S1. Derivation of effective stiffness ratio

Figure S1- (a) The displacement $x_{\text{bulk}}$ as a result of force $F_{\text{bulk}}$ of a sample of bulk material. (b) The displacement $x_{\text{nano}}$ as a result of force $F_{\text{nano}}$ for a nanostructured sample. The effective stiffness $k$ is defined as the ratio of force to displacement.

The effect of nanostructuring a surface can be quantified by considering the effective stiffness.

The force $F_{\text{bulk}}$ required to give a displacement $x_{\text{bulk}}$ of the bulk material is given by

$$F_{\text{bulk}} = \frac{G A x_{\text{bulk}}}{l}$$
where \( G \) is the shear modulus of the material, \( A \) is the surface area over which the force acts and \( l \) is the thickness of the material. Defining the effective stiffness of the bulk material \( k_{bulk} \) as the ratio of force to displacement gives

\[
k_{bulk} = \frac{F_{bulk}}{x_{bulk}} = \frac{G A}{l}
\]

\[
k_{bulk} = \frac{Y A}{2(1 + \nu) l}
\]

where \( Y \) and \( \nu \) are the Young's modulus and Poisson ratio of the material respectively. A similar treatment can be carried out with the surface of nanostructures. From beam theory

\[
F_{nano} = \frac{3\pi Y r^4 x_{nano}}{2l^3}
\]

where \( r \) is the diameter of the nanostructures, assumed to be cylindrical. From this expression, the nanostructured bending stiffness follows

\[
k_{nano} = \frac{3\pi Y r^4}{2l^3}
\]

The area in this case is \( A = \pi r^2 \) and the aspect ratio is defined by \( \phi = \frac{l}{r} \). Substituting these relationships into the above equation gives

\[
k_{nano} = \frac{3 Y A}{2l} \frac{1}{\phi^2}
\]

\[
k_{nano} = \frac{3(1 + \nu)k_{bulk}}{\phi^2}
\]

and therefore

\[
\frac{k_{nano}}{k_{bulk}} \propto \frac{1}{\phi^2}
\]
S2. Importance of polymer chain alignment in piezoelectric polymers

For PLLA, the ‘3’ direction of the base vectors that describe the $d_{ij}$ piezoelectric tensor is aligned along the length of the polymer chains. It is therefore important to consider how the polymer chains are oriented inside the nanotube, as this will dictate if the applied strains couple to the piezoelectric modes. In nanostructures grown by template wetting, there are two cases of chain orientation to consider: axial and radial alignment. Figure S2 shows simulated nanotubes with each type of chain orientation. Here it is clear that only the axial chain orientation leads to any significant piezoelectric potential. This axial chain orientation is observed in PLLA nanotubes grown by melt-press template wetting, as demonstrated previously by our group $^2$.

![Simulated piezoelectric potential of a PLLA nanotube as a function of polymer chain orientation. (a) Schematic representation of two possible polymer chain orientations. Surface plot of simulated piezoelectric potential in PLLA nanotube having chain orientations corresponding to (b) (001) (chains parallel to length of the tube), and (c) (010) (chains radially aligned in the nanotube). It can be seen that only the axial (001) case leads to any significant piezoelectric potential. This axial chain alignment is observed in nanotubes produced by the melt-press template wetting method.](image)

Figure S2 - Simulated piezoelectric potential of a PLLA nanotube as a function of polymer chain orientation. (a) Schematic representation of two possible polymer chain orientations. Surface plot of simulated piezoelectric potential in PLLA nanotube having chain orientations corresponding to (b) (001) (chains parallel to length of the tube), and (c) (010) (chains radially aligned in the nanotube). It can be seen that only the axial (001) case leads to any significant piezoelectric potential. This axial chain alignment is observed in nanotubes produced by the melt-press template wetting method.
S3. Parametric sweep of tube geometry

The length, radius and wall thickness of the simulated PLLA nanotube (with axial chain alignment) were varied systematically to demonstrate the effect of geometry on the piezoelectric potential. In all cases, the force applied was 1 nN. The potential values were calculated as a surface average over one half of the nanotube surface.

Figure S3(a) shows the influence of nanotube length and radius, with a constant radius-to-wall-thickness ratio of 3. It is evident that the potential is roughly independent of the nanotube length, consistent with beam theory which states that the shear stress along a rigidly fixed end-loaded cantilever is constant along its length. The potential increases with decreasing tube radius.

