Piezoelectric Nylon-11 Nanowire Arrays Grown by Template Wetting for Vibrational Energy Harvesting Applications

*Anuja Datta, Yeon Sik Choi, Evie Chalmers, Canlin Ou and Sohini Kar-Narayan**

[*] Dr. A. Datta, Y. Choi, E. Chalmers, C. Ou, Dr. S. Kar-Narayan
Department of Materials Science and Metallurgy, University of Cambridge, 27 Charles
Babbage Road, Cambridge CB3 0FS, UK, E-mail: sk568@cam.ac.uk

Keywords: piezoelectric nanogenerator, odd-numbered Nylon, nanowires, energy harvesting, template wetting.

Piezoelectric polymers, capable of converting mechanical vibrations into electrical energy, are attractive for use in vibrational energy harvesting due to their flexibility, robustness, ease and low cost of fabrication. In particular, piezoelectric polymers nanostructures have been found to exhibit higher crystallinity, higher piezoelectric coefficients and ‘self-poling’, as compared to films or bulk. The research in this area has been mainly dominated by polyvinylidene fluoride (PVDF) and its co-polymers, which while promising, have a limited temperature range of operation due to their low Curie and/or melting temperatures. Here, we report the fabrication and properties of vertically aligned, and ‘self-poled’ piezoelectric Nylon-11 nanowires with a melting temperature of ~200 °C, grown by a facile and scalable capillary wetting technique. We show that a simple nanogenerator comprising as-grown Nylon-11 nanowires, embedded in an anodized alumina (AAO) template, can produce an open-circuit voltage of 1 V and short-circuit current of 100 nA, when subjected to small-amplitude, low-frequency vibrations. Importantly, the resulting nanogenerator is shown to exhibit excellent fatigue performance and high temperature stability. Our work thus offers the possibility of exploiting a previously unexplored low-cost piezoelectric polymer for nanowire-based energy harvesting, particularly at temperatures well above room-temperature.

1. Introduction

Nanogenerators (NGs) based on piezoelectric materials have attracted increasing interest in light of the growing demand for wireless, portable, embedded, implantable and/or wearable self-powered devices, and the ubiquitous availability of ambient vibrational energy sources as a potential power solution.^[1-4] Piezoelectric polymers, in particular, have been widely studied and exploited in NG design,^[2,5-8] as in spite of exhibiting weaker piezoelectric properties than commonly used ceramics, such as barium titanate,^[9] lead zirconium titanate,^[10] and zinc oxide,^[11-13] they possess a range of advantages over ceramics that render them mechanically stable, chemically robust and possibly biocompatible. Importantly, nanostructures and nanowires of ferroelectric (and hence piezoelectric) polymers, such as polyvinylidene (PVDF) and polyvinylidene fluoride trifluoroethylene (P(VDF-TrFE)), have been found to exhibit superior piezoelectric performance,^[7,14-22] by virtue of their nanoscale confinement. There have been several reports on polymer-based NGs, including nanopressure sensor, acoustic NG and mechanical energy harvester,^[23-27] but the typically low Curie and/or melting temperatures of these polymers limit their use in applications at higher temperatures, for example in early-fault detection systems for heavy machinery that may require a wider operating temperature range. There is thus a growing need to explore alternative piezoelectric polymers with enhanced thermal stability, and in particular to develop low-cost scalable processes to fabricate nanowires based on these materials, which can offer reliable energy harvesting performance at higher temperatures.

In this regard, odd-numbered Nylons with relatively high melting temperatures, are known to possess ferroelectric and piezoelectric characteristics by virtue of the high degree of hydrogen bonding and dipole orientation resulting from the arrangement of polyamide molecules within adjacent chains upon crystallization.^[28] While, non-ferroelectric even-numbered Nylons (Nylon-6,6 and Nylon-6) weaved as fabrics have already been successfully used in textile industry,^[29] and have found suitable applications as integrated

sensors and as components of energy devices,^[30] ferroelectric odd-numbered Nylons^[31] have received considerably less attention. Among odd-numbered Nylons, Nylon-11 (polyamide-11 = $[\text{C}_{11}\text{H}_{21}\text{ON}]_n$) exhibits piezoelectric and ferroelectric properties that are comparable to PVDF at room temperature.^[32-35] Typically, Nylon-11 exhibits five crystalline modifications, including triclinic α and pseudo-hexagonal γ phases, which have different dipole densities and orientation.^[36,37] The high piezoelectricity in Nylon-11 is attributed to its polar crystal structure (γ form), although other configurations may also lead to piezoelectric behavior (see Supporting Information S1). A piezoelectric charge constant d_{31} between 3-12 pC N⁻¹ has been reported for a variety of melt drawn, strained, solution-cast and poled Nylon-11 films,^[36,38-42] with a d_{31} of up to ~15 pC N⁻¹ reported at relatively higher temperature (up to 200 °C).^[43] Nylon-11 has previously been prepared as nanofibers and nanoribbons via electrospinning which requires high voltages,^[32,33] but their performance as energy harvesters has never been studied. Furthermore, scalable solution-based synthesis methods for Nylon-11 nanowires have not been attempted, and the understanding of their piezoelectric properties in relation to the crystal structure in nanowires is yet to be reported.

Here we describe a facile and scalable synthesis technique for Nylon-11 nanowire arrays of uniform size and high aspect ratio of ~200 by a solution-processed capillary template infiltration method within AAO templates. Unlike our previous work on P(VDF-TrFE) nanowires grown within a similar nanoporous template via gravity infiltration,^[7] herein, ultralong Nylon-11 nanowires were prepared by capillary wetting, which was necessary in order to prevent fast drying of the infiltrated Nylon-11 solution and which reproducibly yielded large density of highly crystalline nanowires of narrow size distribution, with a significant presence of the piezoelectric γ phase imparted by the pore confinement of the templates. In order to carry out further characterization, the nanowires could be subsequently transferred to any substrate in the form of nanowire mats that resulted upon preferential dissolution of the AAO template in phosphoric acid. More importantly, the

Nylon-11 nanowires were ‘self-poled’,^[2,7,8,15,44,45] and were incorporated as-grown into template-based NGs for energy harvesting with a wide temperature range of operation and excellent fatigue performance, without the requirement of poling via large external electric fields that are otherwise typically required for piezoelectric performance. Enhanced piezoelectric properties of Nylon-11 nanowires make this material a potentially low-cost candidate for smart fabrics in the wearable technology industry, as has been demonstrated recently with piezoelectric PVDF fibers,^[46,47] with the added advantage of having a wider temperature range of operation.

