Nanophase Separation of Poly(*N*-alkyl acrylamides): The Dependence of the Formation of Lamellar Structures on Their Alkyl Side Chains

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Synthesis of *N*-alkyl acrylamides

N-alkyl amine (TCI, Japan) was dissolved in chloroform to the concentration of 0.1 M. To this solution, triethylamine (1.2 equivalent to *N*-alkyl amine, TCI, Japan) was added. The solution was cooled at 0 ˚C and acryloyl chloride (1.2 equivalent to *N*-alkyl amine) was added dropwise. After addition of acryloyl chloride, the solution was heated to room temperature and reaction was carried out for 3h. Then the reaction solution was washed with 5 wt% HCl, saturated Na_2CO_3, and saturated NaCl. The organic solution was collected and dried with Na_2SO_4. The crude products were purified by vacuum distillation for $n = 4$ (0.3 Torr, 55 ºC,) and $n = 5$ (0.3 Torr, 80 ºC) or recrystallization from chloroform-hexane mixed solvent for $n \geq 6$. The purified compounds were characterized with ^1H NMR spectra.

butylacrylamide (*n*=4)

1H NMR (500 MHz, $CDCl_3$) δ (δ in ppm):6.27 (dd, 1H, $H_2C{=}CH$-), 6.11 (dd, 1H, H*H*C=CH-), 5.85 (s, 1H, -N*H*-CH_2-CH_2-), 5.62 (dd, 1H, *H*HC=CH-), 3.33 (q, 2H, -NH-CH_2-CH_2-), 1.50-1.56 (m, 2H, -NH-CH_2-CH_2-CH_2-CH_3), 1.37 (m, 2H, -NH-CH_2-CH_2-CH_2-CH_3), 0.93 (t, 3H, -NH-CH_2-CH_2-CH_2-CH_3)

pentylacrylamide (*n*=5)

1H NMR (500 MHz, $CDCl_3$) δ:6.27 (dd, 1H, $H_2C{=}CH$-), 6.11 (dd, 1H, H*H*C=CH-), 5.86 (s, 1H, -N*H*-CH_2-CH_2-), 5.62 (dd, 1H, *H*HC=CH-), 3.32 (q, 2H, -NH-CH_2-CH_2-), 1.51-1.57 (m, 2H, -NH-CH_2-CH_2-$(CH_2)_2$-CH_3), 1.30-1.36 (m, 4H, -NH-CH_2-CH_2-(CH_2)$_2$-CH_3), 0.90 (t, 3H, -NH-CH_2-CH_2-$(CH_2)_2$-CH_3)

hexylacrylamide (*n*=6)

1H NMR (500 MHz, $CDCl_3$) δ:6.26 (dd, 1H, $H_2C{=}CH$-), 6.08 (dd, 1H, H*H*C=CH-), 5.63 (dd, 1H, *H*HC=CH-), 5.55 (s, 1H, -N*H*-CH_2-CH_2-), 3.27-3.35 (m, 2H, -NH-CH_2-CH_2-), 1.51-1.56 (m, 2H, -NH-CH_2-CH_2-$(CH_2)_3$-CH_3), 1.25-1.37 (m, 6H, -NH-CH_2-CH_2-(CH_2)$_3$-CH_3), 0.89 (t, 3H, -NH-CH_2-CH_2-$(CH_2)_3$-CH_3)

heptylacrylamide (*n*=7)

1H NMR (500 MHz, $CDCl_3$) δ:6.27 (dd, 1H, $H_2C{=}CH$-), 6.07 (dd, 1H, H*H*C=CH-), 5.63 (dd, 1H, *H*HC=CH-), 5.51 (s, 1H, -N*H*-CH_2-CH_2-), 3.33 (q, 2H, -NH-CH_2-CH_2-), 1.53 (m, 2H, -NH-CH_2-CH_2-$(CH_2)_4$-CH_3), 1.28-1.33 (m, 8H, -NH-CH_2-CH_2-(CH_2)$_4$-CH_3), 0.88 (t, 3H, -NH-CH_2-CH_2-$(CH_2)_4$-CH_3)

octylacrylamide (*n*=8)

