFM principles

## Results

### I. $d_{33}$ measurement

The piezoelectric coefficient,  $d_{33}$ , is used to measure the piezoelectric response of different materials. To measure  $d_{33}$  using PFM, the voltages ranging from 1.0V to 3.5V are applied on the samples with different scanning areas, followed by measuring their piezoresponse amplitudes. The  $d_{33}$  values are then determined from the gradients of the graphs of Amplitude (pm) versus Applied Bias (V) and it is defined as effective  $d_{33}$  as it is an average value over the scanning area.

#### a) Average $d_{33}$ over the scanning area

Table 1 shows the results of measurement of  $d_{33}$  on the four samples.

Sample	Scanning area ( $\mu\text{m}^2$ )	Mean $d_{33}$ (pm/V)
PVDF 30nm	1	151
	5	119
PVDF 400nm	1	35 – 38
	5	27
P(VDF-TrFE) 50nm	1	74 – 79
	5	32
P(VDF-TrFE) 400nm	1	58 – 62
	5	NA

Table 1: Average  $d_{33}$  values of different samples

By comparing the mean  $d_{33}$  values for samples with the same material and scanning area but with different thicknesses, we find that the thickness does affect the magnitude of  $d_{33}$ . Mean  $d_{33}$  values decreases with the increasing thickness of the film. This shows that when the thickness of samples increases, the samples become less responsive to the same applied bias, and thus their piezoresponses are reduced.

When we compare samples of the similar thickness and scanning area but of different materials, we find that P(VDF-TrFE) has a lower  $d_{33}$  value than that of the PVDF film with low thickness. However, when the thickness increases, the  $d_{33}$  of P(VDF-TrFE) decreases much slower than that of PVDF. Thus, as shown in Table 1, the  $d_{33}$  value for P(VDF-TrFE) 400nm is even greater than that of the PVDF 400nm. One of the possible reasons for this is that the thicker film may have different structures from that of the thinner films. For the thinner films, the polymer chains are oriented in parallel to the surface, while in the thicker films the orientations of the polymer chains are random<sup>5</sup>. Therefore the piezoelectric properties of the thicker films are different from that of the thinner films.

For samples with the same thickness and materials, the scan size also affects the value of  $d_{33}$ . When a larger area of samples is scanned, the piezoelectric response decreases instead. This is probably due to a different average value obtained at the smaller area as some smaller areas may have larger piezoelectric response compared to that of the larger area. Furthermore, all our experiments were conducted using the same scanning rate. With a smaller scan area, the tip-stopping time on top of the sample during scanning is more than that of the larger scan. Hence, the sample may have more time to expand/contract with a smaller scan area. Obviously, this is a subject of on-going study.

## b) $d_{33}$ values at selected points

Table 2 shows the  $d_{33}$  at selected points on different samples.

Sample	Location	$d_{33}$	Mean $d_{33}$
PVDF 30nm	X	199	151
	Y	123	
PVDF 400nm	X	42	35-38
	Y	19	
P(VDF-TrFE) 50nm	X	74	74-79
	Y	27	
P(VDF-TrFE) 400nm	X	61	58-62
	Y	41	

Table 2:  $d_{33}$  values at selected points

The point data measurement is performed within the scanning size of  $1 \mu\text{m}^2$ . X and Y refer to the location with high and low piezoresponse amplitudes within the scanning area, respectively. Generally, the spots with higher piezoresponse amplitude demonstrate a larger  $d_{33}$ . For PVDF film, the magnitude of the average  $d_{33}$ , as shown in the Table 1, falls in between this range. In contrast, the average  $d_{33}$  for the P(VDF-TrFE) seems to be at the higher end value from point measurement. This could be due to some difficulties in locating the analyzed spots during point measurement.

## II. Hysteresis Loop Measurement

Fig.4 shows the hysteresis loop (polarization phase) as a function of the applied bias for P(VDF-TrFE) film of 50nm. Negative voltage was first applied in hysteresis measurement 1 (Hys.1) while positive voltage was first applied in the hysteresis measurement 2 (Hys.2). The results show that the P(VDF-TrFE) film has the typical ferroelectric behaviour.

