Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B.

Supporting Information

Biomimetic hierarchical structure with hydrophilic surface and hydrophobic subsurface constructed from waterborne polyurethanes containing self-assembling peptide extender

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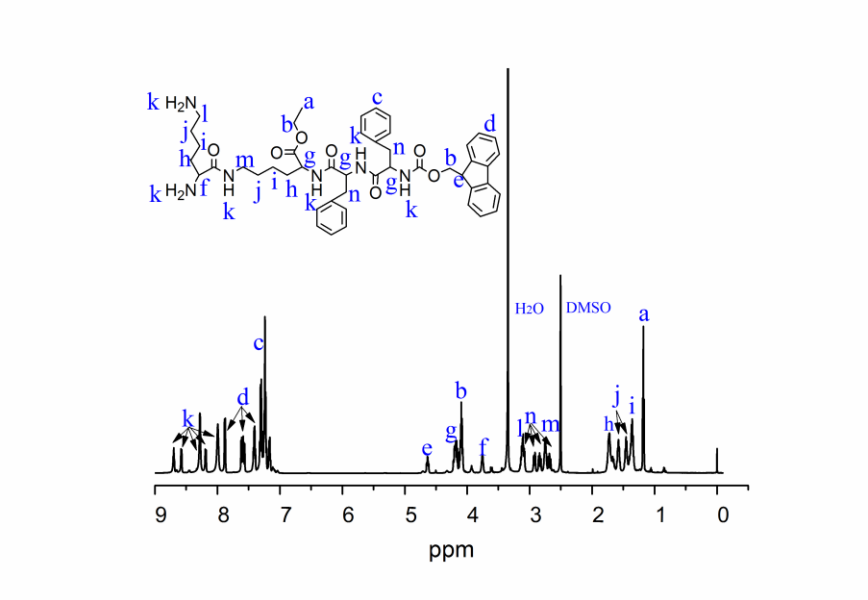

Figure S1. ^{1}H NMR spectrum of PPE.

