Electronic Supplementary Material (ESI) for Biomaterials Science.

Supplemental Materials for

Thermoplastic polyurethane with controllable degradation and critical anti-fouling properties

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This File Includes:

Synthesis of poly(carboxybetaine) degradable urethane (PCBDU)

1. Synthesis of PCBDU-1

A temperature controller and a nitrogen inlet were added to a 250 mL three-necked round bottom flask with a mechanical stirrer to melt PCL-diol (8.92 g, 4.46 mmol). After melting, hexamethylene diisocyanate (HDI) (1.5g, 8.91 mmol) was added dropwise into the flask; moreover, 20 mL DMF was added to reduce the viscosity. This prepolymer solution was stirred for 2 h at 80 ℃. CB-diol (1.17 g, 4.46 mmol) was added to the solution dropwise, and the solution was stirred for a further 30 min. The resulting solution was poured into a PTFE plate, which was subsequently placed in an oven at 100 ℃ for 12 h to enable the reaction to complete, and another 12 h to remove the residual solvent.

2. Synthesis of PCBDU-3

A temperature controller and a nitrogen inlet were added to a 250 mL three-necked round bottom flask with a mechanical stirrer to melt PCL-diol (4.46 g, 2.23 mmol). After melting, hexamethylene diisocyanate (HDI) (1.5 g, 8.91 mmol) was added dropwise into the flask; moreover, 20 mL DMF was added to reduce the viscosity. This prepolymer solution was stirred for 2 h at 80 ℃. CB-diol (1.75g, 6.69 mmol) was added to the solution dropwise, and the solution was stirred for a further 30 min. The resulting solution was poured into a PTFE plate, which was subsequently placed in an oven at 100 ℃ for 12 h to enable the reaction to complete, and another 12 h to remove the residual solvent.

3. Synthesis of PCBDU-5

A temperature controller and a nitrogen inlet were added to a 250 mL three-necked round bottom flask with a mechanical stirrer to melt PCL-diol (2.98 g, 1.49 mmol). After melting, hexamethylene diisocyanate (HDI) (1.5 g, 8.91 mmol) was added dropwise into the flask; moreover, 20 mL DMF

was added to reduce the viscosity. This prepolymer solution was stirred for 2 h at 80 ℃. CB-diol (1.95 g, 7.43 mmol) was added to the solution dropwise, and the solution was stirred for a further 30 min. The resulting solution was poured into a PTFE plate, which was subsequently placed in an oven at 100 ℃ for 12 h to enable the reaction to complete, and another 12 h to remove the residual solvent.

4. Synthesis of PCBDU-7

A temperature controller and a nitrogen inlet were added to a 250 mL three-necked round bottom flask with a mechanical stirrer to melt PCL-diol (2 g, 1 mmol). After melting, hexamethylene diisocyanate (HDI) (1.34 g, 8 mmol) was added dropwise into the flask; moreover, 20 mL DMF was added to reduce the viscosity. This prepolymer solution was stirred for 2 h at 80 ℃. CB-diol (1.84g, 7 mmol) was added to the solution dropwise, and the solution was stirred for a further 30 min. The resulting solution was poured into a PTFE plate, which was subsequently placed in an oven at 100 ℃ for 12 h to enable the reaction to complete, and another 12 h to remove the residual solvent.

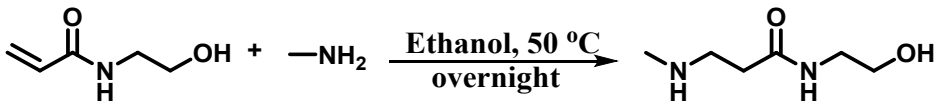
5. Synthesis of Poly(ethylene glycol-co-carprolactone) urethane (PEGCU)

A temperature controller and a nitrogen inlet were added to a 250 mL three-necked round bottom flask with a mechanical stirrer to melt PCL-diol (2.22 g, 1.11 mmol). After melting, hexamethylene diisocyanate (HDI) (1.5 g, 8.91 mmol) was added dropwise into the flask; moreover, 20 mL DMF was added to reduce the viscosity. This prepolymer solution was stirred for 2 h at 80 ℃. PEG 300 (2.34 g, 7.80 mmol) was added to the solution dropwise, and the solution was stirred for a further 30 min. The resulting solution was poured into a PTFE plate, which was subsequently placed in an oven at 100 ℃ for 12 h to enable the reaction to complete, and another 12 h to remove the residual solvent.

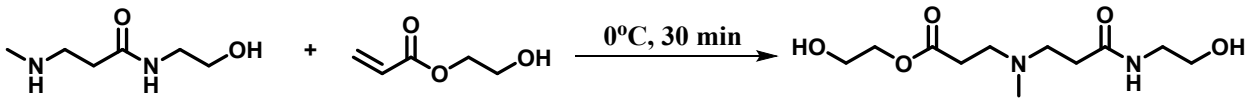
6. Synthesis of Poly(carprolactone) degradable urethane (PCLDU)

A temperature controller and a nitrogen inlet were added to a 250 mL three-necked round bottom flask with a mechanical stirrer to melt PCL-diol (5.94 g, 2.97 mmol). After melting, hexamethylene diisocyanate (HDI) (0.5 g, 2.97 mmol) was added dropwise into the flask; moreover, 20 mL DMF was added to reduce the viscosity. The resulting solution was poured into a PTFE plate, which was subsequently placed in an oven at 100 ℃ for 12 h to enable the reaction to complete, and another 12 h to remove the residual solvent.