1H NMR (500 MHz, $CDCl_3$) δ:6.25 (dd, 1H, $H_2C=CH$-), 6.05 (dd, 1H, H*H*C=CH-), 5.61 (dd, 1H, *H*HC=CH-), 5.47 (s, 1H, -N*H*-CH_2-CH_2-), 3.26-3.33 (m, 2H, -NH-CH_2-CH_2-), 1.49-1.59 (m, 2H, -NH-CH_2-CH_2-$(CH_2)_5$-CH_3), 1.18-1.31 (m, 10H, -NH-CH_2-CH_2-$(CH_2)_5$-CH_3), 0.86 (t, 3H, -NH-CH_2-CH_2-$(CH_2)_5$-CH_3)

nonylacrylamide (*n*=9)

1H NMR (500 MHz, $CDCl_3$) δ:6.27 (dd, 1H, $H_2C=CH$-), 6.07 (dd, 1H, H*H*C=CH-), 5.63 (dd, 1H, *H*HC=CH-), 5.49 (s, 1H, -N*H*-CH_2-CH_2-), 3.33 (q, 2H, -NH-CH_2-CH_2-), 1.56 (m, 2H, -NH-CH_2-CH_2-$(CH_2)_6$-CH_3), 1.26-1.31 (m, 12H, -NH-CH_2-CH_2-$(CH_2)_6$-CH_3), 0.88 (t, 3H, -NH-CH_2-CH_2-$(CH_2)_6$-CH_3)

decylacrylamide (*n*=10)

1H NMR (500 MHz, $CDCl_3$) δ:6.27 (dd, 1H, $H_2C=CH$-), 6.06 (dd, 1H, H*H*C=CH-), 5.62 (dd, 1H, *H*HC=CH-), 5.49 (s, 1H, -N*H*-CH_2-CH_2-), 3.32 (q, 2H, -NH-CH_2-CH_2-), 1.51 (m, 2H, -NH-CH_2-CH_2-$(CH_2)_7$-CH_3), 1.25-1.30 (m, 14H, -NH-CH_2-CH_2-$(CH_2)_7$-CH_3), 0.87 (t, 3H, -NH-CH_2-CH_2-$(CH_2)_7$-CH_3)

undecylacrylamide (*n*=11)

1H NMR (500 MHz, $CDCl_3$) δ:6.27 (dd, 1H, $H_2C=CH$-), 6.07 (dd, 1H, H*H*C=CH-), 5.63 (dd, 1H, *H*HC=CH-), 5.49 (s, 1H, -N*H*-CH_2-CH_2-), 3.33 (q, 2H, -NH-CH_2-CH_2-), 1.55 (m, 2H, -NH-CH_2-CH_2-$(CH_2)_8$-CH_3), 1.21-1.31 (m, 16H, -NH-CH_2-CH_2-$(CH_2)_8$-CH_3), 0.88 (t, 3H, -NH-CH_2-CH_2-$(CH_2)_8$-CH_3)

dodecylacrylamide (*n*=12)

1H NMR (500 MHz, $CDCl_3$) δ:6.27 (dd, 1H, $H_2C=CH$-), 6.08 (dd, 1H, H*H*C=CH-), 5.63 (dd, 1H, *H*HC=CH-), 5.53 (s, 1H, -N*H*-CH_2-CH_2-), 3.31-3.35 (m, 2H, -NH-CH_2-CH_2-), 1.50-1.56 (m, 2H, -NH-CH_2-CH_2-$(CH_2)_9$-CH_3), 1.26-1.31 (m, 18H, -NH-CH_2-CH_2-$(CH_2)_9$-CH_3), 0.88 (t, 3H, -NH-CH_2-CH_2-$(CH_2)_9$-CH_3)

tridecylacrylamide (*n*=13)

