Supporting Information

Hierarchical Crosslinked Poly[caprolactone-co-urethane] toward Connective tissue-like Properties and Multifunctional Integration

Yawei Sun, Zhao Liu, Fang Chen, Mi Xu, Jinli Zhang and Wei Li*

Preparation of double layer actuator Firstly, the PU samples were cut into 13 × 36 mm sheets with 0.15 mm in thickness. Two sheets for each sample. Secondly, Pt electrodes, with a size of 10 mm in width, 24 mm in length and ~20 nm in thickness, were deposited on both surfaces of one PU sheet (call as active layer) leaving uncoated margins of ~1.5 mm along three sides and 10.5 mm along one side. The electrode area was smaller than the area of the beam so as to minimize electrical breakdown around the edges of the beam. Then, four aligned polyvinyl chloride (PVC) fibers (1 mm diameter) placed in parallel to one another and sandwiched between two sheets of PU sample to provide unidirectional stiffening. The uncoated PU sheet was used as a fixed end (call as passive layer). Finally, the two sheets were pressed together. Unlike P(CL-BDO), the adhesion performance of TA allowed P(CL-TA_1/BDO_1) able to strong bonding with each other. The double layer actuator was fabricated completely. The actuation voltage was provided by a high voltage power supply (DW-P103-1ACFO).