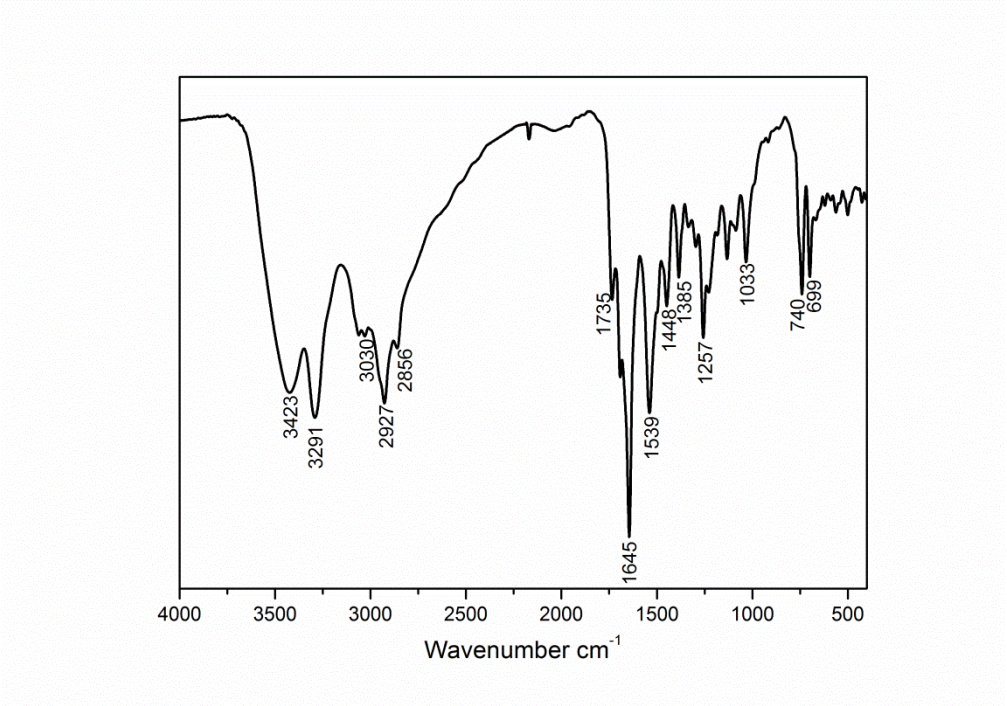

Figure S2. FTIR spectrum of PPE. 740cm^{-1}, 699cm^{-1}: δ_{CH} (benzene ring). 3030cm^{-1}: $\nu_{=C-H}$ (benzene ring). 1033cm^{-1}, 1257cm^{-1}: ν_{C-O} (ethyl ester). 1735cm^{-1}: $\nu_{C=O}$ (ethyl ester). 1385cm^{-1}, 1448cm^{-1}: ν_{CH} (methyl, methylene). 2856cm^{-1}, 2927cm-1: δ_{CH} (methyl, methylene). 1645cm^{-1}: $\nu_{C=O}$ (amide). 1539cm^{-1}: δ_{NH} (amide). 3291cm^{-1}: ν_{NH} (amide). 3423cm^{-1}: ν_{NH} (carbamate, amino).

