Supporting Information for

Optically-Healable Polyurethanes with Tunable Mechanical Properties

Rui Yan,[1] Bixin Jin,[1] Yunjun Luo,[1,2] Xiaoyu Li[1,2*]*

[1] School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081, China

[2] Key Laboratory of High Energy Density Materials, Ministry of Education, Beijing Institute of Technology

Table of Contents

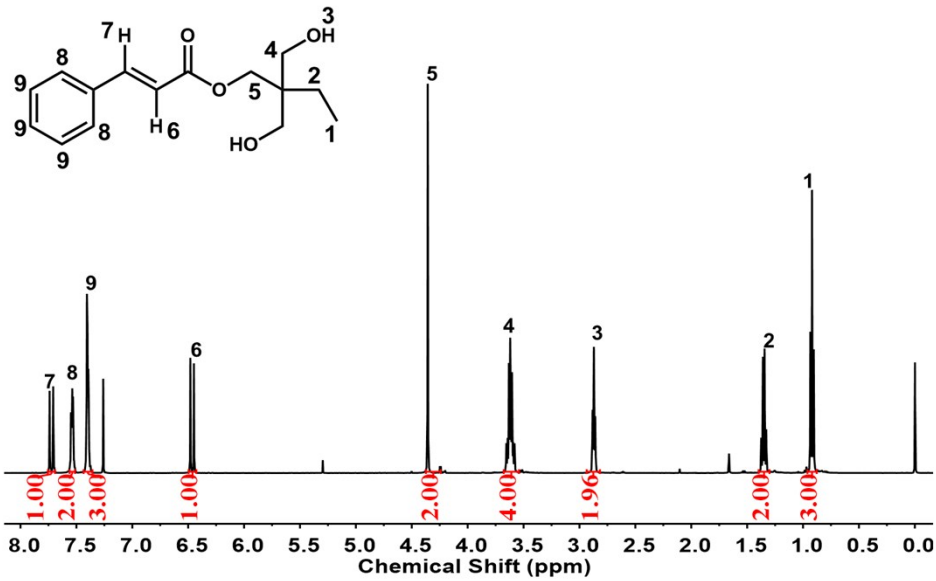

Figure S1. [1]H NMR spectra of CTMP.

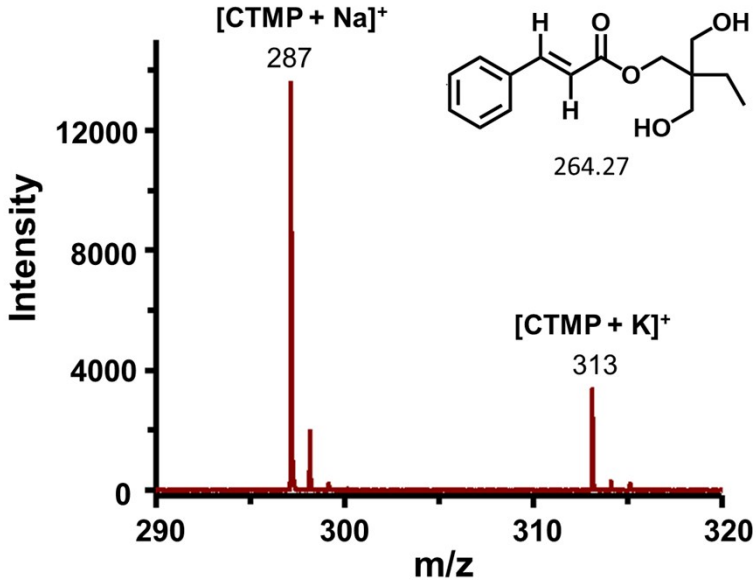

Figure S2. MALDI-TOF spectra of CTMP.

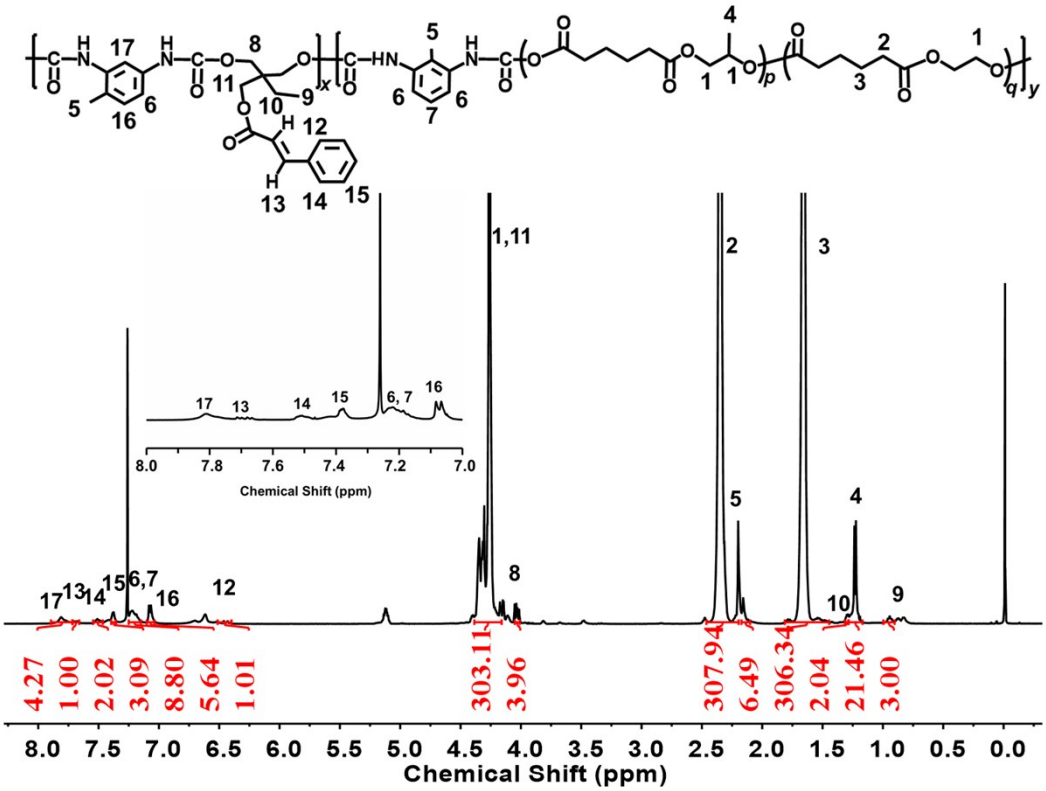

Figure S3. ^{1}H NMR spectra of C_2-PU.

