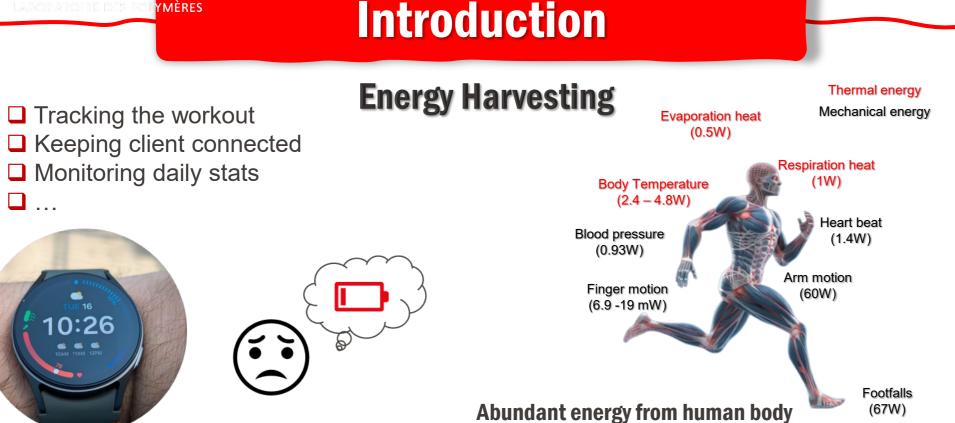
# Spontaneous Piezo- and Pyroelectricity of Polyacrylonitrile -**Brushes Prepared via Surface-initiated polymerization**

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### **Polar Polymer Film**

**Electrostatic self-assembly** 

**Polypeptides** 

Science. 1997, 276, 384 Angewandte Chemie, 2000, 112, 8 Nature 1999, 398, 137

Chem 2017. 3. 764 Polymers **2024**, 16, 2097 × Complex building blocks

- **×** Weak, non-covalent interactions
- × Stability
- **×** Difficult to control chemical composition

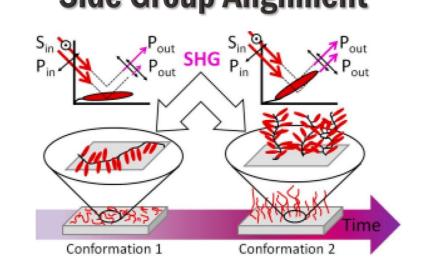
**Polymer Brush** 

# **Side Group Alignment**

**Conformal coating** 

**× Solution processing** 

× Melt-based processing





- High grafting density
- **Stretched polymer chain**

Chemical Reviews, 2009, 109, 5437-5527 Chemical Reviews, 2017, 117, 1105-1318.

Polymer brush is an effective way to modify surface properties.

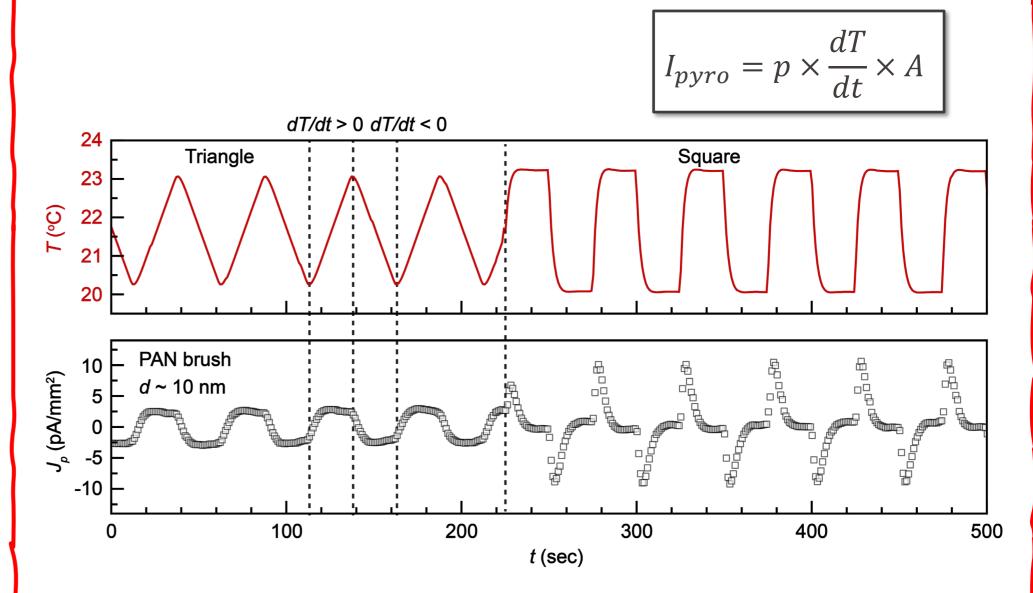
#### **Characterized by second harmonic generation**

Langmuir, 2017, 33, 4157-4163

The orientation of dipolar liquid crystalline side chains in polymer brushes evolves progressively with brush thickness