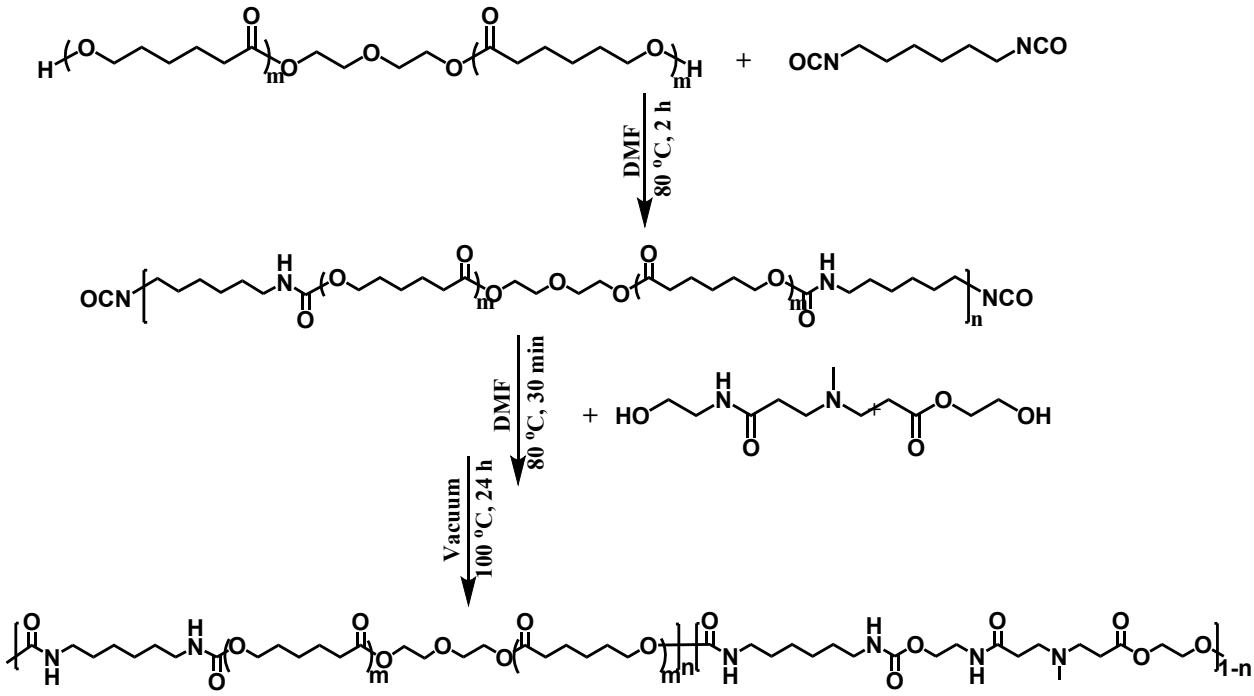
(a)



(b)



(c)



Scheme S1. Synthetic route of (a) HMP, (b) CB-diol and (c) PCBDU.

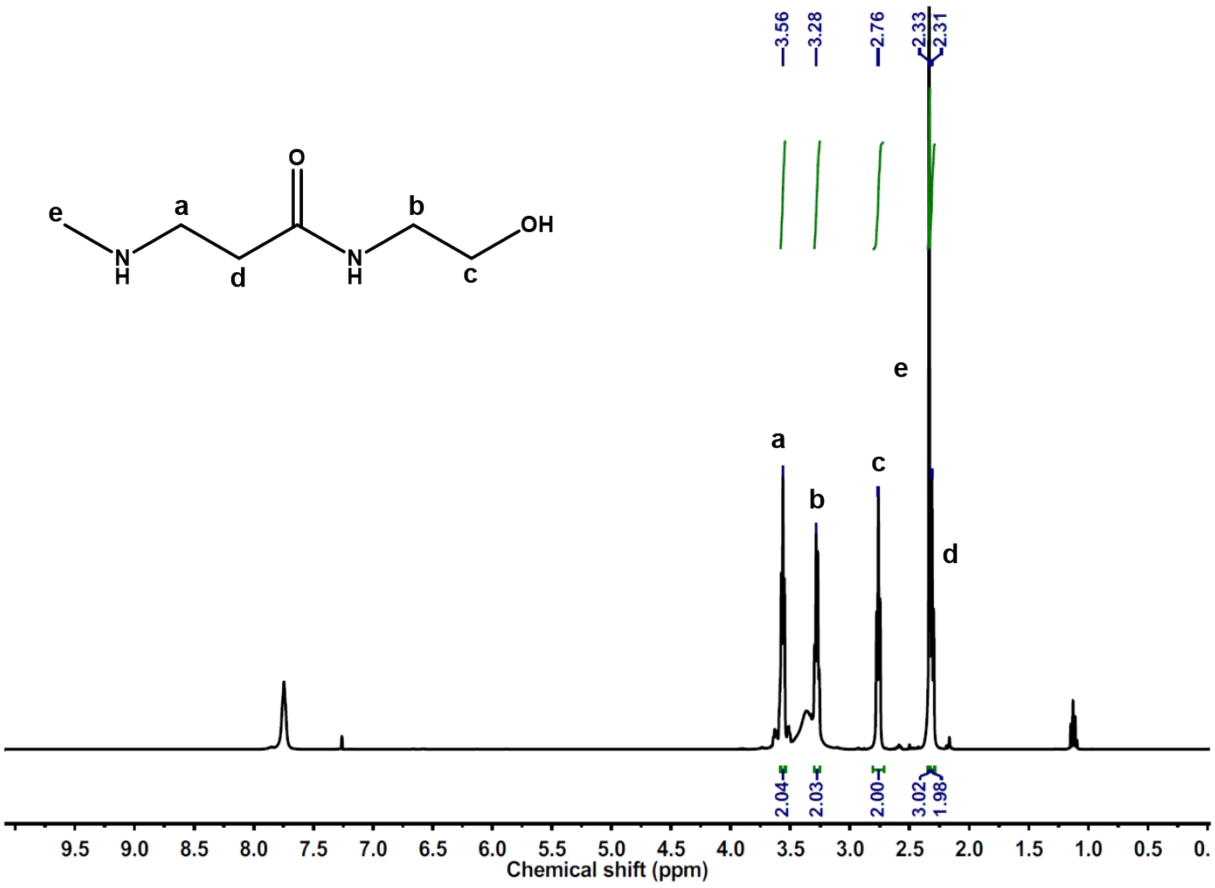


Figure S1. ^{1}H NMR spectrum for HMP.