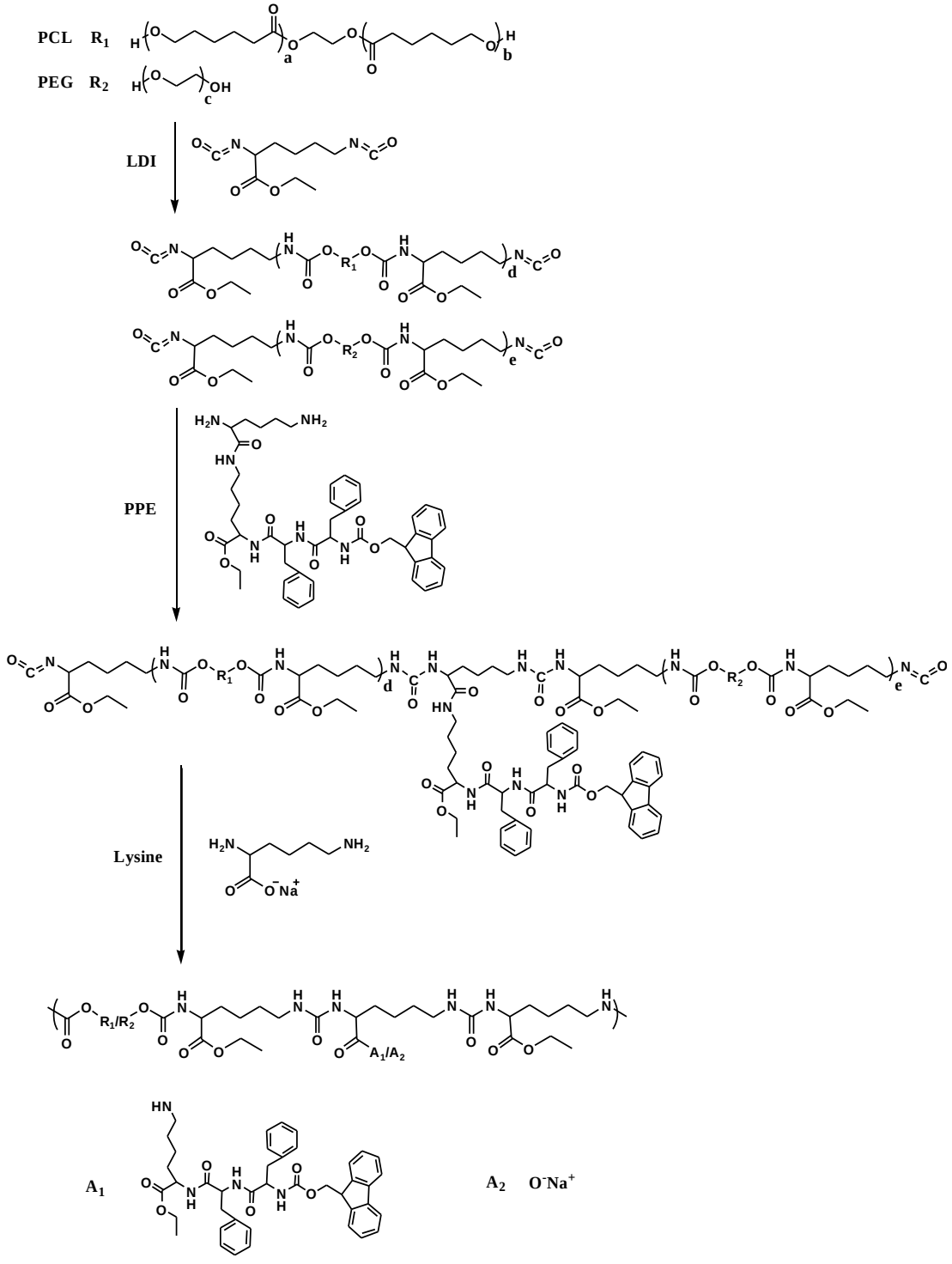

Figure S3. Synthesis route of WPU.

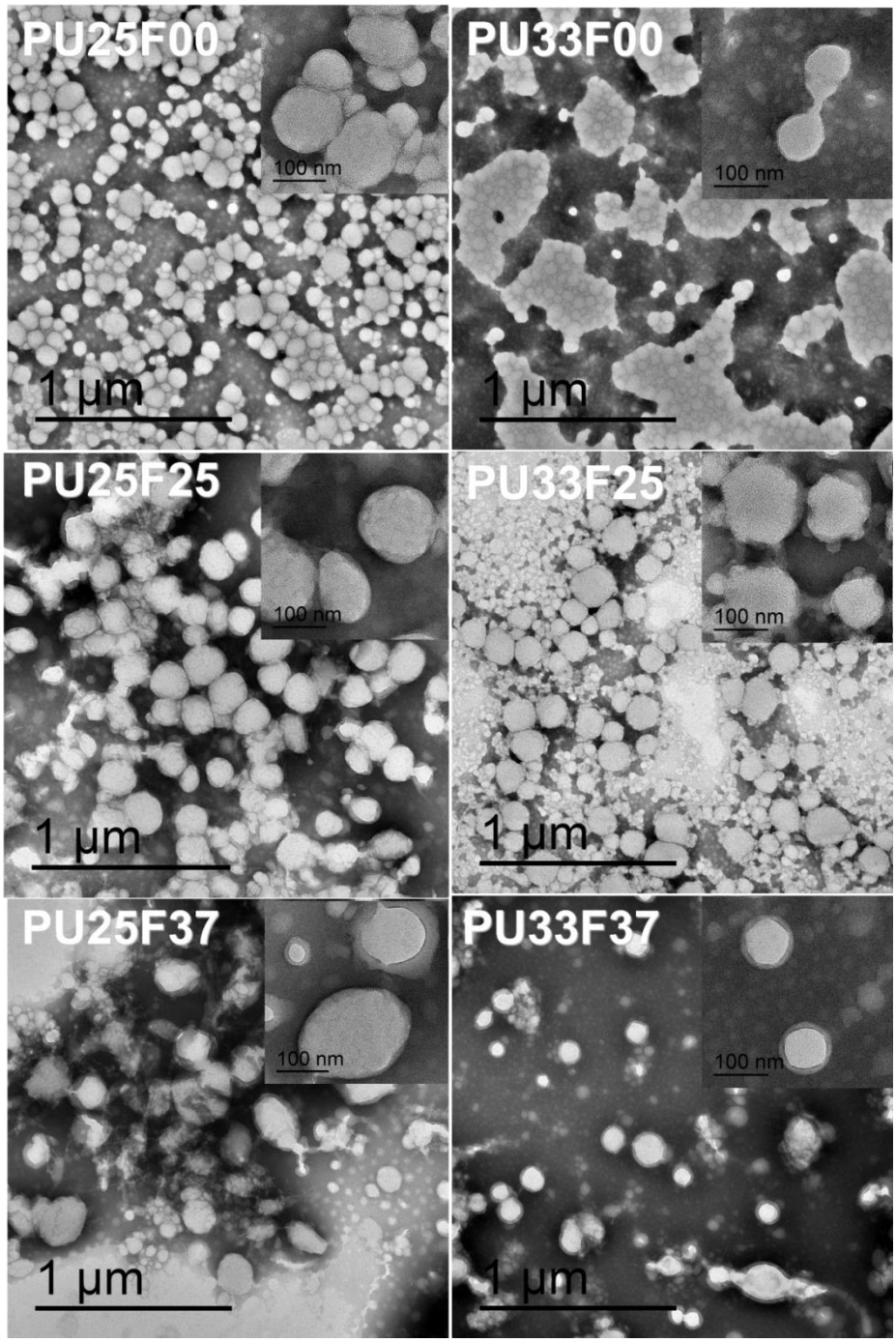

Figure S4. TEM images of various WPU emulsion particles.

