

Supporting Information for:

Shape-Persistent, Thermoresponsive Polypeptide
Brushes Prepared by Vapor Deposition
Surface-Initiated Ring-Opening Polymerization of
 α -Amino Acid N-Carboxyanhydrides

Yong Shen,¹ Solenne Desseaux,² Bethany Aden,³ Bradley S. Lokitz,⁴ S. Michael Kilbey, II,³

Zhibo Li^{1} and Harm-Anton Klok^{2*}*

1. Beijing National Laboratory for Molecular Sciences (BNLMS), Institute of Chemistry,
Chinese Academy of Sciences, Beijing 100190, China.

2. École Polytechnique Fédérale de Lausanne (EPFL), Institut des Matériaux and Institut des
Sciences et Ingénierie Chimiques, Laboratoire des Polymères, Bâtiment MXD, Station 12,
CH-1015 Lausanne, Switzerland.

3. Departments of Chemistry and Chemical & Biomolecular Engineering, University of
Tennessee, Knoxville TN, 37996-1600, USA.

4. Center for Nanophase Materials Sciences, Oak Ridge National Laboratory,
Oak Ridge, TN, 37831 USA.

* E-mail: harm-anton.klok@epfl.ch; zbli@iccas.ac.cn.

Table S1. Water contact angles of poly(L-EG₂-Glu) and poly(L-EG₃-Glu) brushes measured at different temperatures.

Sample	Water contact angle (°)	
	20 °C	60 °C
poly(L-EG ₂ -Glu)	69 ± 1.7	73 ± 0.2
poly(L-EG ₃ -Glu)	56 ± 0.7	66 ± 0.4

Table S2. Dry and Swollen Thicknesses for PPEG₂MEMA Brushes by In Situ Multi-angle Ellipsometry

Sample Name	Dry (nm)	Swollen at 25 °C (nm)	n	Swollen at 50 °C (nm)	n	Swelling Ratio ^a
PPEG ₂ MEMA-a	54±1	108±9	1.40 ₃	109±13	1.40 ₄	2.02
PPEG ₂ MEMA-b	53±1	115±6	1.40 ₂	108±9	1.40 ₅	2.18
PPEG ₂ MEMA-c	52±1	129±29	1.40 ₂	126±2	1.40 ₀	2.47
PPEG ₂ MEMA-d	52±1	125±17	1.40 ₅	124±2	1.39 ₄	2.42
Average	53±1	117±16	1.40±0.005	114±11	1.40±0.007	2.22

^a Ratio of swollen (at 25°C) to dry thickness (nm)

Table S3. Dry and Swollen Thicknesses for Poly(D-EG₂-Glu) Brushes by In Situ Multi-angle Ellipsometry

Sample Name	Dry (nm)	Swollen at 25 °C (nm)	n	Swollen at 50 °C (nm)	n	Swelling Ratio ^a
Poly(D-EG ₂ -Glu)-a	60±1	135±5	1.40 ₈	122±2	1.41 ₀	2.25
Poly(D-EG ₂ -Glu)-b	56±1	123±8	1.41 ₃	127±2	1.41 ₁	2.19
Poly(D-EG ₂ -Glu)-c	72±1	134±5	1.42 ₆	133±9	1.42 ₆	1.85
Poly(D-EG ₂ -Glu)-d	73±7	139±22	1.42 ₅	133±7	1.41 ₂	1.90
Average	65±9	133±11	1.42±0.010	128±6	1.41±0.007	2.03

^a Ratio of swollen (at 25°C) to dry thickness (nm)

Table S4. Dry and Swollen Thicknesses for Poly(L-EG₂-Glu) Brushes by In Situ Multi-angle Ellipsometry

Sample Name	Dry (nm)	Swollen at 25 °C (nm)	n	Swollen at 50 °C (nm)	n	Swelling Ratio ^a
Poly(L-EG ₂ -Glu)-a	55±3	123±10	1.40 ₄	124±3	1.40 ₀	2.25
Poly(L-EG ₂ -Glu)-b	58±1	125±2	1.41 ₃	131±3	1.41 ₁	2.17
Poly(L-EG ₂ -Glu)-c	63±7	139±9	1.41 ₄	133±2	1.41 ₀	2.21
Poly(L-EG ₂ -Glu)-d	53±1	135±7	1.40 ₈	128±4	1.40 ₈	2.57
Average	57±5	130±10	1.41±0.006	128±4	1.41±0.005	2.27