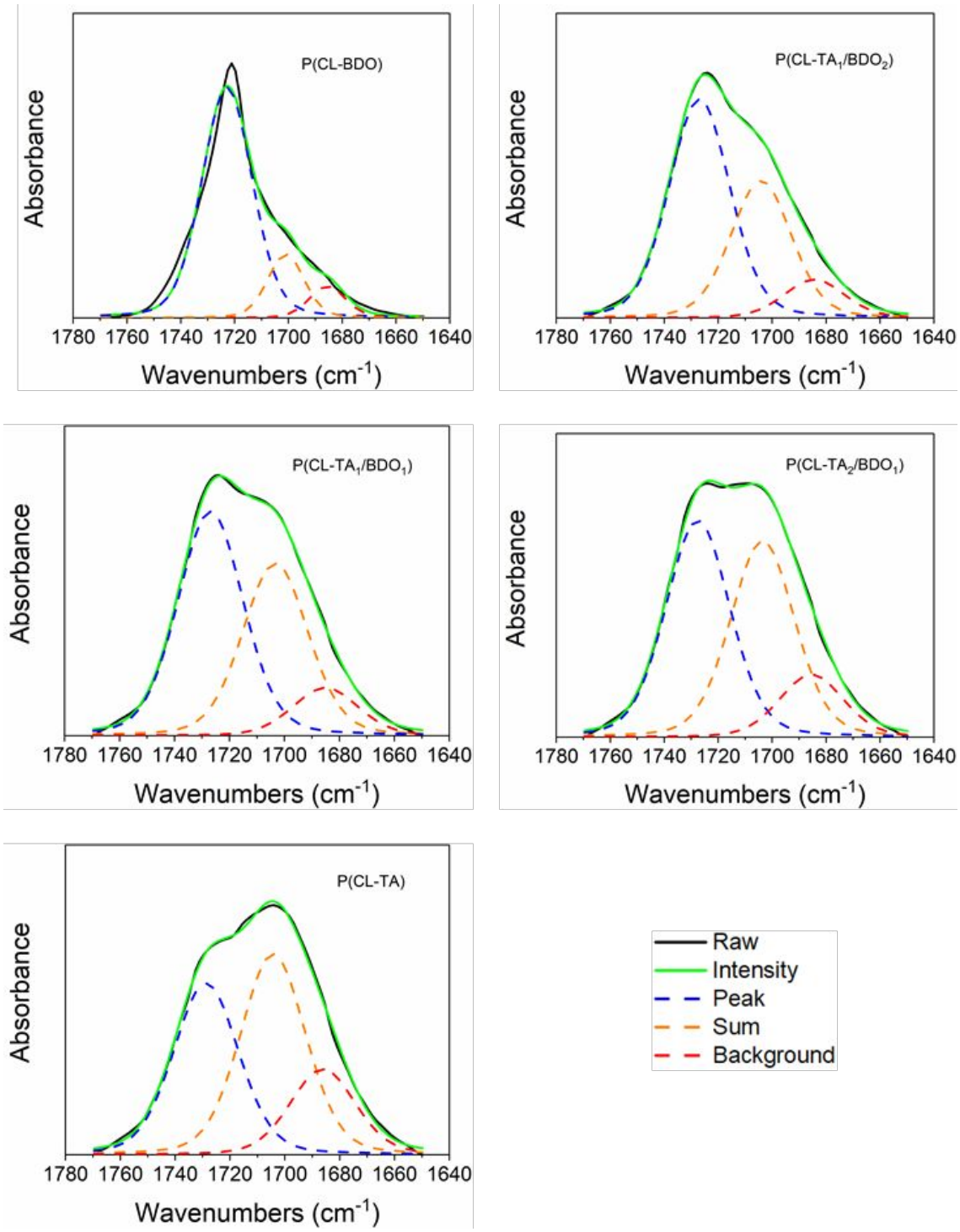


Figure S1 ATR-IR spectra in the C=O stretching regions of various PU samples. The bands at 1726 cm^{-1} (blue dash line), 1703 cm^{-1} (orange dash line) and 1686 cm^{-1} (red dash line) are due to the free C=O stretching vibration, hydrogen-bonded C=O stretching vibration in soft domain and hydrogen-bonded C=O stretching vibration in hard domain, respectively.

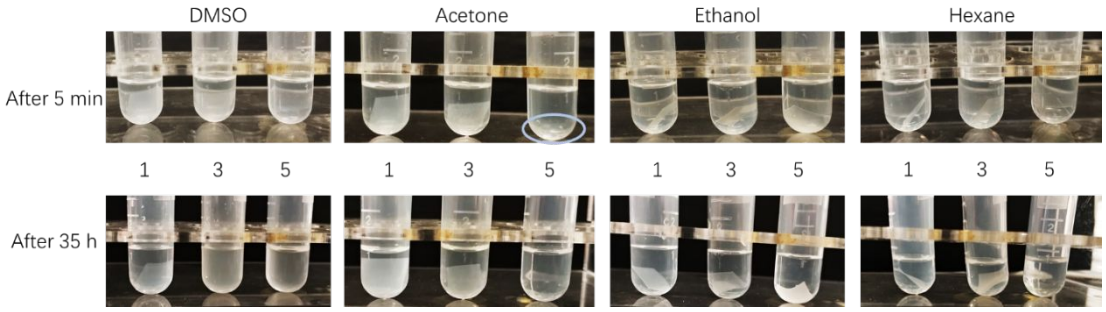


Figure. S2 Variations of three samples immersed in organic solvent for the period of 5 min or 35 h, 1,3,5 represent the sample of P(CL-BDO), P(CL-TA$_1$/BDO$_1$) and P(CL-TA), respectively.

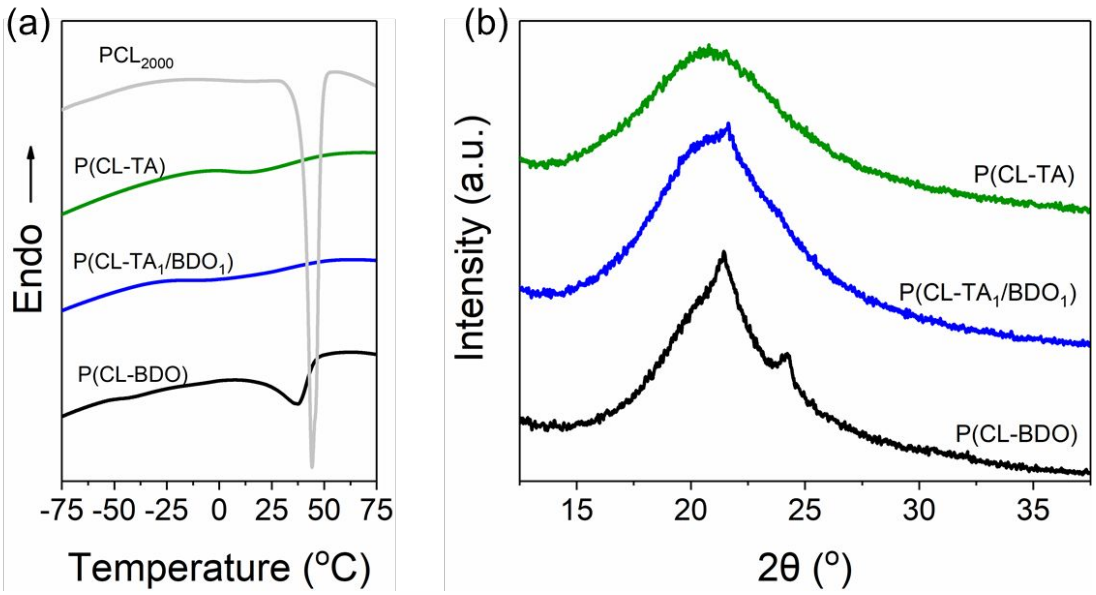
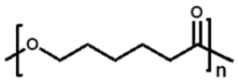