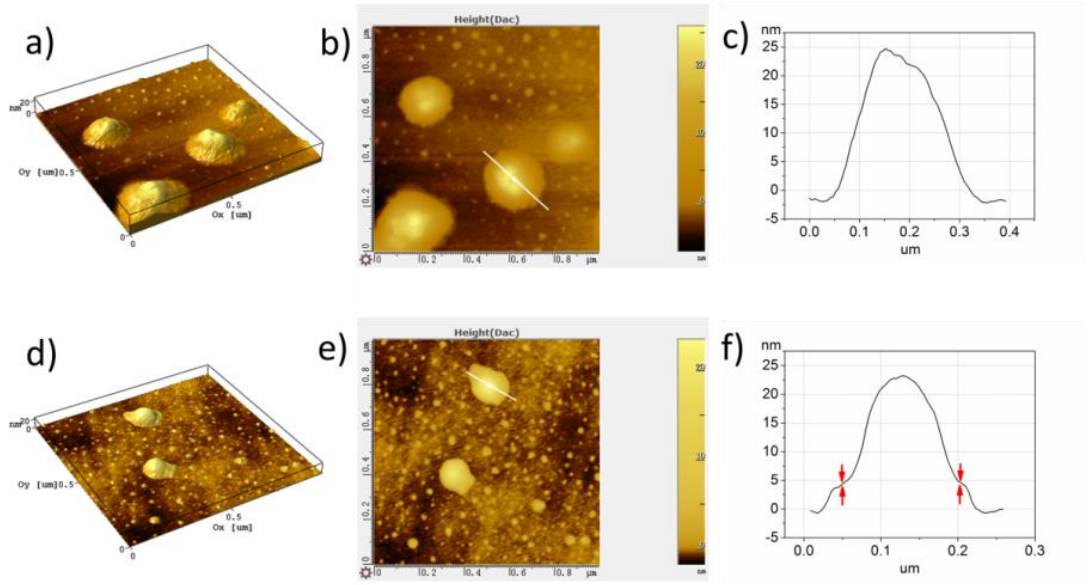

Figure S5. AFM images of polyurethane emulsion particles deposited on silica wafer. a) stereogram and b) height graph of PU33F00 particles, c) section of emulsion particle located on white line in b). d) stereogram and e) height graph of PU33F37 particles, f) section of emulsion particle located on white line in e), the red arrow marks a step which represents a loop surrounding the emulsion particle.

