

Supporting Information

Supramolecular additive initiated controlled atom transfer radical polymerization of zwitterionic polymers on ureido-pyrimidinone-based biomaterial surfaces

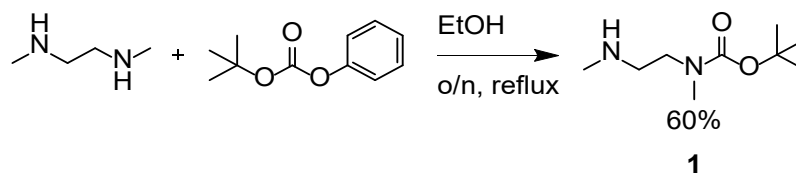
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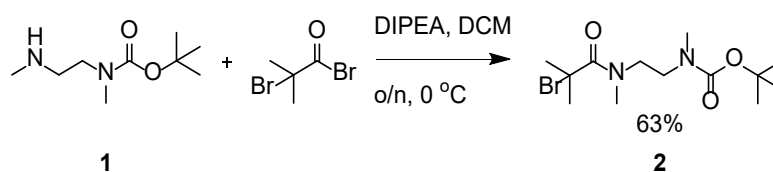
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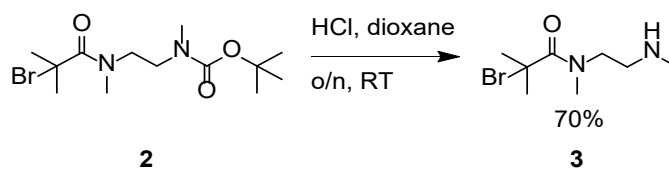
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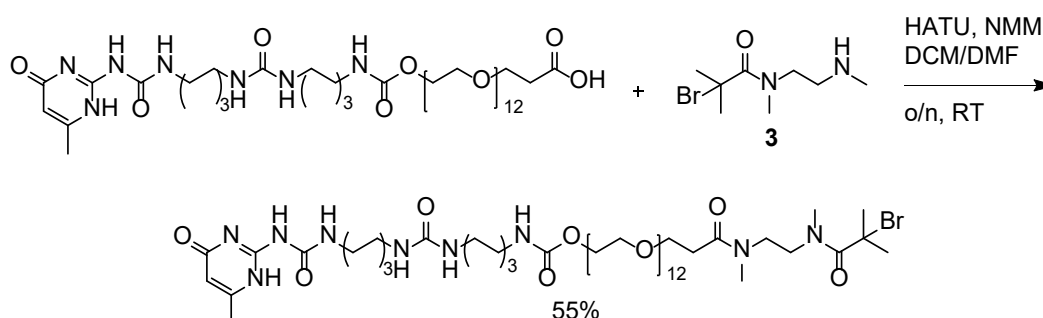
Scheme S1: Synthesis of tert-butyl methyl(2-(methylamino)ethyl)carbamate



Scheme S1: Synthesis of tert-butyl (2-(2-bromo-N,2-dimethylpropanamido)ethyl)(methyl) carbamate



Scheme S2: Synthesis of 2-bromo-N,2-dimethyl-N-(2-(methylamino)ethyl)propanamide



Scheme S3: Synthesis of UPy-BiB.