1H NMR (500 MHz, $CDCl_3$) δ:6.27 (dd, 1H, $H_2C=CH$-), 6.07 (dd, 1H, $HHC=CH$-), 5.63 (dd, 1H, $HHC=CH$-), 5.50 (s, 1H, -$NH-CH_2-CH_2$-), 3.33 (q, 2H, -$NH-CH_2-CH_2$-), 1.50-1.57 (m, 2H, -$NH-CH_2-CH_2-(CH_2)_{10}-CH_3$), 1.21-1.31 (m, 20H, -$NH-CH_2-CH_2-(CH_2)_{10}-CH_3$), 0.88 (t, 3H, -$NH-CH_2-CH_2-(CH_2)_{10}-CH_3$)

tetradecylacrylamide (*n*=14)

1H NMR (500 MHz, $CDCl_3$) δ:6.27 (dd, 1H, $H_2C=CH$-), 6.07 (dd, 1H, $HHC=CH$-), 5.63 (dd, 1H, $HHC=CH$-), 5.49 (s, 1H, -$NH-CH_2-CH_2$-), 3.33 (q, 2H, -$NH-CH_2-CH_2$-), 1.50-1.56 (m, 2H, -$NH-CH_2-CH_2-(CH_2)_{11}-CH_3$), 1.25-1.31 (m, 22H, -$NH-CH_2-CH_2-(CH_2)_{11}-CH_3$), 0.88 (t, 3H, -$NH-CH_2-CH_2-(CH_2)_{11}-CH_3$)

pentadecylacrylamide (*n*=15)

1H NMR (500 MHz, $CDCl_3$) δ:6.27 (dd, 1H, $H_2C=CH$-), 6.07 (dd, 1H, $HHC=CH$-), 5.63 (dd, 1H, $HHC=CH$-), 5.49 (s, 1H, -$NH-CH_2-CH_2$-), 3.33 (q, 2H, -$NH-CH_2-CH_2$-), 1.50-1.56 (m, 2H, -$NH-CH_2-CH_2-(CH_2)_{12}-CH_3$), 1.25-1.31 (m, 24H, -$NH-CH_2-CH_2-(CH_2)_{12}-CH_3$), 0.88 (t, 3H, -$NH-CH_2-CH_2-(CH_2)_{12}-CH_3$)

hexadecylacrylamide (*n*=16)

1H NMR (500 MHz, $CDCl_3$) δ:6.27 (dd, 1H, $H_2C=CH$-), 6.07 (dd, 1H, $HHC=CH$-), 5.63 (dd, 1H, $HHC=CH$-), 5.49 (s, 1H, -$NH-CH_2-CH_2$-), 3.33 (q, 2H, -$NH-CH_2-CH_2$-), 1.52-1.56 (m, 2H, -$NH-CH_2-CH_2-(CH_2)_{13}-CH_3$), 1.25-1.31 (m, 26H, -$NH-CH_2-CH_2-(CH_2)_{13}-CH_3$), 0.88 (t, 3H, -$NH-CH_2-CH_2-(CH_2)_{13}-CH_3$)

hepthadecylacrylamide (*n*=17)

1H NMR (500 MHz, $CDCl_3$) δ:6.27 (dd, 1H, $H_2C=CH$-), 6.07 (dd, 1H, $HHC=CH$-), 5.63 (dd, 1H, $HHC=CH$-), 5.51 (s, 1H, -$NH-CH_2-CH_2$-), 3.33 (q, 2H, -$NH-CH_2-CH_2$-), 1.53 (m, 2H, -$NH-CH_2-CH_2-(CH_2)_{14}-CH_3$), 1.25-1.31 (m, 28H, -$NH-CH_2-CH_2-(CH_2)_{14}-CH_3$), 0.88 (t, 3H, -$NH-CH_2-CH_2-(CH_2)_{14}-CH_3$)

octadecylacrylamide (*n*=18)

