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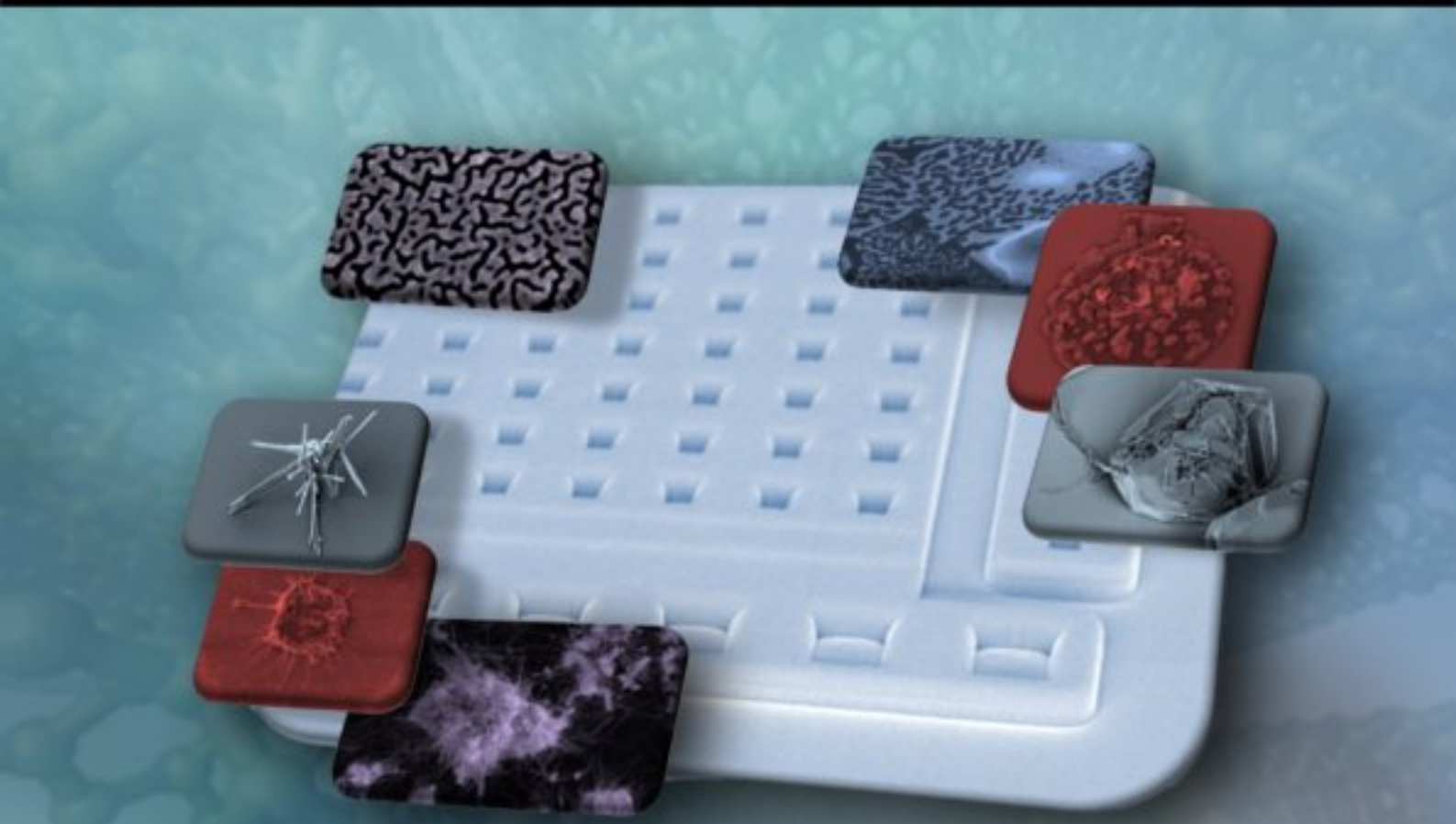