^a Ratio of swollen (at 25°C) to dry thickness (nm)

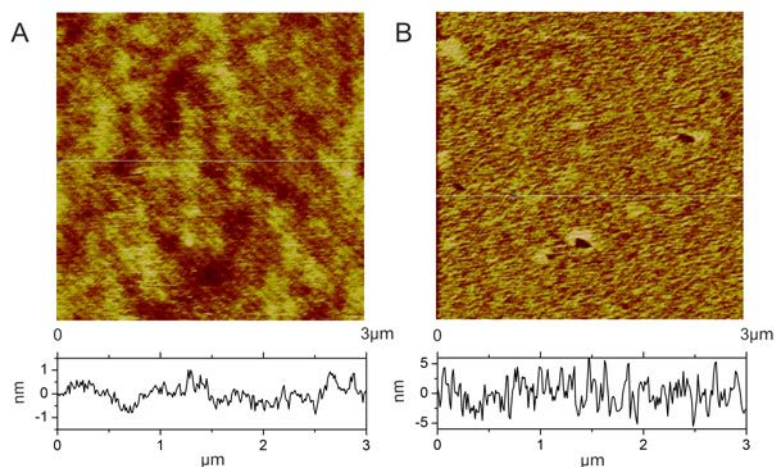


Figure S1. AFM topography scans and cross sectional images of poly(rac-EG₂-Glu) brushes (A: film thickness = 43 nm) and poly(L-EG₃-Glu) brushes (B: film thickness = 24 nm) measured in water.

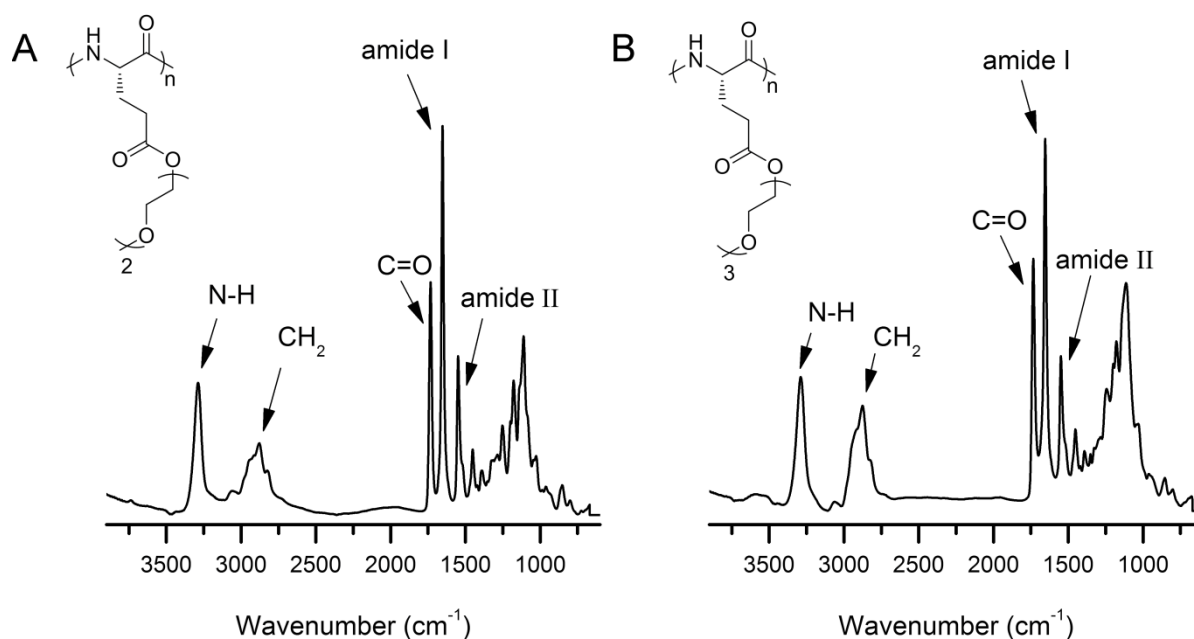


Figure S2. FTIR spectra of (A) poly(L-EG₂-Glu) (d = 78 nm) and (B) poly(L-EG₂-Glu) (d = 24 nm) brush functionalized silicon wafers.