2. Results and Discussion

2.1. Growth Mechanism of Nylon-11 Nanowires

A schematic of the Nylon-11 nanowire-array growth process via capillary wetting of the pores of an AAO template is shown in **Figure 1**. A three-step process was adopted to control the growth of Nylon-11 nanowires inside the AAO template which comprised: (i) preparation of the Nylon-11 solution in formic acid by dissolving the required concentration (10 wt. % optimum) of Nylon-11 pellets; (ii) promoting the growth of Nylon-11 nanowires via capillary action by placing the AAO templates on a Nylon-11 solution pool; and (iii) cleaning the resulting loosely adhered Nylon-11 nanoparticles from the surfaces of the templates following the capillary wetting process and subsequent evaporation of the formic acid solvent. In order to study the density, morphology and the phase of the prepared Nylon-11 nanowires, the AAO template was dissolved in phosphoric acid and a mat of nanowires could be obtained and transferred to any desired substrate. The Nylon-11 polymer concentration (wt. %) in solution was varied at the start of the growth process, and scanning electron microscopy (SEM) imaging was carried out on the resulting nanowires to get an understanding of the growth mechanism.

The advantage of capillary wetting process in the preparation of Nylon-11 nanowires was verified by carrying out complementary experiments using the more conventional gravity-induced template infiltration method that was previously reported by our group for the fabrication of P(VDF-TrFE) nanowires.^[7] This method was found to be unsuitable for Nylon-11 nanowire formation as can be seen in **Figure 2(a)** and (b). In the case of conventional gravity-induced template wetting where the solution was drop-cast on to the top surface of the template, incomplete pore-infiltration of Nylon-11 solution resulted (Figure 2(a)) due to fast drying out of the drop of formic acid solution. As a result, a thick film of Nylon-11 was obtained on top of the template surface (Figure 2(b)), preventing further soaking of the pores, and hence no nanowires were obtained using this method.

Capillary wetting (Figure 1) was therefore adopted as a viable alternative to ensure complete infiltration of the template pores, for the template-assisted fabrication of Nylon-11 nanowires. It has been shown that the maximum height at which the polymer solution can reach via “capillary wetting” is inversely proportional to the radius of the template pore, given by Jurin’s law as $h = 2\gamma (\cos \theta) / \rho g r$,^[48] where γ is the surface tension of the polymer solution, θ is the contact angle of the meniscus at the pore wall, ρ is the density of the polymer solution, g is the acceleration due to gravity, and r is the radius of the nanopore. In this case, taking $\gamma = 0.033\text{-}0.043 \text{ N m}^{-1}$,^[31] $\theta = 75\text{-}82^\circ$,^[49,50] $\rho = 1.01\text{-}1.03 \text{ gm cm}^{-3}$,^[31] and $r = 125 \text{ nm}$ (pore diameter $\sim 250 \text{ nm}$), respectively, the maximum height that the Nylon-11 solution can reach via capillary force is calculated to be $\sim 2.2 \times 10^7 \text{ }\mu\text{m}$, which is much higher than the length of the pore channels (thickness of the template $\sim 60 \text{ }\mu\text{m}$). However, the time required for filling the pores is also controlled by the viscosity of the Nylon-11 pool solution,^[32] which in turn depends on the concentration of the pool solution (i.e. wt. % of the Nylon-11 pellets dissolved in formic acid), and importantly, the rate of evaporation of the formic acid.^[51] Thus in practice, the actual height that the solution can successfully infiltrate is significantly lower. Also it has been observed that when templates were wetted with polymers slightly above their

solidification temperatures,^[52] the elevated temperature of the polymer solution enhanced the mobility of the molecules and the liquid polymer infiltrated the pores as a liquid thread preceded by a meniscus during capillary wetting.^[52] Thus, in our fabrication process, a warm (~ 60 °C) formic acid solution of Nylon-11 was used to infiltrate the AAO template pores by the aid of capillary action. As the solution travelled through the pore channels, the viscosity increased due to rapid evaporation of formic acid (heat of vaporization = + 23.1 kJ mol⁻¹ as compared to + 31.3 kJ mol⁻¹ for acetone, + 40.66 kJ mol⁻¹ for water),^[53] forming micro-droplets of Nylon-11 which appeared as a nano-particulate film on reaching the opposite template surface and on cooling thereafter (Figure S2 in Supporting Information). The film thus obtained was loosely attached to the template surface and could be easily removed by mechanical polishing, leaving a nanowire-filled AAO template.

2.2. Morphology and structure of template-grown Nylon-11 nanowires

The proposed growth mechanism was verified through SEM imaging of the nanowires prepared by varying the starting Nylon-11 polymer concentration in the solution. On varying the wt.% of Nylon-11 polymer in the solution, either continuous or beaded nanowires were obtained at high concentration (10 – 20 wt.%) solution, or a mixture of nanoparticles and nanowires were obtained at low concentration (2 wt. % and 5 wt.%), as can be observed from the SEM images, taken after removal of the template, in **Figure 3**. In the case of 2 wt.% Nylon-11 in formic acid, no one-dimensional (1D) nanowire growth was observed and only particulate deposition of diameter similar to that of the pore channels resulted instead (Figure 3(a)). With increasing concentration of the Nylon-11 solution, the percentage of nanowires increased, as observed for 5 wt.% Nylon-11 sample in which low aspect ratio (average length 4 µm and diameter ~250 nm) nanowires and a considerable (40-50 vol. %) growth of Nylon-11 nanoparticles was obtained (Figure 3(b)). Figure 3(c) shows the dependence of nanowire length with increasing wt. % of Nylon-11 in formic acid, indicating that the capillary wetting process is feasible to obtain high aspect ratio (40-50 µm long) Nylon-11 nanowires at an

optimum solution concentration of 10 wt. %. Beyond this concentration, the length of the nanowires was found to decrease (Figure 3(c)), as the viscosity of the solution increased with increasing concentration,^[33] thus inhibiting the infiltration of the pore channels. Figure 3(d) shows a cross-sectional SEM image of Nylon-11 nanowire-filled AAO template, verifying the uniform growth of ultra-long Nylon-11 nanowires within the confinement of the template pores at an optimum concentration of 10 wt. %.

