

Polythiophene precursor electrochemical nanolithography: highly local thermal and morphological characterization

Jin Young Park,[‡] Prasad Taranekar^a and Rigoberto Advincula^{a*}

^aDepartment of Chemistry and Department of Chemical Engineering, University of Houston, Houston, TX 77204, USA. Tel: 1-713-743-1755; Fax: 1-713-743-1755; E-mail: radvincula@uh.edu

[‡] Current address: Department of Polymer Science and Engineering University of Massachusetts 120 Governors Drive, Amherst, MA 01003

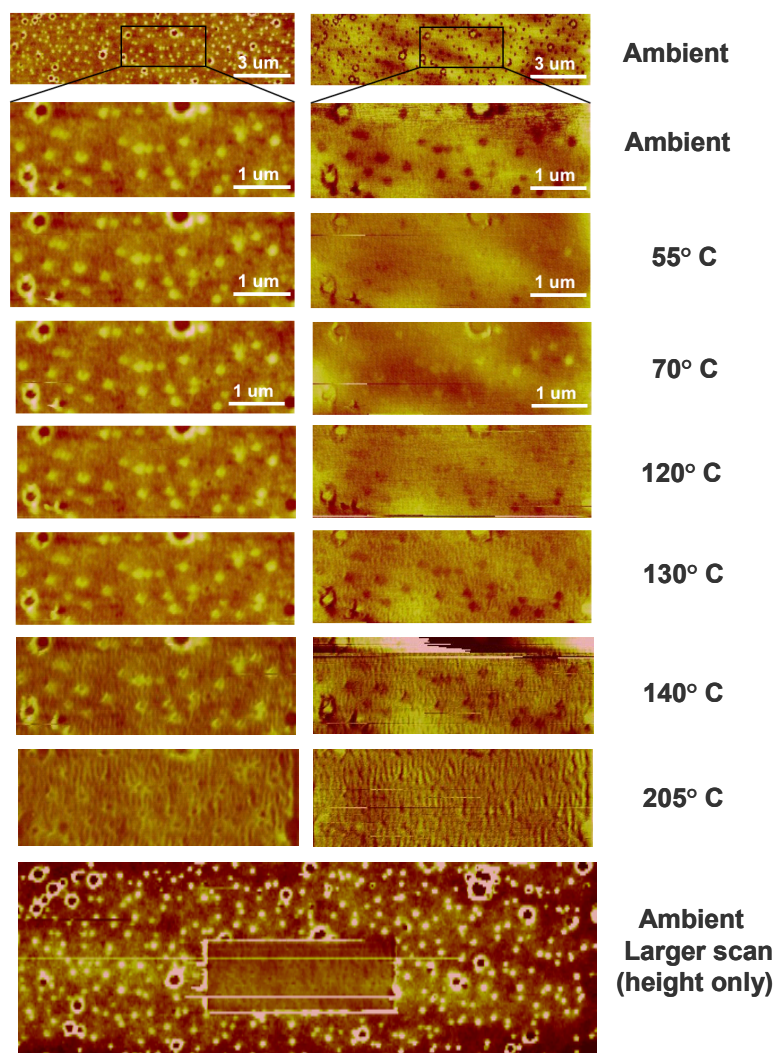


Figure S1. Surface morphological (left) and friction (right) change of the spin-casting P3T:PMMA ($w/w = 25:75$) blend film formed in an incremented temperature of 55, 70, 120, 130, 140, 205 °C, respectively.

Conductivity calculation

Figure 4



Original Film thickness (by spin-coating): 50-55 nm

Total thickness on the pattern dot: ~61.83 nm

Current: 27.14 ± 52.5 pA

$$\Omega = V/I$$

$$\text{Electric conductivity} = 1/(\Omega \cdot \text{thickness}) \\ = \mathbf{1.46 \times 10^{-6} \text{ S/cm}}$$



Total thickness on the pattern dot: ~63.17 nm

Current: 54.20 ± 7.92 pA

$$\Omega = V/I$$

$$\text{Electric conductivity} = 1/(\Omega \cdot \text{thickness}) \\ = \mathbf{2.86 \times 10^{-6} \text{ S/cm}}$$



Total thickness on the pattern dot: ~66.26 nm

Current: 64.85 ± 11.77 pA

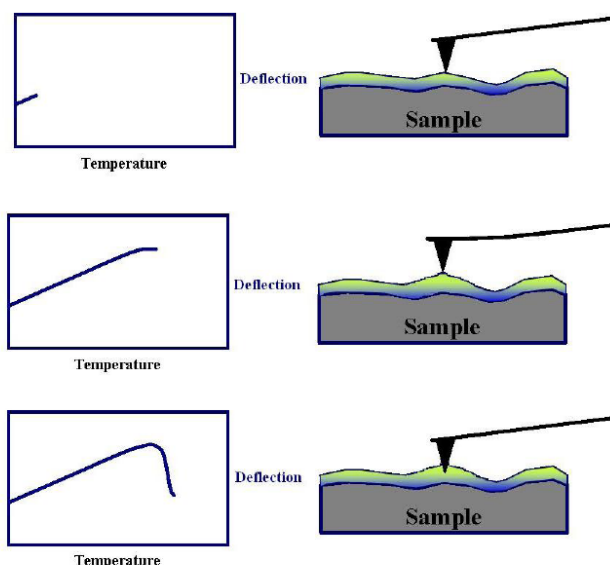
$$\Omega = V/I$$

$$\text{Electric conductivity} = 1/(\Omega \cdot \text{thickness}) \\ = \mathbf{3.26 \times 10^{-6} \text{ S/cm}}$$