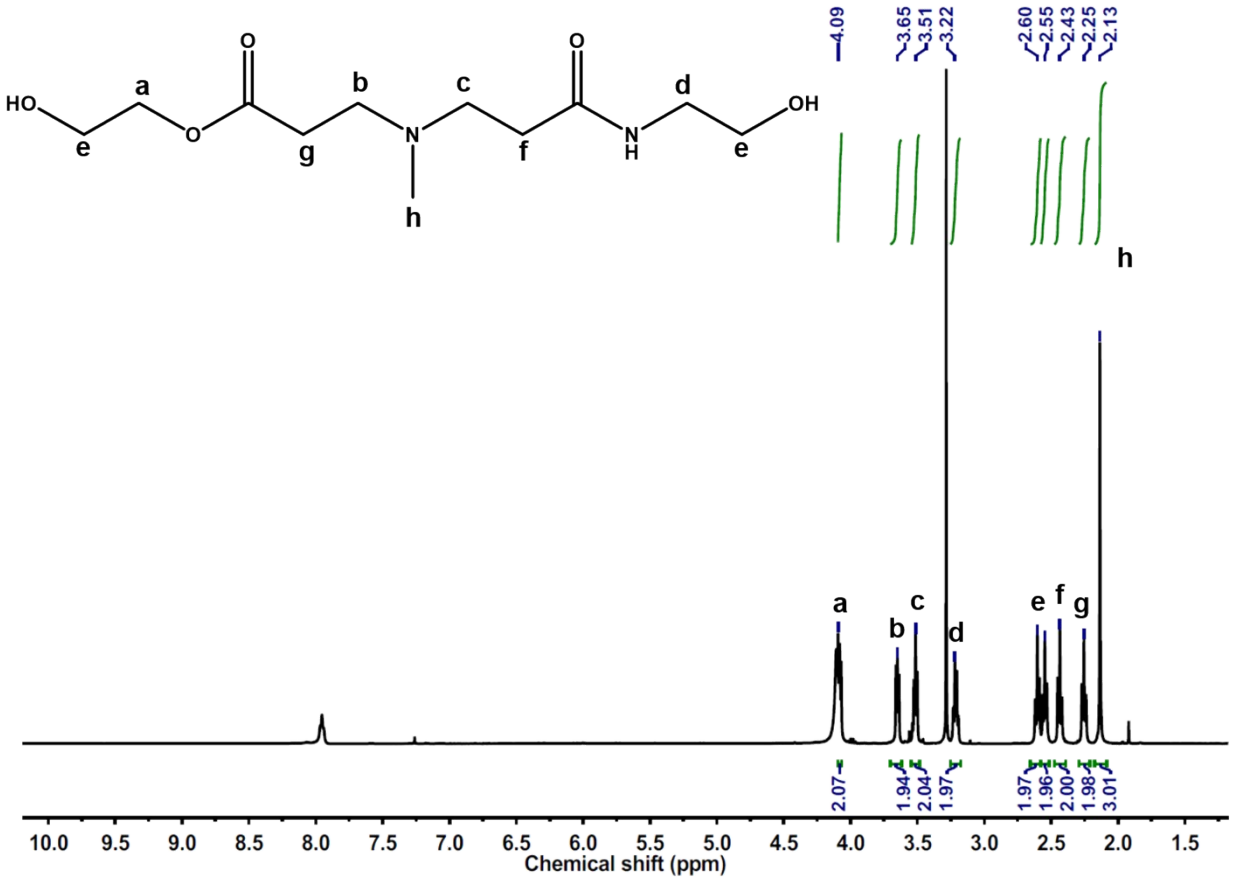


Figure S2. ^{1}H NMR spectrum for HAMAP.

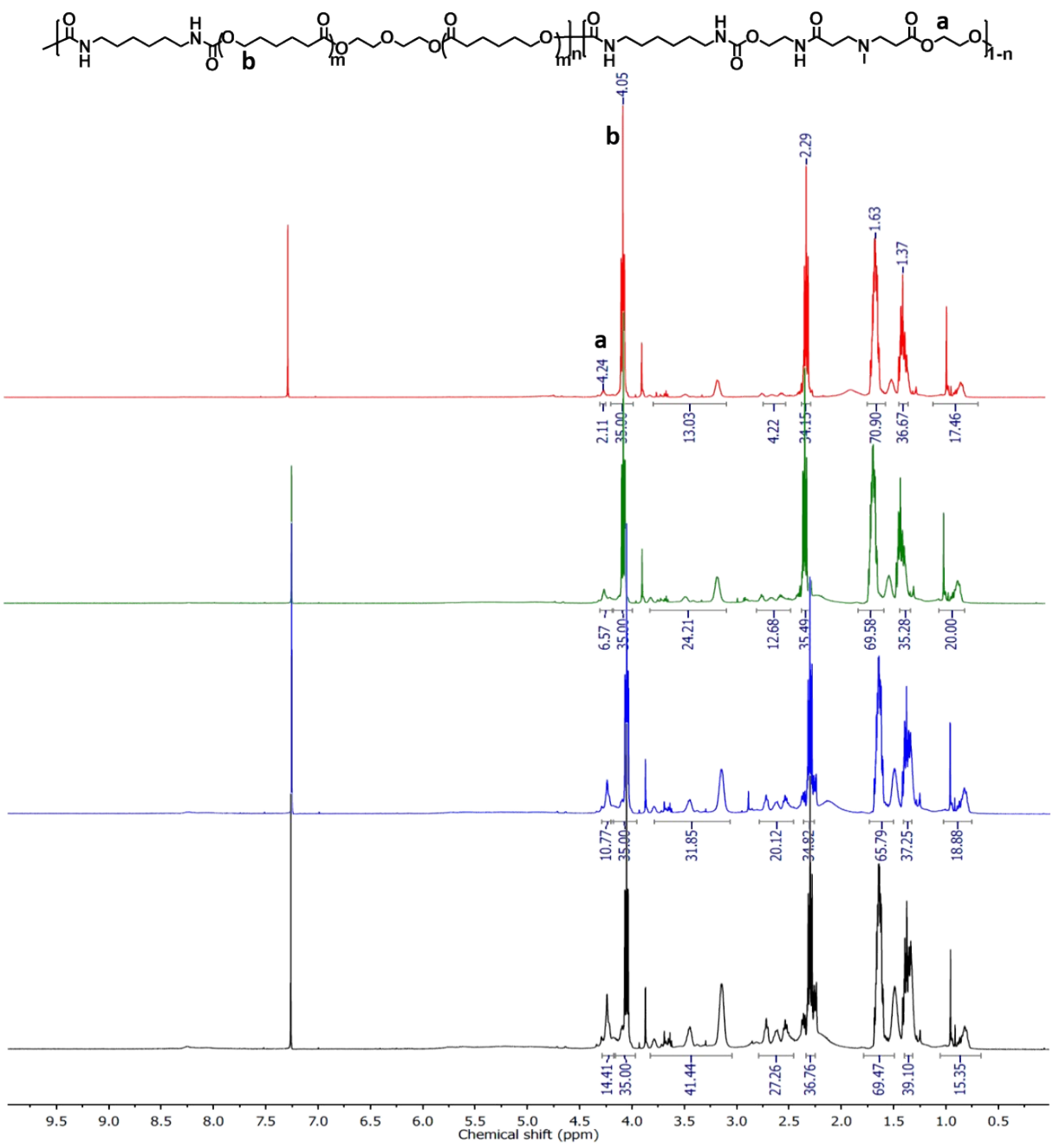


Figure S3. ^{1}H NMR spectrum for PCBDU.

Table S1. The mole percentage and weight percentage of different diols in each sample.