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Contents

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Distributed Array of Polymeric Piezo-nanowires through Hard-Templating Method into Porous Alumina

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Abstract: We report on the preparation of ferroelectric polymeric nanowires through hard-templating strategy. Wet-impregnation of poly(vinylidene fluoride) (PVDF) and its copolymer poly(vinylidene fluoride-tri fluoro ethylene) [P(VDF TrFE)] was performed into commercially available porous Anodic Alumina Membrane (AAM). The polymeric nanowires show a diameter ranging from 144 to 166 nm, a length of tenth of micron and a high filling ratio of the alumina pores. X-ray diffraction pattern and infrared spectroscopy show the crystallization of both polymers into the ferroelectric β phase. In addition, Curie temperature (T_c) tests show an increase to higher T_c for the PVDF-TrFE polymeric nanowires with respect to the bulk polymeric material, thus revealing the importance of confined crystallization into mono-dimensional structures. A piezoelectric behavior was also observed by a voltage generation upon mechanical pressure, without pre-poling or mechanically orienting the polymer. These crystalline piezoelectric nanowires distributed in a vertical array would potentially address applications like mechanical pressure sensors, e.g., in robotics. *Copyright © 2011 IFSA.*

Keywords: Piezoelectric polymeric nanowires, Confined crystallization, Hard-templating, Anodic porous alumina membrane, Dielectrical properties.

1. Introduction

Poly(vinylidene fluoride) (PVDF) is a very attractive polymer, whose remarkable piezoelectrical and pyroelectrical properties [1] gave rise to a broad range of applications, in particular for electronic

devices [2]. In general piezoelectricity can be obtained by orienting the molecular dipoles of polar PVDF in the same direction by subjecting the material to mechanical stretching or to an intense electric field (poling) [3]. Recently, arrays of PVDF wires supported within a non-polar matrix, like the porous Anodic Alumina Membrane (AAM) have been reported [4], thus obtaining high aspect ratio one-dimensional nanostructures. Garcıa-Gutiérrez *et al* carefully studied the polymer crystallization into the alumina restricted geometry, showing that the degree of crystal orientation increases due to confinement into the alumina pores.

Copolymers of (vinylidene fluoride-tri fluoro ethylene) [P(VDF TrFE)] have been also prepared in the form of nanowires into AAM for potential applications as sensors and actuators in microelectromechanical systems[5]. PVDF-TrFE readily crystallizes into the ferroelectric β crystal phase and also its crystallization and properties are affected by confinement.

In the present work, we report on a comparison of the crystallization and Curie temperature behavior between the PVDF and PVDF-TrFE nanowires templated into porous AAM. A wet-impregnation strategy is applied, based on a phase transition of the polymers from a liquid phase (upon dissolution in an appropriate solvent) to a crystalline form, induced by the confinement into the pores of the AAM. This process leads in one step to an already distributed array of nanowires confined in an insulating matrix. Applications of these polymeric nanowires are envisioned mainly in electronics, sensing and actuation where flexibility of the matrix, piezoelectric properties and wide operating temperatures range are needed.

2. Materials and Methods

AAM (Anodisc® membrane 47 mm, nominal pore size 100 nm, average pore size 200 nm, thickness 60 μm) were purchased from Whatman, cut in 4 pieces of about 20 × 20 mm an placed on the top of the vacuum sample holder of a spin coater (Spin150 VT BG 66-0, SPS-Europe). 100 μL (2.5%wt) of both poly(vinylidene fluoride) (PVDF, Aldrich) dissolved in N-methyl-pyrrolidinone (NMP, Aldrich) and of poly(vinylidene fluoride trifluoro ethylene) (PVDF-TrFE, molar ratio PVDF/TrFE=2.33, Piezotèch) in methyl ethyl ketone (MEK, Aldrich) were respectively spin coated for 2 min at 500 rpm and 1 min at 1500 rpm on the AAM. In order to completely fill the pores of alumina, both sides of the AAM were impregnated and spin coated. The samples were then dried in oven at 130 °C for 2 hours (sample codes: PVDF@AAM, PVDF-TrFE@AAM) and carefully mechanically polished to remove the eventual polymeric film on the membrane. To compare the result with bulk material, thin films of PVDF-TrFE and PVDF were prepared by spin coating the same solutions on platinized silicon wafers.

