Supporting Information

Towards cell-adhesive, 4D printable PCL Networks through dynamic covalent chemistry

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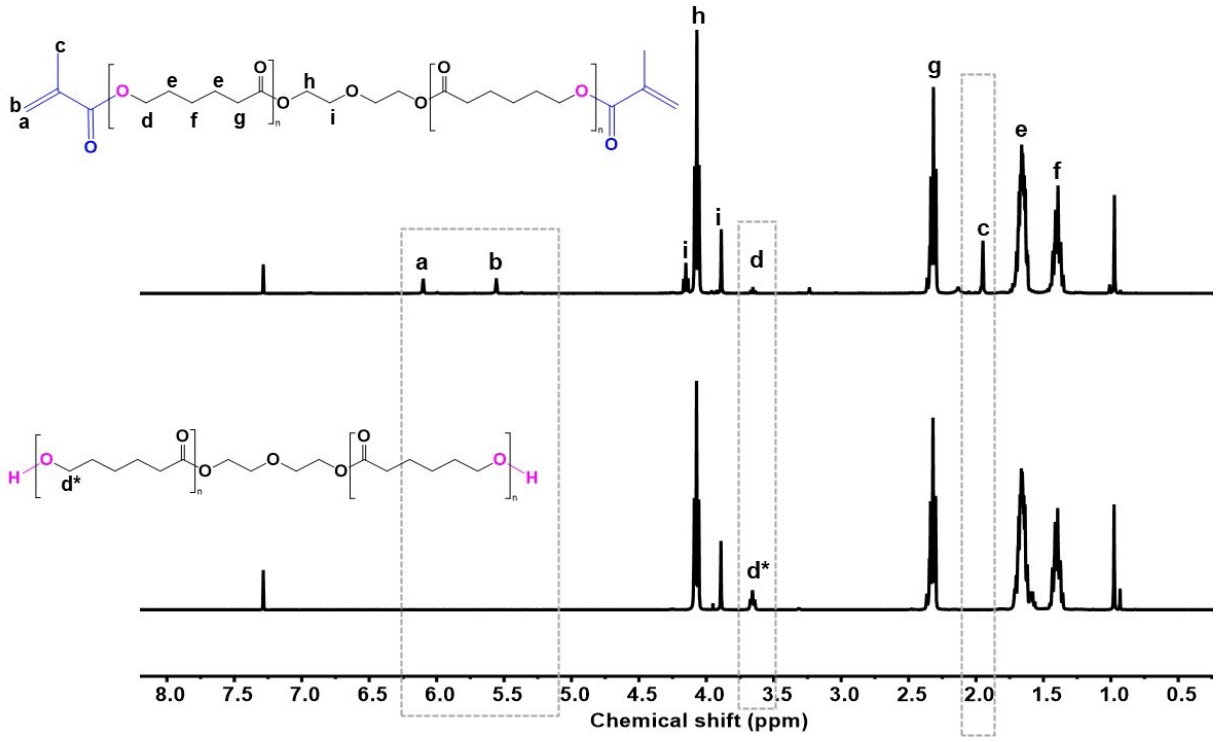