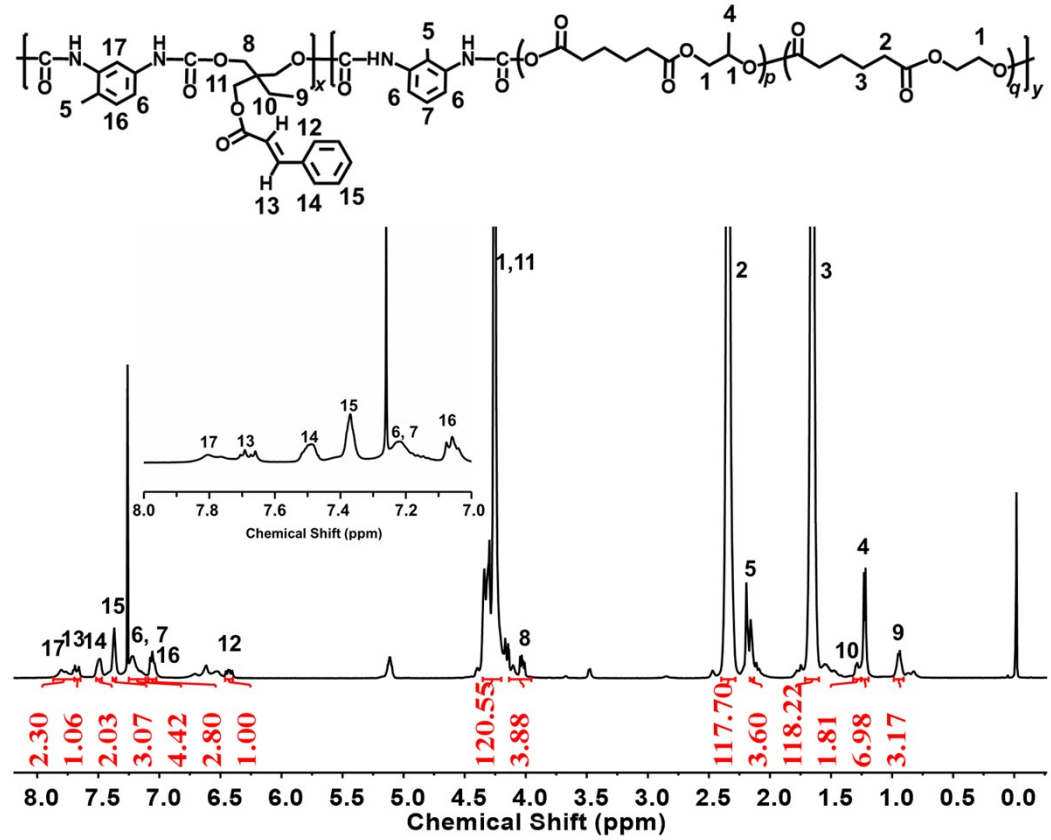

Figure S4. ^{1}H NMR spectra of C_5-PU.

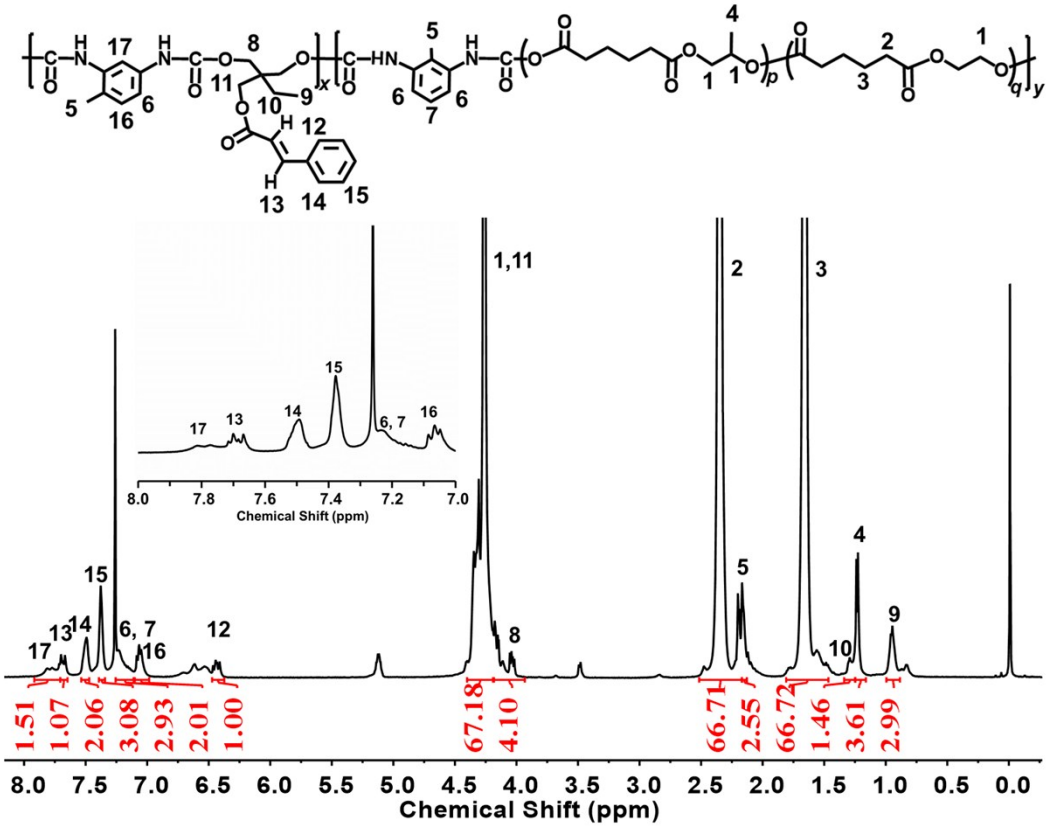

Figure S5. ^{1}H NMR spectra of C_8-PU.