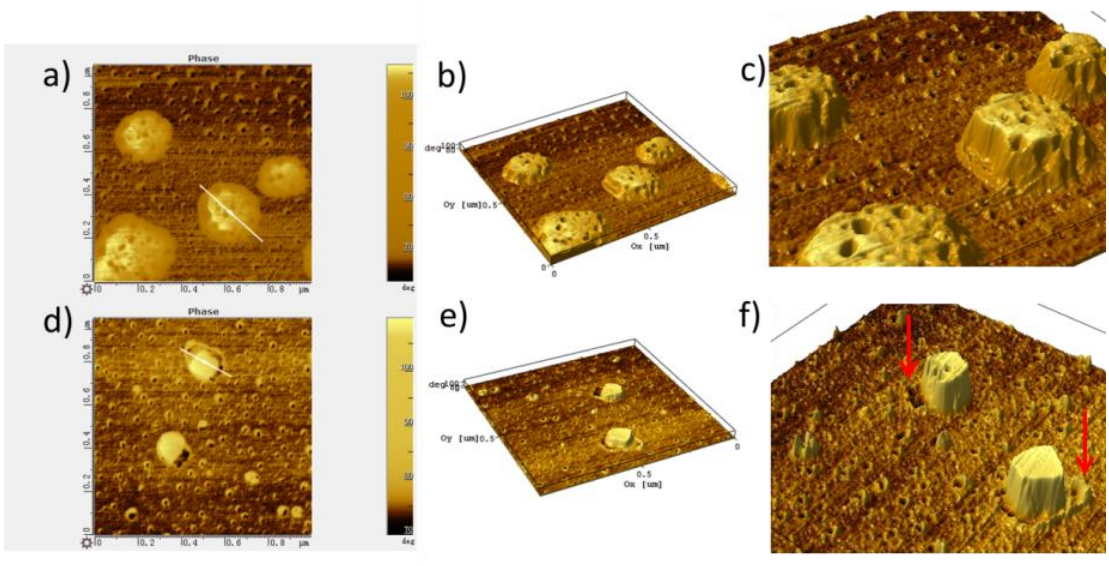

Figure S6. AFM images of polyurethane emulsion particles deposited on silica wafer. a) phase graph and b) c) stereogram of PU33F00 particles. d) phase graph and e) f) stereogram of PU33F37 particles, the red arrows in f) mark a loop surrounding the emulsion particle with different phase structure from the core of emulsion particle.

Table S1. Emulsion particles size (nm) in different pH.

Sample	pH				
	2	5	7	8	10
PU25F00	2664±743	1974±350	180.1±37	179.0±6.4	182.6±6.8
PU25F25	170.6±2.7	168.6±3.4	171.2±2.9	176.2±3.4	176.5±4.0
PU25F37	203.8±6.3	255.4±13	206.3±4.2	214.0±7.8	214.1±5.7
PU33F00	4529±1062	3540±539	268.8±32	225.4±1.3	205.7±4.9
PU33F25	188.7±3.8	181.9±6.3	196.4±1.6	192.3±7.0	196.7±6.2
PU33F37	152.9±3.9	174.0±5.3	146.2±2.7	148.6±3.5	155.6±0.7

Table S2. Emulsion particles zeta potential (mV) in different pH.

Sample	pH				
	2	5	7	8	10
PU25F00	5.1±0.1	9.7±1.5	-17.7±0.6	-32.7±0.8	-30.6±1.2
PU25F25	8.7±1.5	8.7±0.6	-28.5±1.0	-33.1±1.5	-21.1±0.9
PU25F37	12.3±3.0	5.4±0.2	-26.8±0.8	-34.0±6.4	-24.6±1.2
PU33F00	3.4±1.6	2.7±0.2	-27.9±0.4	-36.5±1.5	-26.3±0.7
PU33F25	5.2±0.8	11.1±1.0	-24.8±0.5	-33.0±1.2	-23.2±1.0
PU33F37	4.9±0.2	6.7±0.6	-34.8±0.8	-33.6±0.8	-21.8±0.7

Table S3. Emulsion particles size (nm) in different salt concentration.

Sample	Salt concentration		
	0%	4%	7%
PU25F00	180.1±37	185.5±3.1	191.6±2.7
PU25F25	171.2±2.9	186.4±2.8	190.3±11.6
PU25F37	206.3±4.2	216.3±3.6	237.1±10.4
PU33F00	268.8±32	199.9±4.6	1051.7±120.3
PU33F25	196.4±1.6	210.9±3.5	207.6±13.1
PU33F37	146.2±2.7	173.7±1.1	192.2±9.7

Table S4. Emulsion particles zeta potential (mV) in different salt concentration.

Sample	Salt concentration		
	0%	4%	7%
PU25F00	-17.7±0.6	-6.2±1.5	-5.3±0.4
PU25F25	-28.5±1.0	-4.2±1.3	-4.2±0.4
PU25F37	-26.8±0.8	-5.8±1.2	-5.4±0.9
PU33F00	-27.9±0.4	-6.9±0.3	-5.9±0.5
PU33F25	-24.8±0.5	-5.5±0.6	-4.3±2.2
PU33F37	-34.8±0.8	-4.2±1.0	-5.8±1.2