Figure S2. Conductivity calculations of localized nanopatterned areas using the current, thickness, and a particular bias voltage (-3 V).

nano-TA

nano-TA schematic



In the nano-TA mode, the user visualizes the sample at a typical resolution of better than 30 nm, identifies the regions of interest and then positions the probe using the AFM to subject the region in contact with the probe to a thermal ramp. Shown to the left is a schematic of the nano Thermal Analysis mode showing the initial upwards deflection of the cantilever due to thermal expansion followed by the penetration of the probe due to softening or melting. This will typically happen at the glass transition or melt transition of the sample. The heating of the probe is due to a high resistance region incorporated into a silicon probe that is otherwise much like a standard silicon probe. This allows rapid, controllable heating by controlling the voltage applied to the probe using the NanoTA2 electronics. During the ramp, the operator can monitor, using the

nano-TA/HT-AFM Specifications:

Measurement Mode:	Single or Dual Probe (SW selectable)
Ramp Modes:	Voltage, Power (single), Resistance (single) Delta Power (dual)
Imaging Modes:	Contact Mode / Intermittent Contact Mode (SPM Dependent)
Temp. Ramp Rate:	Up to 600,000°C / min
Max. Controllable Temp. of Probe:	400°C (dependent on probe)
Probe Spring Const:	ranges from 0.1 N/m to 5 N/m
Probe Res. Freq.:	ranges from 20 to 80 kHz
Tip Radius:	10-30 nm
Tip Height:	3-6 microns
Cantilever Length:	200 - 350 μm

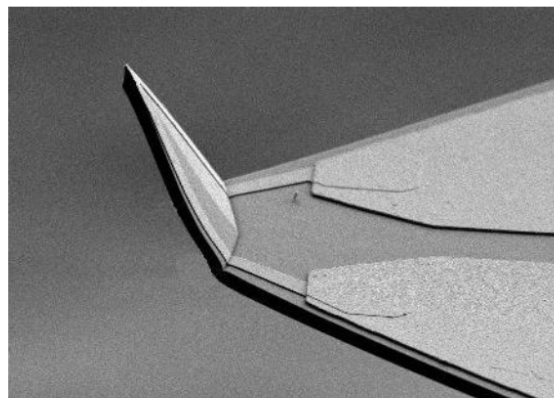


Figure S3. Summary and specifications of the nano-TA technique, specifications on the Anasys Instrument and SEM of cantilever tip.

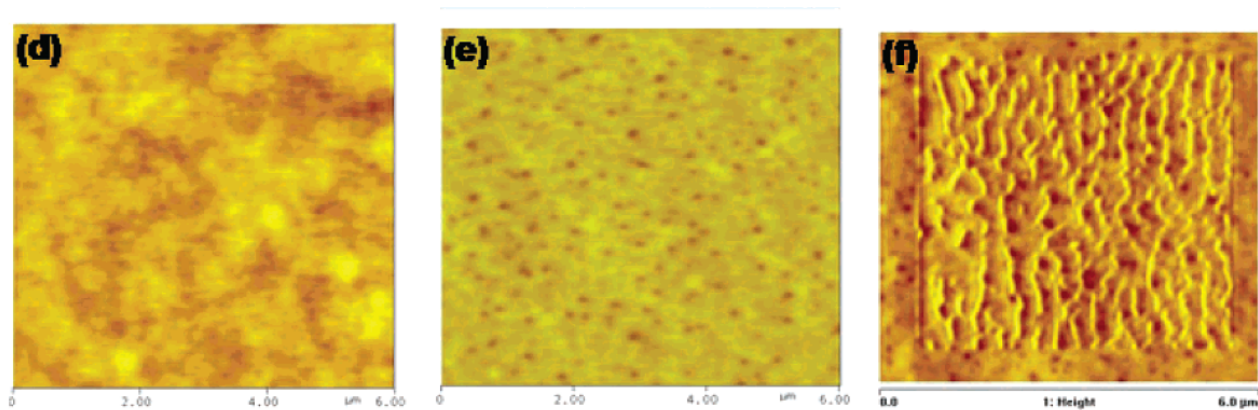


Figure S4. (d) Morphology of the polystyrene film after attempted square ($1 \mu\text{m}^2$) patterning at -12 V and a tip speed of $2 \mu\text{m}^2/\text{s}$ with no pattern observed. (e) Morphology of the polymer A and polystyrene blends coated on a Si(100) substrate prior to patterning. (f) Square patterning of a polymer blend surface of $5 \mu\text{m}^2$ at -9 V with a tip speed of $10 \mu\text{m}^2/\text{s}$. REFERENCE: Jegadesan, S.; Sindhu, S.; Taraneekar, P.; Advincula, R.*; Valiyaveetil, S.* "Electrochemically Nanopatterned Conducting Coronas of a Conjugated Polymer Precursor: SPM Parameters and Polymer Composition" *Langmuir* 2006, **22**, 3807-3811.