Field Emission Scanning Electron Microscopy was performed on a Zeiss SupraTM 40 equipped with an Energy Dispersive X-rays detector EDX (EDAX) on the polymer-filled AAM membranes or after the alumina dissolution in a water solution of NaOH (4 M) for 6 hours, after supporting one side of the membrane with a PVC tape. Wide-angle X-ray diffraction pattern were collected on a Bruker D8 Discover with Ni-filtered CuK_{α}-radiation and a position-sensitive detector (Vantec). Infrared spectroscopy was carried out in absorption mode with a Bruker Equinox 55.

For electrical tests, both sides of the samples were sputtered with platinum, using an electrode mask with a known surface area ($S = 2.60 \times 10^{-5}$ m^2). Copper wires were connected with silver paste to both sides of the samples. The dielectric constant ε and loss factor tgδ frequency dependences were obtained using impedance analyzer (Agilent Techn. 4294, basic accuracy 0.08 %) under applied DC voltage of 100 mV (for composited) and 50 mV (for thin film) from 100 Hz to 1 MHz. The Curie temperature (T_c) was tested at 100 kHz and 500 mV from 20 to 200°C (temperature step of 10 °C from 20 to 90 °C, and step of 5 °C from 90 to 200 °C) by immersing the contacted sample in a heated silicon oil bath. The piezoelectric behavior was tested with an ad-hoc prepared hammer, which apply a

mechanical pressure on one side of the sample and generated electrical output is observed through a digital oscilloscope.

3. Results and Discussion

Commercially available anodic alumina membrane from Whatman shows randomly organized pores with a diameter varying from 150 to 280 nm (average pore size 200 nm, average porosity 55 %, Fig. 1a). The polymeric nanowires from samples PVDF@AAM and PVDF-TrFE@AAM are shown in Fig. 1b-d. The high percentage of pore filling by both polymers was established upon partial dissolution of the alumina membrane (Figs. 1c and d). In particular the PVDF nanowires show a diameter ranging from 85 to 230 nm (average size 166 nm), whereas the PVDF-TrFE ranges from 65 to 267 nm (average size 144 nm). Both polymers are several tenths of μm in length, thus showing a high aspect ratio. In addition the nanowires are not self-standing, thus the presence of the insulating alumina matrix plays also the important role of sustaining the wires in a vertical and distributed array.