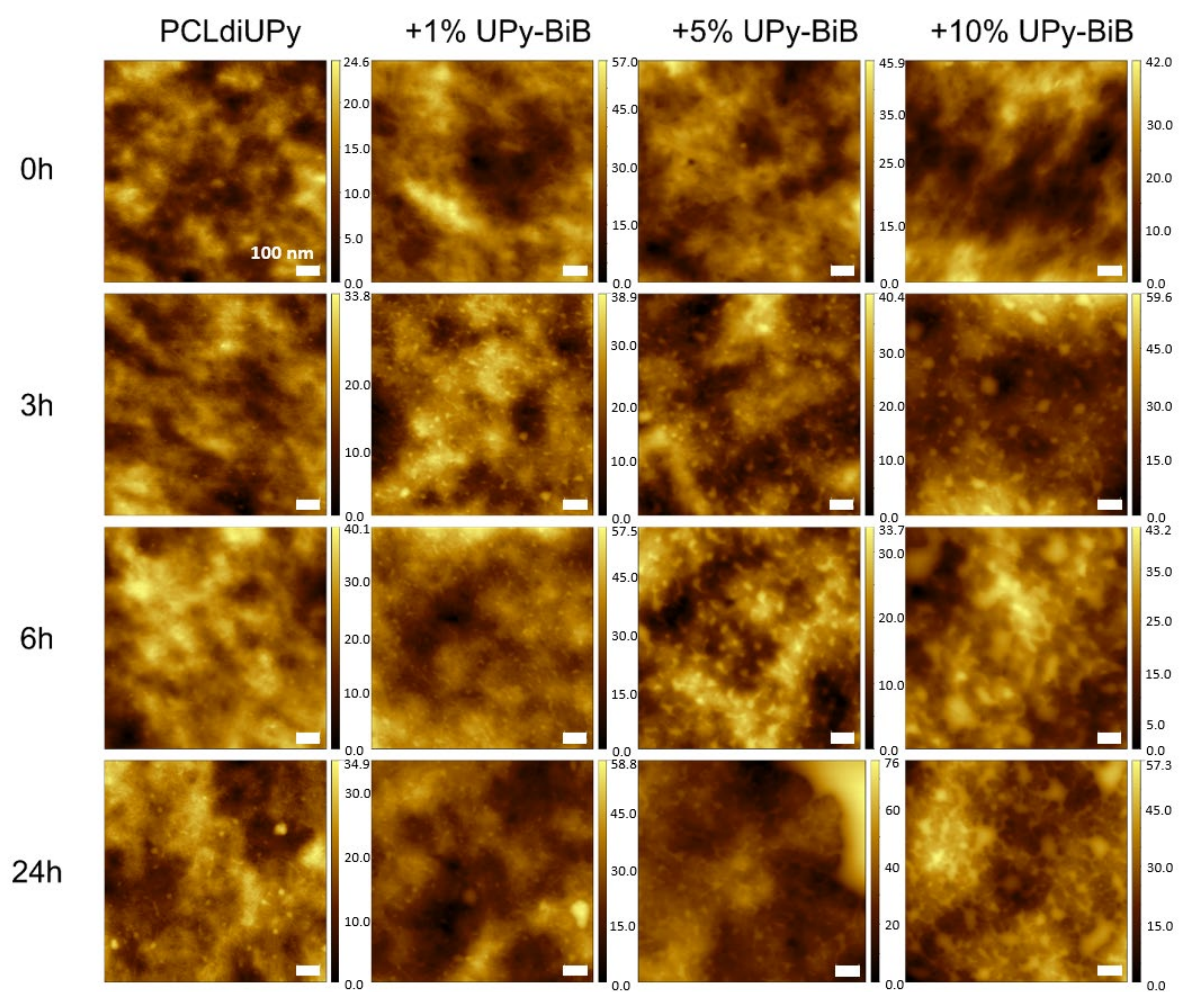


Figure S1: Atomic Force Microscopy height images recorded in tapping mode in air of solution-cast films of PCLdiUPy with 0, 1, 5, and 10% UPy-BiB additive before and after 3, 6, and 24 hours of polymerization on the surface. Scale bars represent 100 nm.

24h

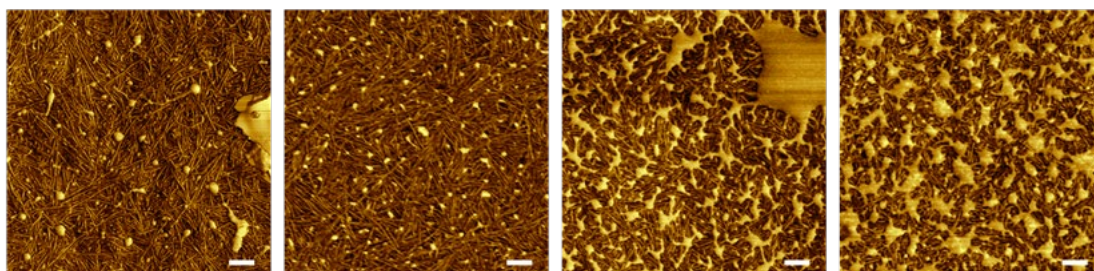


Figure S2: Atomic Force Microscopy phase images recorded in tapping mode in air of solution-cast films of PCLdiUPy with 0, 1, 5, and 10% UPy-BiB additive (from left to right) after 24 hours of reaction on the surface. Scale bars represent 100 nm.

Table S1: Fiber diameter as determined from AFM phase images, mean \pm SD.

	PCLdiUPy [nm]	+1% UPy-BiB [nm]	+5% UPy-BiB [nm]	+10% UPy-BiB [nm]
0h	7.3 \pm 1.0	7.6 \pm 1.2	7.7 \pm 1.2	7.2 \pm 1.1

