

## **Supplementary Information**

### **Crystal Orientation of Poly(ethylene oxide) Confined within the Nanorod Templated by Anodic Aluminum Oxide Nanochannels**

Chien-Liang Liu<sup>1</sup> and Hsin-Lung Chen<sup>2\*</sup>

<sup>1</sup>National Synchrotron Radiation Research Center, 101 Hsin-Ann Road, Hsinchu Science Park, Hsinchu 30076, Taiwan

<sup>2</sup>Department of Chemical Engineering, National Tsing Hua University, Hsin-Chu 30013, Taiwan

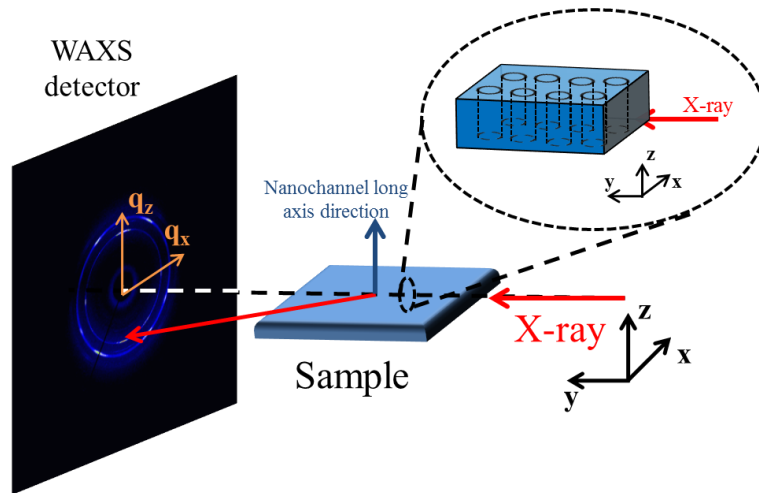


Fig S1. Schematic illustration of the configuration of the WAXS experiment; the incident beam traveled along the edge of sample. The long axis of the AAO nanochannels was along z direction.

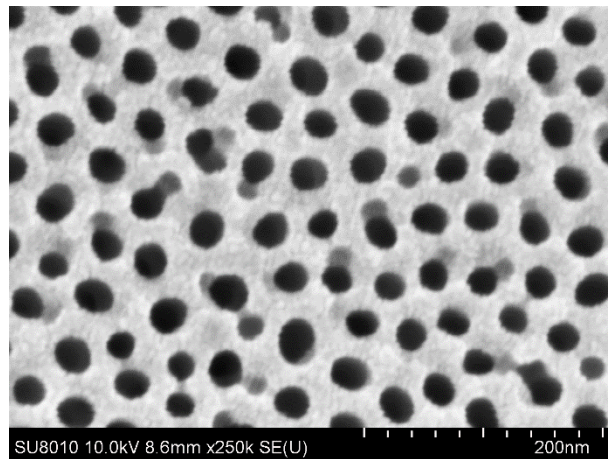
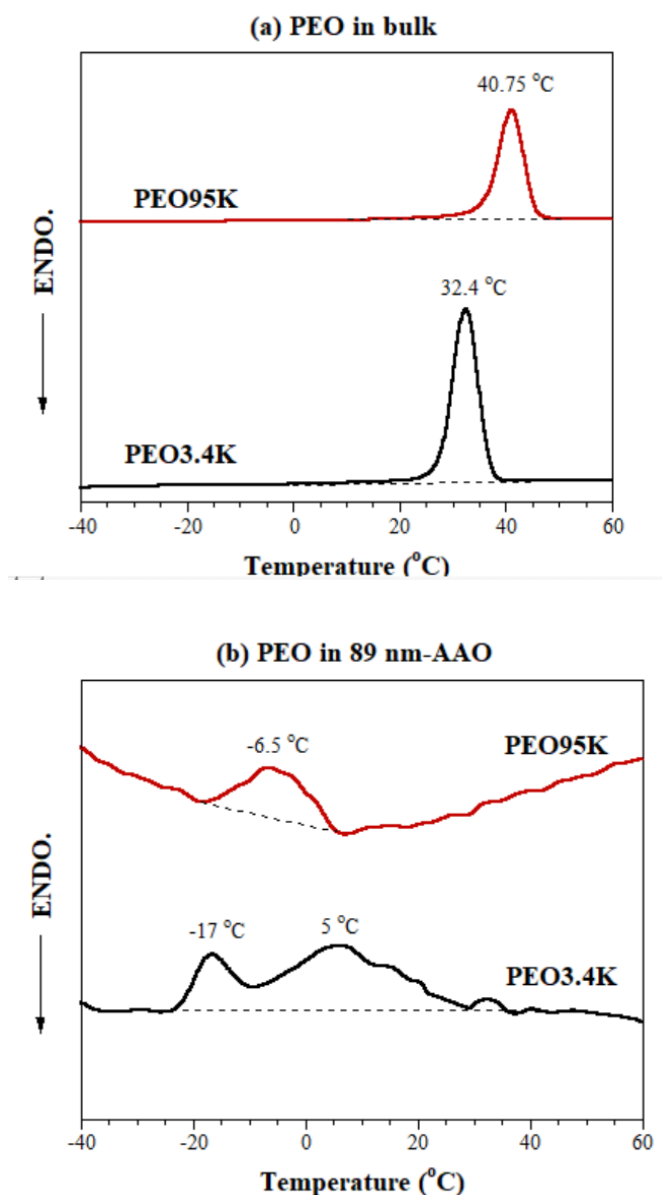


Fig. S2 The top-view SEM image of neat 23 nm-AAO membrane

### DSC cooling scans of the PEO-containing AAO membranes

Differential scanning calorimetry (DSC) measurement was performed with a NETZSCH 2000 DSC. For the cooling scan, the sample was first heated to 90 °C for melting annealing for 5 min to erase the thermal history. A cooling scan was then conducted to -50 °C at the cooling rate of 5 °C /min for recording the crystallization exotherms. The DSC thermograms thus obtained are displayed in Figure S4.