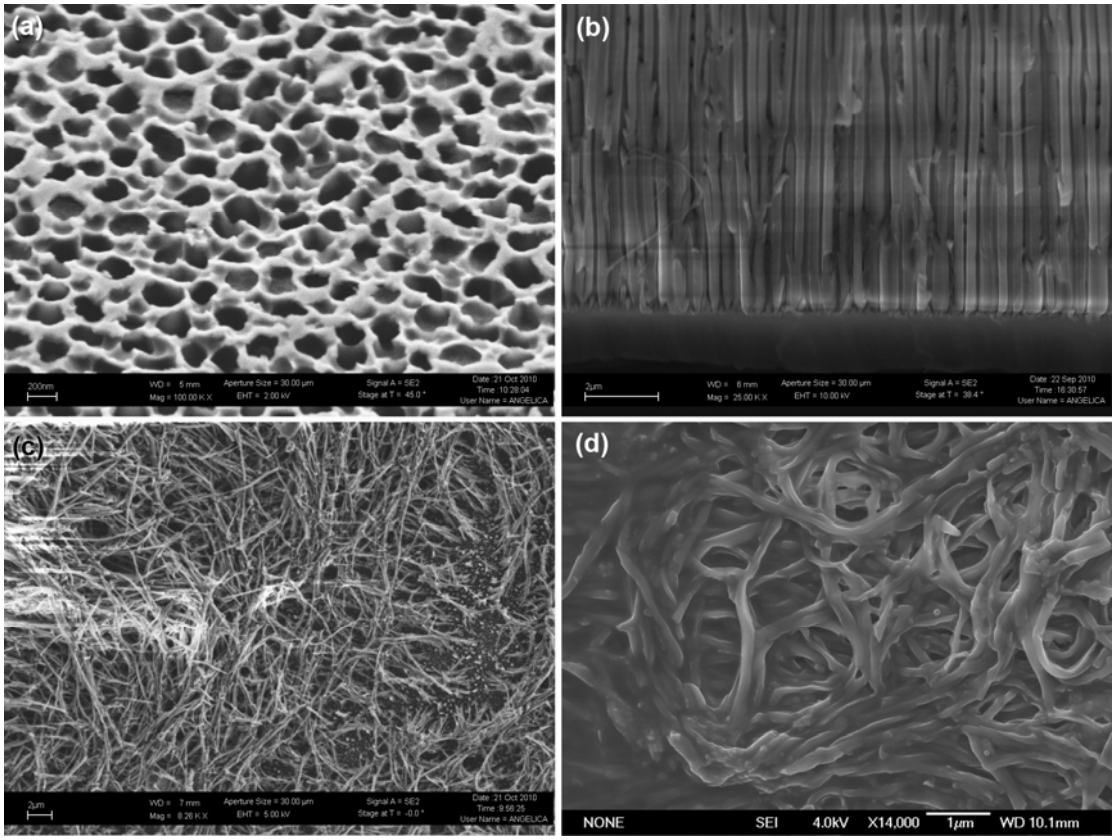
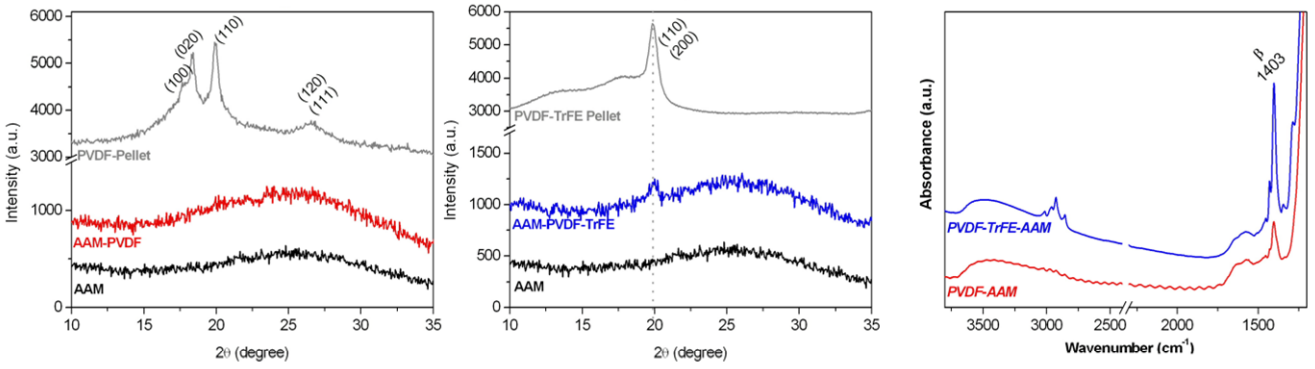


Fig. 1. (a) Porous anodic alumina membrane (AAM, Anodisc®) from Whatman; (b) Cross section of the PVDF-impregnated porous alumina membranes; (c) PVDF-nanowires, and (d) PVDF-TrFE nanowires after dissolution of the alumina membrane.

Wide-angle X-ray diffraction pattern (Fig. 2a) shows two intense diffraction peaks of the PVDF in powder form (grey spectrum) corresponding to the (110) and (020) reflections. Absence of any reflection in the measured range (from 10° to 37°) is observed for the PVDF-filled AAM membrane (PVDF@AAM, red spectrum) and for the empty alumina membrane (AAM, black spectrum). In Fig. 2b the PVDF-TrFE@AAM sample shows a diffraction peak at 19° (blue spectrum) corresponding to the overlapping of (110) and (200) reflection of the β-phase of PVDF-TrFE in powder form (grey spectrum).