From Fig.4, the symmetrical shape of the hysteresis loop indicates that a same value of the positive and negative bias is required to cause any polarization switching for the P(VDF-TrFE) 50nm film. For instance, the polarization domains of the sample begin to switch their direction at  $\sim +5\text{V}$  until a saturated state is reached at  $\sim +8\text{V}$ . The application of a reverse voltage at this saturated state, however, does not cause any significant changes in their polarization direction until another critical switching voltage in the negative range is achieved. Therefore, the sample remains in a single-poled condition after the removal of the applied bias. This type of hysteresis loop suggests that P(VDF-TrFE) may be a promising candidate for the memory storage devices because it can register a change in bias and maintain its polarization direction even when the applied bias is removed. Furthermore, it can switch the polarization direction when an opposite critical voltage is reached. This kind of property makes P(VDF-TrFE) ‘rewritable’, and therefore suitable for storing data.

A comparison of the topography, amplitude and phase image before and after the hysteresis loop measurement is shown in Fig.5. Some changes of height are noticed, which may be related to the poling effect.

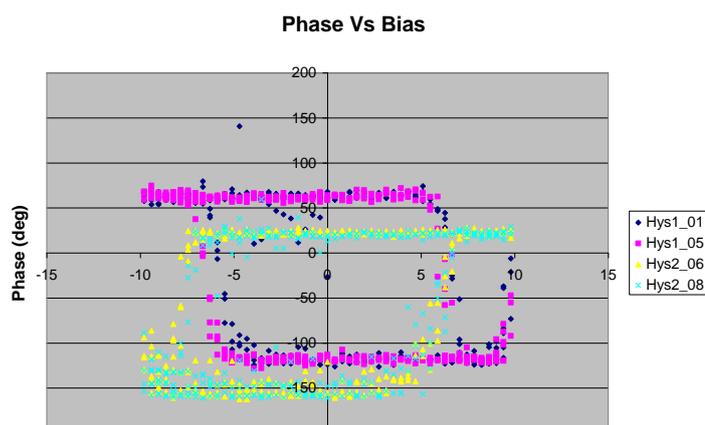


Fig. 4. Hysteresis loop of P(VDF-TrFE)

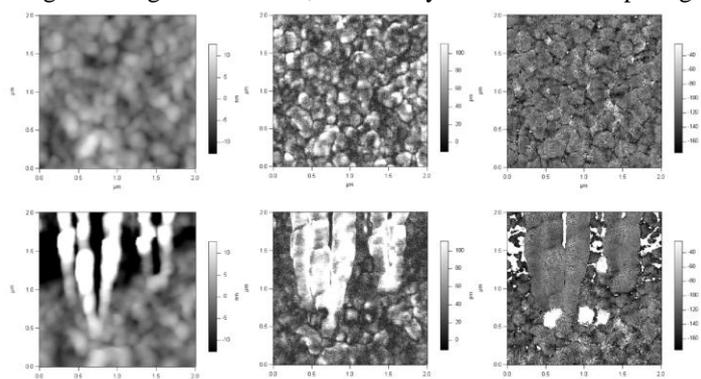


Fig. 5 Nanoscale image of P(VDF-TrFE) before and after hysteresis

Hysteresis loop measurements on PVDF films were also conducted but no conclusive results were obtained. One possible reason is that the domain switch for PVDF is more difficult and therefore need higher applied voltage which is beyond the capability of the current PFM set-up (+/- 10V).

### III. Poling effect

The poling experiment is only performed for P(VDF-TrFE) films because the hysteresis loop measurement did not obtain the meaningful information for the PVDF film samples. Therefore, the change of the amplitude/phase may be only pronounced for the P(VDF-TrFE) samples, another possibility is that PVDF requires higher voltage to be poled.

To analyze the poling effects of opposite voltages on P(VDF-TrFE) 50nm, we utilized direct current poling technique. The sample was first scanned without bias for a scale of  $5\mu\text{m}^2$ . Then a positive voltage is applied to the central portion with a scale of  $3\mu\text{m}^2$ . Eventually a negative voltage is applied on the central  $1.5\mu\text{m}^2$  portion. The sample phase and amplitude showed different response to different voltages.