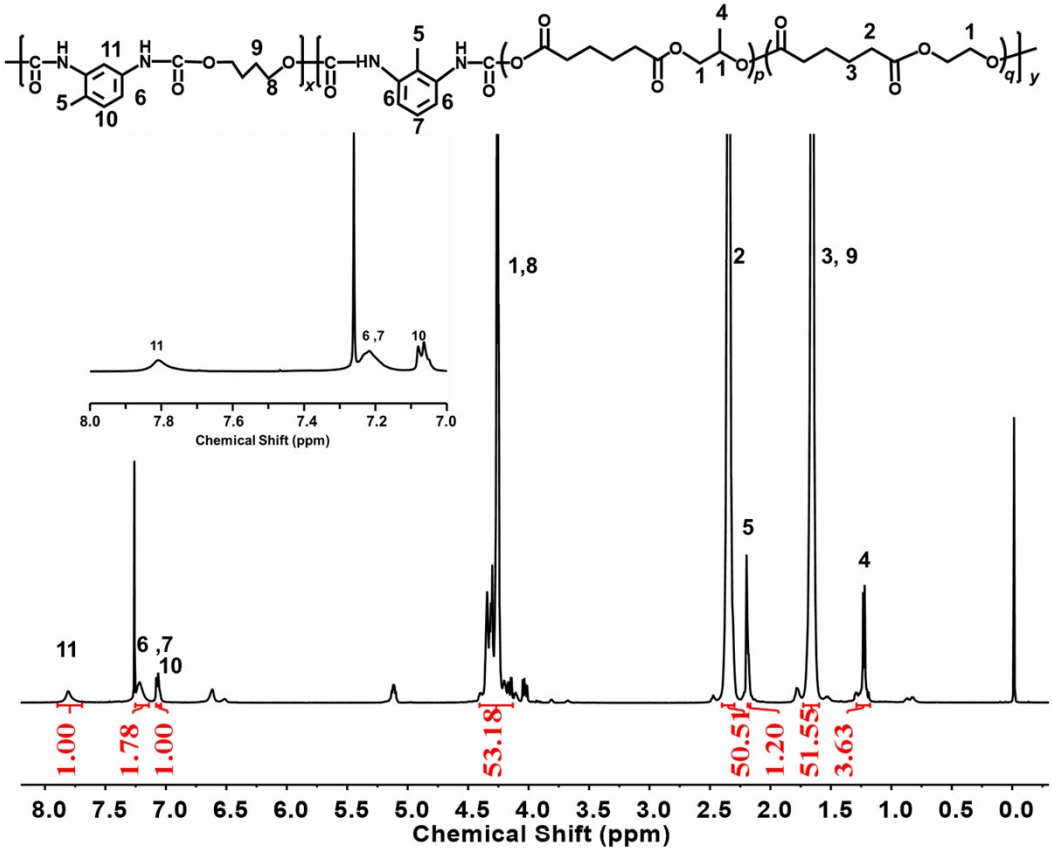

Figure S6. ^{1}H NMR spectra of B_2-PU.

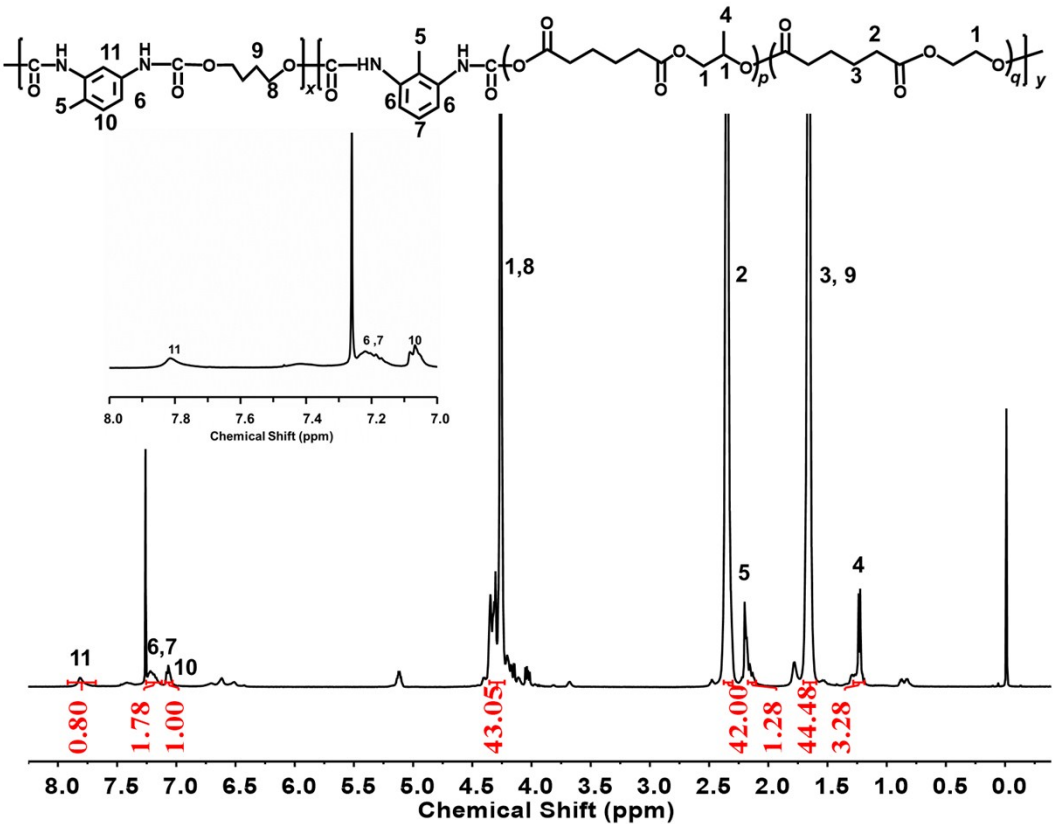

Figure S7. ^{1}H NMR spectra of B_5-PU.