Figure S3(b) shows the influence of radius and wall thickness on a nanotube 3 μm long. At a given radius, a thicker walled tube will result in a greater surface potential. Likewise, for a given wall thickness a smaller radius will give a higher potential. Inspecting the surface plot suggests that a radius-to-wall-thickness ratio might be the governing factor on the magnitude of the developed potential. However, Figure S3(c) demonstrates that this is not the case. The contours in part (b) are not actually parallel, and fitting the contours with linear regression gives a different gradient for each potential value, hence the radius-to-wall-thickness ratio is not the only important parameter, the absolute values of radius and wall thickness are also important.
Figure S3 – The average surface potential of a PLLA nanotube, deformed as an end-loaded cantilever by a 1 nN load, as a function of outside radius, length and wall thickness. (a) and (b) are surface plots representing the parameter space for each variable. (c) shows how the surface potential varies as the radius is increased, with a proportional increase in wall thickness governed by the ratios show. As the radius is increased, the potential decreases, even though the wall thickness is increased proportionally. This indicates that the radius-to-wall-thickness ratio is not the sole governing factor in the piezoelectric performance of the nanotube.
S4. Convergence of FEA modelling

Figure S4 - A convergence test on the PLLA nanotube mesh, observing how (a) the averaged surface potential from the outer face of one side of a PLLA nanotube and (b) the average total displacement of the top face vary as the mesh is refined. The ‘mesh element length’ is the length of mesh nodes along the axis of the tube. The ‘mesh ratio’ is the ratio of the maximum element size to the tube wall thickness. Decreasing values represent a finer mesh. The values for each parameter used in all simulations in this work are marked with vertical dashed lines. It can be seen that refining the mesh beyond these points leads to no significant change in the results. Parameter values used for subsequent simulation: element length = 50 nm, mesh ratio = 0.5.
S5. Additional SEM images of cell/nanotube interaction

**Figure S5** – Human dermal fibroblast cells on amorphous PLLA nanotubes after 72 hours of cell culture. (a – f) are representative SEM images taken from different parts of the sample surface, across different length scales, as indicated by the respective scale bars. The geometric patterning seen in part (b) is a feature of the nanotube surface and is not created by the cells. It is believed that the formation of these clumps is related to capillary forces when drying the samples. Parts (e) and (f) demonstrate that nanotubes part of the same group are pulled in opposite directions by two different cells.
S6. Upper and lower bounds of bending stiffness and effective shear modulus

The maximum displacement \( x \) of an end loaded cantilever is given by

\[
x = \frac{Fl^3}{3IY}
\]

where \( F \) is the force, \( Y \) is the Young’s modulus, \( I \) is the second moment of area of the cantilever and \( l \) is the cantilever length. For a hollow cylindrical beam, the second moment of area is given by

\[
I = \frac{\pi}{4}(R^4 - r^4)
\]

where \( r \) is the inner diameter and \( R \) is the outer diameter. The bending stiffness can therefore be written as

\[
k = \frac{F}{x} = \frac{3IY}{l^3}
\]

The experimentally observed values, together with a literature value of Young’s modulus, can be used to calculate a bending stiffness. For the lower bound, the dimensions of a single nanotube were used. For an upper bound, a cluster of nanotubes was assumed to behave as a single, much larger nanotube. Observations of the SEM images in Figure S5 indicate that each cluster contains between 10 and 30 nanotubes. A close-packed array of 19 tubes was therefore used in this estimation, and approximated to a single nanotube as shown in Figure S6. Outer and inner radii were taken to be five times that observed for a single tube. It is clear that this is a gross overestimate of the actual bending stiffness and that the true value is likely to be much closer to the lower bound.
To calculate an effective shear modulus, the displacement due to shear deformation a bulk material

\[ x_{\text{shear}} = \frac{Fl}{G'A} \]

and the displacement due to beam bending

\[ x_{\text{beam}} = \frac{F l^3}{3IY} \]

are set equal, where \( G' \) is the effective shear modulus and \( A \) is the area over which force \( F \) is acting, taken to be the cross-sectional area of the tube (c.f. Figure S1). The effective modulus can then be expressed as

\[ G' = \frac{3IY}{AI^2} \]

Table S1 lists the parameter values used to calculate the bending stiffness and effective modulus values, as well as the calculated values.
| Parameter | Lower bound | Upper bound |
|-----------|-------------|-------------|
| $R$       | 152.5 nm    | 762 nm      |
| $r$       | 96.5 nm     | 482.5 nm    |
| $l$       | 30 μm       | 30 μm       |
| $Y^{(3)}$ | 4 GPa       | 4 GPa       |
| $k$       | 0.32 nN/μm  | 200 nN/μm   |
| $G'$      | 220 kPa     | 5.4 MPa     |