#### a) Poled first by positive and then negative voltage

Fig. 6 shows the poling effect on P(VDF-TrFE) of 50nm. It is clear that the positive voltage causes no visible effects in the scanning area, but the negative voltage results in an obvious decrease in the piezoresponse amplitude within the central  $1.5\mu\text{m}^2$  scanning area.

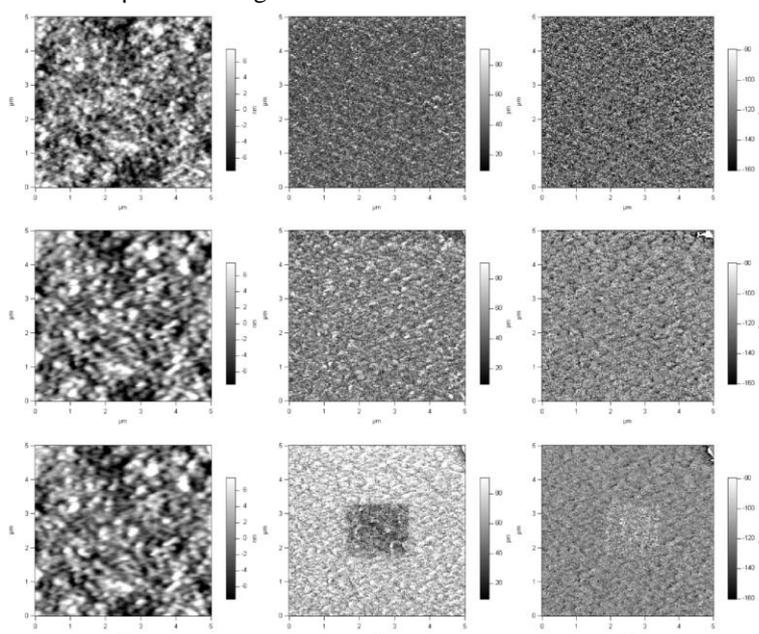


Fig.6 Location A, PVDF-TrFE, +10V, -10V

From top: topography, amplitude and phase before poling (field of view  $5\mu\text{m}^2$ ), after +10V DC applied to  $3\mu\text{m}^2$  area in the middle, and after -10V DC applied to  $1.5\mu\text{m}^2$  area in the middle.

Area	Amplitude/pm	Phase/degree
Unpoled	217	-124
+10V	667	-128
-10V	400	46

Table 3. hysteresis loop on Location A

Table 3 shows that both positive and negative voltages cause changes in the amplitude. When a positive 10V is applied, the amplitude increases by nearly three times, but the polarization phase does not change. On the other hand, when a negative 10V is applied subsequently in a smaller region; the amplitude decreases by an extent smaller than the increment, the phase angle also changes significantly, indicating the switching of the polarization by a negative voltage to nearly  $180^\circ$ . Furthermore, the morphology has markedly changed. It is unclear of the reason for this and more studies may be needed for a conclusive finding.

#### b) Poled first by negative and then positive bias

A reverse poling procedure are carried out on the sample, by applying negative voltage (-10V) first, followed by positive voltage (+10V). The results are shown in Fig.7. It is obvious that both positive and negative voltages induce poling effects on the sample of PVDF-TrFE. The amplitude and phase angle change remarkably.