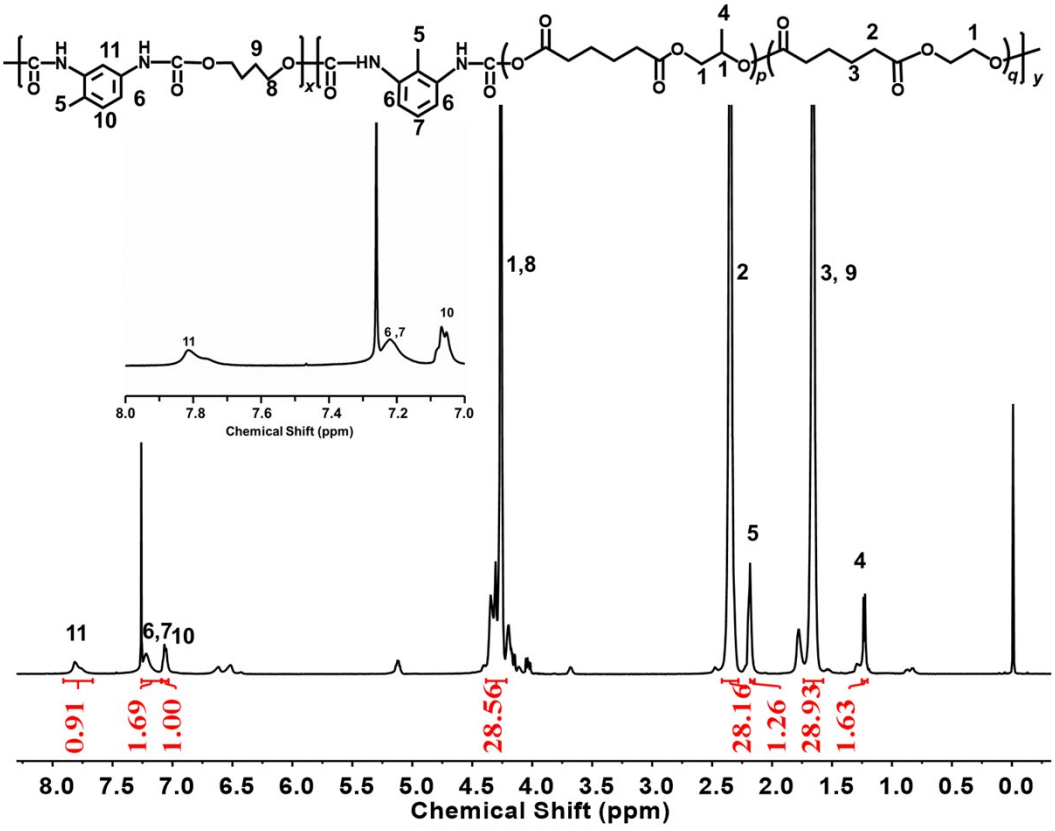

Figure S8. ^{1}H NMR spectra of B_8-PU.

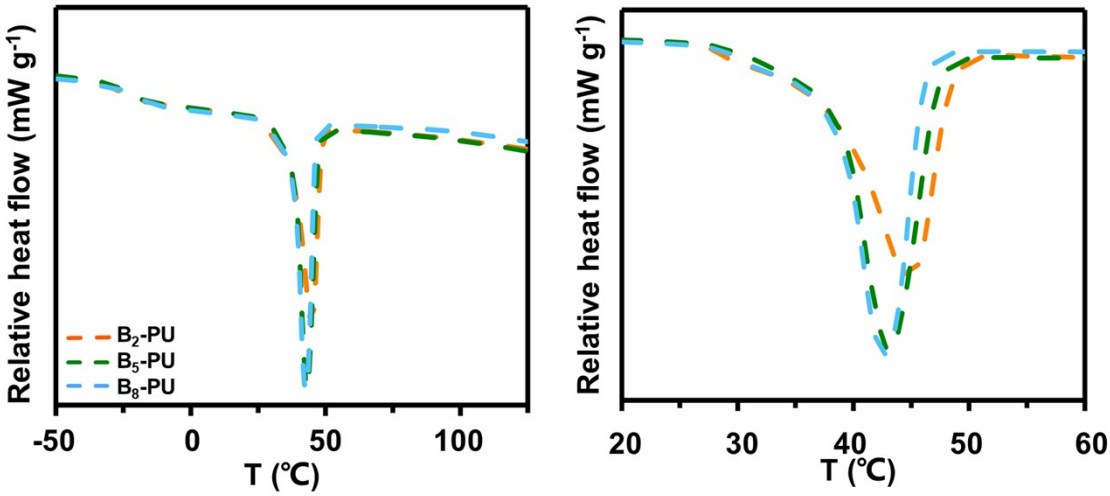

Figure S9. The heating thermograms from the first DSC scan of B_2-PU (orange), B_5-PU (cyan) and B_8-PU (green) samples.