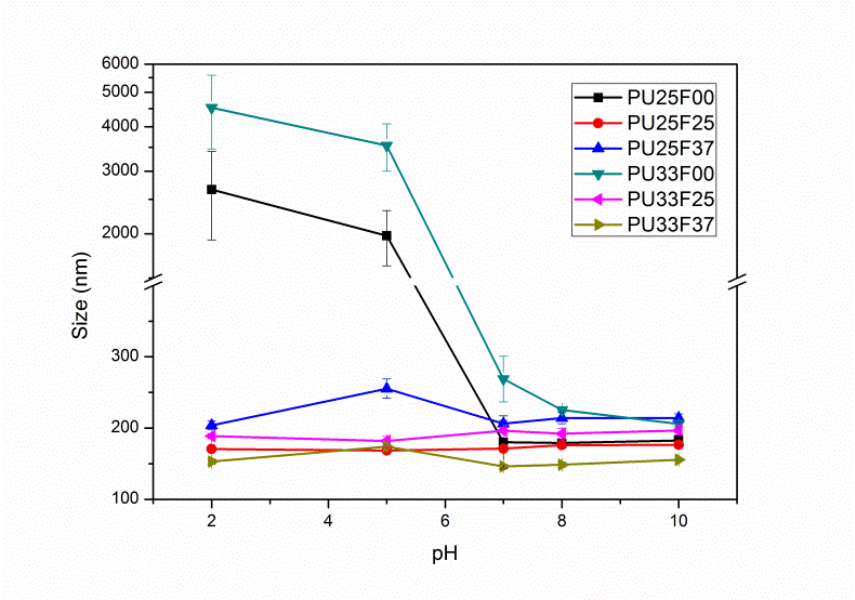

Figure S7. Emulsion particles size in different pH.

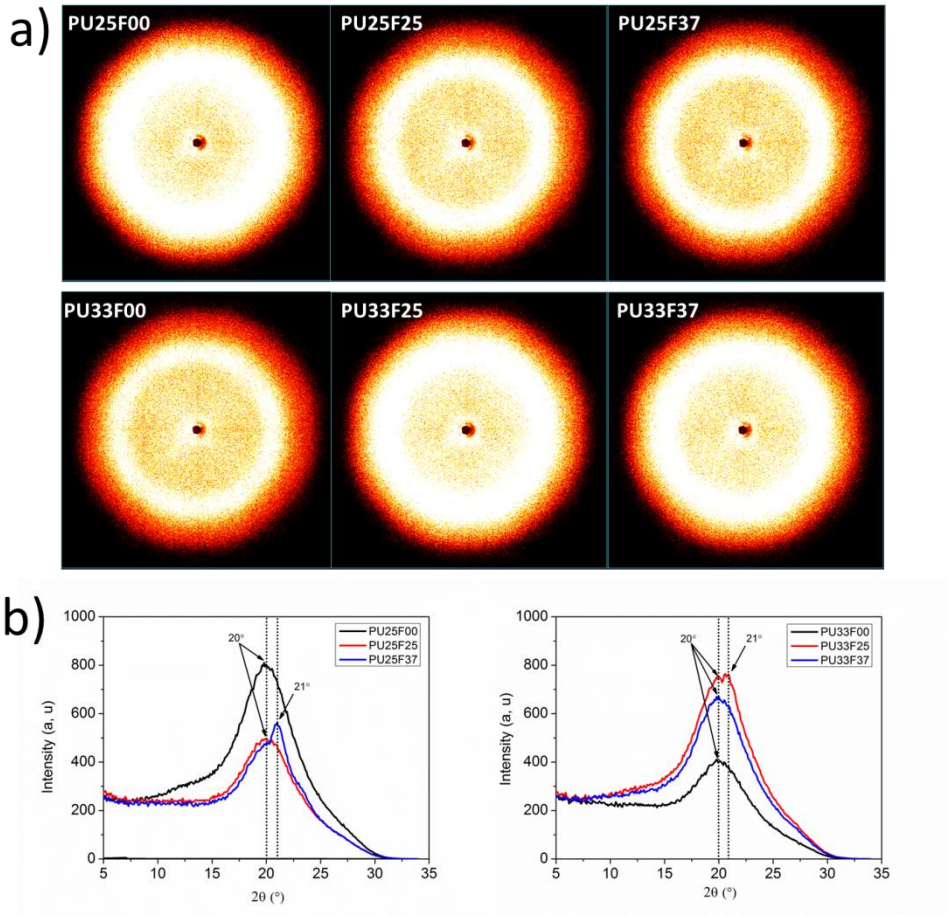

Figure S8. Wide Angle X-ray Scattering (WAXS) patterns a) and curves b) of PU films measured by D8 DISCOVER (BRUKER Germany) operated at 40 kV and 40 mA with Cu (λ=1.54178 Å) irradiation.