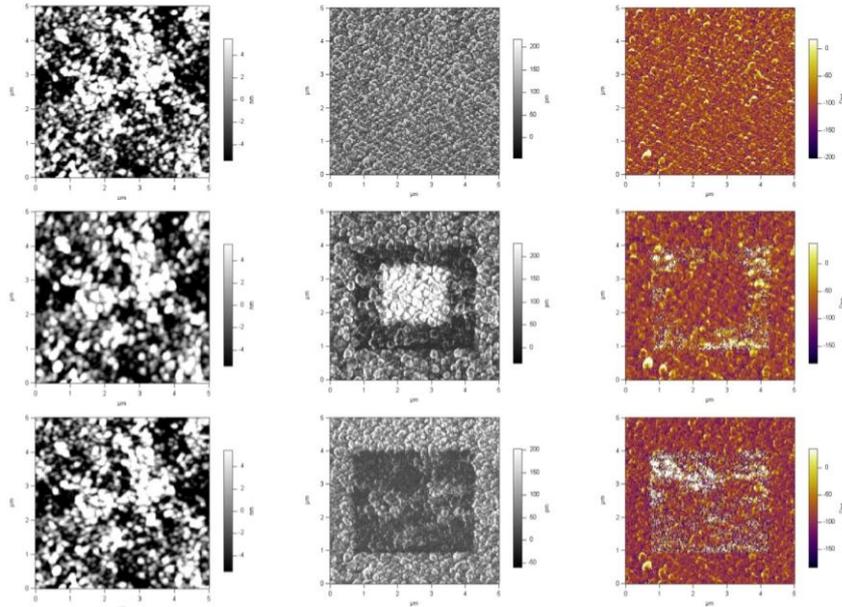


Fig.7 Location B, PVDF-TrFE, -10V, +10V

From top: topography, amplitude and phase before poling (field of view  $5\mu\text{m}^2$ ), after -10V DC applied to  $3\mu\text{m}^2$  area in the middle, and after +10V DC applied to  $1.5\mu\text{m}^2$  area in the middle.

Table 4 shows that the amplitude first decreases with a negative voltage applied, and then the amplitude increases significantly when a positive voltage is applied. The phase decreases by nearly 180 degrees after -10V is applied while returning to its original value after applied with a +10V. The morphology has changed significantly. Again, further confirmations are needed.

It can be deduced that negative voltage will completely reverse the phase, while positive voltage will make the phase return to its original value.

Area	Amplitude/pm	Phase/degree
Unpoled	310	70
-10V	270	-115
+10V	740	70

Table 4. Hysteresis loop on Location B

### c) The switching voltage

In the above experiments, extreme voltages of +/- 10V were applied to the sample to examine the poling effect. However, during the experiment, the sample showed no response when a smaller voltage (in terms of absolute value) is applied. Therefore it was suspected that there should be a critical switching voltage such that the sample may not respond until this critical voltage is achieved. From the hysteresis loop measurement, it can also be deduced that there is a critical voltage that cause the domain to switch. This might be helpful to explain why a positive 10V voltage imposes no effect on the unpoled sample.

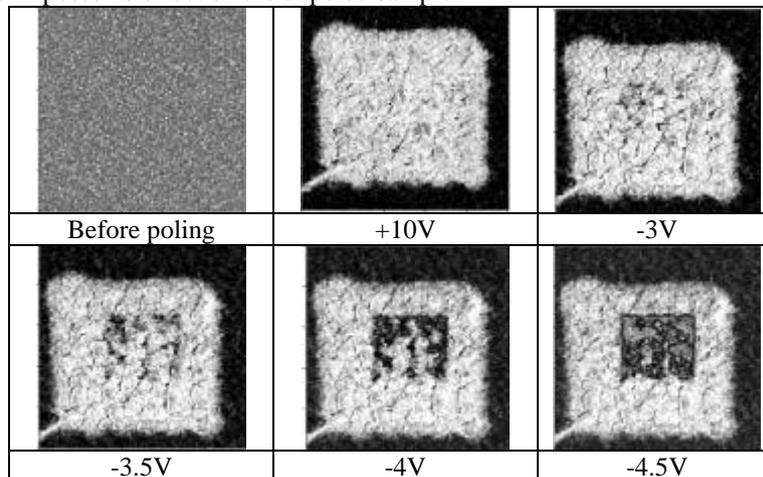


Fig.8 amplitude image during poling (positive first)

To further confirm the critical switching voltage, the applied dc voltage was gradually increased until a change in the phase is able to observe. Due to the limitation of the PFM machine, we are not able to apply voltages greater than 10V. A voltage of +10V was first applied to an area of  $3 \mu\text{m}^2$ , and then a negative voltage was applied within a  $1.5 \mu\text{m}^2$  area. The negative voltage was increased gradually until a noticeable change was found from the amplitude image. Fig. 8 shows the change in their amplitude.

From Fig.8 it can be seen that after the application of a positive voltage of +10V, the negative switching voltage is about -4.5V, the phase of the sample is completely inverted.