	PCL_{2000}-diol (mol%)	CB-diol (mol%)	PEG_{300}-diol (mol%)	PCL_{2000}-diol (wt%)	CB-diol (wt%)	PEG_{300}-diol (wt%)
PCBDU-1	25.0	25.0	\	77.0	10.1	\
PCBDU-3	12.5	37.5	\	57.8	22.7	\
PCBDU-5	8.3	41.7	\	46.3	30.4	\
PCBDU-7	6.3	43.8	\	38.6	35.4	\
PEGCU-7	6.3	\	43.8	36.7	\	38.6
PCLDU-10	50.0	\	\	92.2	\	\

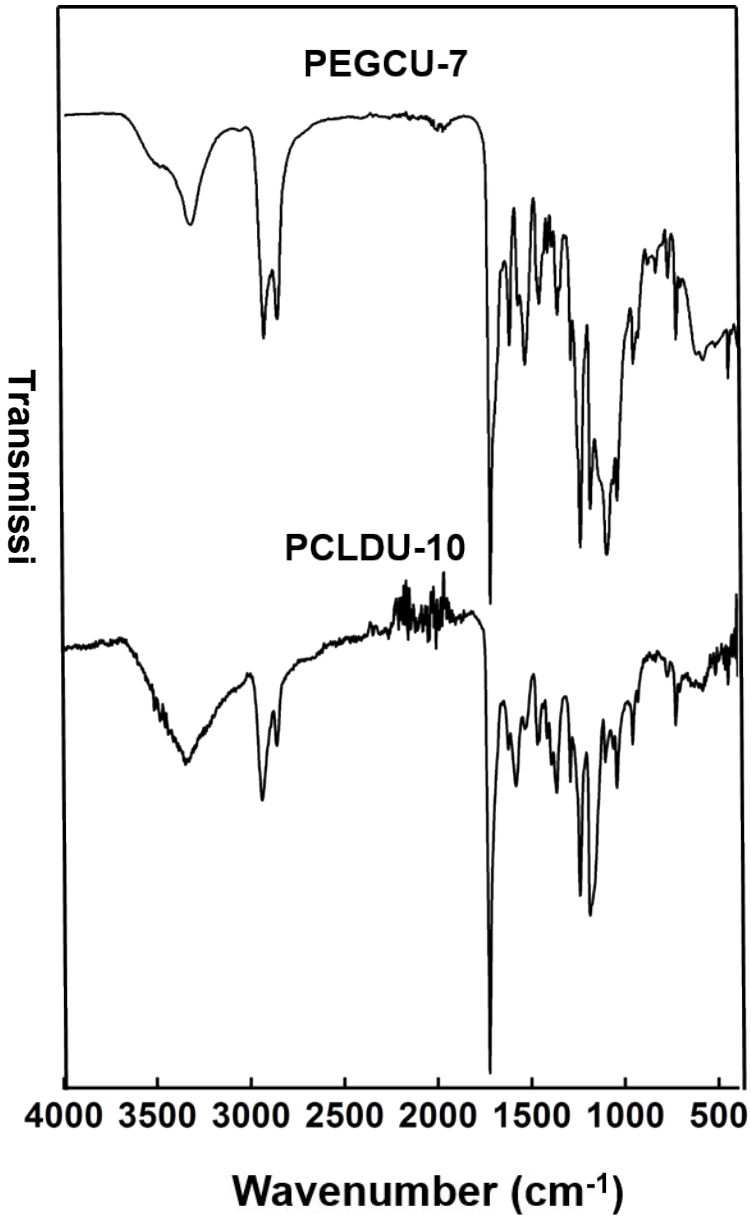


Figure S4. FT-IR spectra for PCLDU-10 and PEGCU-7.

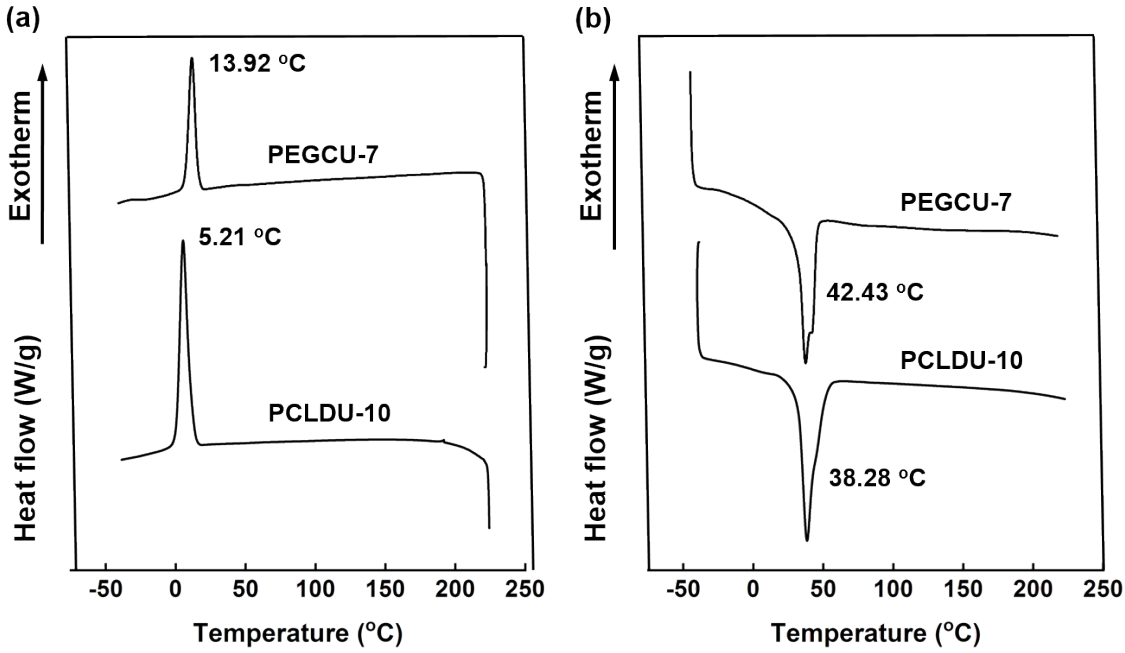


Figure S5. DSC profiles for PCLDU-10 and PEGCU-7 (a) cooling curve (b) heating curve.