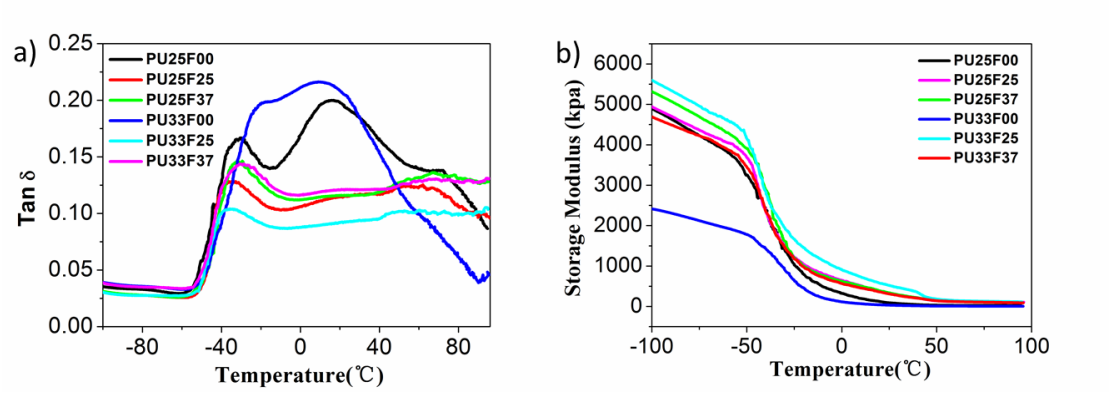

Figure S9. DMA curves of WPU films. The measurement was performed on a Dynamic Mechanical Thermal Analyzer (DMA) Q800 (TA instruments) using rectangular test film. The testing was done at a heating rate of 5 ℃ /min and at a frequency of 10 Hz.

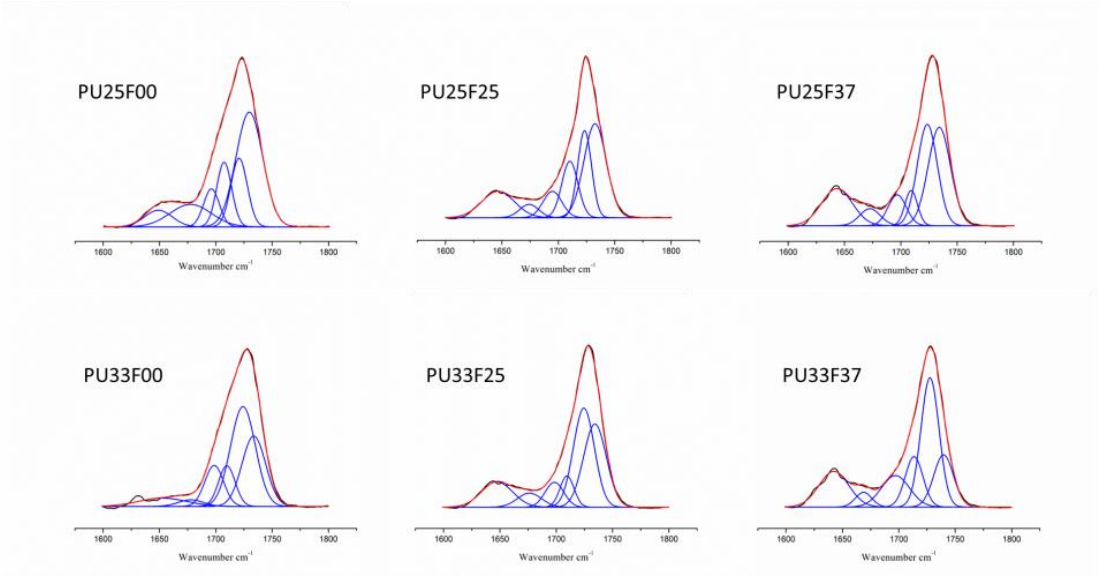

Figure S10. FTIR curve-fitting of polyurethane films in carbonyl stretching region

Table S5. FTIR curve-fitting results of polyurethane films in carbonyl stretching region.