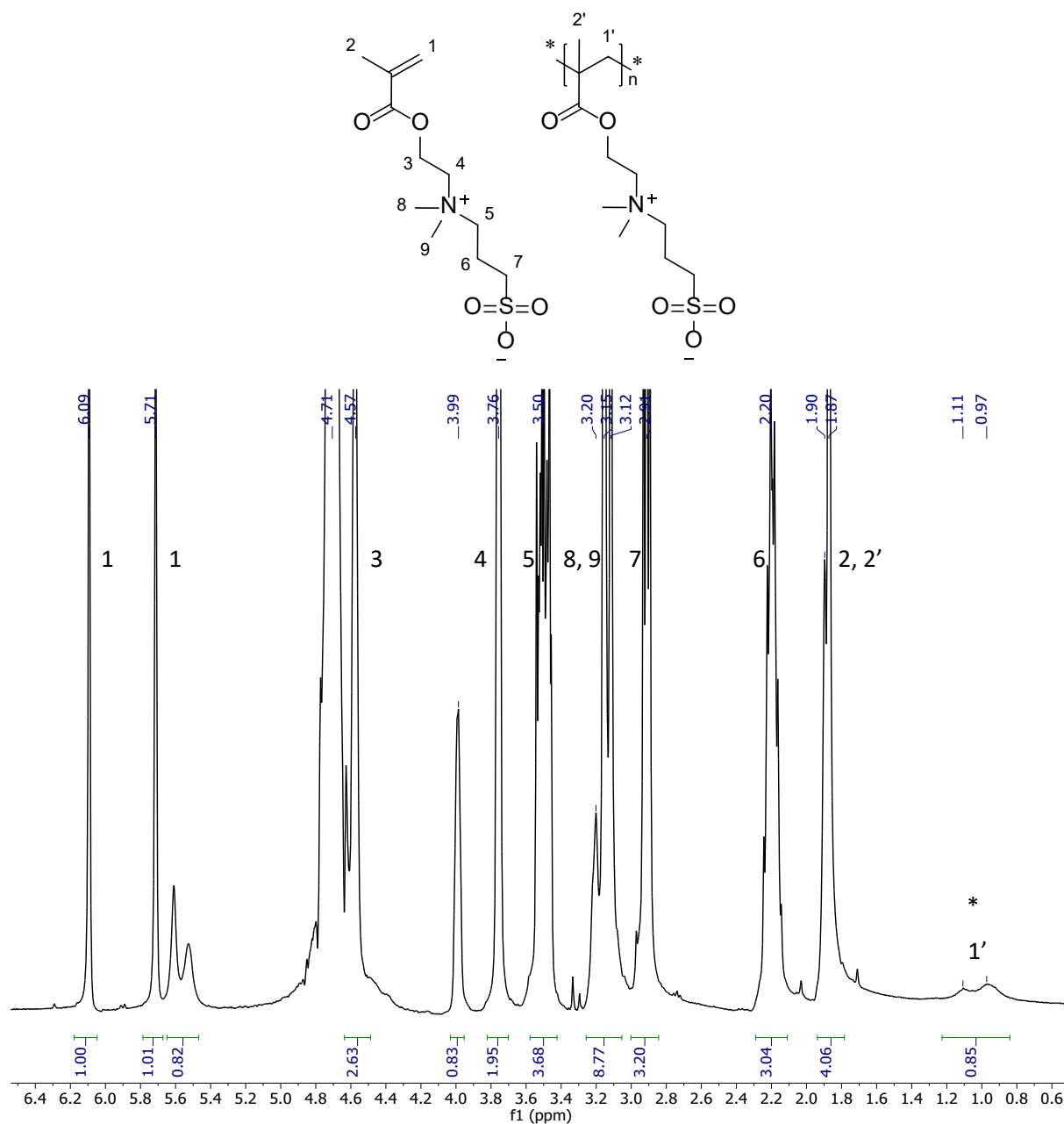


Figure S3: ^1H NMR spectrum of the reaction mixture after 2 hours of polymerization, showing polymer backbones indicated with asterix (recorded in D_2O).

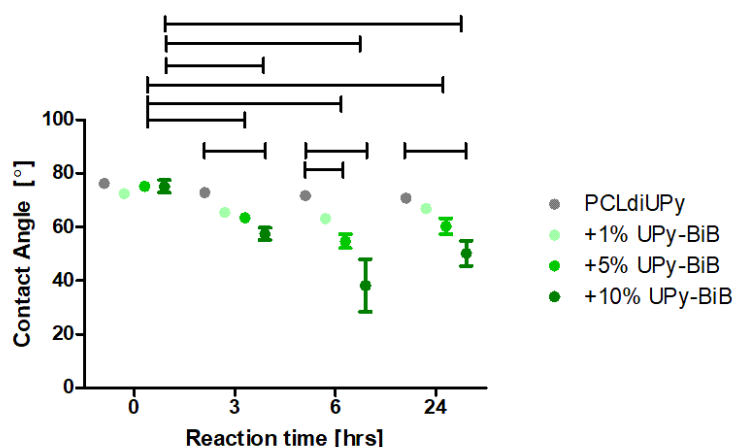


Figure S4: Water contact angles measured on solution-cast films with 0, 1, 5, and 10% UPy-BiB before and after 3, 6, and 24 hours of polymerization on the surface. Data are represented as mean \pm SD. Statistically significant differences are depicted by the overhead lines. Error bars are on the order of graph symbol size.

Table S2: Root Mean Square (RMS) roughness of solution-cast films.

	PCLdiUPy [nm]	+1% UPy-BiB [nm]	+5% UPy-BiB [nm]	+10% UPy-BiB [nm]
0h	4.6 \pm 1.4	8.7 \pm 0.8	6.3	5.1 \pm 0.1
3h	4.5 \pm 0.4	7.7 \pm 2.3	7.5 \pm 1.6	8.2 \pm 0.8
6h	5.6 \pm 1.0	7.6 \pm 0.4	6.0 \pm 0.2	7.1 \pm 0.2
24h	5.8 \pm 0.5	7.2 \pm 1.6	11.1 \pm 1.5	7.5 \pm 0.1

Table S3: Atomic surface composition of solution-cast films with 0, 1, 5, and 10 mol% UPy-BiB before and after exposure to the SI-ATRP reaction conditions for 3, 6, and 24 hour.