Figure S1: ^{1}H NMR of polycaprolactone diol and PCLDMA

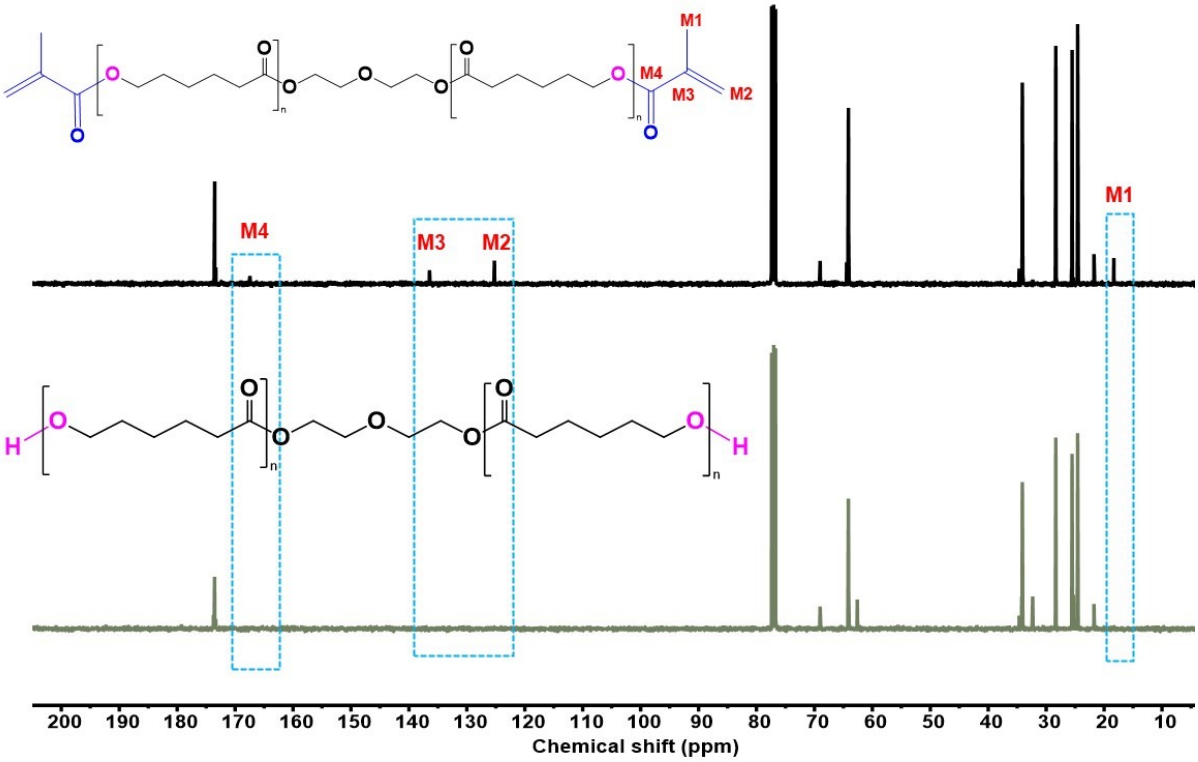

Figure S2: ^{13}C NMR of polycaprolactone diol and PCLDMA

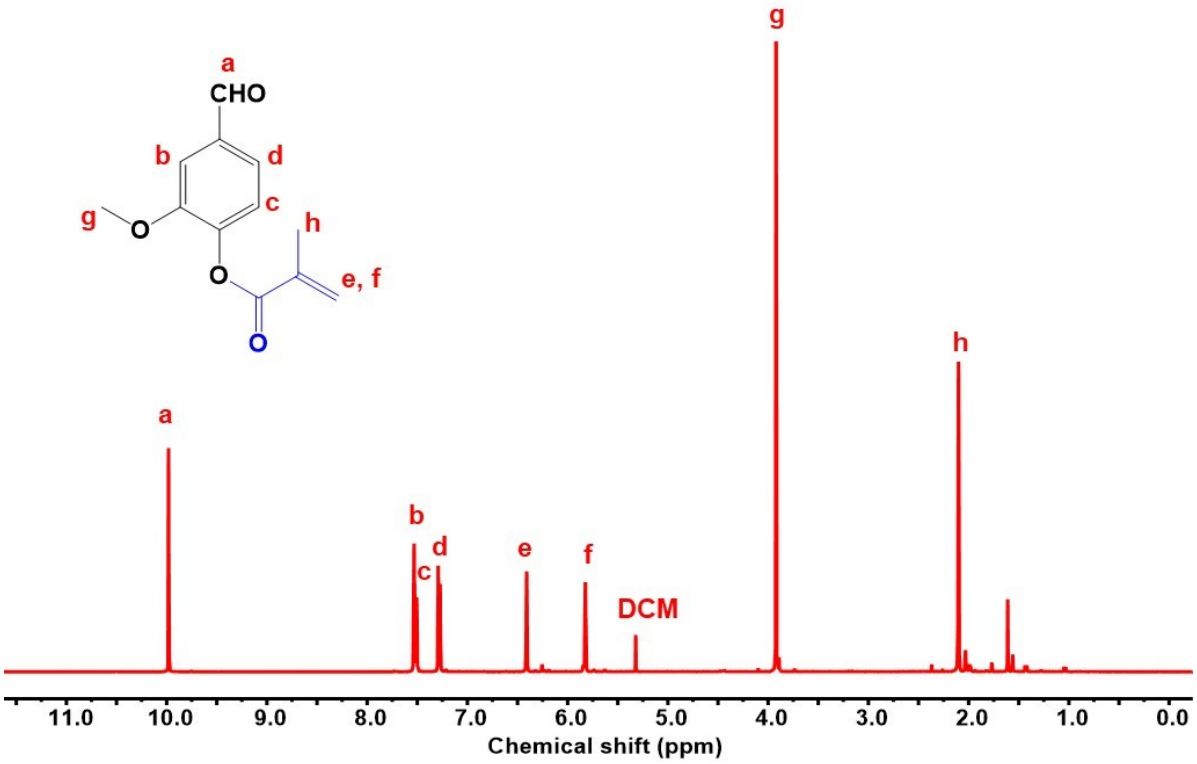

Figure S3: ^{1}H NMR of methacrylated vanillin