A significant reduction of the beaded structure (< 5 vol.%) with a maximum yield of nanowires at 10 wt. % can also be observed from the SEM images taken after removal of the template, as shown in **Figure 4(a) & (b)**. Figure 4 (c) the exposed nanowire tips in partially dissolved templates (Supporting Information S3) from which an average diameter of 196 nm was measured (histogram shown in the inset of Figure 4(c)). Dense long nanowire arrays freed from the template by dissolution in phosphoric acid (inset of Figure 4(d)) were also occasionally observed to roll as mats (Figure 4(d)), assisted by the support of a residual thin Nylon-11 film (10-20 nm thick) formed as a result of joining of the soft nanowire bases (Figure 4(d) and Figure S4) during cleaning and dissolution of the template. Furthermore, Nylon-11 nanowires freed from the AAO template underwent noticeable stretching (indicated by arrows in Figure 4(b) and observed in Figure S5), and sometimes appearing as nanoribbons (see Figure S5), presumably due to their high mechanical strength.^[54]

Detailed structural characterization was subsequently carried out by X-ray diffraction (XRD) studies. XRD spectra of the parent Nylon-11 pellets did not reveal any ordered crystallinity, as seen in **Figure 5(a)**. A multi-peak Gaussian fitting however resulted in the presence of two possible XRD peaks around $2\theta \sim 21.4^\circ$ and $\sim 23^\circ$, suggestive of both un-oriented γ and α phases. In contrast, for Nylon-11 nanowires prepared within AAO templates, sharp crystalline XRD peaks were observed due to the γ phase at about $2\theta = 21.6^\circ$ corresponding to (200) (hydrogen bond direction according to Kawaguchi et al. in Ref [37]), along with possible α contribution observed around $2\theta = 22.8^\circ$ and 12.5° . The ratio of the

intensity between γ/α phases increased in the Nylon-11 nanowires freed from the template as well as in a spin-cast Nylon-11 film (see Supporting Information S6). Differences in the XRD patterns for template-protected nanowires as compared to the freed nanowires suggest that the Nylon-11 structure of the nanowires was formed under the influence of two simultaneous ordering (γ and α). Crystallization from formic acid solution might have resulted in more ordered α form and less γ form in template-protected nanowires, whereas partial re-crystallization from α to γ might have taken place under mechanical deformation during template dissolution in the freed nanowires.^[32] Similar changes in the crystal form have been observed in Nylon-6 and Nylon-11 electrospun fibers,^[33,55] attributed to the formation of γ phase due to the high stress experienced by Nylon fibers during the fabrication process. Herein, the orientation of the Nylon-11 chains prior to crystallization inside the pores may possibly be responsible for the difference in the crystallinity observed, as also seen in other polymers.^[56,57]

2.3. Absorption spectroscopy of Nylon-11 nanowires

Room-temperature Fourier transform infrared (FTIR) spectroscopy data for the template-protected and freed Nylon-11 nanowires, as compared to the parent Nylon-11 pellets and a blank AAO template, are shown in Figure 5(b). Typically, in Nylon-11, the region 500-800 cm^{-1} comprises the amide V and VI bands, whereas, the 1000-1400 cm^{-1} zone is sensitive to the methylene segments. The region 1500-1700 cm^{-1} contains the amide I and II bands and is characteristic to N-H bending from ordered, disordered, and free N-H groups and C-O bonds. The regions typical to hydrogen bonding are from 1600 to 1800 cm^{-1} and from 3000 to 3600 cm^{-1} .^[48,55] FTIR of Nylon-11 pellets showed intense bands resulting from the absorption of active H_2O , CO and CO_2 molecules.^[51,58] Stretching and bending of C=O and O-H units gave rise to strong FTIR signals between 1700 - 2300 cm^{-1} and 3200 – 3600 cm^{-1} , thereby suppressing the bands from Nylon chains.^[51,58] Both the pellet and Nylon-11 nanowires showed sharp bands observable at 1469, 1543 and 1643 cm^{-1} due to intense N-H

stretching in amide groups. A strong transmittance band $\sim 2352\text{ cm}^{-1}$ in the nanowires was due to absorbance of CO_2 molecules in the AAO template for the template-protected sample. A slight difference between the ratio of the bands at 2852 and 2925 cm^{-1} is observed between Nylon-11 pellet and nanowires, which are assigned to symmetric and antisymmetric CH_2 stretch, respectively.^[59-61] The amide A band occurring at about 3310 cm^{-1} in both Nylon-11 pellet and nanowires was due to the N-H stretching vibration that is sensitive to the strength of the hydrogen bond. A somewhat increased transmittance and varying ratios in the transmittance bands in the Nylon-11 nanowires as compared to Nylon-11 pellets suggests that the hydrogen bonds might break and the dipoles rotate to re-form bonds in a new direction due to the nanowire formation. It should however be noted that differentiation of the FTIR data between α and γ phases in Nylon-11 nanowires is difficult due to their close overlap.^[58,60,61]