		Surface composition [at%]					
		C	O	N	N+	S	Br
PCLdiUPy	0h	74.45	22.17	3.38	0.00	0.00	0.00
	3h	75.20	20.67	4.00	0.08	0.03	0.00
	6h	76.64	19.60	3.65	0.04	0.07	0.00
	24h	75.36	20.48	3.80	0.12	0.23	0.00
+1% UPy-BiB	0h	74.72	21.30	3.95	0.00	0.03	0.00
	3h	74.23	21.36	3.65	0.24	0.48	0.04
	6h	74.93	20.69	3.75	0.21	0.36	0.04
	24h	74.81	20.82	4.02	0.13	0.22	0.00
+5% UPy-BiB	0h	73.81	22.23	3.85	0.00	0.07	0.03
	3h	73.15	22.21	3.41	0.41	0.69	0.11
	6h	74.87	20.64	3.42	0.36	0.60	0.10
	24h	73.48	22.31	3.24	0.34	0.55	0.07
+10% UPy-BiB	0h	74.23	21.16	4.46	0.00	0.07	0.08
	3h	71.38	23.78	3.37	0.47	0.82	0.16
	6h	70.76	23.66	2.97	0.82	1.58	0.22
	24h	72.21	22.23	3.23	0.84	1.37	0.12

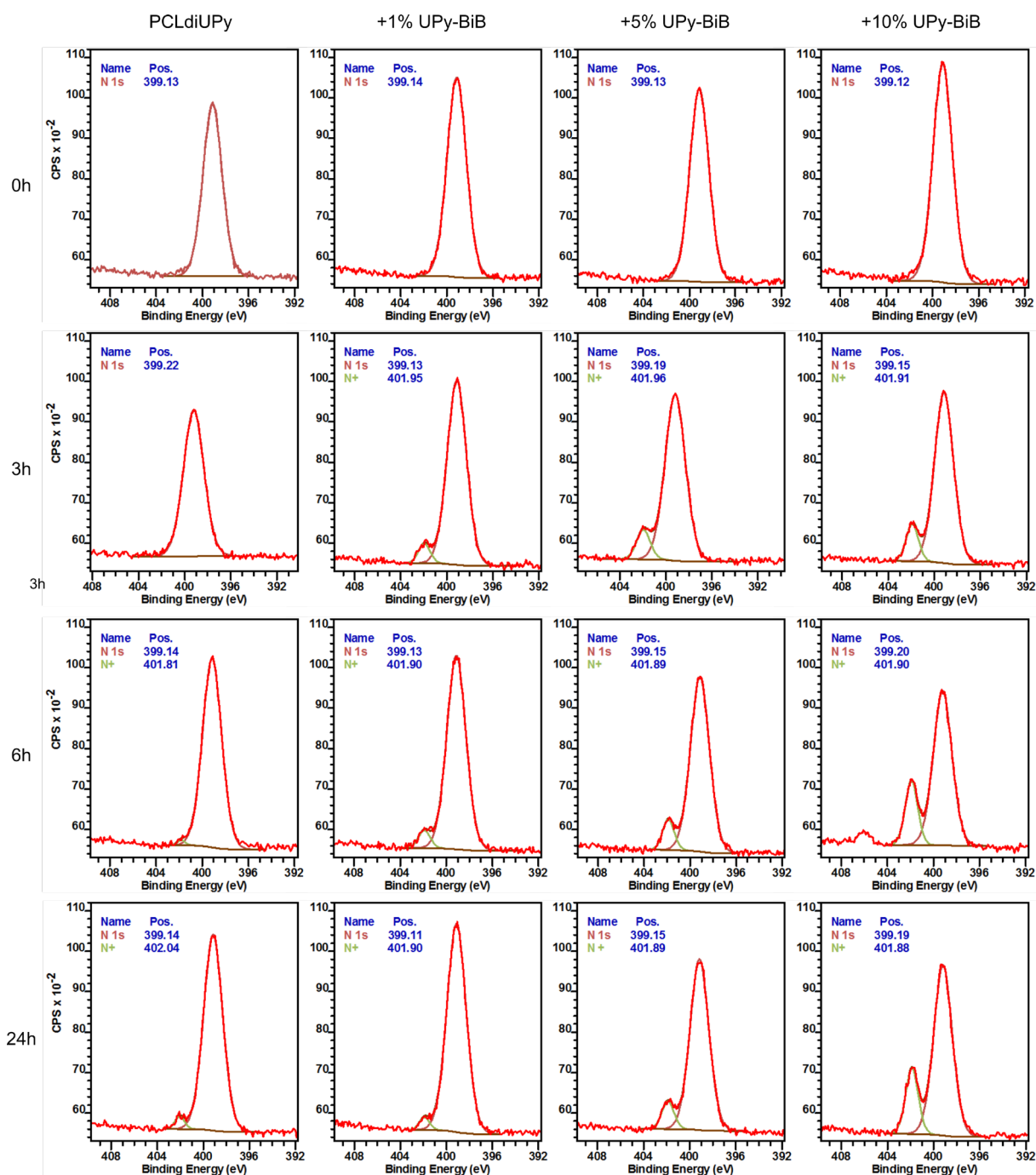


Figure S5: XPS N 1s narrow scan spectra of solution-cast films of PCLdiUPy with 0, 1, 5, and 10 mol% UPy-BiB additive before, and after 3, 6, and 24 hours polymerization reaction.