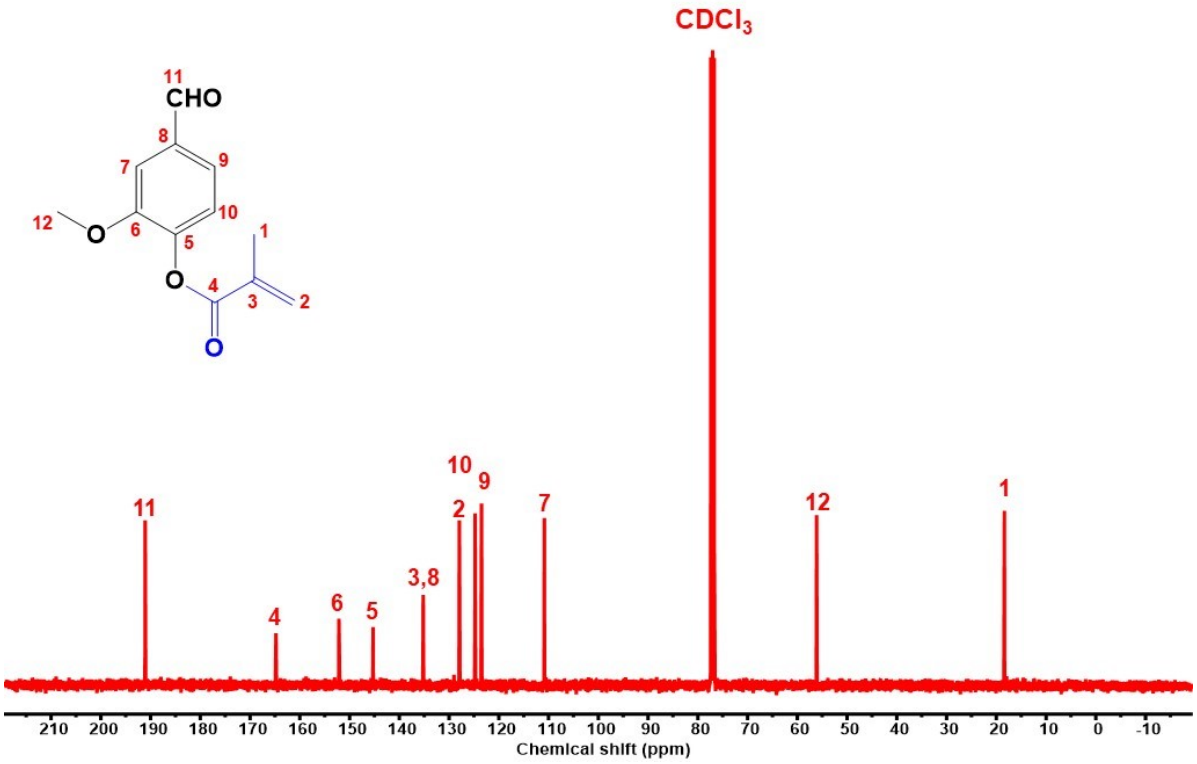

Figure S4: ^{13}C NMR of methacrylated vanillin

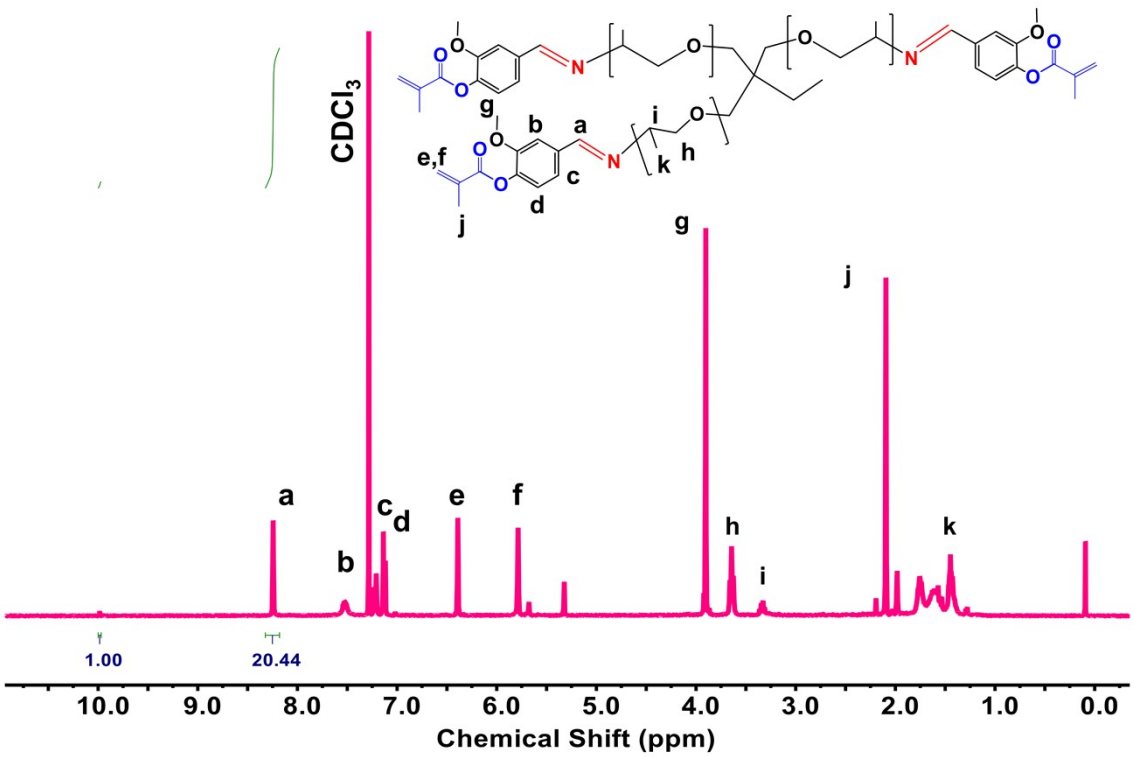

Figure S5: ^{1}H NMR of imination of methacrylated vanillin