Sample	PCL		Urethane		Urea		Hard Segment	
	Free	H-bond*	Free	H-bond	Free	H-bond	Free	H-bond
Wavenumber (cm^{-1})	1733	1723	1709	1697	1674	1644		
PU25F00	43.0	15.7	13.6	8.3	12.9	6.4	26.5	14.7
PU25F25	36.1	20.4	15.7	8.5	4.4	14.5	20.1	23.0
PU25F37	32.8	30.0	6.6	8.4	5.2	17.0	11.8	25.4
PU33F00	27.0	40.2	11.0	12.5	2.7	6.54	13.7	19.0
PU33F25	31.5	34.6	7.3	7.8	5.7	13.2	13.0	21.0
PU33F37	16.0	36.2	13.8	13.8	3.7	16.5	17.6	30.0

* Means hydrogen-bonded carbonyl.

Table. S6 Peaks percentage in C1s core-level XPS spectra of the polyurethane film surfaces.

Samples	C-C, C-H 284.7ev	C-O 286.1ev	C=O 288.7ev	C-O/C=O
PU25F00	67.8	20.7	11.5	1.79
PU25F25	59.0	27.8	13.2	2.11
PU25F37	53.3	32.8	13.9	2.37
PU33F00	45.3	39.5	15.2	2.60
PU33F25	43.4	43.5	13.1	3.32
PU33F37	29.8	55.9	14.3	3.91

Table S7. Static contact angle of polyurethane films.

Sample	H_2O (°) stationary	CH_2I_2 (°) stationary	Total surface energy		
			γ (mN/m) (disperse part)	γ (mN/m) (polar part)	γ (mN/m)
PU33F00	55.9±4.21	38.8±2.56	32.96	17.65	50.61
PU33F25	50.3±1.81	43.2±1.55	29.91	22.80	52.71
PU33F37	51.5±1.55	37.1±2.31	33.18	20.31	53.49

Table S8. Dynamic contact angle of polyurethane films.

Sample	Stationary contact angle (°)	Advancing contact angle (°)	Receding contact angle (°)
PU33F00	69.4±0.80	68.0±2.05	42.9±1.28
PU33F25	64.2±1.50	56.7±1.15	25.6±0.47
PU33F37	64.7±2.14	63.4±1.42	33.6±2.07

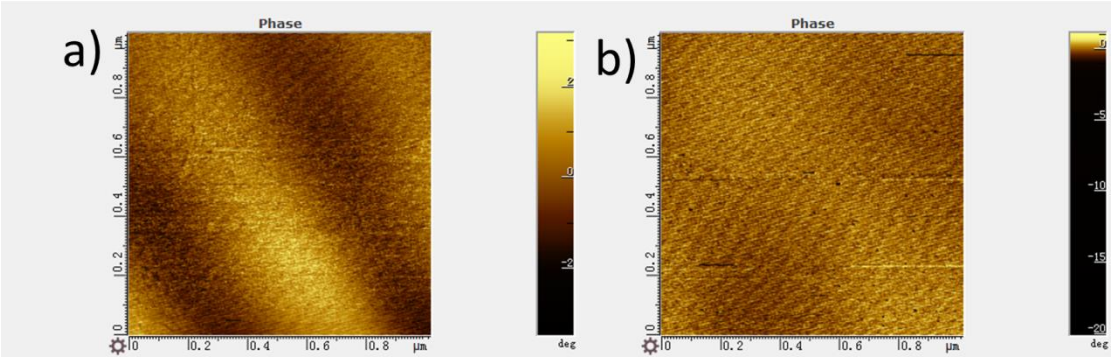

Figure S11. a) AFM phase images of films in wet condition of PU33F00 and b) PU33F37.