Figure. S3 DSC thermograms (a) and XRD patterns (b) of P(CL-BDO), P(CL-TA$_1$/BDO$_1$) and P(CL-TA).

The electron density (η) can be estimated by equation (R2) using method of group contribution.

$$\eta_i = \frac{\rho_i n}{M_{w_i}} \quad \text{(R2)}$$

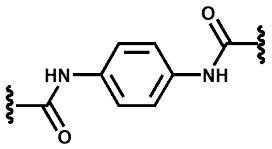
where ρ_i is mass density of the segment, n is the number of electrons and Mw_i is molecular weight. The SLD calculation of some specific fragments in P(CL-TA/BDO) as followed below:



Number	Group	Mw (g/mol)	Mv (cm^3/mol)	ρ (g/cm^3)	N (e)
5	-CH$_2$-	14	16.5	0.85	8

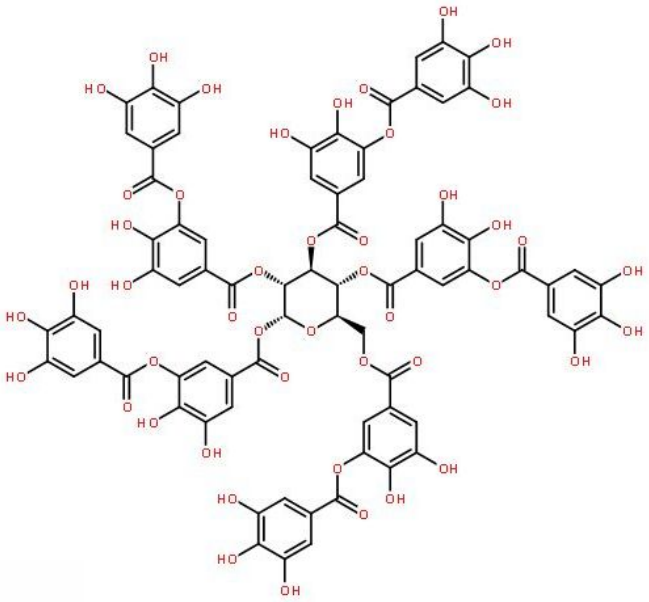
1	-C(=O)-	28	10.7	2.62	14
1	-O-	16	5.1	3.13	8
Sum		114	98.3	1.16	62

η_{PCL}=1.16×62/114=0.63 mol e/cm^3=0.38 e/Å^3

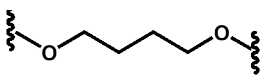


Number	Group	M_w (g/mol)	M_V (cm^3/mol)	ρ (g/cm^3)	N (e)
2	-C(=O)-	28	10.7	2.62	14
2	-NH-	15	8.5	1.76	8
1	-C_6H_4-	76	58.8	1.29	40
Sum		162	97.2	1.67	84

η_{PPDI}=1.67×84/162=0.87 mol e/cm^3=0.52 e/Å^3



η_{TA}=2.13×876/1701.2=1.10 mol e/cm^3=0.66 e/Å^3



Number	Group	Mw (g/mol)	Mv (cm^3/mol)	ρ (g/cm^3)	N (e)
4	-CH_2-	14	16.5	0.85	8
2	-O-	16	5.1	3.13	8
Sum		88	76.2	1.15	48