### **Pyro- and Piezoelectric Measurement**

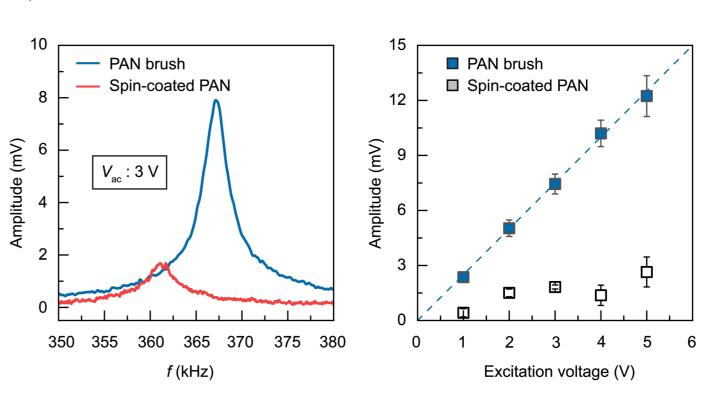
#### **Dynamic Pyroelectric Measurement**



➤ The pyroelectric coefficient is comparable with commercial poled PVDF!

### Piezoelectric Force Microscope (PFM)

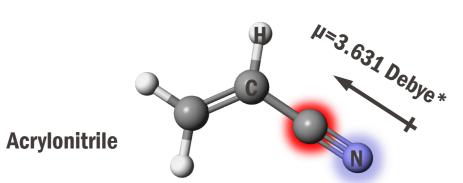
Science, 2024, 383, 1492-1498



PFM showed that PAN in the brush architecture has much higher piezoelectricity than the spin-coated form, suggesting the structure promotes macroscopic polarization.

### **Model System**

#### **Polar Side Group**



- Large dipole moment
- **Suitable for SIP**
- **Hydrophobic polymer**

\*Calculated by



### **Preparation of Polyacrylonitrile Brush**

Angew. Chem. Int. Ed., 2018, 57, 13433

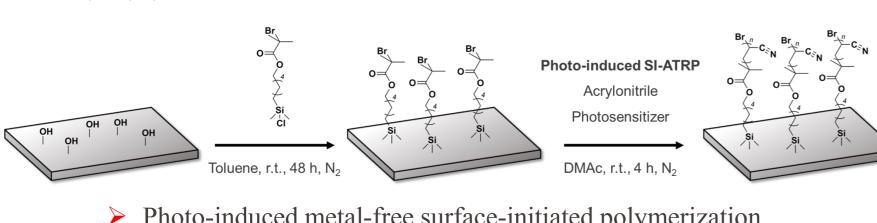
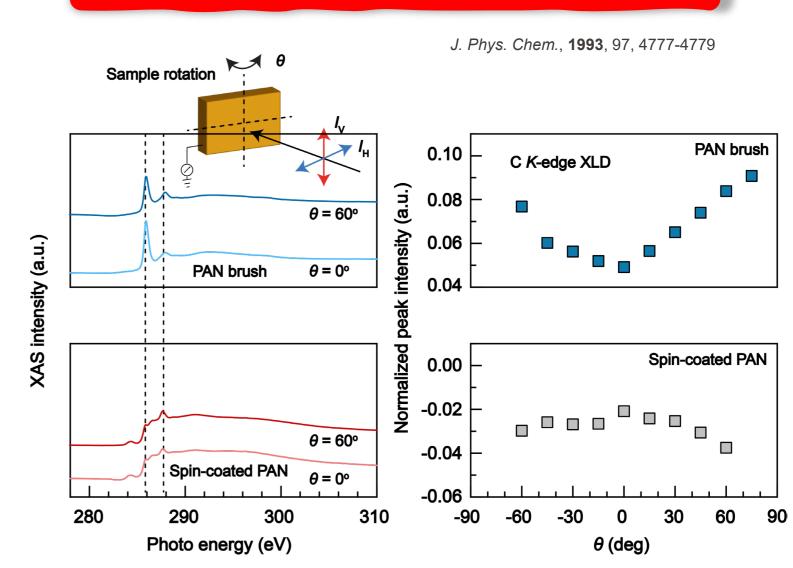


Photo-induced metal-free surface-initiated polymerization

## **Synchrotron Radiation**



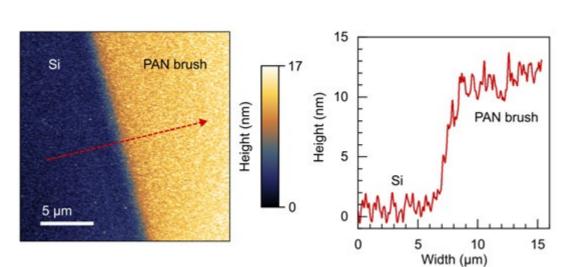
➤ NEXAFS revealed the spatial anisotropy in the distribution of -CN groups.

### **Polymer Brush Thickness**

#### **Ellipsometry**

Ellipsometry confirmed the film thickness around 10 nm

#### **Atomic Force Microscope (AFM)**



> AFM verified the uniformity of the thin PAN brush film and was consistent with Ellipsometry data.

#### **Summary**

Our study shows:

- > The polymer brush structure can reorient polar side groups.
- This further induces spontaneous macroscopic polarization.
- Pyro- and Piezoelectricity emerge without post-treatment.

## Acknowledgements

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