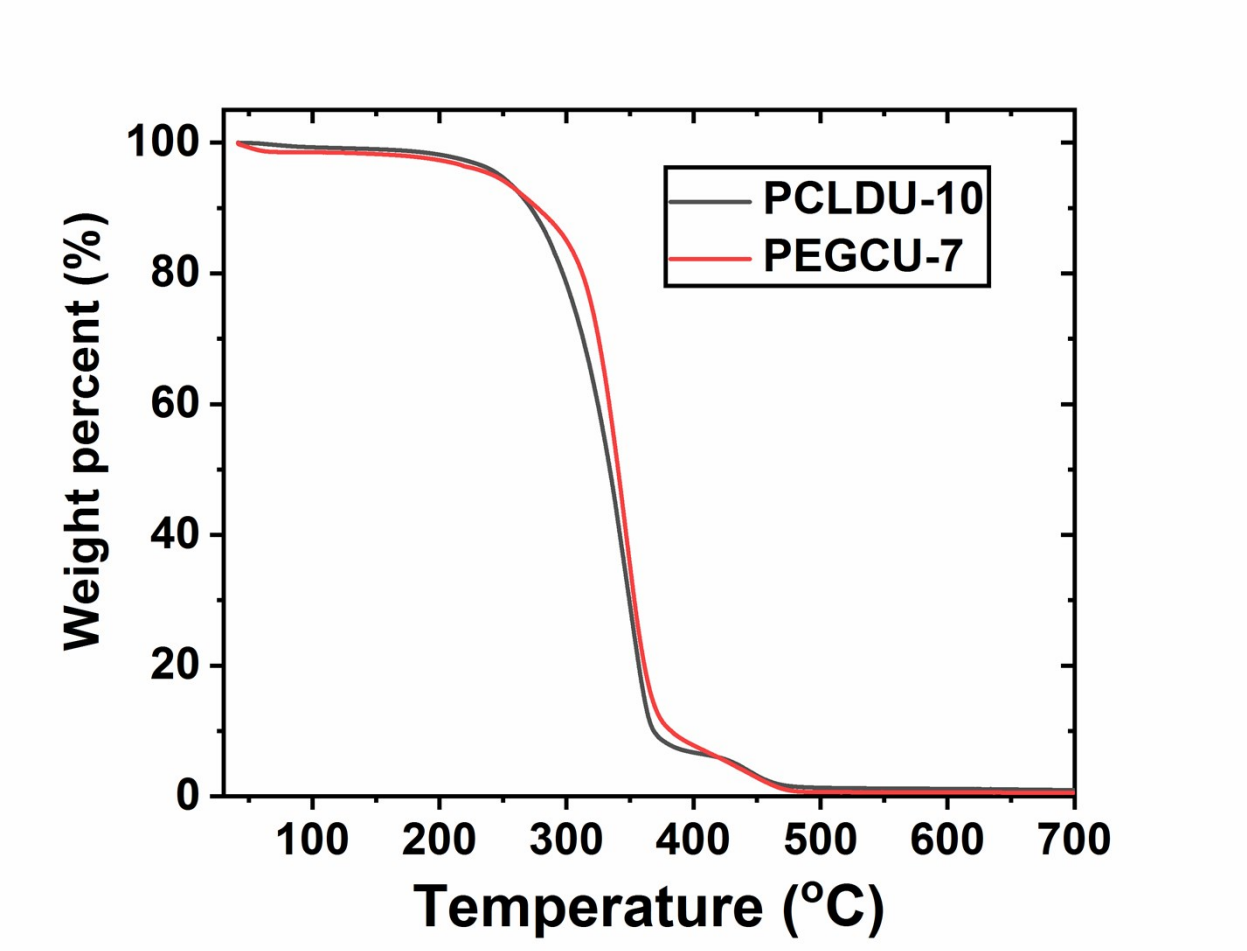


Figure S6. TGA profiles for PCLDU-10 and PEGCU-7.

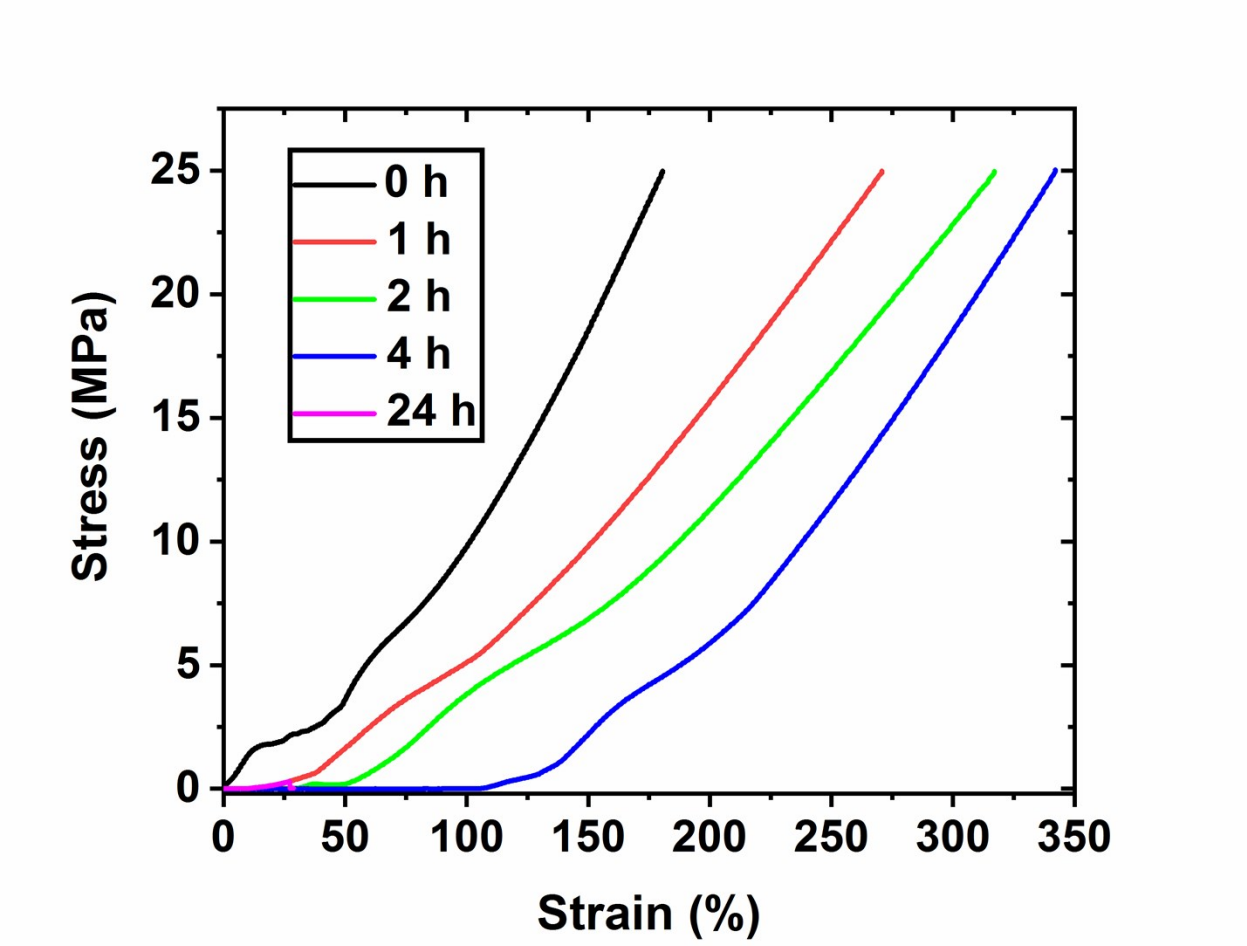


Figure S7. Compression test of PCBDU-1 with different hydrolysis time.