1H NMR (500 MHz, $CDCl_3$) δ:6.27 (dd, 1H, $H_2C=CH$-), 6.07 (dd, 1H, $HHC=CH$-), 5.63 (dd, 1H, $HHC=CH$-), 5.49 (s, 1H, -$NH-CH_2-CH_2$-) 3.33 (q, 2H, -$NH-CH_2-CH_2$-), 1.50-1.58 (m, 2H, -$NH-CH_2$-

CH_2-$(CH_2)_{15}$-CH_3), 1.22-1.31 (m, 30H, -NH-CH_2-CH_2-$(CH_2)_{15}$-CH_3), 0.88 (t, 3H, -NH-CH_2-CH_2-$(CH_2)_{15}$-CH_3)

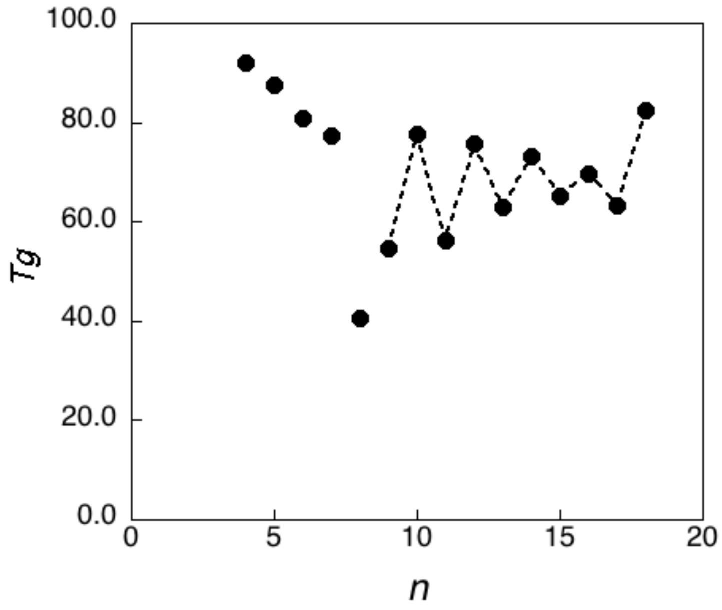

Figure S1. Tg for p(AlkylAms). The dotted line is a guide for the eye.

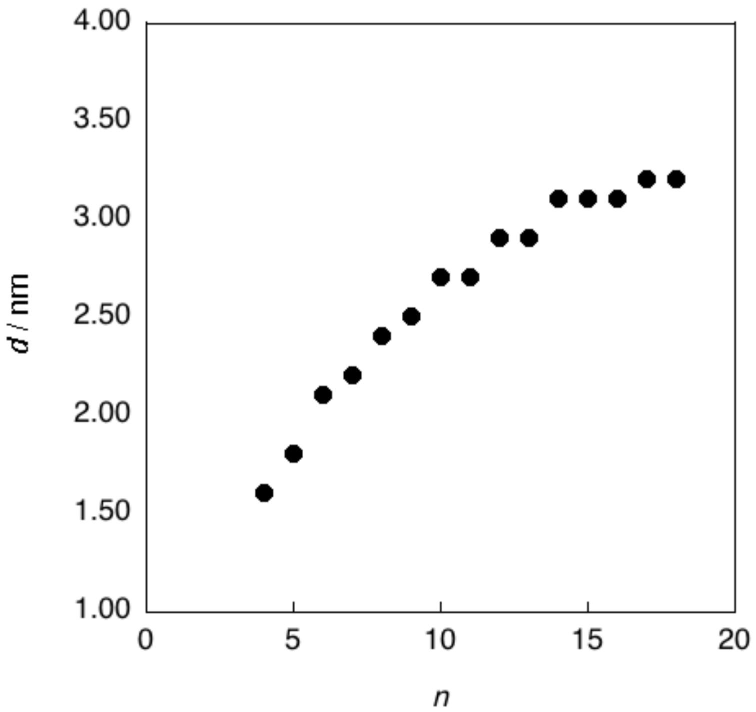

Figure S2. Dependence of alkyl nanodomain sizes with *n*.