2.4. Temperature-dependent characterization of Nylon-11 nanowires

Differential scanning calorimetry (DSC) measurements on Nylon-11 pellets, spin-cast Nylon-11 film, as well as template-grown Nylon-11 nanowires are shown in **Figure 6(a)** and **6(b)**. During the heating cycle, a single melting peak at $T_m = 189.5\text{ }^\circ\text{C}$ was recorded for Nylon-11 pellets as well as spin-cast Nylon-11 film ($T_m \sim 186\text{ }^\circ\text{C}$). The DSC data on Nylon-11 nanowires indicates a change in the crystal structure of the Nylon-11, which was absent in the pellet or the film that had a single melting peak.^[62] However, for template-protected nanowires, the melting peak was split into two distinct peaks, at $183.9\text{ }^\circ\text{C}$ and $186.9\text{ }^\circ\text{C}$, corresponding to typical melting points for α and γ phases respectively. In case of the freed nanowires, the doublet peaks shifted to a higher temperature at $186\text{ }^\circ\text{C}$ and $189\text{ }^\circ\text{C}$, respectively, possibly due to the strain induced in the nanowires on freeing from the template, as also seen in the SEM images (**Figure 4(b) & (c)**). During the DSC cooling cycle (**Figure 6(b)**), Nylon-11 nanowires (both template-protected and freed) recrystallized at relatively higher temperature ($\sim 167\text{ }^\circ\text{C}$) as compared to the Nylon-11 film and pellets, indicating higher

crystalline order present in the nanowires. The higher T_m observed in Nylon-11 nanowires suggests the suitability of Nylon-11 nanowires for higher operational temperature as compared to other ferroelectric polymers.^[2,7,44,63]

Figure 6(c) shows the temperature dependence of dielectric permittivity, ϵ , of freed Nylon-11 nanowires and Nylon-11 nanowires in AAO template in comparison to the spin-cast Nylon-11 film, measured between -160 °C and 220 °C. Both Nylon-11 film and nanowires showed similar trends in ϵ at all temperature ranges, with a relatively higher magnitude of ϵ observed for the film. Typically, Nylon-11 exhibits three noticeable relaxation processes which can be observed from dielectric permittivity measurements. The high temperature relaxation appearing above 80 °C, is commonly designated as α relaxation. As the temperature decreases below room temperature, the β relaxation due to water adsorption and dipolar amide group may appear, followed by γ relaxation below 150 °C due to local mode-motion.^[42] For both Nylon-11 film and Nylon-11 nanowires, only α relaxation was observed, with a steady decrease of ϵ to very low values below room temperature. Upon increasing the temperature, both film and nanowires were found to reach the melting point without showing any further phase relaxation phenomenon (Figure 6(c)). Figure 6(d) shows the ϵ and loss factor of the freed Nylon-11 nanowires above room temperature, where a thick nanowire-mat as discussed earlier was used for the electrical measurement (inset of Figure 6(d)) without using any other polymer filler. Here, a clear α transition at ~120 °C and a broad melting zone around ~189 °C were identified. In freed nanowires, ϵ reached a value of about 177 at ~120 °C for a testing frequency of 10 kHz. Correspondingly, the loss factor, $\tan \delta$, also showed a peak at the same temperature.^[42,43] The nature of the dielectric properties of Nylon-11 samples are commensurate to the reports for Nylon-11 films prepared from both melt quenching as well as casting from trifluoroacetic acid solution,^[42,43] where it was proposed that as the temperature gradually increases, the micro-Brownian motion of hydrocarbon sections of the Nylons is excited in the non-crystalline regions, while the amide

groups stay as unexcited states, possibly due to hydrogen bonding. The hydrocarbon sections of Nylon-11 are much longer than the amide group and only the amide group has a strong dipole moment. It is also to be noted that the Nylon-11 nanowires, similar to Nylon-11 film reported earlier, do not show a dielectric anomaly, which would indicate a Curie transition, up to the melting temperature.^[42,43] We argue that this feature of Nylon-11 nanowires could be important in terms of high temperature piezoelectric applications as compared to other polymers such as PVDF and P(VDF-TrFE).^[44]

2.5. Energy harvesting performance of Nylon-11 nanowires

An NG based on template-grown vertically aligned Nylon-11 nanowires was fabricated by sputter-coating both sides of the template with gold for electrical access to the nanowires within (see Section 4 for details). The electrical output was measured in response to periodic impacting perpendicular to the long axis of the nanowires, by an oscillating mechanical arm at a set frequency in a bespoke energy harvesting measurement setup (see Supporting Information S7 for details).^[7,12,13] **Figure 7(a)** shows the schematic of the NG structure and the impacting arrangement, where the NG is rigidly fixed at the mean position of the oscillating arm in order to generate maximum compressive force upon impacting. It is ensured that the Nylon-11 nanowire filled template are totally free of any residual film, and crack-free before Au electrodes are deposited on both sides of the template. The device structure is typical for template-based NGs, allowing both mechanical and electrical access to the vertical array of nanowires within.^[7,12,13,64-66] **Figure 7(b)** and **(c)** show the output open circuit voltage (V_{OC}) and short-circuit current (I_{SC}) respectively, measured in response to the periodic impacting at a frequency (f) ranging from 5 - 20 Hz and amplitude of 0.5 mm. (NG output data taken at frequencies up to 150 Hz on a nominally identical NG are shown in Supporting Information Figure S8.) We observed a peak V_{OC} of ~ 1 V and a peak I_{SC} of ~ 100 nA from the device when impacted at a frequency of 5 Hz and amplitude 0.5 mm,

which is comparable to that reported from the P(VDF-TrFE) nanowire-based NG reported earlier by our group.^[7] The electrical output of the nanogenerator was measured across different resistors for $f = 5$ Hz, as shown in Figure 7(d), and a peak in output power density of $\sim 0.03 \mu\text{W cm}^{-2}$ was observed across a load resistance of $\sim 10 \text{ M}\Omega$ (Figure 7(e)). The electrical output was found to increase with increasing impact frequencies and amplitudes (see Figure S8). The output power density can be readily improved by stacking several devices connected electrically in series.^[7] The corresponding figures of merit as defined in Reference [8] are 0.17 GJ/m^3 and $77 \text{ pJ}/(\text{m}^3 \cdot \text{Pa}^2)$, for stress-driven and strain-driven excitations respectively (see Supporting Information S9 and Figure S10).