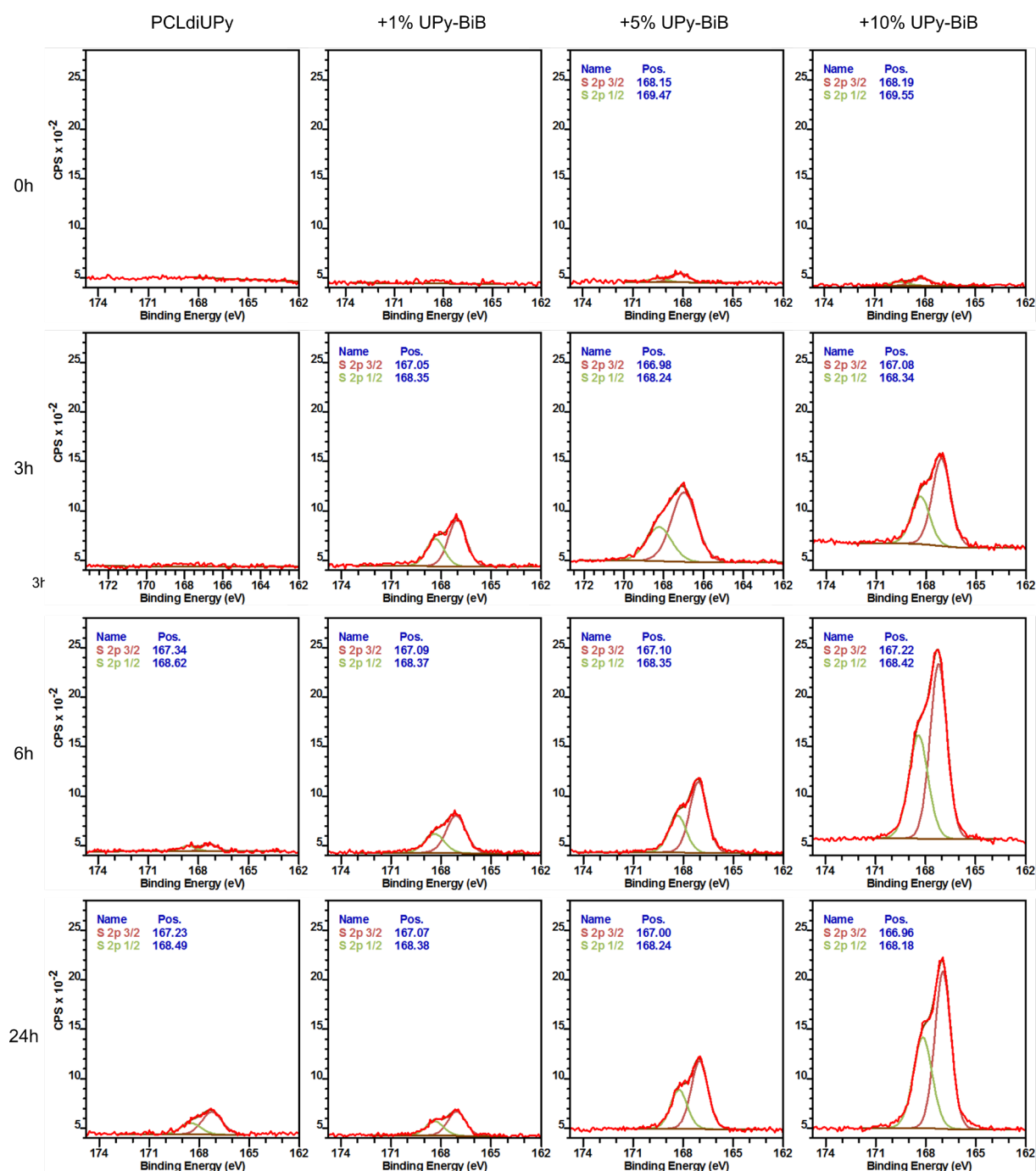


Figure S6: XPS S 2p narrow scan spectra of solution-cast films of PCLdiUPy with 0, 1, 5, and 10 mol% UPy-BiB additive before, and after 3, 6, and 24 hours polymerization reaction.

