Supporting Information

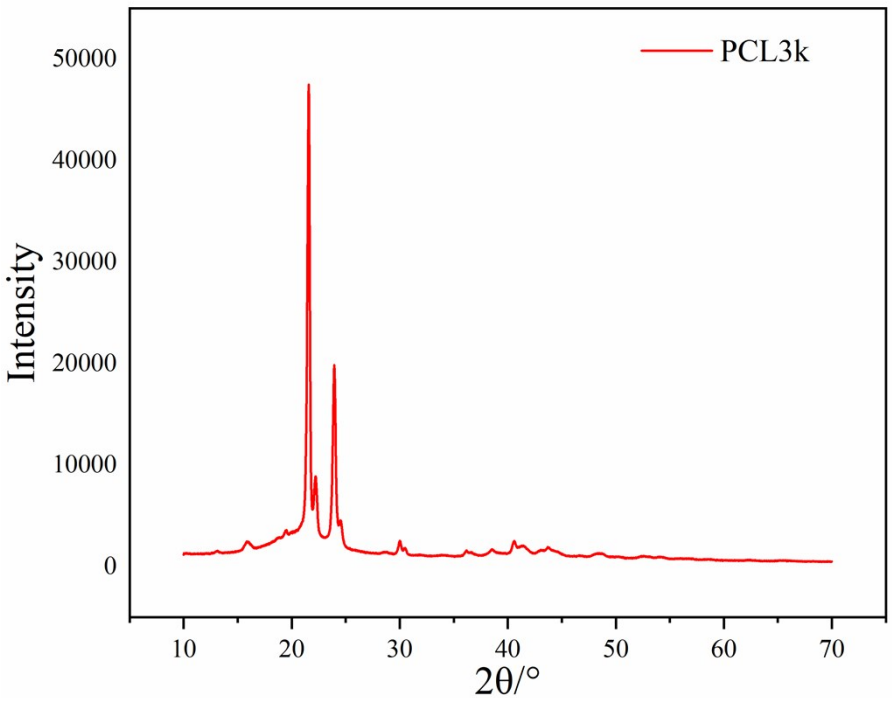

Figure S1. The XRD spectrum of PCL3k

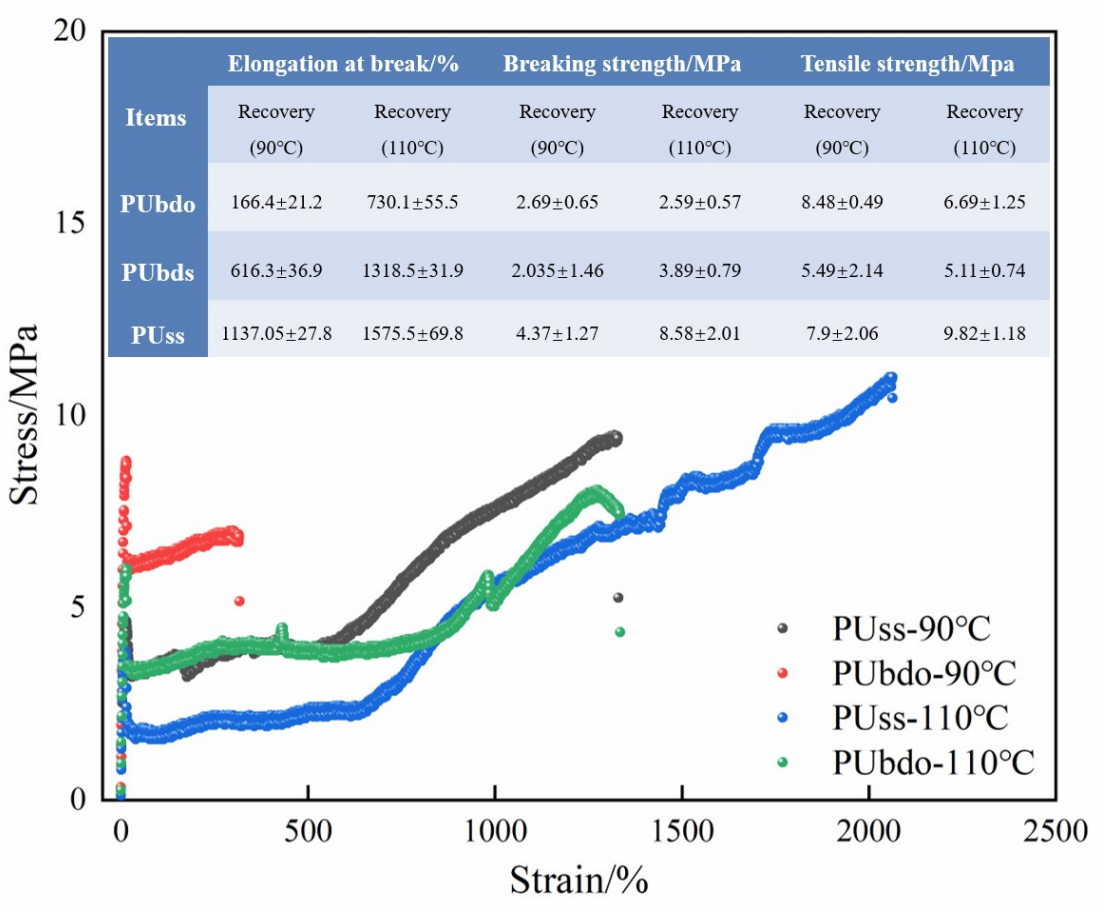

Figure S2. The strain-stress curves of self-healable PUss and PUbdo under 110˚C/90˚C, and the insert table recorded the elongation at break, breaking strength and tensile strength of recovery samples.

Table S1. Composition of PUs.

Samples	PCL-diol/g	HDI/g	SS/g	BDO/g	TMPMP/g	HS/g	HS/wt%	PCL/wt%
PUbdo	30	3.7	0	0.43	1.91	6.04	16.76	83.24
PUbds	30	3.7	0	0.74	1.91	6.35	17.47	82.53
PUss	30	3.7	1.2	0	1.91	6.81	18.50	77.28
PU2ss	30	4.51	2.4	0	1.91	8.01	21.07	78.93
PUbdo-HS	0	2.02	0	0.43	1.91	4.36		
PUbds-HS	0	2.02	0	0.74	1.91	4.67		
PUss-HS	0	2.02	1.2	0	1.91	5.13		

Table S2. FTIR assignments, bands percentage areas of PUs and the calculated relevant parameters for determination of microphase separation in PUs.

Peak/cm^{-1}	Associations	PCL3k	PUbdo	PUbds	PUss
1680	Ordered H-bonded carbonyl (PU)		8.21%	10.86%	0.86%
1700	Disordered H-bonded carbonyl (PU)		23.99%	29.23%	23.26%
1716	H-bonded carbonyl (PCL)	53.95%	22.11%	4.99%	24.06%
1721	Bonded carbonyl (PCL)	34.44%	7.91%	11.71%	6.18%
1730	Free carbonyl (PU)		30.90%	33.77%	37.69%
1738	Free carbonyl (PCL)	11.61%	6.88%	9.44%	7.95%
X_b (the weight fraction of H-bonded urethane groups)			0.379	0.410	0.272