η_{BDO}=1.15×48/88= 0.63 mol e/cm^3=0.38 e/Å^3

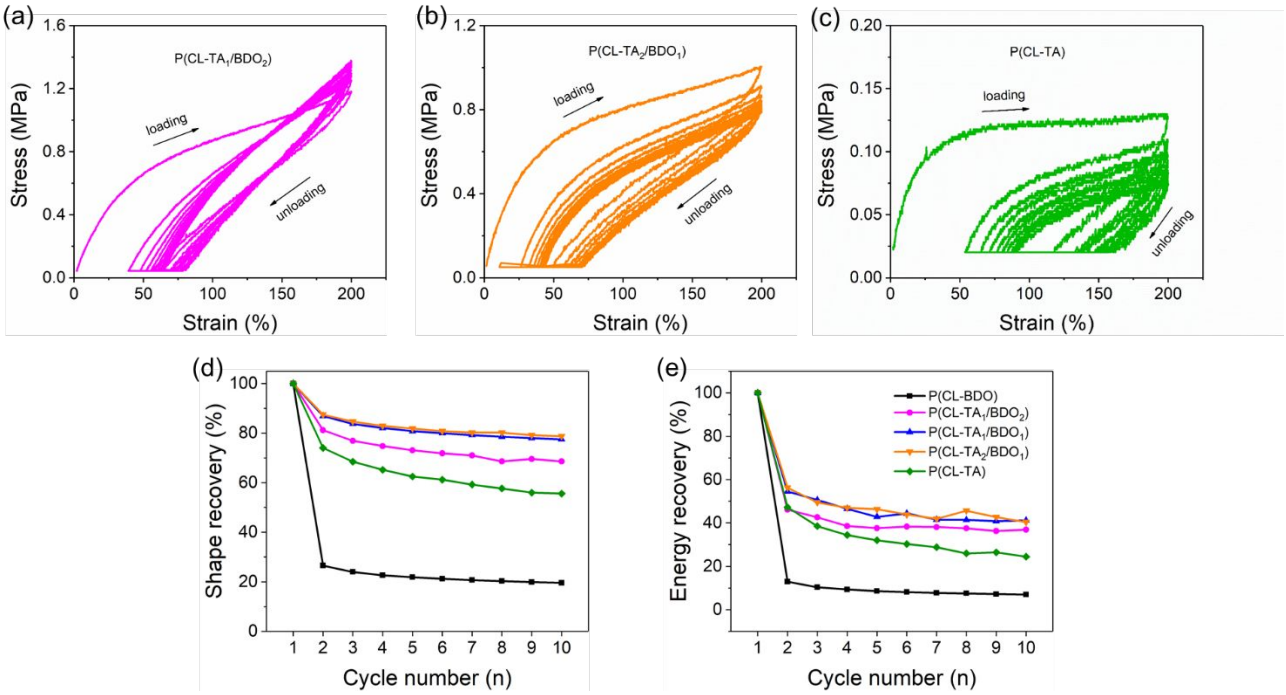


Figure S4. Successive cyclic stretching of P(CL-TA_1/BDO_2) (a), P(CL-TA_2/BDO_1) (b) and P(CL-TA) (c); (d) the shape recovery and (e) energy recovery profiles of these samples.

Table S1 DMA data for two samples.

sample	Tg (°C) by E″	Tg (°C) by Tan δ	Maximum of Tan δ
P(CL- BDO)	-33.56	-24.86	0.22
P(CL- TA_1/ BDO_1)	-3.32	20.37	0.88

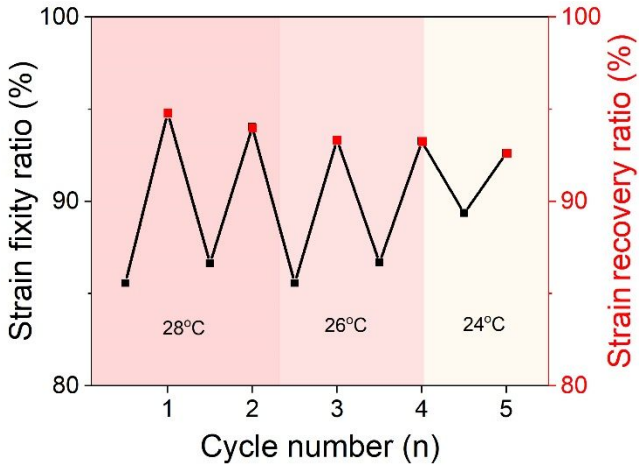


Figure S5. Shape memory properties of P(CL-BDO) as a function of thermo-mechanical cycle, red dots represent strain recovery ratio after heating.