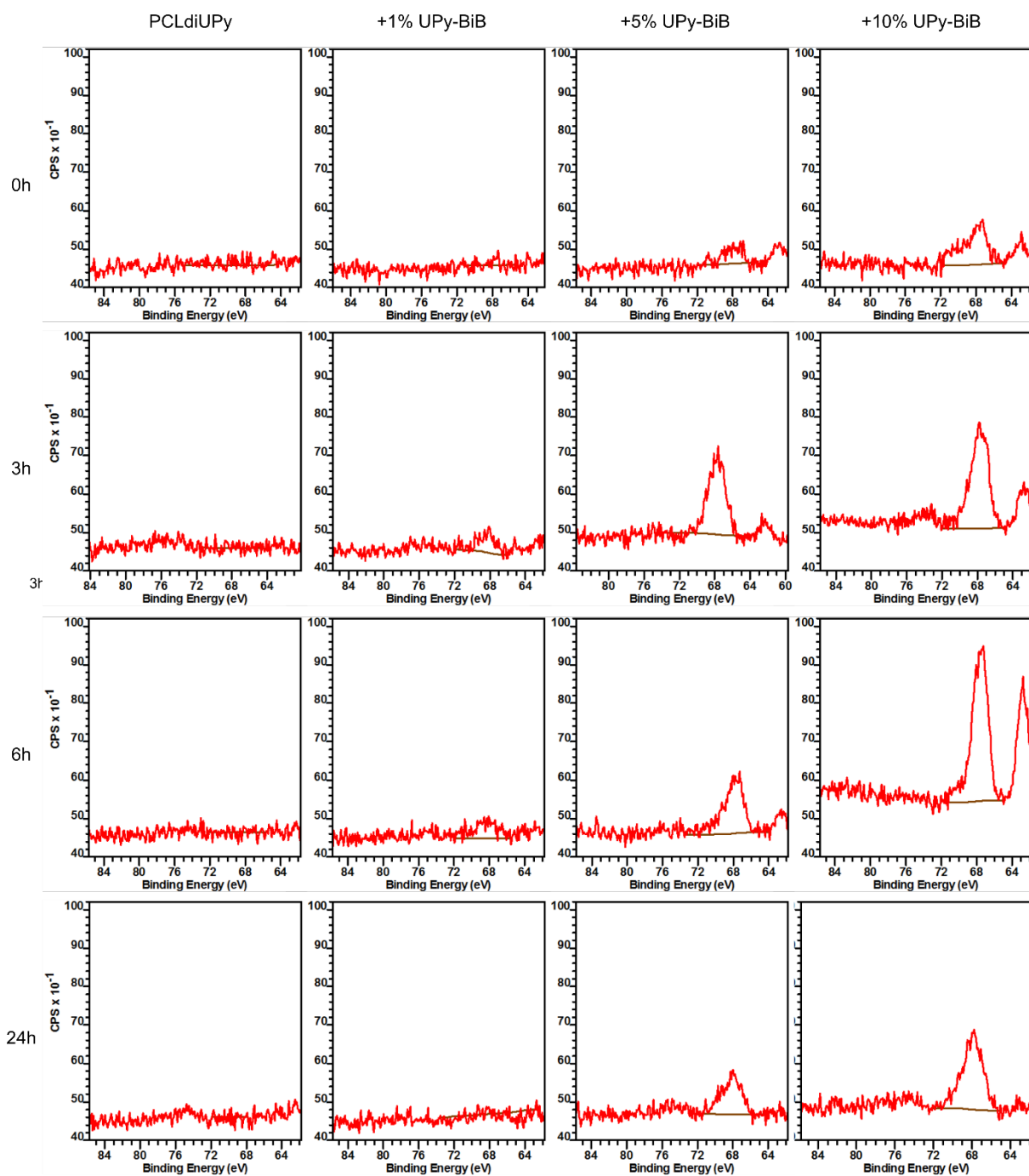


Figure S7: XPS Br 3d narrow scan spectra of solution-cast films of PCLdiUPy with 0, 1, 5, and 10 mol% UPy-BiB additive before, and after 3, 6, and 24 hours polymerization reaction.