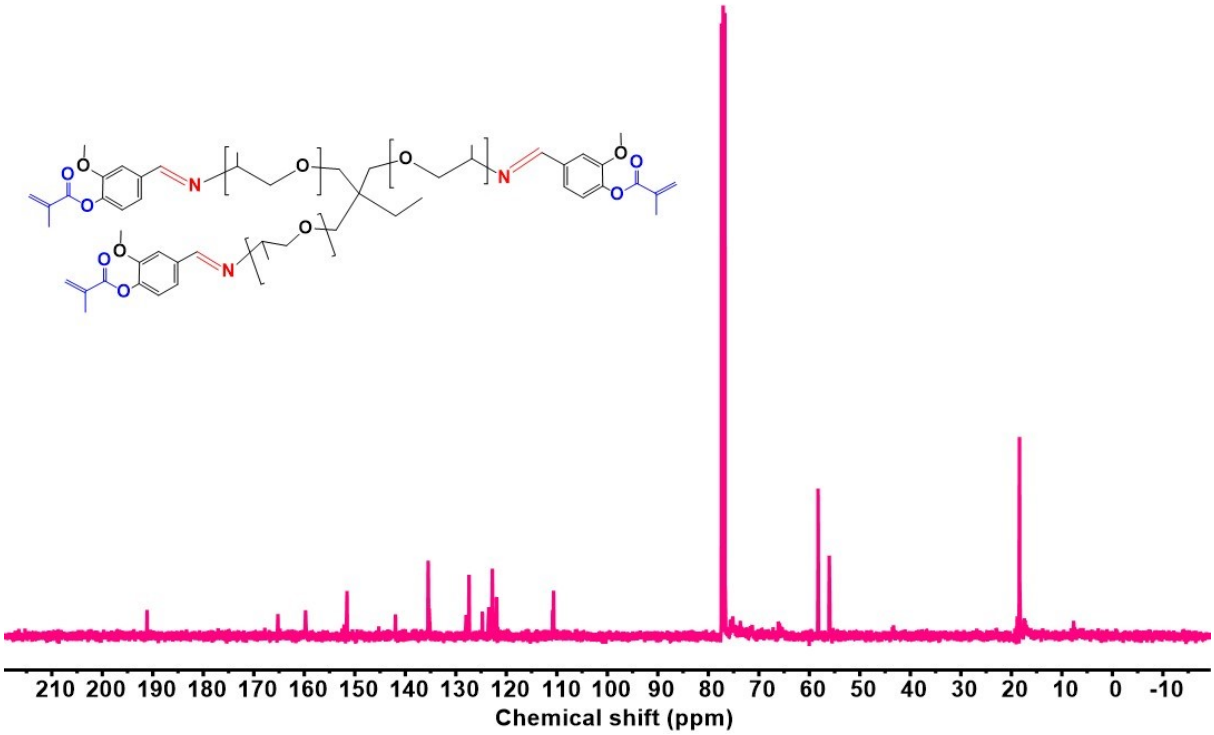

Figure S6: ^{13}C NMR of imination of methacrylated vanillin

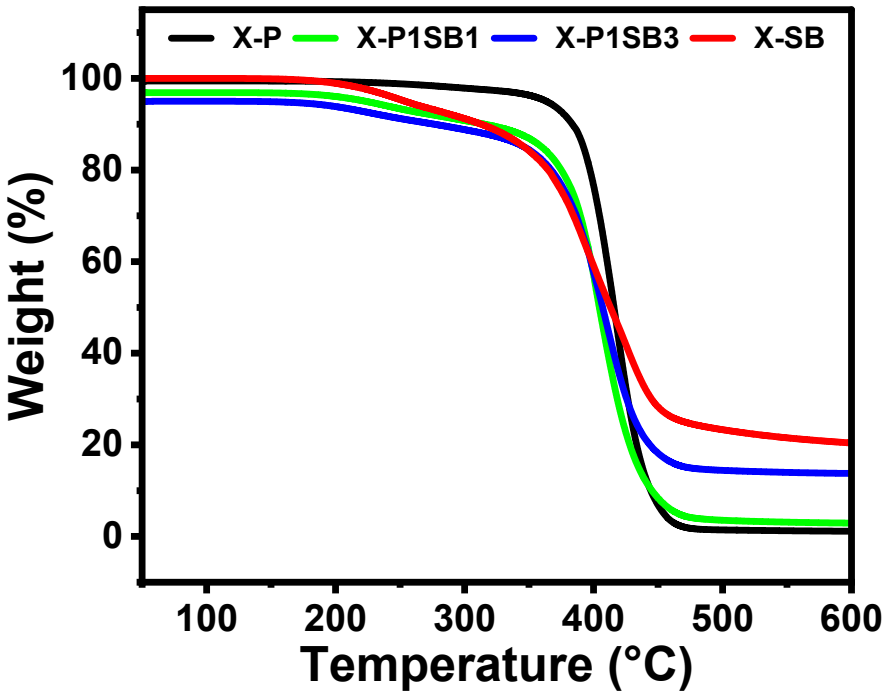

Figure S7: TGA thermogram of prepared scaffolds

Table S1: Thermal properties of X-P_1SB_1 and X-P_1SB_3

Sample	**DMA T_g**	**T_5**	**T_d**	**Residue at 600°C**	**G'_{37} (Mpa)**	**ϑ_e (mol/m³)**
X-P_1SB_1	-22±3	274±5	406±6	3.0±1.1	7.9 ± 1.8	2.43±0.02
X-P_1SB_3	17.5±2	271±2	409±3	14.4±0.6	21.9 ± 3.1	3.21±0.1