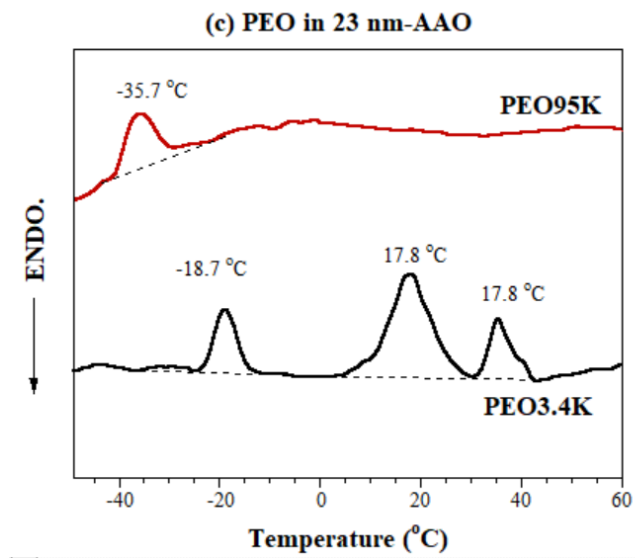


Fig S3. DSC cooling scans of PEO3.4K and PEO95K in (a) the bulk state, (b) 89 nm-AAO membrane, and (c) 23 nm-AAO membrane.

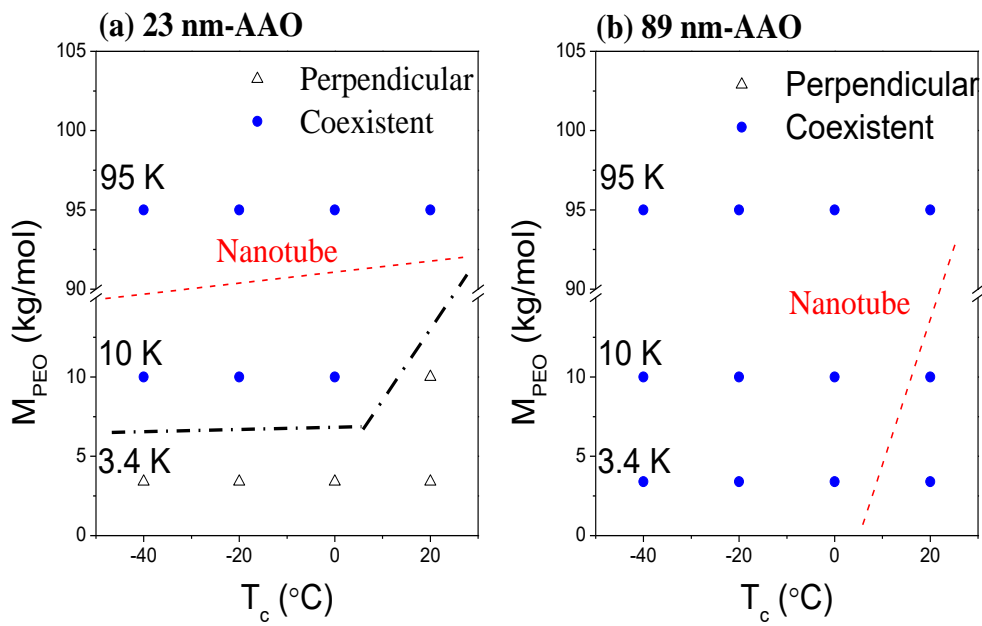


Fig S4. Overlay of the orientation diagrams of PEO crystallites in the nanotubes and nanorods templated by: (a) 23 nm-AAO and (b) 89 nm-AAO. The data points in the plots mark the type of orientation attained in nanorod system. The red dashed lines and black dot-dashed line define the boundary between the perpendicular orientation and coexistent orientation for the nanotube and nanorod, respectively. It can be seen that the window of the perpendicular orientation was much smaller in the nanorod than that associated with the nanotube, as manifested particularly by the fact that no pure perpendicular crystal orientation was observed for the nanorod in 89 nm-AAO.

**Table S1.** Summary of PEO crystal orientation in AAO nanochannels reported in the selected literature.

Reference in the present paper	Type of orientation	Molecular weight of PEO (g/mol)	$D_{AAO}$ (nm)	$T_c$ (°C)	Morphological entity of PEO in nanochannels
Ref. 1	Perpendicular	$M_n= 41,000$	20	Not specified	Not specified
Ref. 22	Parallel <sup>a</sup>	$M_w= 100,000$	400	-30	nanotube
Ref. 23	Perpendicular	$M_w= 2000$	30, 60, 100	Not specified	nanorod
	Parallel <sup>b</sup>	$M_w= 2000$	10	Not specified	nanorod
Ref. 26	Perpendicular, (Perpendicular+ Tile) <sup>c</sup>	$M_n= 3400, 10000, 95000$	23, 89	20, 0, -20, -40	nanotube
This work	Perpendicular, (Perpendicular+ Tile) <sup>c</sup>	$M_n= 3400, 10000, 95000$	23, 89	20, 0, -20, -40	nanorod
<sup>a</sup> Parallel orientation formed due to surface nucleation. <sup>b</sup> Parallel orientation formed due to the development of fully-extended chain crystals. <sup>c</sup> Coexistent orientation preferred at higher nucleation density and weaker confinement (larger $D_{AAO}$ ).					