High-temperature operation up to 150°C was also demonstrated, as shown in Figure 7(f), by impacting the NG while it was mounted on a temperature-controlled heating stage (see Figure S11). The ability of the Nylon-11 NG to withstand such high temperatures is noteworthy and indicates its suitability for operation in high-temperature vibration environments, for example, for energy harvesting applications in vibrating car engines and/or heavy machinery where temperatures typically reach $\sim 150^\circ\text{C}$. While there is a slight decrease in the measured electrical output at higher temperatures, the NG performance was found to be almost fully recoverable upon returning to room temperature as indicated in Figure 7(f).

Finally, fatigue testing was carried out by continuously impacting the device for up to 15 h at 5 Hz ($\sim 2.7 \times 10^5$ cycles). **Figure 8(a)** shows that the Nylon-11 NG exhibited negligible change in V_{OC} over the entire period of continuous testing. Cross-sectional SEM images taken before and after fatigue testing are shown in Figure 8 (b) and (c), indicating no significant change in the morphology of the nanowires and/or the AAO template. The mechanical-to-electrical energy conversion efficiency of the Nylon-11 nanowires was found to be $\sim 11.5\%$ for an impedance-matched load, (as calculated in Supporting Information S9

and Figure S10), although the device efficiency is considerably lower due to the presence of the stiff AAO template.^[7]

3. Conclusions

In conclusion, we have reported, for the first time, the fabrication of high-quality vertically aligned Nylon-11 nanowire arrays by capillary wetting process within nanoporous AAO templates, which in contrast to parent pellets and films deposited by spin casting, showed high crystallinity and intense orientation of the piezoelectric γ phase. The flexible and chemically resilient Nylon-11 nanowire arrays were easily transferable to other substrates as flexible mats, supported by very thin Nylon-11 film, thus allowing access to the nanowires outside the AAO template for characterization. Measurement of dielectric permittivity of the nanowires between -160 °C and 200 °C revealed no dielectric anomaly and indicated the absence of a Curie transition up until the melting temperature of ~189 °C. The measured thermal response indicated that Nylon-11 nanowires may be a viable and cheap alternative for high-temperature piezoelectric applications as compared to commonly used polymers such as PVDF and P(VDF-TrFE). The energy harvesting performance of the NG based on the as-grown template-grown Nylon-11 nanowire arrays was investigated, and revealed high energy conversion efficiency with stable operation over 15 h of continuous impacting. Notably, we have demonstrated, for the first time, stable NG performance at temperatures as high as 150 °C in piezoelectric polymer nanowires.

The ‘self-poled’ nature of the Nylon-11 nanowires render them particularly attractive for use in low-cost and simple NG designs as they require minimal post-processing steps. Our findings also provide important experimental evidence of the dimensionality related crystalline morphology of odd-numbered Nylon nanowires, paving the way for tunable NG design and properties, in particular for applications well above room temperature. The enhanced piezoelectric performance observed in our template-grown Nylon-11 nanowires

makes this material an attractive candidate for future electronic textiles and wearable sensor industry.^[30,46,47]

4. Experimental section

Fabrication of Nylon-11 nanowires: Nylon-11 nanowire arrays were prepared by template-based capillary wetting method from a solution of Nylon-11 pellets (Sigma Aldrich, $[-\text{NH}(\text{CH}_2)_{10}\text{CO-}]_n$) in formic acid (Sigma Aldrich, Reagent grade $\geq 95\%$). Nanowires were obtained in 25 mm diameter AAO (Anapore, Whatman) templates with nominal pore diameters of 200 – 250 nm and of thickness 60 μm . All the chemicals were used without further processing. Initially, calculated wt.% of Nylon-11 pellets were dissolved in formic acid under constant stirring at 60 °C. When dissolved, a pool of Nylon-11 solution in formic acid was created in a shallow depth petridish and an AAO template was gently kept afloat on top of this. The formic acid solution was allowed to dry naturally at room temperature. After 1 h, the Nylon-11 solution-treated AAO template was gently released from the dried Nylon-11 film at the bottom by using warm deionised water to loosen it from excess attached Nylon-11 bottom layer. Further cleaning steps were undertaken as described in Supporting Information S12.

Obtaining Nylon-11 Nanowire Arrayed Mats: In order to study and compare the properties of bare Nylon-11 nanowires, the nanowires were released by dissolving the AAO template by soaking in a solution of 40 vol. % phosphoric acid in water for 4 h (Figure S13). Semi-transparent and delicate Nylon-11 nanowire mats were obtained which were then carefully transferred to substrates (rigid or flexible) by drawing the substrates close to the floating nanowire mats on the phosphoric acid solution (scheme in Figure 1). The Nylon-11 nanowire mats were then repeatedly washed with gentle spray of deionized water and dried naturally on substrates (scheme in Figure 1).

Preparing Nylon-11 film: Nylon-11 pellets were dissolved in formic acid (20 wt%) under constant stirring at 80 °C. The film was made by spin coating (1000 rpm/30 s) the prepared Nylon-11 solution, and then allowed to dry naturally over 30 min. at room temperature.