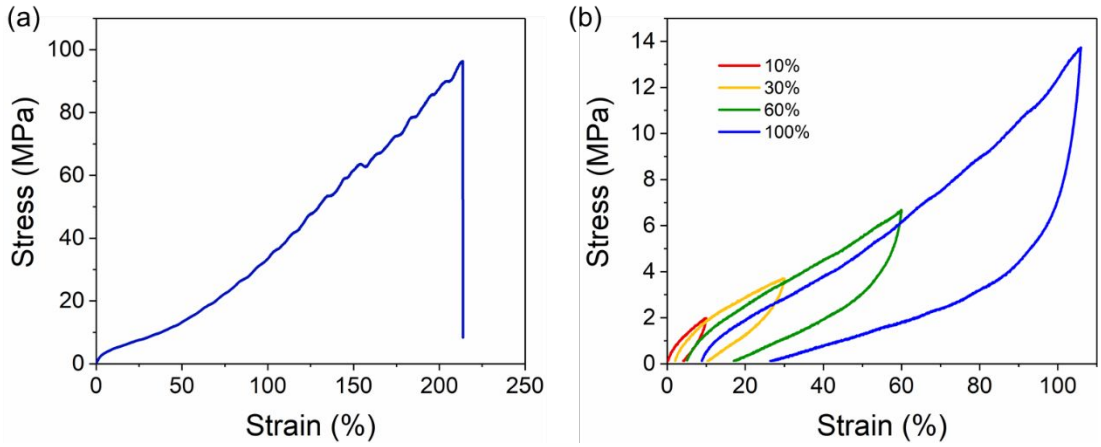


Figure S6. Tensile stress–strain curves (a) and cyclic stretching with different range (b) of pre-stretched P(CL-TA_1/BDO_1).

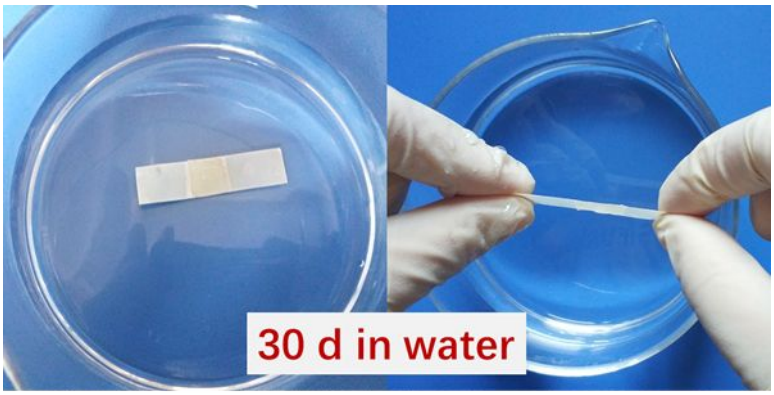


Figure S7. Adhesion demonstration of P(CL-TA_1/BDO_1) tape having been immersed in water for 30 d.