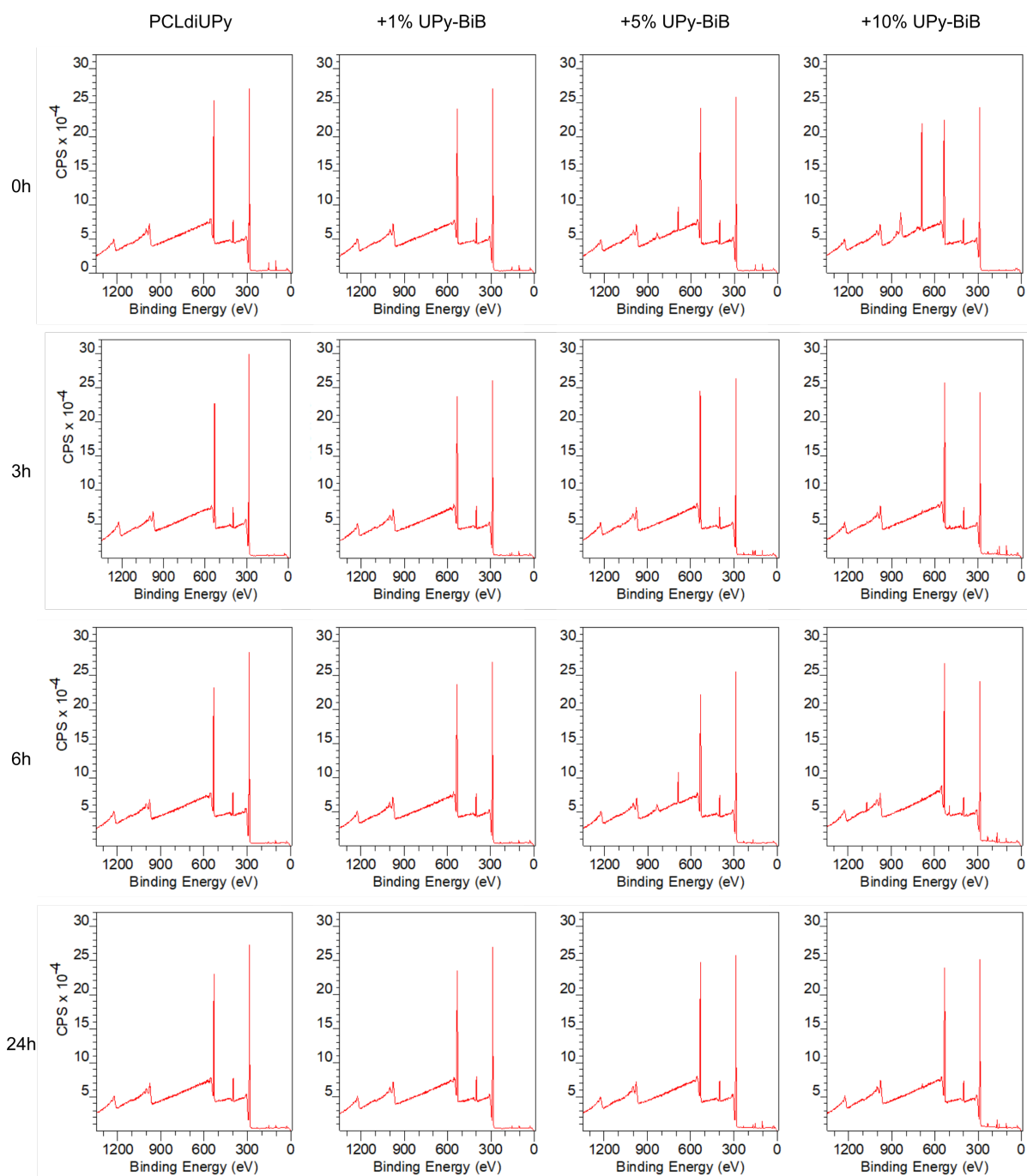
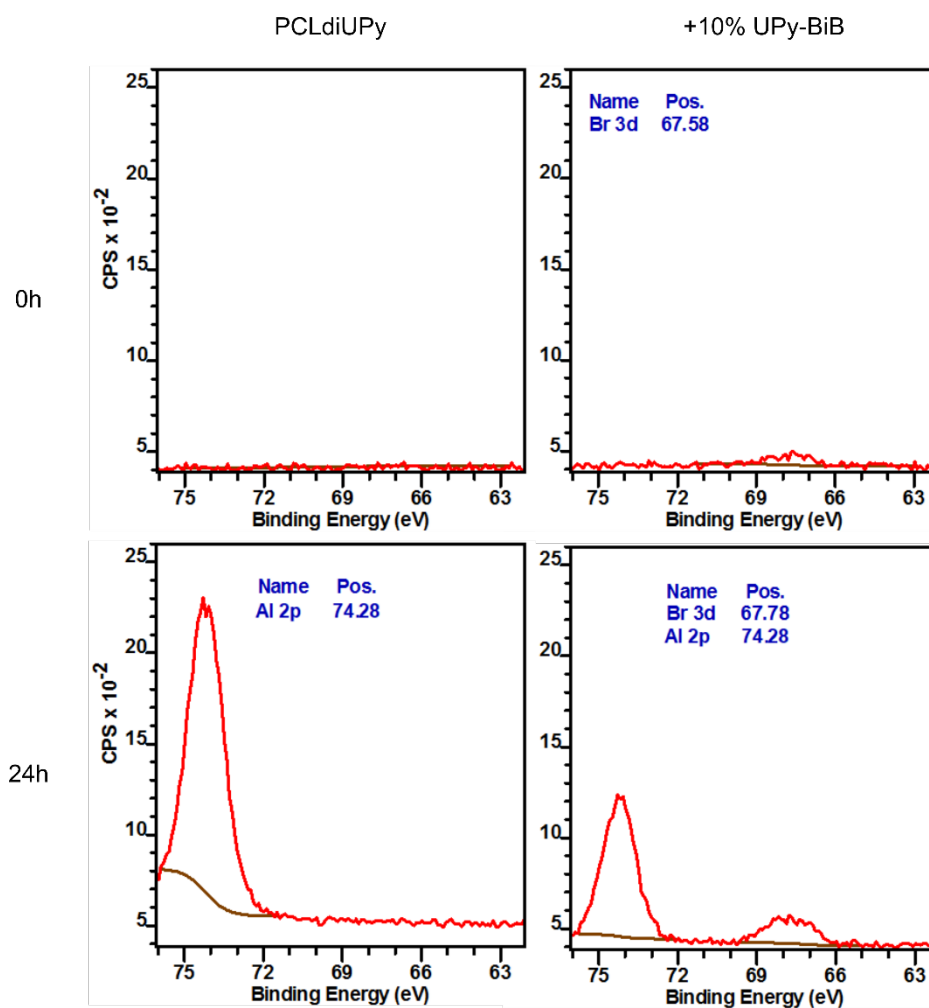


Figure S8: XPS survey spectra of solution-cast films of PCLdiUPy with 0, 1, 5, and 10 mol% UPy-BiB additive before, and after 3, 6, and 24 hours polymerization reaction.

Table S4: Surface composition of electrospun scaffolds

	Surface composition [at %]						
	C	O	N	N ⁺	S	Br	Al
PCLdiUPy 0h	75.16	20.68	4.16	0.00	0.00	0.00	0.00
PCLdiUPy 24h	65.63	25.65	2.01	1.10	1.94	0.00	3.68
10% UPy-BiB 0h	74.59	20.89	4.48	0.00	0.00	0.03	0.00
10% UPy-BiB 24h	69.90	23.82	2.88	0.71	1.18	0.09	1.42

**Figure S9:** XPS narrow scan spectra of the Br 3d and Cu 3p region of electrospun scaffolds of PCLdiUPy with 0 and 10% UPy-BiB before and after 24 hours polymerization reaction.