Characterization: The phase and crystalline quality of the Nylon-11 nanowires inside the AAO template and that of the released nanowires were characterized by X-ray diffraction (XRD) with a Bruker D8 diffractometer equipped with Lynx Eye position-sensitive detector using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). Peak shifts due to sample misalignment was adjusted while performing the XRD scans and background correction was taken care of by using a zero diffraction silicon substrate for mounting. In case of collecting the data for bare Nylon-11 nanowires, the nanowire mat was directly transferred and collected on the zero background silicon reference substrate. Morphological analyses including the evolution of nanowire growth on changing the wt. % of Nylon-11 polymer in formic acid was systematically studied by field-emission scanning electron microscopy (FE-SEM, FEI Nova NanoSEM)). DSC measurements of the samples were carried out using a Q2000 TA Instruments differential scanning calorimeter with heating and cooling rates of 5 °C/min. DSC measurement of bare Nylon-11 nanowires were carried out after carefully peeling off the nanowire mat from the substrates. All the samples were sealed into T-zero pans (TA Instruments) prior to the measurements. FTIR measurements were carried out using a Bruker Tensor 27 IR spectrometer with attenuated total internal reflection attachment. Following a baseline measurement, the samples were placed on an IR transparent high refractive index crystal on which the IR beam is incident and pressure was applied from a small metal disk to ensure contact between the sample and the crystal. IR spectrograms were generated with an average of 20 spectra taken for each measurement. Dielectric permittivity versus temperature measurement of the bare Nylon-11 nanowires was carried out by transferring Nylon-11 nanowires on Au sputtered silicon (using k550 Emitech) acting as the bottom electrode and

then depositing ~50 μm electrodes on top by using conductive silver epoxy and attaching copper wires. The measurement was carried out in an inert sealed bespoke chamber with a heating and cooling rate of 2 $^{\circ}\text{C}/\text{min}$ (using 336 Temperature Controller, Lakeshore), while the dielectric properties were recorded between frequencies of 500 Hz and 100 kHz using an impedance analyser (4294A, Agilent Technologies).

Fabrication of the Nanogenerator: The nanogenerator geometry depicted in the schematic shown in Figure 7(a) was achieved by depositing electrodes on either side of a Nylon-11 nanowire-filled AAO template (of diameter ~ 25 mm) by sputter coating ~ 100 nm thick Au film using k550 Emitech sputter-coater. A shadow mask was used to prevent Au from being deposited to the edge of the template, with a few mm being left around the edge to prevent the possibility of shorting the top and bottom Au electrodes. Thin copper wires were attached on these surfaces using conductive silver paint for electrical access to the Nylon-11 nanowires within the template.

Supporting Information

Supporting Information is available from the author.

Acknowledgements

This work was financially supported by a grant from the European Research Council through an ERC Starting Grant (Grant no. ERC-2014-STG-639526, NANOGEN). S.K-N., Y.C., C.O and A.D. are grateful for financial support from this same grant. A.D., Y.C., and E.C. fabricated the samples and A.D., Y.C., E.C., and C.O performed the measurements reported. A.D. and S.K-N. designed and guided the experimental work. A.D., Y.C. and S.K-N. co-wrote the paper. All authors discussed the results and commented on the paper.

- [1] Z. L. Wang, J. Song, *Science* **2006**, 312, 242.
- [2] S. Crossley, R. A. Whiter, S. Kar-Narayan, *Mater. Sci. Technol.* **2014**, 30, 1613.
- [3] S. Xu, Y. Qin, C. Xu, Y. Wei, R. Yang, Z. L. Wang, *Nat. Nanotechnol.* **2010**, 5, 366.
- [4] R. Yang, Y. Qin, L. Dai, Z. L. Wang, *Nat. Nanotechnol.* **2009**, 4, 34.
- [5] V. Cauda, G. Canavese, S. Stassi, *J. Appl. Polym. Sci.* **2015**, 132, 41667.
- [6] E. Fukada, *IEEE Trans. Ultrason. Ferroelectr. Freq. Control.* **2000**, 47, 1277.
- [7] R. A. Whiter, V. Narayan, S. Kar-Narayan, *Adv. Energy Mater.* **2014**, 4, 1614.
- [8] S. Crossley, S. Kar-Narayan, *Nanotechnology* **2015**, 26, 344001.
- [9] A. Koka, H. A. Sodano, *Adv. Energy Mater.* **2014**, 4, 1301660.
- [10] S. Xu, B. J. Hanse, Z. L. Wang, *Nat. Commun.* **2010**, 1, 93.
- [11] Z. L. Wang, J. Song, *Science* **2006**, 312, 242.
- [12] C. Ou, P. E. Sanchez-Jimenez, A. Datta, F. L. Boughey, R. A. Whiter, S. Sahonta, S. Kar-Narayan, *ACS Appl. Mater. Interfaces* **2016**, 8, 13678.
- [13] F. L. Boughey, T. Davies, A. Datta, R. A. Whiter, S. Sahonta, S. Kar-Narayan, *Nanotechnology (Letters)* **2016**, 27, 28LT02.
- [14] J. L. Lutkenhaus, K. McEnnis, A. Serghei, T. P. Russell, *Macromolecules* **2010**, 43, 3844.
- [15] V. Cauda, S. Stassi, K. Bejtka, G. Canavese, *ACS Appl. Mater. Interfaces* **2013**, 5, 6430.
- [16] Y. Wu, Q. Gu, G. Ding, F. Tong, Z. Hu, A. M. Jonas, *ACS Macro Lett.* **2013**, 2, 535.
- [17] V. Cauda, B. Torre, A. Falqui, G. Canavese, S. Stassi, T. Bein, M. Pizzi, *Chem. Mater.* **2012**, 24, 4215.
- [18] W. H. Liew, M. S. Mirshekarloo, S. Chen, K. Yao, F. E. H. Tay, *Sci. Rep.* **2015**, 5, 9790.
- [19] L. Persano, C. Dagdeviren, C. Maruccio, L. De Lorenzis, D. Pisignano, *Adv. Mater.* **2014**, 26, 7574.
- [20] C. Fu, X. Wang, X. Shi, X. Ran, *RSC Adv.* **2015**, 5, 87429.
- [21] L. Persano, C. Dagdeviren, Y. Su, Y. Zhang, S. Girardo, D. Pisignano, Y. Huang, J.A. Rogers, *Nat. Comm.* **2013**, 4, 1633.