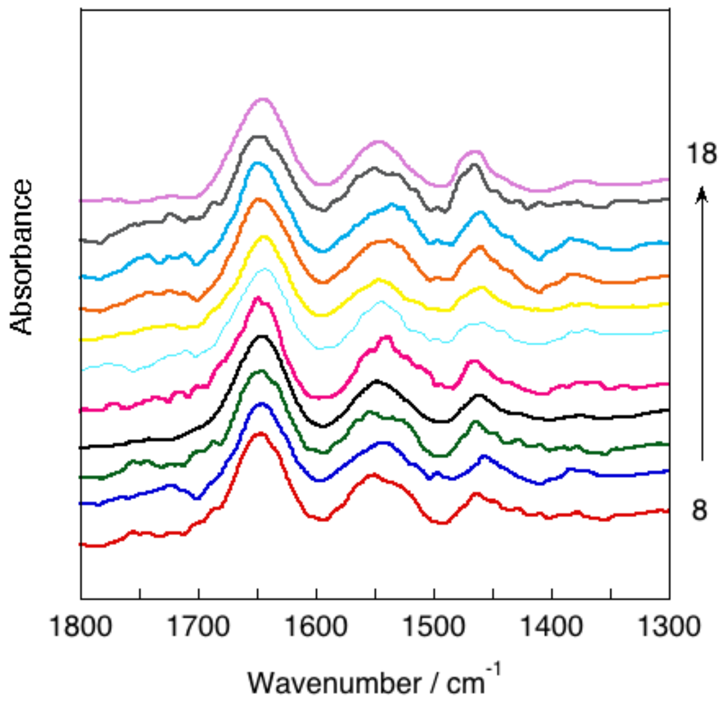

Figure S3. FT-IR spectra of lamellar film of p(AlkylAms) (n = 8-18) at the amide region.