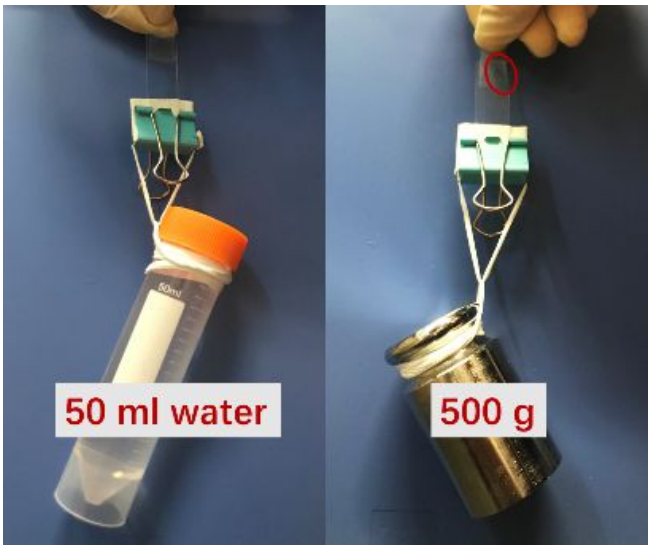


Figure S8. Glass-adhesion demonstration of P(CL-TA_1/BDO_1) tape having been storied under the atmosphere for 6 months. The red circle is the part that has not fallen off.

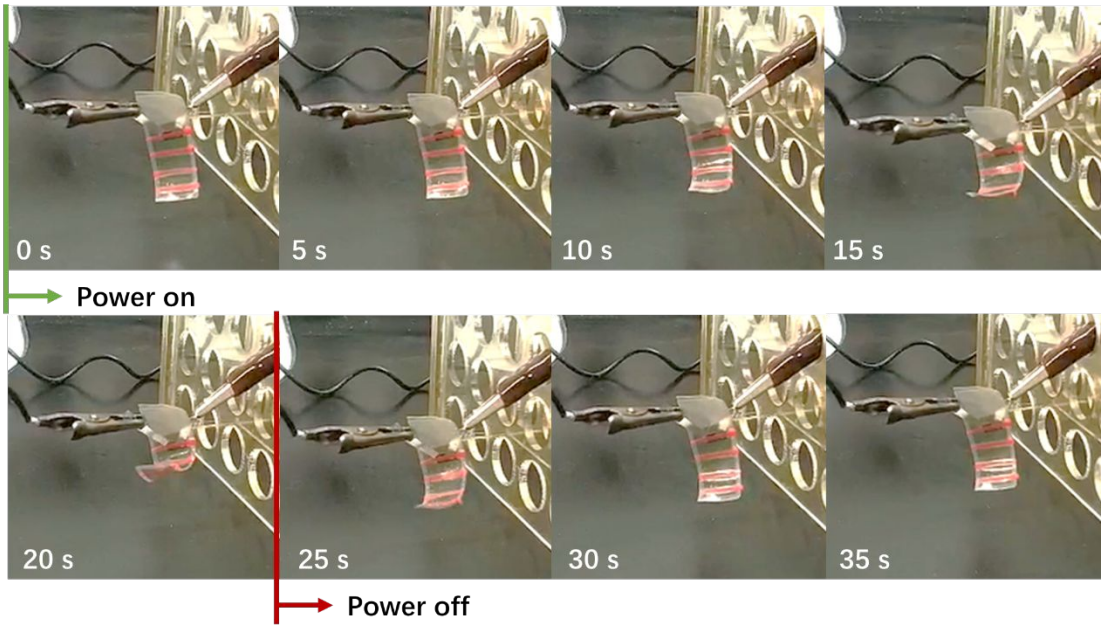


Figure S9. Curving and recovery process by electricity stimulation.

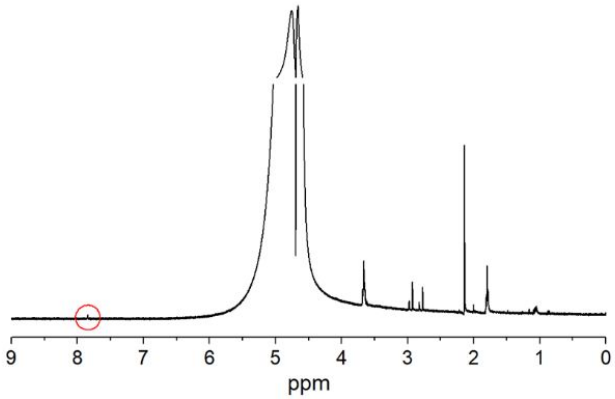


Figure S10. ^{1}H NMR spectra of degradation products generated during the degradation of P(CL-TA_1/BDO_1) within the period of 60-90 d.