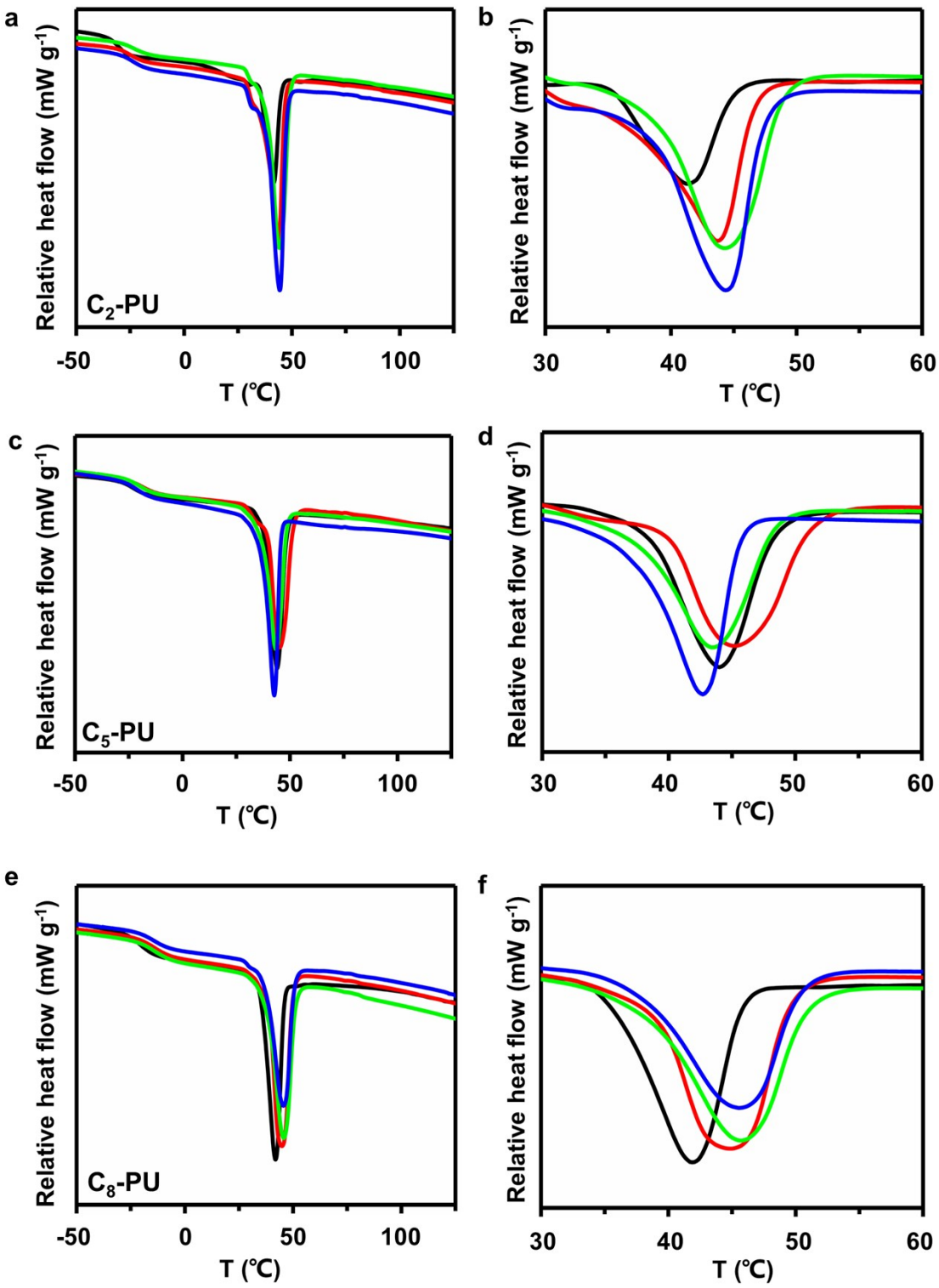

Figure S10. The heating thermograms from the first DSC scan of (a) C_2-PU, (c) C_5-PU and (e) C_8-PU samples before (black) and after illumination for 24 h (red), 48 h (green) and 72 h (blue). Zoom-in images of the results were shown in (b), (d) and (f) for C_2-PU, C_5-PU and C_8-PU, respectively. The results of these tests are listed in Table S1.

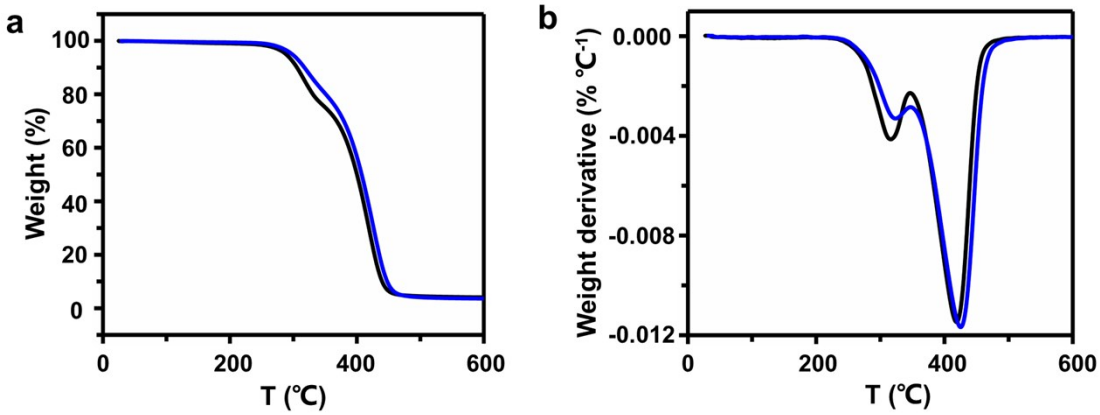

Figure S11. (a) TGA and (b) DTG thermograms of pristine C_8-PU samples (black) and the sample after UV irradiation at 300 nm for 72 h (blue).

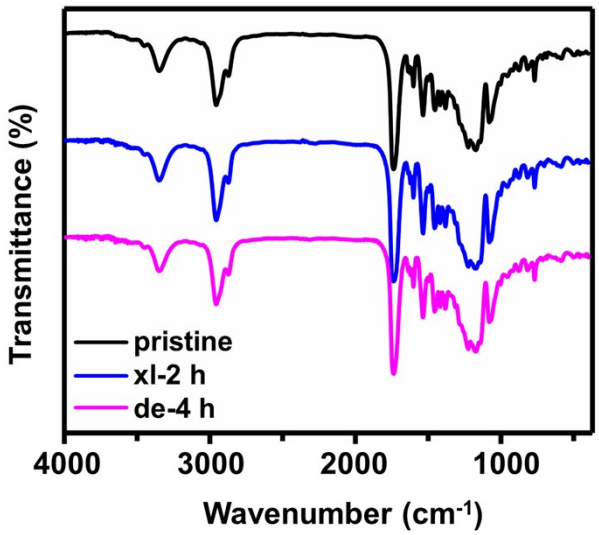

Figure S12. The variation of FT-IR spectra of C_8-PU after UV irradiation at 300 nm and 250 nm.