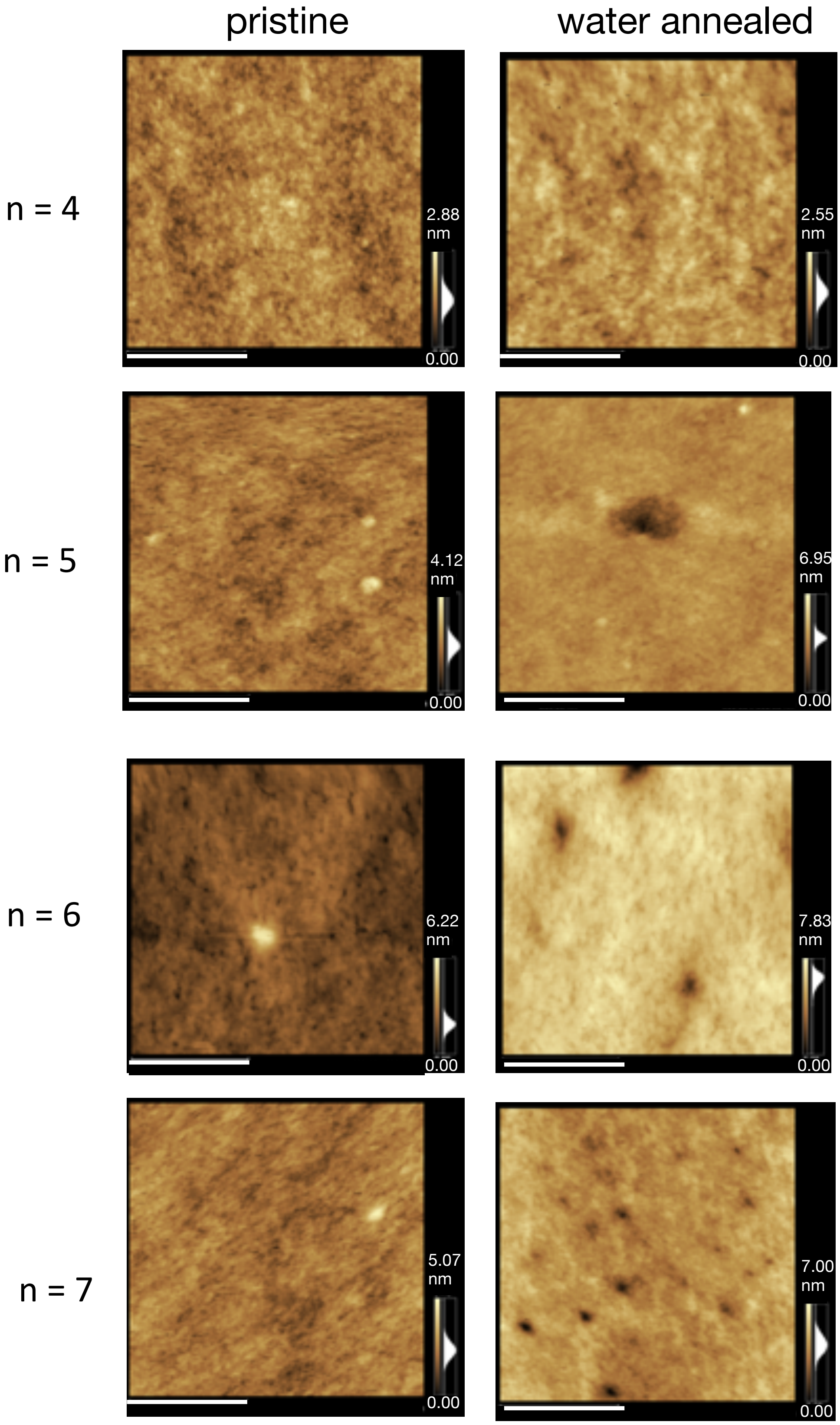

Figure S4 AFM images for p(AlkylMA). Left pristine and right water annealed film. White scale bar in the images indicate 200 nm