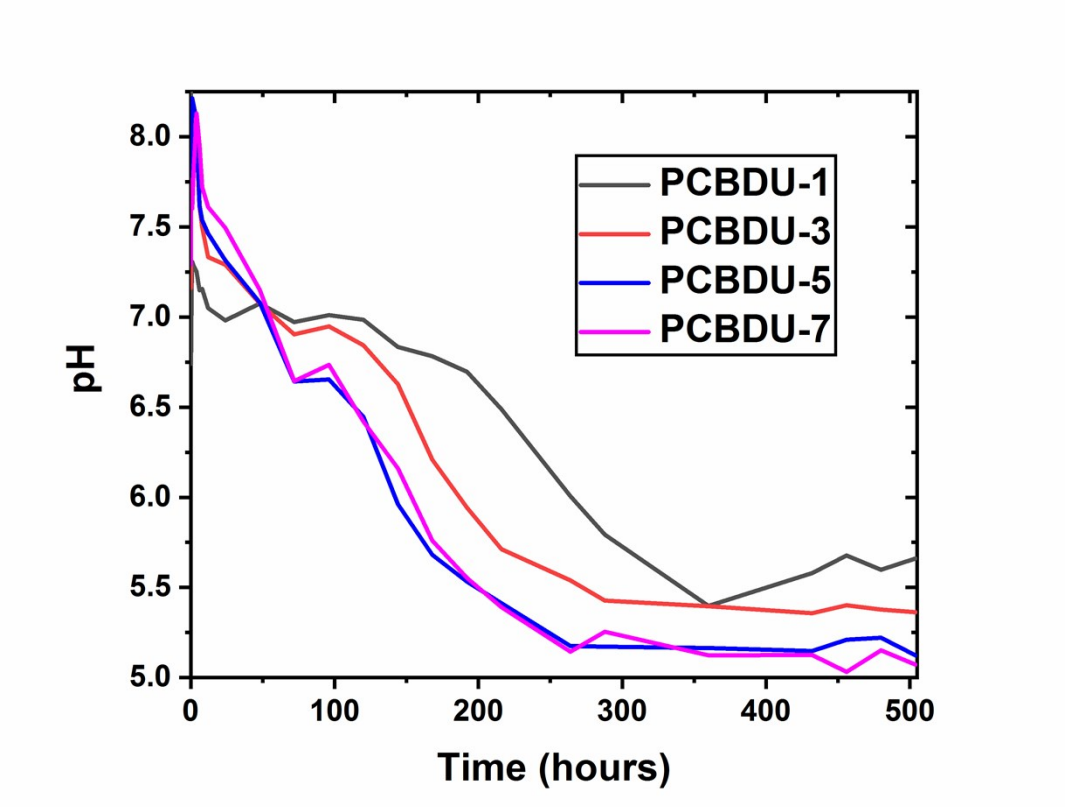


Figure S8. The pH change of the solution (DI water) during the hydrolysis of PCBDUs .

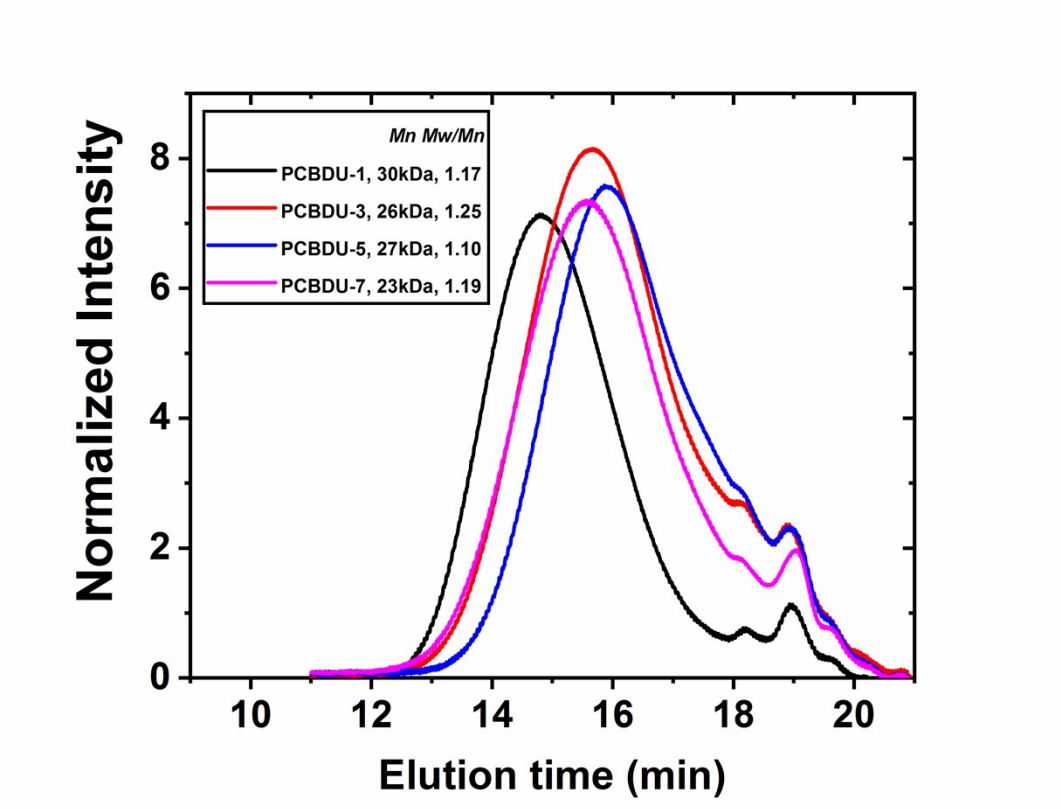


Figure S9. GPC spectrum for PCBDUs.