(a) (b) (c)

Fig. 2. Wide-angle X-ray diffraction pattern of (a) PVDF-impregnated and (b) PVDF-TrFE-impregnated membranes; (c) Fourier-transform infrared (FT-IR) spectra. Sample codes: PVDF@AAM: red spectrum, PVDF-TrFE-AAM: blue spectrum; PVDF and PVDF-TrFE in powder form are shown in grey, empty alumina in black.

The infrared spectroscopy measurement confirms not only the crystallization in the ferroelectric β phase of the PVDF-TrFE polymer into the alumina membrane, but also of the PVDF-AAM sample (Fig. 2c). The β crystalline phase shows a vibration peak at 1403 cm^{-1}, as observed in both spectra [4, 6] and is more intense in the case of PVDF-TrFE polymer.

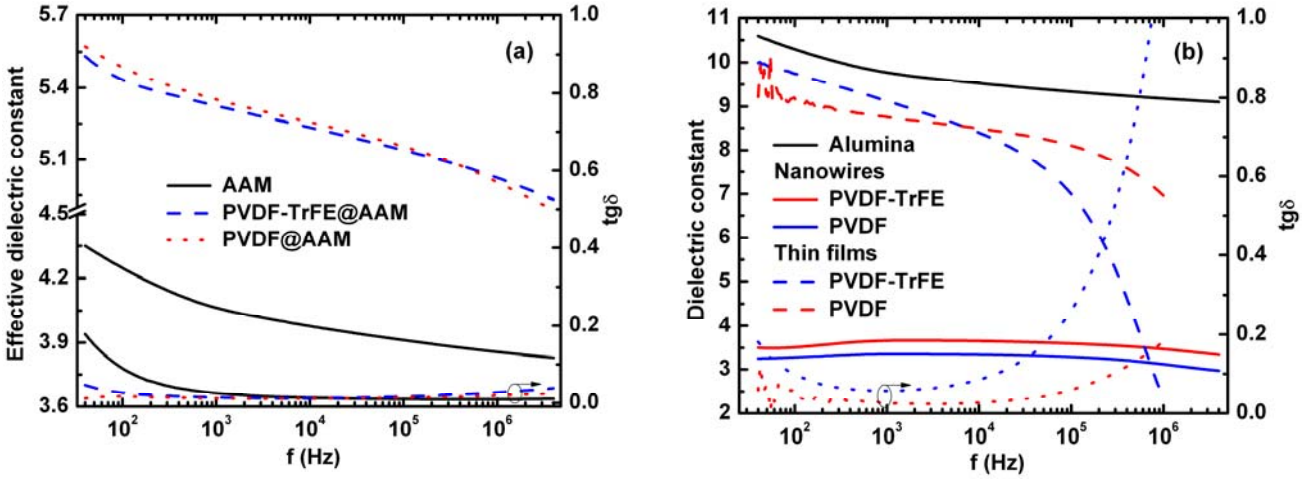
Electrical measurements on all the polymer-impregnated samples show a decrease of the effective dielectric constant and a quasi-constant behavior of the loss factor tgδ (Fig. 3a). The effective dielectric constant contains both impact from the alumina and filled material in the pores (air or polymer). To extract dielectric constant of alumina and polymer nanowires, simple parallel capacitance relation was applied. The pores of AAM can be assumed as a parallel connection of multiple capacitors. If total measured capacity C_{tot} represents the capacity of the composite of alumina C_{al} with an air C_{air} or with the polymers C_{pol}, we can write that

$$C_{tot} = C_{al} + C_{air} \text{ and } C_{tot} = C_{al} + C_{pol}.$$

Since the porosity of the AAM is known, the surface area of the top electrodes for alumina and air (or polymer) can be calculated. As follows capacity of the air can be calculated and C_{al} and C_{pol} can be extracted, on the supposition that all pores are filled. Dielectric constant of the air was considered to be 1.00059 and constant with the frequency.