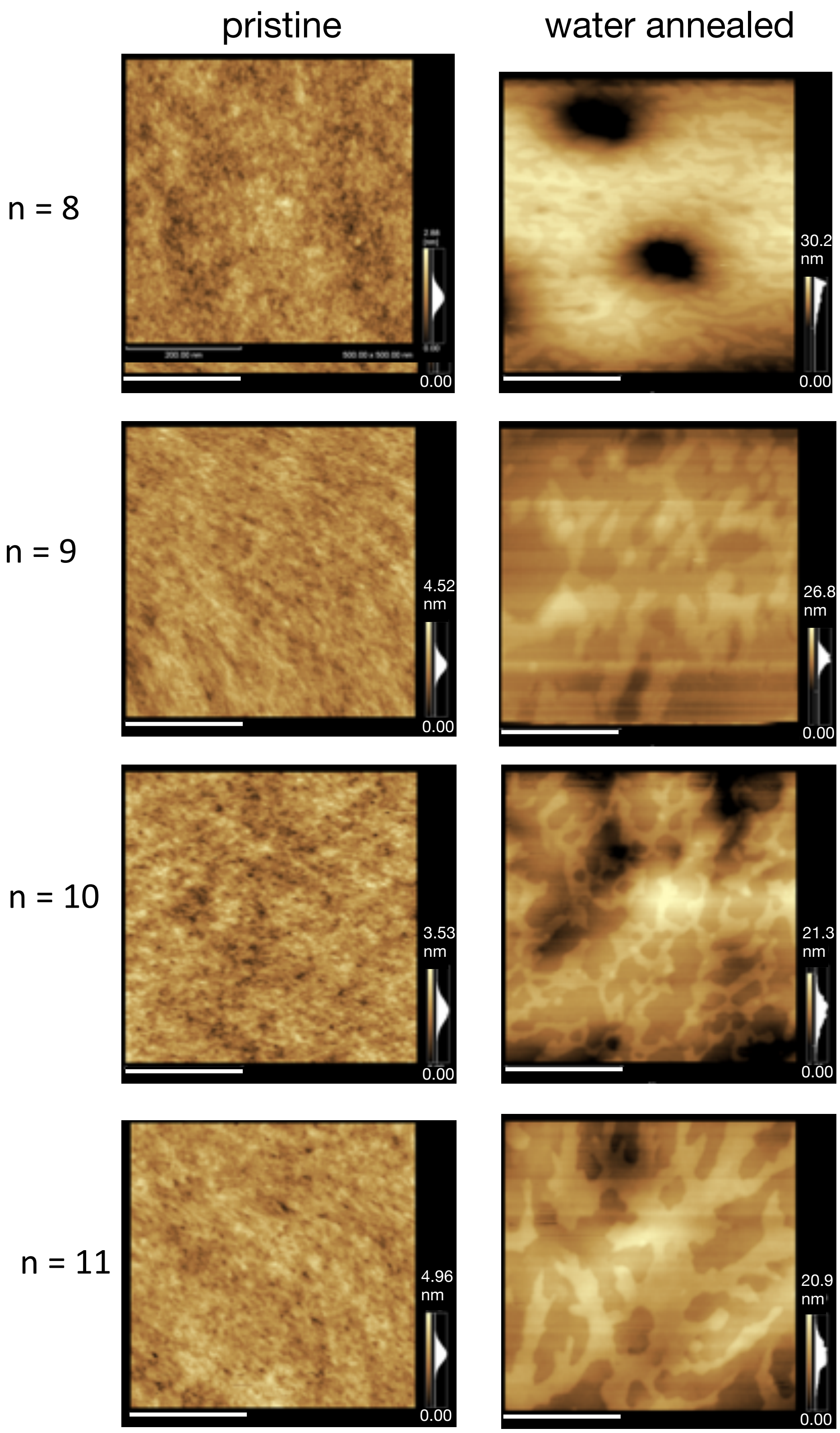

Figure S4 Continued

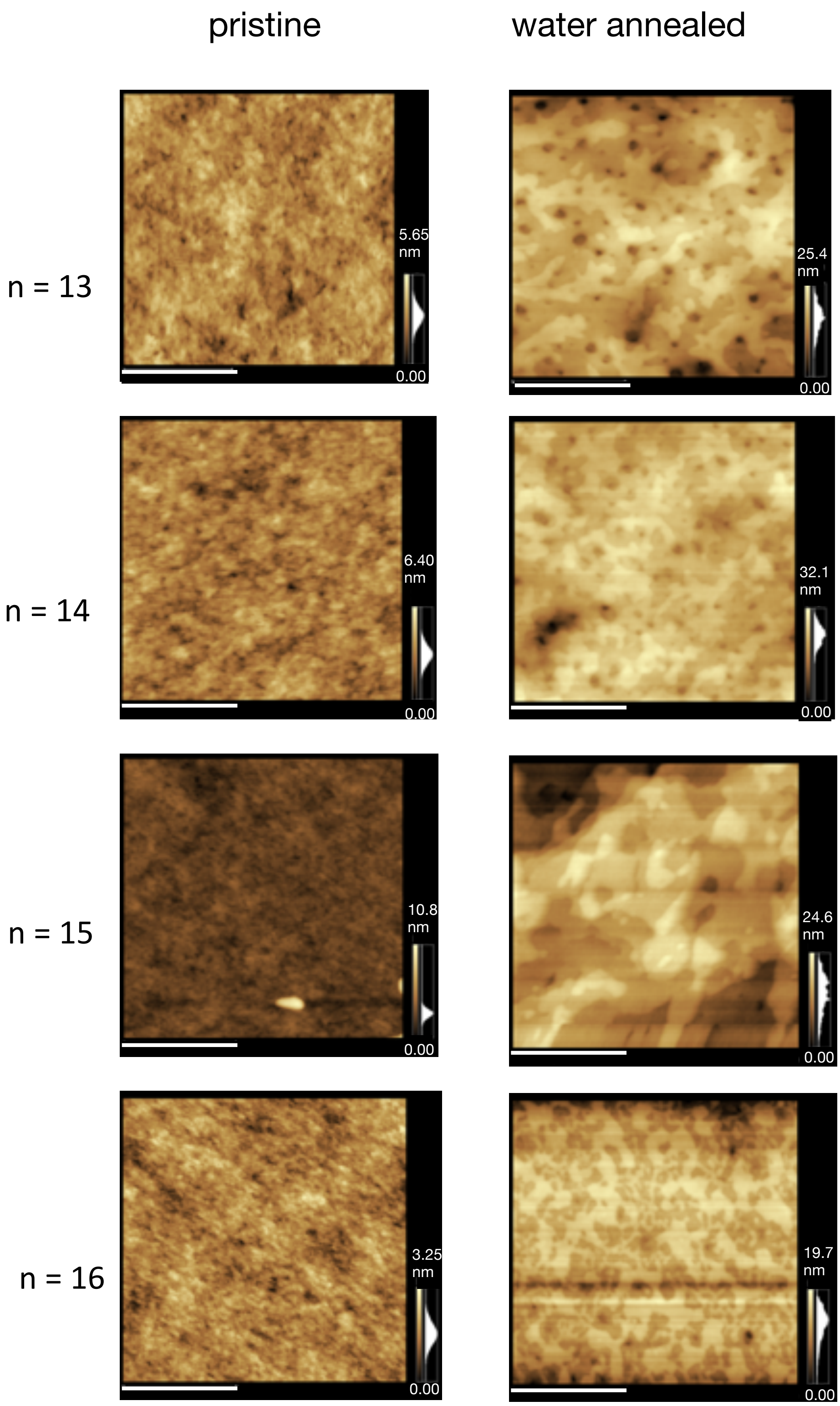