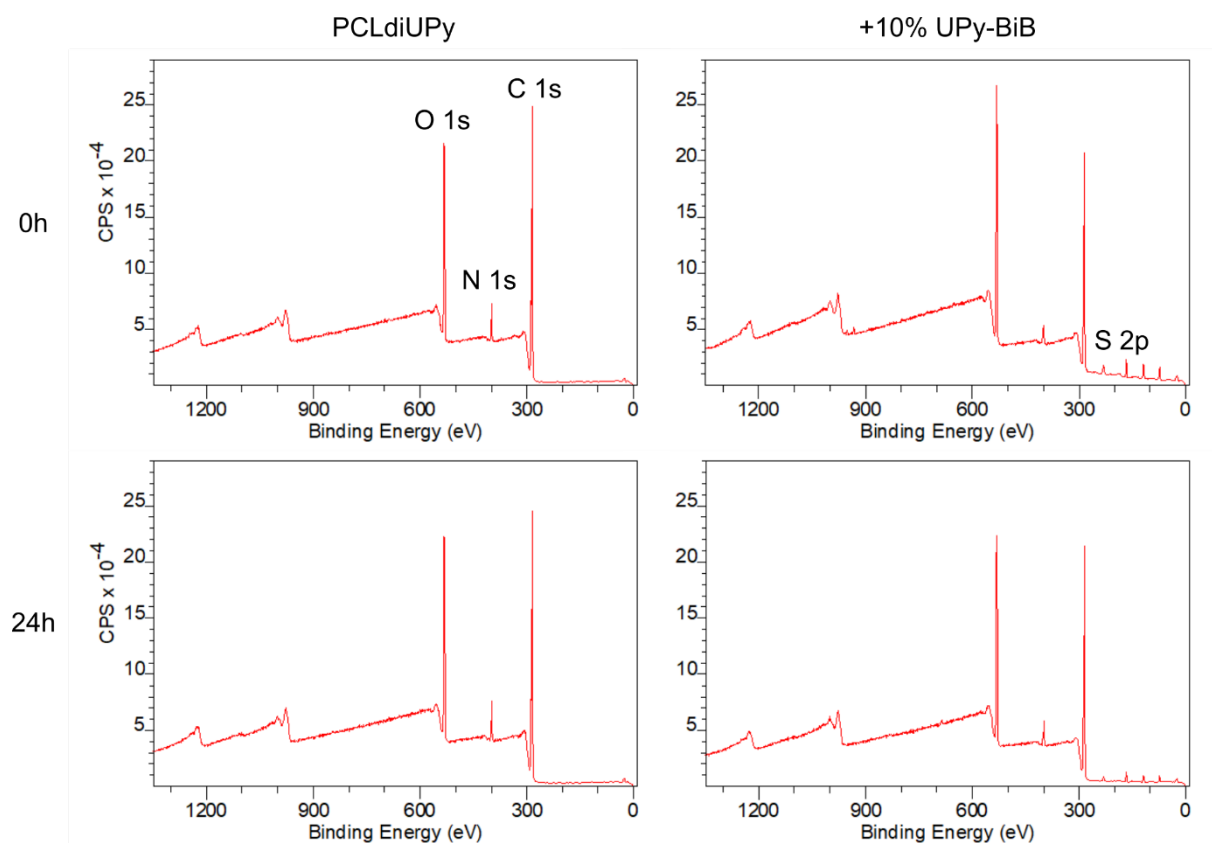


Figure S10: XPS survey scan spectra of electrospun scaffolds of PCLdiUPy with 0 and 10% UPy-BiB before and after 24 hours polymerization reaction.

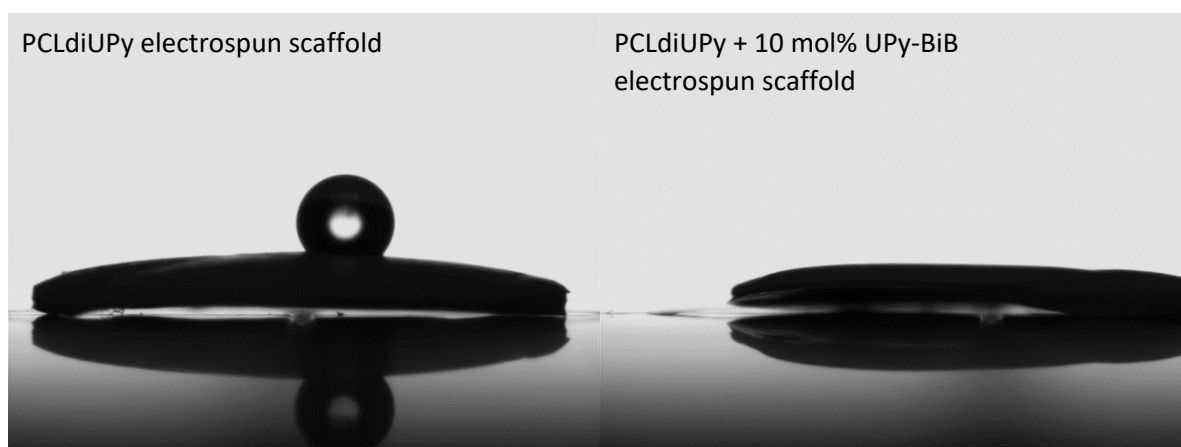


Figure S11: Contact angle of water droplets on PCLdiUPy electrospun scaffolds without additive (left) and with 10 mol% UPy-BiB additive (right) 30 seconds after droplet deposition (2 μ L).