Using this simple model, the dielectric permeability of alumina and polymer nanowires were calculated (Fig. 3b). For comparison the dielectric constant of polymer thin films are also presented. The dielectric constant values for alumina and thin films are comparable with those for the bulk. The permeability of polymer thin films is larger and significantly decreases with increase of frequency regarding polymer nanowires. The dielectric properties of a polymer are determined by the charge distribution and also by statistical thermal motion of its polar group. The electronic polarization occurs during a very short interval of time of order of 10^{-10} s, but longer then for electronic polarization, i.e. 10^{-3}-10^{-2} s required for the process of ionic polarization. To set in dipole polarization it requires longer time. Evidently also in case of polar polymers, the dielectric constant begins to drop at a certain frequency. At high frequencies, the periodic reversal of the electric field occurs so fast that the switching of the polar regions of the polymer in the direction of the field is depressed: the polarization due to the charge accumulation decreases, leading to the decrease in the values of dielectric constant

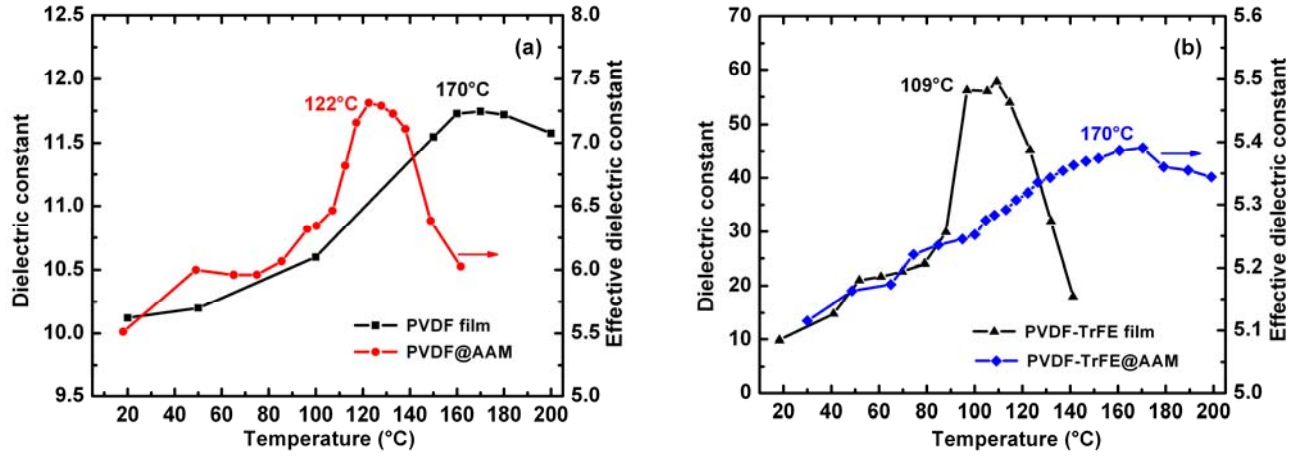
and increase in the tgδ[7, 8]. The switching of polarization in the case of nanowires might be suppressed by the alumina pores. Low dielectric constant for polymer nanowires in comparison with bulk and films can be attributed to the weak crystallinity.



(a) (b)

Fig. 3. (a) Effective dielectric constant and loss factor tgδ for PVDF-TrFE@AAM and PVDF@AAM systems. (b) Extracted dielectric constant for AAM, PVDF-TrFE and PVDF nanowires, and dielectric constant and tgδ for PVDF-TrFE and PVDF thin films.

T_c measurements on both polymeric nanowires into the alumina matrix and both polymer thin films are shown in Fig. 4. A shift to higher T_c values is clearly shown when comparing the PVDF-TrFE polymer as thin film (109 °C, Fig. 4a) with the same material confined into the alumina pores of 200 nm (170 °C). The Fig. 4b presents effective dielectric constant behavior versus T of the PVDF-nanowires into alumina and a PVDF-sheet obtained from Sigma.