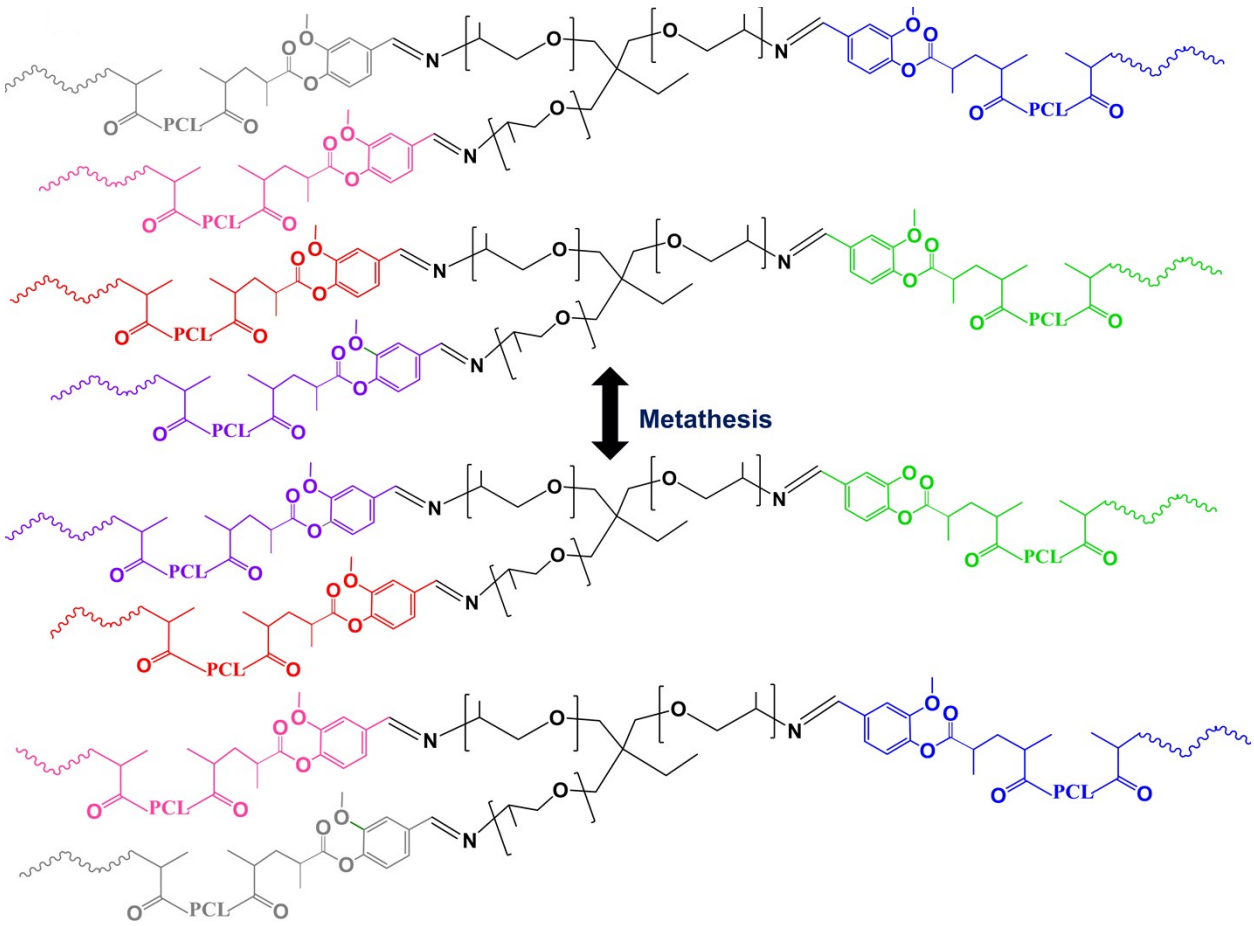

Figure S8: Mechanism of self-healing through imine metathesis for X-P_1SB_3 scaffolds.