**Table S1** - Parameter values and calculated values of the bending stiffness ($k$) and effective shear modulus ($G'$). Radii and lengths are experimentally observed; Young’s modulus is taken from literature. Calculated values are given to two significant figures.
Figure S7 - The relative change in modulus of PLLA films as a result of crystallisation. Modulus values were determined fitting the experimental data to the DMT indentation model. The flat geometry of this sample means that the DMT model is appropriate.
S8. FEA modelling of nanotube side wall deflection

**Figure S8** - (a) Surface plot of the deformation in a PLLA nanotube as a result of a 10 nm indent from an AFM tip. The nanotube is in cross-section, with the remainder of the structure omitted due to symmetry. (b) Surface plot of the deformation of a PLLA film as a result of a 10 nm indent from an AFM tip. The intrinsic mechanical properties of the material in (a) and (b) are identical. The colour scale for both plots is also the same. (c) Simulated force - distance curves for 200 nm diameter PLLA nanotubes of differing wall thickness. Also shown is the force - distance curve of a 200 nm film of the same material. (d) Simulated force vs. displacement curves for nanotubes of different wall thicknesses (t) and radii (r), but constant r/t ratio. The deformation characteristics are similar in each case. (e) The simulated deformation of a PLLA nanotube, loaded with 4 nN in the geometry shown in part (a), as a function of elastic modulus. At a constant force, the deformation d is inversely proportional to the elastic modulus E.

Quantitative Nanomechanical Mapping is so called because in principal, values can be assigned to material properties. In practice, however, determining accurate values is challenging. Accurate material properties require various aspects of the tip and cantilever to be accurately known. Routines exist to estimate the cantilever spring constant and tip apex radius, but these are both subject to large errors. The uncertainty in the tip calibration propagates into the values of mechanical properties, meaning that absolute values should be treated with caution. It is therefore far more trustworthy to perform comparative measurements, looking for trends rather...
than absolute values. In this instance, even if the tip calibration is inaccurate, the results are still reliable.

The system is complicated further when considering the behaviour of nanoscaled materials. Leaving aside any potential changes in intrinsic material properties that can occur in nanomaterials (e.g. graphene vs. graphite), the physical dimensions of nanostructured samples can cause problems in QNM. Typically, the modulus values returned by QNM are determined by fitting the Derjagin-Muller-Toropov (DMT) model to the force-distance curves at each pixel. This model assumes a spherical indenter (the tip) deforming an infinite flat plane (the sample). In nanomaterials, the curvature of the sample is of a similar order of magnitude to that of the tip apex. The sample cannot, therefore, be approximated to a flat plane. If the DMT model is used to determine modulus values of nanoscaled materials, the values will not be accurate even if the tip calibration is perfect.

Indentation of nanotubes, as in the present case, adds more uncertainty to the system. This is highlighted in Figure S6. Parts (a) and (b) show the distribution in deformation of a nanotube and film, each with identical material parameters and each subjected to a 10 nm indent from the tip. In the film, the majority of the deformation is localised to the region immediately beneath the tip. The relatively unclamped nature of the nanotube, however, allows for the same tip displacement to be accommodated by deformation distributed throughout the nanotube structure. An indentation of a film therefore mostly probes material deformation, whereas in a nanotube the deformation can be considered as structural. The difference in behaviour is further shown by the force-distance curves in Figure S6(c). For a given force, the tube structure deforms to a greater extent than the nanotube, even though the material in each has the same properties. This effect is amplified as the wall thickness is reduced.
Since the estimated modulus values from QNM are not valid, a different metric must be used to assess the mechanical properties. The deformation data is a more appropriate channel to use for this comparison. The deformation is the amount the sample deforms as a result of the 'peak force' applied by the tip. This data is extracted directly from the raw force-distance curves - i.e. no assumptions are made about the loading geometry, and no models are fitted to the data - and is therefore more appropriate for analysis of QNM data from PLLA nanotubes.