- [22] L. Persano, A. Catellani, C. Dagdeviren, Y. Ma, X. Guo, Y. Huang, A. Calzolari, P. Pisignano, *Adv. Mater.* **2016**, 28, 7633.
- [23] S. Garain, S. Jana, T. K. Sinha, D. Mandal, *ACS Appl. Mater. Interfaces* **2016**, 8, 4532.
- [24] M. M. Alam, D. Mandal, *ACS Appl. Mater. Interfaces* **2016**, 8, 1555.
- [25] S. K. Karan, D. Mandal, B. B. Khatua, *Nanoscale* **2015**, 7, 10655.
- [26] K. H. Kim, K. Y. Lee, J. S. Seo, B. Kumar, S. W. Kim, *Small* **2011**, 7, 2577.
- [27] D. M. Shin, H. J. Han, W. G. Kim, E. Kim, C. Kim, S. W. Hong, H. K. Kim, J. W. Oh, Y. H. Hwang, *Energy Environ. Sci.* **2015**, 8, 3198.
- [28] B. Z. Mei, J. I. Scheinbeim, B. A. Newman, *Ferroelectrics* **1993**, 144, 51.
- [29] M. Stoppa, A. Chiolerio, *Sensors* **2014**, 14, 11957.
- [30] S. Jung, S. Hong, J. Kim, S. Lee, T. Hyeon, M. Lee, D.-H. Kim, *Sci. Rep.* **2015**, 5, 17081.
- [31] B. Ellis, R. Smith (eds) *Polymers: A Property Database*, CRC Press, Taylor & Francis, Florida, USA, **2008**, pp. 287-291.
- [32] Z. Zhong, M. C. Wingert, J. Strzalka, H. H. Wang, T. Sun, J. Wang, R. Chen, Z. Jiang, *Nanoscale* **2014**, 6, 8283.
- [33] M. Dhanalakshmi, J. P. Jog, *eXPRESS Polym. Lett.* **2008**, 2, 540.
- [34] S. L. Wu, J. I. Scheinbeim, B. A. Newman, *J. Polym. Sci. Part B: Polym. Phys.* **1999**, 37, 2737.
- [35] M. H. Litt, C. H. Hsu, P. Basu, *J. Appl. Phys.* **1977**, 48, 2208.
- [36] J. I. Scheinbeim, *J. Appl. Phys.* **1981**, 52, 5939.
- [37] A. Kawaguchi, T. Ikawa, Y. Fujiwara, M. Tabuchi and K. Monobe, *J. Macromol. Sci., Part B: Phys.* **1981**, B20, 1.
- [38] B. A. Newman, P. Chen, K. D. Pae, J. I. Scheinbeim, *J. Appl. Phys.* **1980**, 51, 5161.
- [39] V. Gelfandbein, D. Katz, *Ferroelectrics* **1981**, 33, 111.
- [40] S. C. Mathur, J. I. Scheinbeim, B. A. Newman, *J. Appl. Phys.* **1984**, 56, 2419.
- [41] J. I. Scheinbeim, S. C. Mathur, B. A. Newman, *J. Polym. Sci. Part B* **1986**, 24, 1791.

- [42] G. Wu, O. Yano, T. Soen, *Polym. J.* **1986**, *18*, 51.
- [43] Y. Takase, J. W. Lee, J. I. Scheinbeim, B. A. Newman, *Macromolecules* **1991**, *24*, 6644.
- [44] R. A. Whiter, Y. Calahorra, C. Ou, S. Kar-Narayan, *Macromolecular Mater. Eng.* **2016**, *301*, 1016.
- [45] J. L. Lutkenhaus, K. McEnnis, A. Serghei, T. P. Russell, *Macromolecules* **2010**, *43*, 3844.
- [46] K. Magniez, A. Krajewski, M. Neuenhofer, R. Helmer, *J. App. Polymer. Sci.* **2013**, *129*, 2699.
- [47] D. Matsouka, S. Vassiliadis, K. Prekas, D. V. Bayramol, N. Soin, E. Siores, *J. Elec. Mater.* **2016**, DOI. 10.1007/s11664-016-4710-3.
- [48] P. G. de Gennes, F. Brochard-Wyart, D. Quere, *Capillarity and Wetting Phenomena*; Springer: New York, **2004**.
- [49] T. Fort, Jr., in *Contact Angle, Wettability and Adhesion*, F.M. Fowkes, ed., American Chemical Society, Washington, DC, **1964**, p. 302-316.
- [50] J. R. Dann, *J. Coll. Interface Sci.*, **1970**, *32*, 302.
- [51] D. J. Skrovanek, P. C. Painter, M. M. Coleman, *Macromolecules* **1986**, *19*, 699.
- [52] M. Zhang, P. Dobriyal, J. T. Chen, T. P. Russell, J. Olmo, A. Merry, *Nano Lett.* **2006**, *5*, 1075.
- [53] J. W. Stout, Leon H. Fisher, *J. Chem. Phys.* **1941**, *9*, 163.
- [54] J.W. Gooch (ed) *Encyclopedic Dictionary of Polymers*, Springer, Atlanta, USA, **2010**, pp 495.
- [55] J. S. Stephens, D. B. Chase, J. F. Rabolt, *Macromolecules* **2004**, *37*, 877.
- [56] J. T. Chen, T. H. Wei, C. W. Chang, H. W. Ko, C. W. Chu, M. H. Chi, C. C. Tsai, *Macromolecules* **2014**, *47*, 5227.
- [57] H. Wu, W. Wang, H. Yang, S. Zhaohui, *Macromolecules* **2007**, *40*, 4244.
- [58] H. Isoda, Y. Furukawa, *J. Phys. Chem. B* **2015**, *119*, 14309.

- [59] J. Jakes, S. Krimm, *Spectrochim. Acta, Part A* **1971**, 27, 19.
- [60] S. S. Nair, C. Ramesh, *Macromolecules* **2004**, 37, 454.
- [61] D. Doskocilova, H. Pivcova, B. Schneider, P. Cefelin, *Collect. Czech. Chem. Comm.* **1963**, 28, 1867.
- [62] J. O. Fernandez, G. M. Swallowe, S. F. Lee, *J. Appl. Polym. Sci.* **2001**, 80, 2031.
- [63] Q. M. Zhang, V. Bharti, G. Kavarnos, M. Schwartz, (eds) (2002) *Encyclopedia of Smart Materials*, John Wiley & Sons, pp. 807–825
- [64] D-M. Shin, H. J. Han, W-G. Kim, E. Kim, C. Kim, S. W. Hong, H. K. Kim, J-W. Oh, Y-H. Hwang, *Energy Environ. Sci.* **2015**, 8, 3198.
- [65] V. Bhavanasi, D. Y. Kusuma, P.S. Lee, *Adv. Energy Mater.* **2014**, 4, 1400723.
- [66] S. Stassi, V. Cauda, C. Ottone, A. Chiodoni, C. F. Pirri, G. Canavese, *Nano Energy* **2015**, 13, 474.