(a) (b)

Fig. 4. Curie temperature (T_c) measurements on the (a) PVDF-TrFE, and (b) PVDF- nanowires into alumina in comparison with thin films.

It seems that the sheet has a higher T_c (170 °C) than the PVDF-nanowires (122°C). However the melting point of PVDF is about 175 °C, thus the disordering of crystalline domains decreases the capacitance value. In this sense the T_c of PVDF-films cannot be directly measured. In the case of PVDF-nanowires the T_c measurements shows a peak at 122 °C, corresponding to the ferroelectric (β) to paraelectric (α) phase transition. By comparing the T_c behavior of the PVDF-TrFE@AAM sample with the PVDF@AAM one, it can be stated that the higher T_c of the first sample is due to its higher percent of crystallinity, as also confirmed by XRD and FT-IR measurements.

The sample PVDF@AAM also showed a piezoelectric response under mechanical stimulus at room temperature. In Fig. 5 the blue line shows the force applied to the hammer hitting the sample, and the yellow line the voltage generated across the sample. It has to be noted that the sample was not pre-poled in the direction of the applied force.

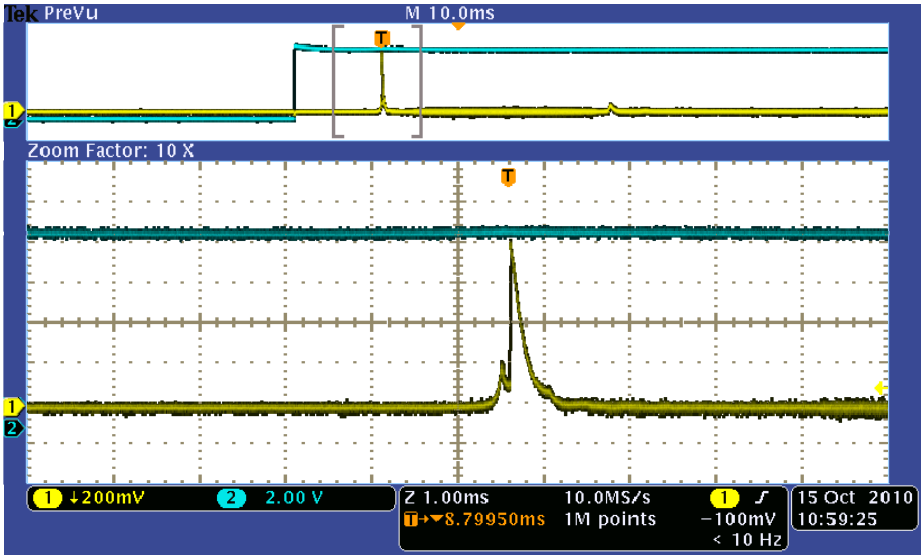


Fig. 5. Piezoresponse of the PVDF@AAM sample: voltage out-put 400 mV (yellow line) upon mechanical stimulus (blue line).

4. Conclusions

In summary, we show an effective and fast wet-impregnation method to prepare crystalline ferroelectric polymeric nanowires made by PVDF and its copolymer PVDF-TrFE into porous alumina membrane in a distributed vertical array. We showed that the crystallization of these polymers into confined geometries enhances their crystallinity into the desired β ferroelectric phase. In addition the increase of the Curie temperature of these ferroelectric polymers when in the form of nanowires allows their use in a broader range of temperatures. The higher crystallinity and T_c of the PVDF-TrFE nanowires with respect to the PVDF ones is indeed reported. A piezoelectric response under mechanical stimulus without applying pre-poling is obtained thus showing the efficiency of confined crystallization method. Further work has to be carried out in order to bring this nanowires into a pressure sensing device (by impregnation of piezoelectric polymer, e.g., in flexible porous matrixes), for application as a sensing skin in the field of robotics.

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