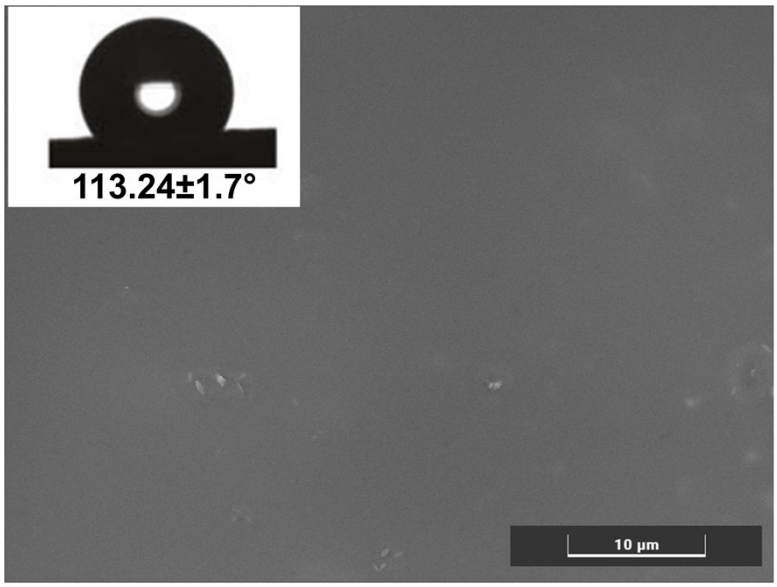

Figure S9: Surface morphology of pristine PCL scaffold.

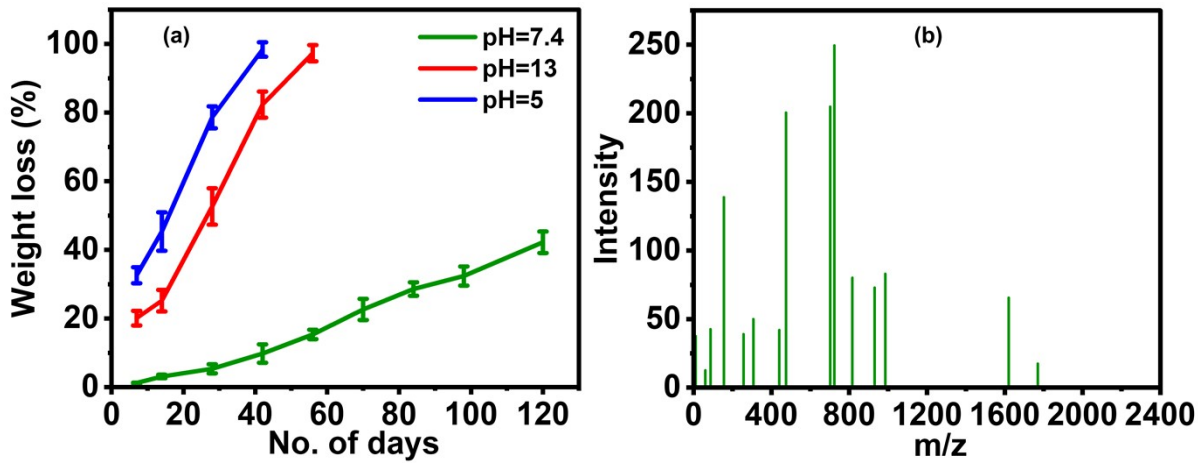

Figure S10: (a) Degradation profile of X-P_1SB_3 under various pH levels, (b) mass spectra of X-P_1SB_3 after hydrolytic degradation for 120 days at 37 °C.

Table S2: Peaks assignment for different *m/z* showing linear water-soluble degradation products

m/z	Degraded product
11.108	-
60.434	-
86.425	Methacrylic acid
155.143	6-hydroxy caproic acid + Na
256.728	-
306.852	Oligomer of Vanillin
440.295	Jefm
474.623	H-CL_4-OH
701.955	H-CL_6-OH
723.877	H-CL_6-OH+Na
816.420	H-CL_7-OH
930.450	H-CL_8-OH
985.345	-
1619.672	H-CL_{14}-OH
1620.502	H-CL_{14}-OH
1729.814	H-CL_{15}-OH

Demonstration of Shape memory effect for X-P_1SB_3: Video VS1 and VS2

SM_XP1SB3_VS1

SM_3DP_XP1SB3_VS2