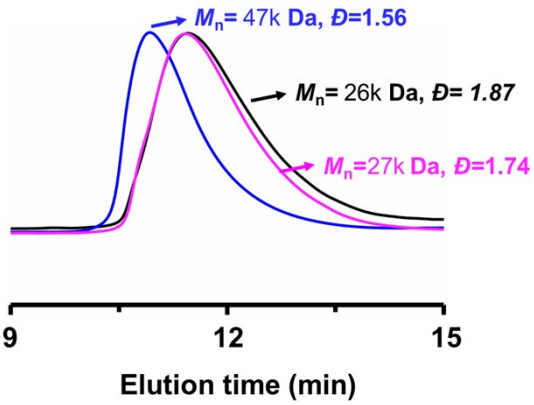

Figure S13. GPC traces of pristine C_8-PU (black), after UV irradiation at 300 nm for 24 h (blue), and then UV irradiation at 250 nm for another 48 h (pink).

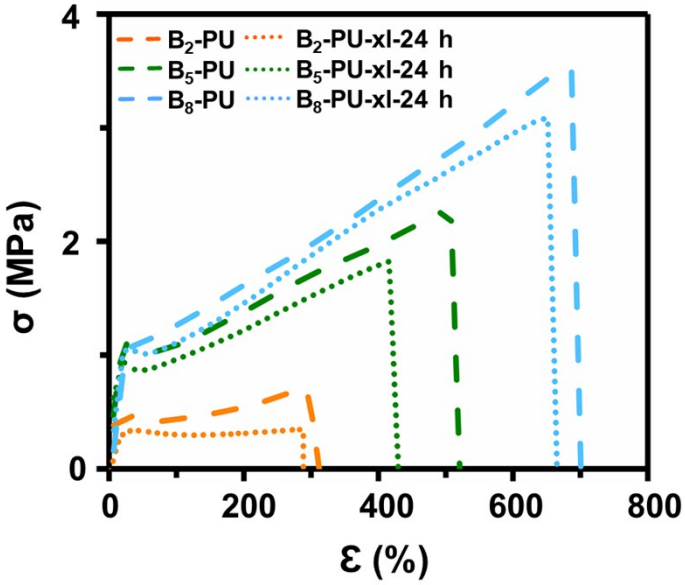

Figure S14. The strain-stress curves of B-PU samples before (dash) and after (dot) UV irradiation at 300 nm for 24 h.

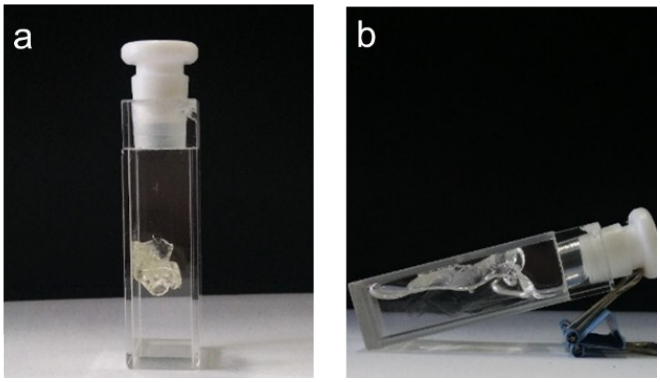

Figure S15. Photographs of a small piece of C_8-PU after UV irradiation at 300 nm for 120 h (a), and after dipped in THF for overnight (b).

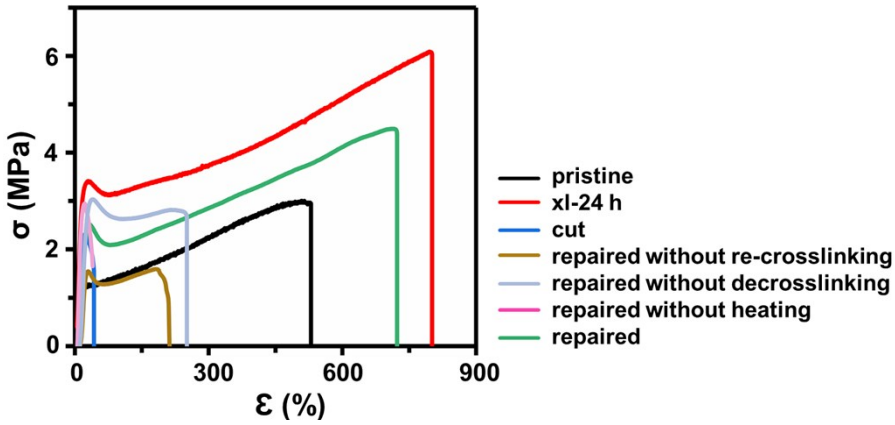

Figure S16. Stress-strain curves of pristine C_8-PU specimen (pristine, black); after UV-irradiation at 300 nm for 24 h (xl-24 h, red); then damaged with a cut in the middle (cut, blue); after 250 nm UV irradiation for 24 h and heating at 60 ℃ for 3 min but no 300 nm UV irradiation (repaired without re-crosslinking, brown); after heating, without 250 nm UV irradiation, after 300 nm UV irradiation for 24 h (repaired without decrosslinking, gray); without heating, after 250 nm UV irradiation for 24 h and 300 nm UV irradiation for 24 h (repaired without heating, pink); and after 250 nm UV irradiation for 24 h, heating at 60 ℃ for 3 min and 300 nm UV irradiation for 24 h (repaired, green).