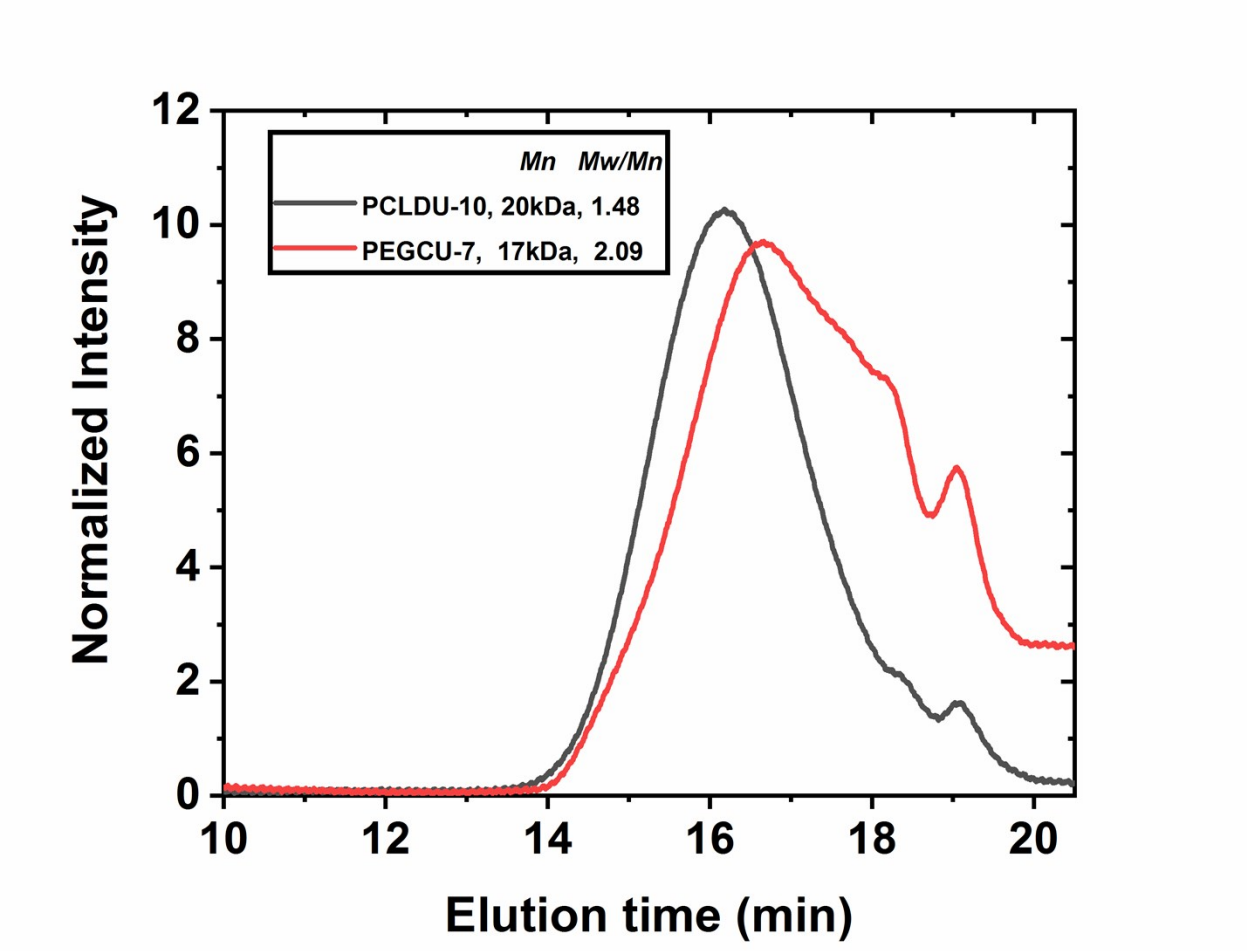


Figure S10. GPC spectrum for PCLDU-10 and PEGCU-7.

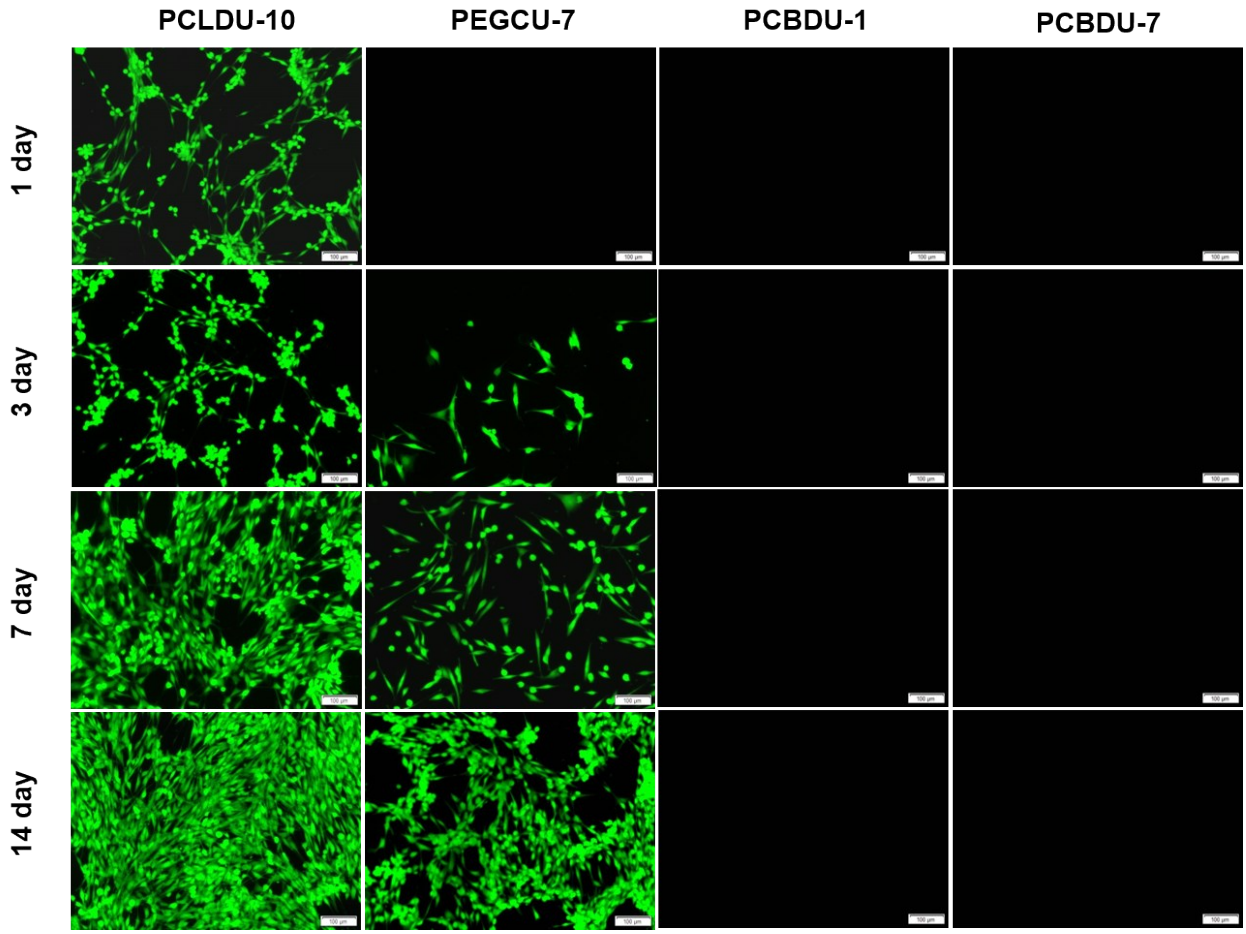


Figure S11. Images of the attachment of NIH-3T3 fibroblast cells on PCLDU-10, PEGCU-7, PCBDU-1 and PCBDU-7(after hydrolysis) after 1, 3, 7 and 14 days immersed in 100% FBS. The scale bar is 100 μm.