Figure S6(d) shows that provided the wall thickness to radius ratio is constant, the deformation characteristics are the same. The constant r/t ratio is known to be a feature of melt-grown polymer nanotubes. Figure S6(e) demonstrates that all else being equal, the amount of nanotube side wall deflection for a given load is inversely proportional to the material elastic modulus. This allows for comparative modulus values to be determined.
Figure S9 - Surface potential of amorphous and crystalline PLLA films, as determined by KPFM. A significant increase in potential is seen between amorphous and crystalline material. This can even be observed qualitatively when handling the samples, as the crystalline films are far more susceptible to the effects of static electricity.
Figure S10 – The attachment of cells to tissue culture plastic (TCP) with and without the magnets used to hold the PLLA samples in place. There is no significant difference in cell attachment, indicating that the presence of the magnet is not influencing the results.
Figure S11 – (a) Height and (b) deformation data channels from QNM on amorphous PLLA nanotube. PeakForce set point = 100 nN. (c) Cut-lines of data, red arrow indicates the point that the deformation data was selected. (d) Average deformation of amorphous and crystalline nanotubes.
S12. Extended KPFM data

Figure S12 – (a) Height and (b) deformation data channels from KPFM on crystalline PLLA nanotube. (c) Cut-lines of height and potential data. (d) Average potential of amorphous and crystalline nanotubes. Potential values were averaged over the entire projected area of the nanotube.
S13. Extended PFM data

The variation in intensity of the crystalline PFM signal shown in Figure S11(b) was observed in several separate nanotubes. Its origin is not currently understood, but could be a result of the underlying crystal structure. PFM Scans were also performed in the absence of an oscillating potential (0V line in Figure S11(c)) to ensure that the signals were of electromechanical origin. These scans mostly consist of noise, however some slight activity can be seen as the tip approaches the edges of the nanotube, which could be attributed to electrostatic interaction between the tip side-wall and the nanotube.

**Figure S13** — (a) Height and (b) deformation data channels from PFM on crystalline PLLA nanotube. (c) Cut-lines of height and PFM data, including a PFM scan with zero applied potential to indicate the electro-mechanical origin of the signal. (d) Average PFM signal gradients of amorphous and crystalline nanotubes.
S14. PeakForce QNM of PLLA nanotubes to observed surface morphology

The PeakForce error signal in PF-QNM displays the difference between the peak force set point and the recorded peak force at each pixel. It is especially useful at highlighting changes in height, rather than absolute values of height. The peak force error signal was therefore used to visualize the surface morphology on the nanotubes. Peak force error signals of amorphous and crystalline nanotubes are shown in Figure S14. There are no discerning features of either group.

Figure S14 – Peak Force error signals, plotted in a non-linear adaptive scale, of (a-c) amorphous and (d-f) crystalline nanotubes (1 hour, 120 °C).
– both amorphous and crystalline nanotubes have some interesting surface features, but there are no significant differences between the two groups. The surface roughness of each nanotube is likely dictated by the inner surface of the AAO template used for growth. Experimental details of how these images were obtained can be found in reference 6.
S15. Attachment of HDFs to polypropylene nanotubes

Figure S15 – (a) SEM image of crystalline isotactic polypropylene (PP) nanotubes. (b) X-ray diffraction of annealed and quenched PP samples, demonstrating the difference in crystallinity. Annealed samples were ≈ 40 % crystalline (by volume). (c) Attachment of HDFs to amorphous and crystalline polypropylene (PP) nanotubes, with standard TCP as a control. Significance assessed with two sample t-test ($N = 4$ for each condition, ns = not significant; * = $p < 0.05$; ** = $p < 0.01$).

Wide-angle X-ray diffraction (WAXD) was performed with a Bruker D8 diffractometer in Bragg-Brentano geometry with Cu Kα radiation.

PP has been used here as a control against the influence of piezoelectricity. Comparing crystalline PP NTs to crystalline PLLA NTs is of little benefit, given that there are several other differences between these polymers besides the absence or presence of piezoelectric behaviour. Surface chemistry will be different between PP and PLLA, as will the exact geometry of each
type of nanotube given the different processing conditions used in their growth. Comparing amorphous PP to crystalline PP, and then amorphous PLLA to crystalline PLLA, removes these inconsistencies. The outcome of each of these comparisons can then be directly contrasted. Using this differential method, the PP NTs act as a control against the effects of piezoelectricity.
S16. Material parameters for FEA modelling

The following material parameters were used for the finite element model:

| Parameter                      | Value (units) | Reference |
|--------------------------------|---------------|-----------|
| Young’s modulus                | 4 GPa         | 3         |
| Poisson ratio                  | 0.36          | 3         |
| Density                        | 1.25 g/cm³    | 3         |
| Piezoelectric coefficient \(d_{14}\) | 10 pC/N      | 7,8       |
| Dielectric constant            | 3.8           | 9         |

Table S2 – Material parameters for FEA of piezoelectric PLLA nanotubes
S17. References

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