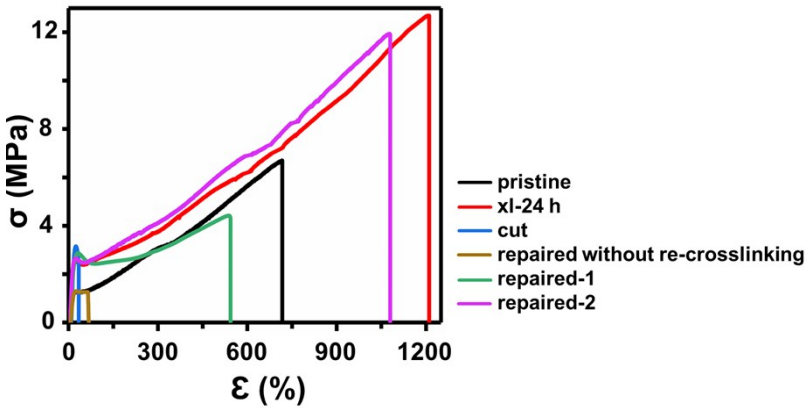

Figure S17. Stress-strain curves of pristine C_5-PU specimen (pristine, black); specimen after UV- irradiation at 300 nm for 24 h (xl-24h, red); crosslinked specimen with a cut in the middle (cut, blue); after 250 nm UV irradiation for 24 h and heating at 60 ℃ for 3 min but no 300 nm UV irradiation (repaired without re-crosslinking, brown); damaged specimen after 250 nm UV irradiation for 24 h, heating at 60 ℃ for 3 min and 300 nm UV irradiation for 24 h (repaired-1, green); damaged specimen after 250 nm UV irradiation for 24 h, heating at 60 ℃ for 3 min and 300 nm UV irradiation for 120 h (repaired-2, purple).

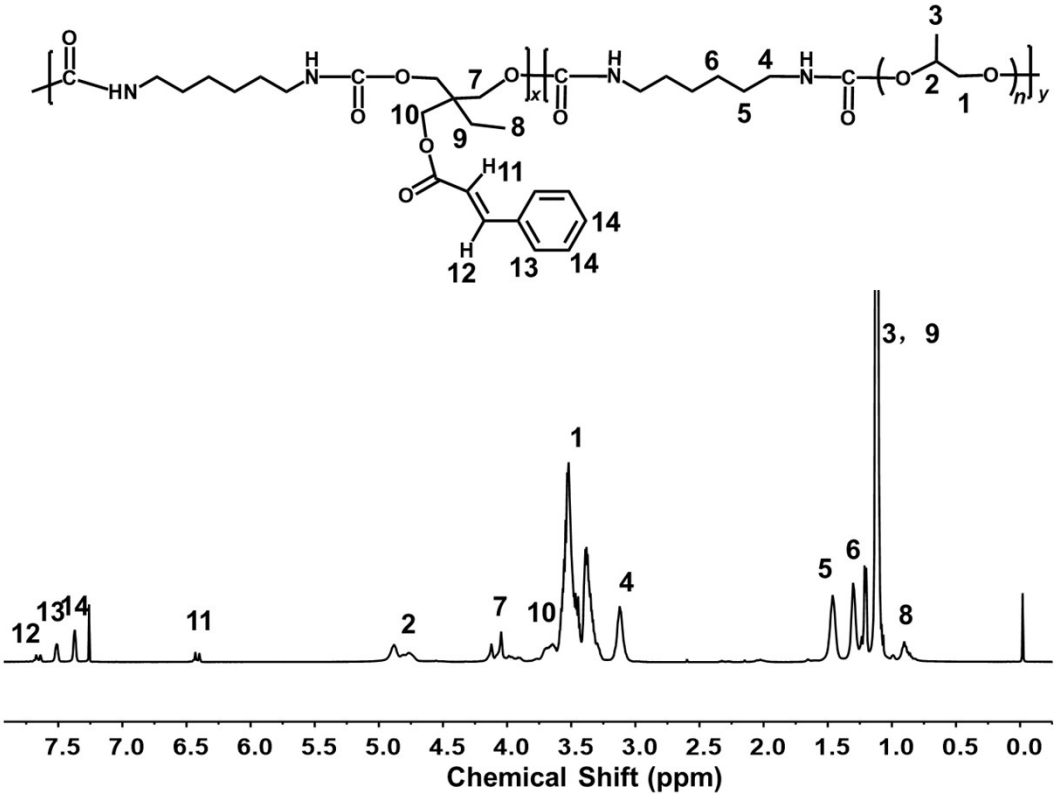

Figure S18. ^{1}H NMR spectra of PPG-PU.

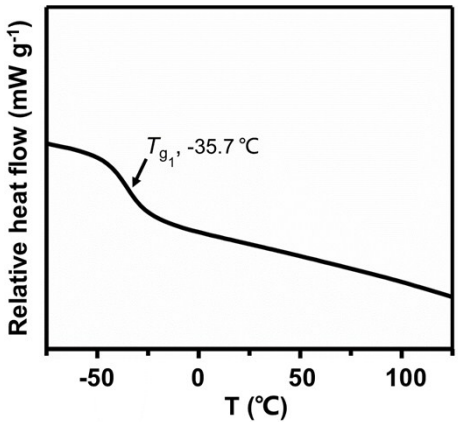

Figure S19. DSC trace of PPG-PU.