Figure S4 Continued

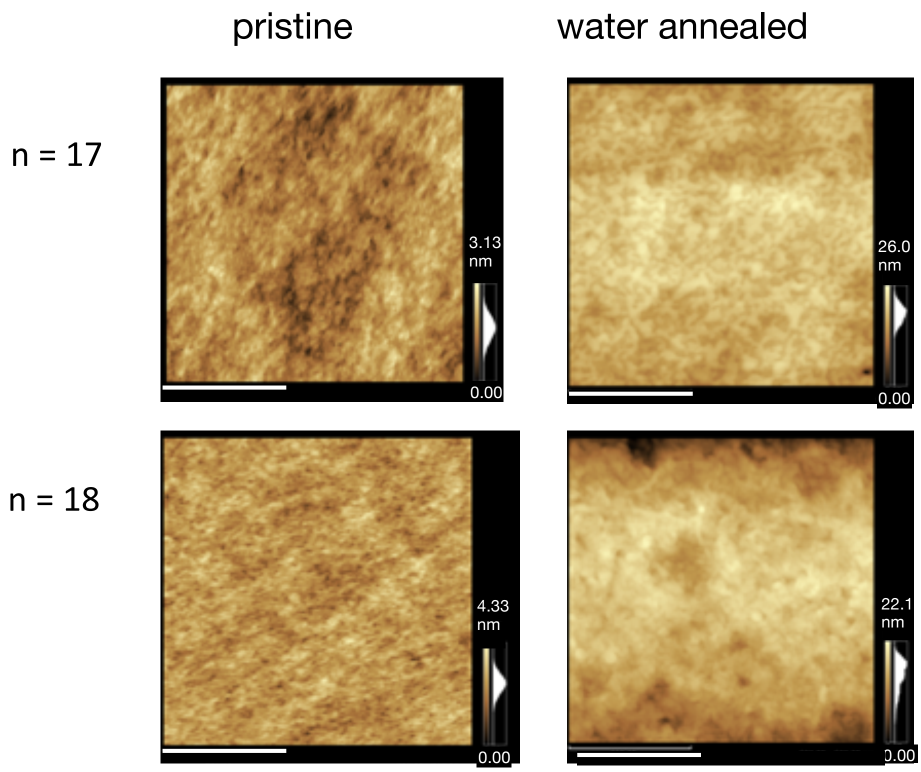

Figure S4 Continued