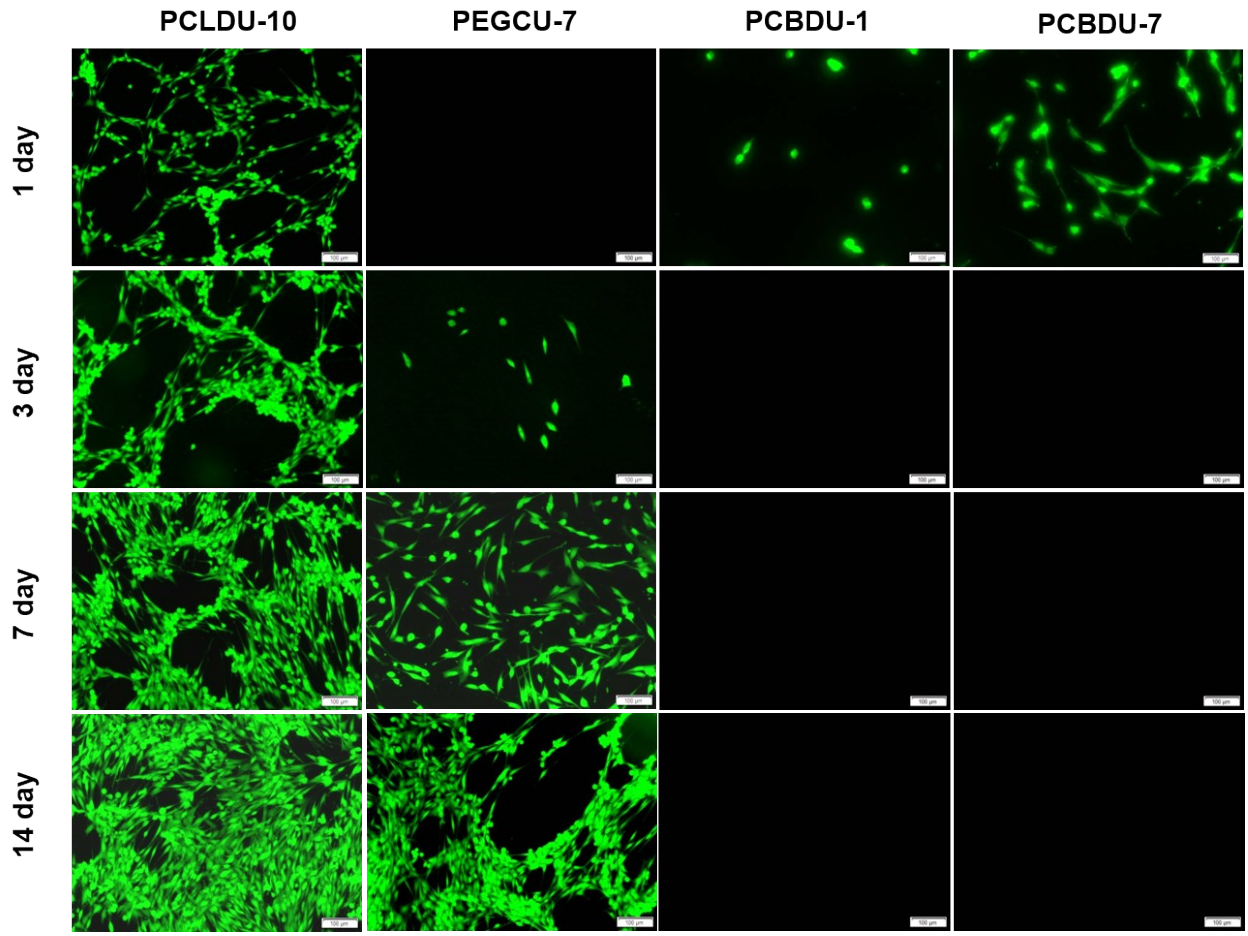


Figure S12. Images of the attachment of NIH-3T3 fibroblast cells on PCLDU-10, PEGCU-7, PCBDU-1 and PCBDU-7 (before hydrolysis) after 1, 3, 7 and 14 days immersed in 100% FBS. The scale bar is 100 μm.

Table S2. Cell densities on PCBDUs (after hydrolysis) and control surfaces with different times immersed in FBS.

	Cell densities ($\times 10^4$ cells/cm^2)					
	PCLDU-10	PEGCU-7	PCBDU-1	PCBDU-3	PCBDU-5	PCBDU-7
1 Day	11.9±1.1	\	0.3±0.03	0.2±0.02	3.2±0.2	1.6±0.2
3 Days	14.3±0.5	0.4±0.1	\	\	\	\
7 Days	21.2±0.9	5.3±0.5	\	\	\	\
14 Days	23.5±0.9	16.6±0.8	\	\	\	\

Table S3. Cell densities on PCBDUs (before hydrolysis) and control surfaces with different times immersed in FBS.

	Cell densities ($\times 10^4$ cells/cm^2)					
	PCLDU-10	PEGCU-7	PCBDU-1	PCBDU-3	PCBDU-5	PCBDU-7
1 Day	10.6±0.6	\	\	\	\	\
3 Days	12.6±0.9	1.6±0.7	\	\	\	\
7 Days	21.6±0.2	5.1±0.4	\	\	\	\
14 Days	29.6±0.1	21.4±0.7	\	\	\	\

Table S4. Cell densities on PCBDUs (before hydrolysis) and control surfaces with different times immersed in cell solution.

	Cell densities ($\times 10^4$ cells/cm^2)					
	PCLDU-10	PEGCU-7	PCBDU-1	PCBDU-3	PCBDU-5	PCBDU-7
1 Day	20.5±1.5	2.9±0.4	\	\	\	\
3 Days	24.1±1.2	13.6±1.1	\	\	\	\
7 Days	25.1±1.6	36.7±3.5	\	\	\	\
14 Days	26.4±1.9	38.9±2.9	\	\	\	\