Figure 1. Schematic of the growth mechanism of Nylon-11 nanowires inside AAO template via capillary wetting.

Figure 2. SEM images showing (a) incomplete infiltration of Nylon-11 in formic acid solution inside AAO template by classical “template-wetting” process. (b) Rapid drying of the droplets on the template surface causes the formation of thick Nylon-11 film and little infiltration inside the pore channels as observed in (a).

Figure 3. Effect of concentration of starting Nylon-11 solution on the microstructure of nanowires obtained from infiltration of AAO template pores by “capillary wetting”. SEM images of nanowires freed from the template are shown for (a) 2 wt.% Nylon-11 in formic acid where no 1-D growth and only particulate deposition of diameter similar to that of the pore channels (~250 nm) was observed; and (b) 5 wt.% Nylon-11 in formic acid, where low aspect ratio (average length 4 μm and diameter ~250 nm) nanowires and a considerable (40-50 vol. %) growth of Nylon-11 nanoparticles was observed. (c) Graph showing the variation of Nylon-11 nanowire length as a function of concentration of the infiltrating solution. (d) Cross-sectional SEM image of a nanowire-filled template shows the formation of ultralong (40-50 μm) nanowires at an optimum 10 wt. % of Nylon-11 solution concentration resulting in complete infiltration of the template pores.

Figure 4. SEM images of Nylon-11 nanowires upon freeing from the template. (a) Nylon-11 nanowires obtained after completely removing the AAO template. (b) Close-up view of the Nylon-11 nanowires arrays freed from the template showing tips of the nanowires consisting of Nylon-11 nanoparticles (inset). The inset of Figure 4(b) shows a zone of wires revealing the beaded structure, as evidence of the proposed growth mechanism of Nylon-11 nanowires inside the AAO template. (c) Partially dissolved nanowire-filled AAO template revealing the tips of the nanowires for accurate estimation of nanowire diameter. The frequency of the distribution of the diameters of Nylon-11 nanowire is shown in the inset. (d) Flexible Nylon-11 nanowires form a dense mat which can be carefully transferred to any substrate and could roll without mechanical tearing. Inset shows the dense mat-like feature of the nanowires.

Figure 5. (a) XRD patterns of Nylon-11 nanowires synthesized by template wetting process before and after template removal, in comparison to parent Nylon-11 pellets. XRD pattern of a blank AAO template is shown for reference. (b) Room temperature FTIR spectra of Nylon-11 nanowires showing prominent FTIR modes of Nylon-11 α and γ phases. FTIR spectra of a blank AAO template and commercial Nylon-11 pellets are also shown for reference.

Figure 6. DSC thermograms: (a) heating and (b) cooling cycles of Nylon-11 nanowires before and after dissolution of the templates in comparison with parent pellets and Nylon-11 film prepared by spin-casting. (c) Temperature-dependent dielectric permittivity of Nylon-11 film, nanowires within the template and freed nanowires at 10kHz. (d) Dielectric permittivity at the indicated frequency 10kHz above room temperature for Nylon-11 freed nanowires clearly shows the phase relaxation phenomenon. Also shown is the loss tangent graph. Inset illustrates the device structure used for dielectric permittivity measurements.

Figure 7. (a) Schematic showing the structure of the Nylon-11 nanowire-based piezoelectric nanogenerator, where Au electrodes were deposited on both sides of the nanowire-filled AAO template. NG piezoelectric output is generated in response to periodic impacting using a bespoke impacting set-up shown in (a), by which the nanowires are subjected to periodic uniaxial compression and relaxation. (b) Open circuit voltage and (c) short circuit current output of the Nylon-11 nanowire-based NG, in response to periodic impacting for a range of frequencies between 5 – 20 Hz and a fixed amplitude of $\sim 0.5\text{ mm}$. (d) Voltage (blue triangle) and current (green square) and (e) peak power density of a single device, measured across different load resistances. (f) High-temperature electrical output data recorded at room temperature (22 °C) and at temperatures up to 150°C. The nanogenerator output data was also recorded upon cooling back to room temperature.

Figure 8. (a) Fatigue testing: open-circuit voltage recorded over time in response to continuous impacting at a frequency of 5Hz and amplitude of ~0.5 mm on the same Nylon-11 nanogenerator device for 15h (270k impacting cycles in total). Data was recorded after 1h (18k cycles), 5h (90k cycles), 10h (180k cycles) and 15h (270k cycles). Cross-sectional SEM images of the Nylon-11 nanowire-generator (b) before, and (c) after fatigue testing, showing unchanged device structure after 270k impact cycles. Note that the template cleaving process resulted in some of the nanowires being pulled out of the pores.

The table of contents entry

Keywords: : piezoelectric nanogenerator, odd-numbered Nylon, nanowires, energy harvesting, template wetting.

Anuja Datta, Yeonsik Choi, Evie Chalmers, Canlin Ou and Sohini Kar-Narayan*

Piezoelectric Nylon-11 Nanowire Arrays Grown by Template Wetting for Vibrational Energy Harvesting Applications

Vertically aligned arrays of piezoelectric Nylon-11 nanowires with high aspect-ratio are prepared using a capillary template wetting method within nanoporous anodized alumina templates. The template-grown nanowires are self-poled and thus can be directly incorporated into nanogenerators with excellent fatigue performance. The relatively high melting temperature (~ 200 °C) of these nanowires make them suitable for energy harvesting applications at elevated temperatures.