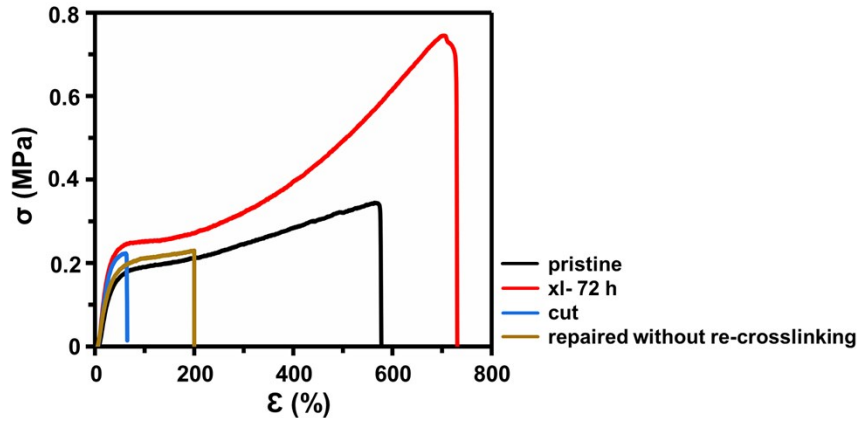

Figure S20. Stress-strain curves of pristine PPG-PU specimen (pristine, black); specimen after UV-irradiation at 300 nm for 72 h (xl-72 h, red); crosslinked specimen with a cut in the middle (cut, blue); after 250 nm UV irradiation for 24 h and heating at 60 ℃ for 3 min but no 300 nm UV irradiation (repaired without re-crosslinking, brown).

Table S1. Thermal properties obtained from the first heating scan of C-PU samples with irradiation at 300 nm for different time via DSC.

	sample	T_m / ℃	Δ H_m / J g^{-1}	crystallinity / %
C_2-PU	**pristine**	41.37	15.57	22.43
	300 nm-24 h	43.69	31.92	45.97
	300 nm-48 h	44.33	36.67	52.82
	300 nm-72 h	44.35	37.41	53.88
C_5-PU	**pristine**	44.20	28.82	43.72
	300 nm-24 h	45.34	33.22	50.39
	300 nm-48 h	43.52	28.92	43.87
	300 nm-72 h	42.70	29.10	44.14
C_8-PU	**pristine**	41.86	23.65	37.90
	300 nm-24 h	45.01	30.11	48.25
	300 nm-48 h	45.69	29.52	47.30
	300 nm-72 h	45.54	26.85	43.02

T_m: The melting temperature of the crystalline portion

ΔH_m (J g^{-1}): The melting enthalpy of the crystalline portion

Table S2. Thermal properties of C-PU samples.

sample	DSC 2nd run		TGA	
	T_{g_1} / ℃	T_{g_2} / ℃	T_{d_1} / ℃	T_{d_2} / ℃
C_2-PU	-31.5	85.1	309.2	410.3
C_5-PU	-27.5	85.8	311.8	410.4
C_8-PU	-21.7	86.3	319.3	418.9

T_d: Peak decomposition temperature obtained from DTG curves.

Table S3. The mechanical properties of pristine B-PU samples.

	B-PU		
	B_2-PU	**B_5-PU**	**B_8-PU**
σ / MPa	0.63±0.06	2.08±0.33	3.55±0.33
ε / %	286±17	503±11	670±98

Table S4. The mechanical properties of C-PUs before and after UV irradiation for different period of time.

	C_2-PU		**C_5-PU**		**C_8-PU**	
	σ / MPa	**ε / %**	**σ / MPa**	**ε / %**	**σ / MPa**	**ε / %**
pristine	1.18±0.18	239±15	6.58±0.92	683±34	3.19±0.43	513±66
xl-24 h	3.08±0.26	406±17	13.23±0.40	1199±23	5.86±0.32	798±10
xl-48 h	5.53±0.60	683±46	15.03±0.63	1291±1	6.64±0.39	924±42
xl-72 h	6.92±0.39	831±32	16.61±0.58	1355±48	7.34±0.22	1086±8
de-24 h	5.16±0.10	712±15	12.75±0.82	1198±90	5.93±0.69	794±25
de-48 h	4.74±0.08	570±27	10.57±0.26	898±53	4.90±0.25	669±13
de-72 h	4.06±0.51	395±16	9.19±0.78	701±12	3.91±0.04	545±32
re-xl -72 h	7.96±0.71	806±56	14.20±1.38	1301±59	7.51±0.38	1038±54
re-de -72 h	6.26±0.33	612±42	12.36±0.06	1124±61	5.47±0.19	670±7

Table S5. The toughness and Young's modulus of C-PUs after 300 nm UV irradiation.

	C_2-PU		C_5-PU		C_8-PU	
	Toughness / MJ m^{-3}	**Young's Modulus / MPa**	**Toughness / MJ m^{-3}**	**Young's Modulus / MPa**	**Toughness / MJ m^{-3}**	**Young's Modulus / MPa**
pristine	1.99±0.35	7.81±4.66	25.72±4.87	13.20±6.11	12.60±3.02	12.63±3.86
xl-24 h	9.21±1.04	18.58±3.65	87.40±6.98	19.21±2.29	33.02±1.24	19.30±2.71
xl-48 h	27.87±3.37	20.58±7.83	103.02±3.06	27.00±6.31	40.80±3.98	20.96±5.08
xl-72 h	40.74±5.52	31.80±6.04	119.92±9.87	27.58±3.78	50.60±1.12	24.37±373

Table S6. Components and molecular characteristics of PPG-PU.

Polymer	**Soft segment**	**Diisocyanate**	**Chain extender**	M_n	*Đ*
PPG-PU	**PPG / g (mmol)**	**HDI / g(mmol)**	**CTMP / g (mmol)**	M_n / **Da**	**Đ**
	10.07 (10.07)	3.67 (21.85)	3.07 (11.62)	20 k	1.75

Table S7. The mechanical properties of PPG-PUs after 300 nm UV irradiation.

	σ / MPa	**ε / %**	**Toughness / MJ m^{-3}**	**Young's Modulus / MPa**
pristine	0.36±0.02	483±76	1.24±0.23	0.45±0.05
xl-24 h	0.42±0.01	591±67	1.76±0.17	0.51±0.08
xl-48 h	0.56±0.04	682±25	2.41±0.12	0.65±0.10
xl-72 h	0.76±0.08	742±29	3.09±0.07	0.79±0.10

References:

1. J. Ling, M. Z. Rong and M. Q. Zhang, *Polymer*, 2012, **53**, 2691-2698.