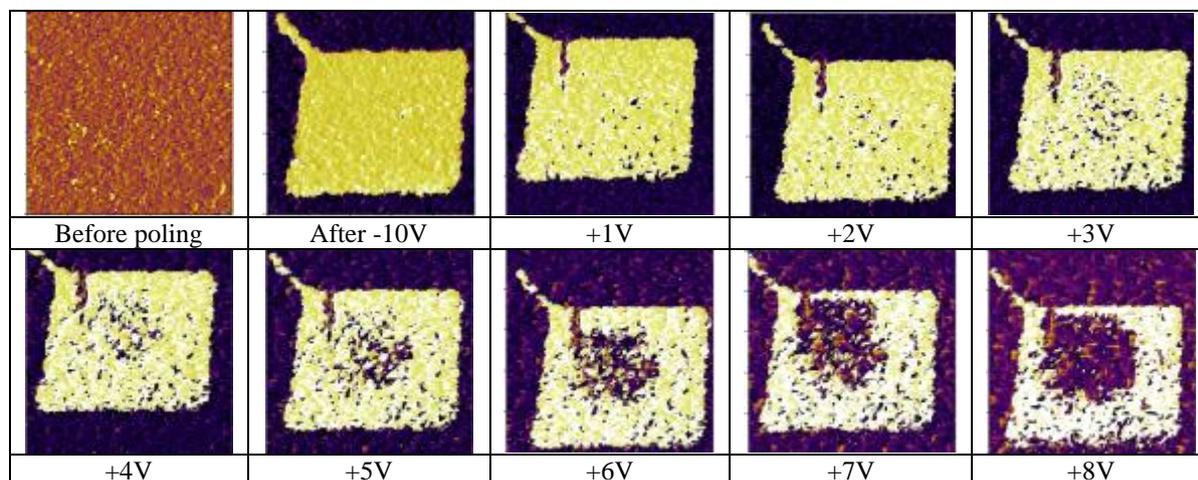


Fig.9 amplitude image during poling (negative first)

The experiment was then repeated by applying a negative voltage of -10V, followed by a gradually increasing positive voltage. As shown in Fig. 9, the switching voltage is now much larger, about +8V.

Comparing the two results showed in Figs. 8 and 9, it can be concluded that positive voltage has a weaker poling effect than negative voltage. This explains why a +10V voltage has no effect on the sample: +10V is most likely smaller than the critical switching voltage.

The results of poling experiments further prove the results of the hysteresis loop measurement in the way that the switching voltage is consistent with that shown on hysteresis loop diagram.

### Conclusion and Discussion

In summary, P(VDF-TrFE) has a lower  $d_{33}$  than PVDF at low thickness. However, when the thickness of the films increases, the  $d_{33}$  of P(VDF-TrFE) ends up at a higher value than that of PVDF. From the hysteresis loop measurement, the critical switching voltage of 5V- 8V in the positive and negative ranges is determined, with the positive switching voltage higher than the negative one. The results are consistent with and further supported by those obtained from the poling experiments. However, there are still many areas needed to be studied further. Firstly, some changes of height on the sample surface of P(VDF-TrFE) were noticed after the hysteresis loop measurement. This may be related to the poling effect of the polymer chains, but further experiments have to be carried out to confirm the result. Secondly, the morphology of each sample changed markedly after the poling experiments. It is unclear of the reasons for this and more studies are therefore needed for a conclusive finding. Lastly, due to technical constraints, we were only able to apply a maximum of +/-10V on samples, but +10V is smaller than the positive switching voltage for P(VDF-TrFE). Hence, a higher voltage must be applied to determine the positive critical voltage.

### Application

P(VDF-TrFE) with its piezoelectric properties is suitable for making sensors and actuators. For example, if it is made as a sensor and placed in a critical spot under stress, the change of stress state may induce a change in the electrical polarization for the P(VDF-TrFE) which produces a detectable electrical voltage. Thus, this kind of switchable polarization is useful in rewritable memory application.

### Acknowledgement

We would like to thank our mentors and teacher in charge for patient and continuous help and support.

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## Appendix:

### Reference

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<sup>3</sup>Fig. 1 and Fig. 2 are adapted from W. Eisenmenger, H. Schmidt and B. Dehlen, *Space charge and dipoles in polyvinylidene fluoride*, *Braz. J. Phys.* Vol. 29 n. 2 Sao Paulo June 1999

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