

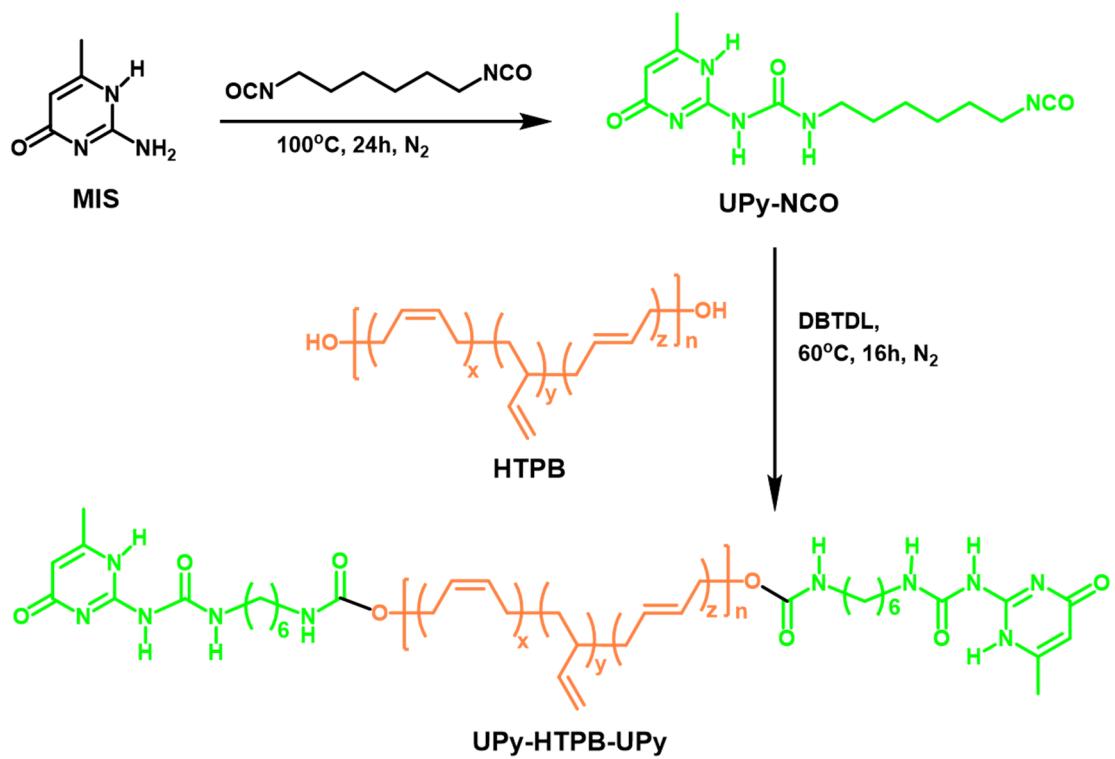
Supplementary

Room temperature solid-state UV cross-linkable vitrimer-like polymers for additive manufacturing

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Scheme S1. Synthetic route of UPy-HTPB-UPy.

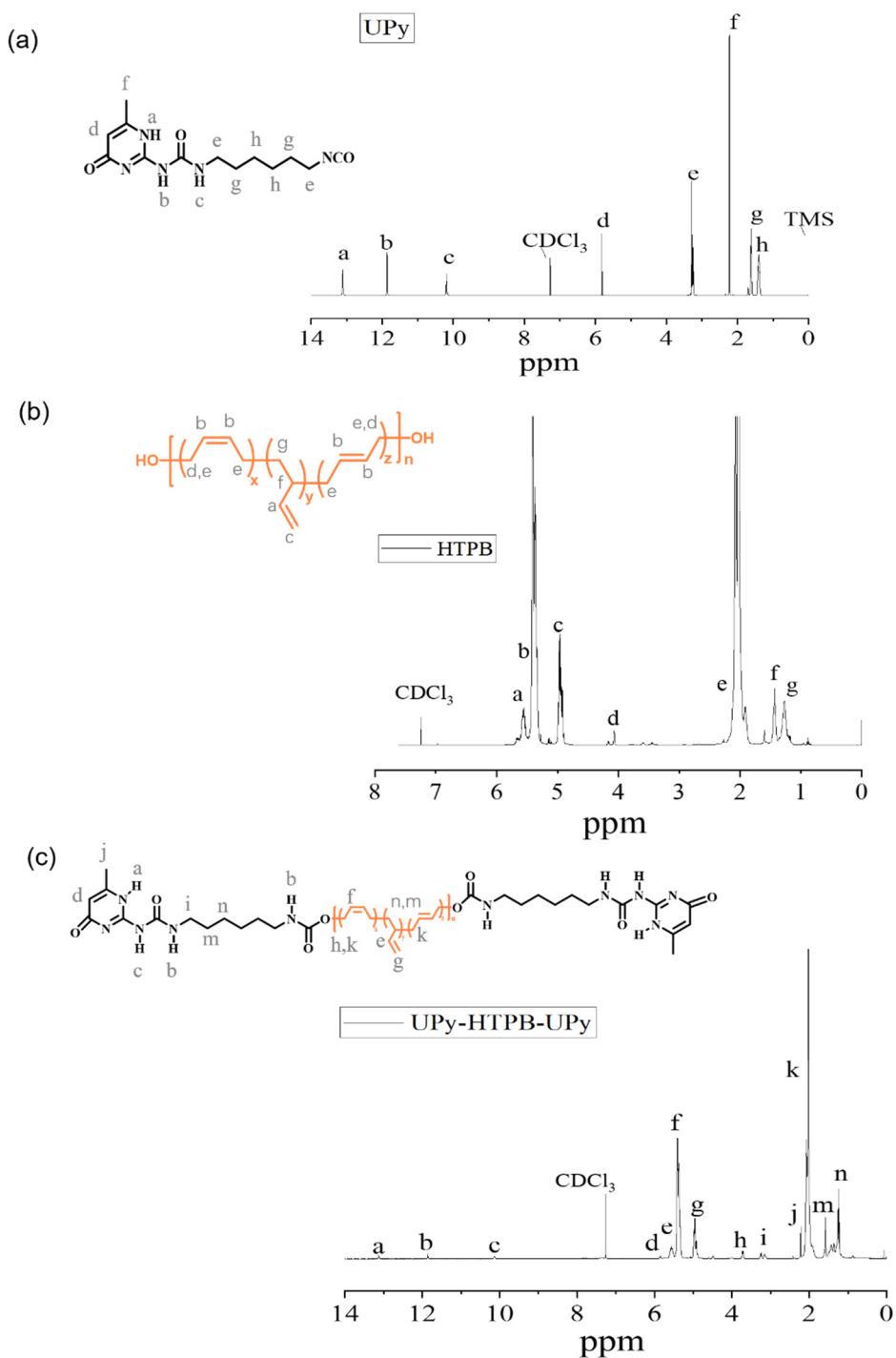


Figure S1. ^1H NMR results of (a) UPy-NCO, (b) HTPB, and (c) UPy-HTPB-UPy confirm that UPy unites are connected to HTPB.

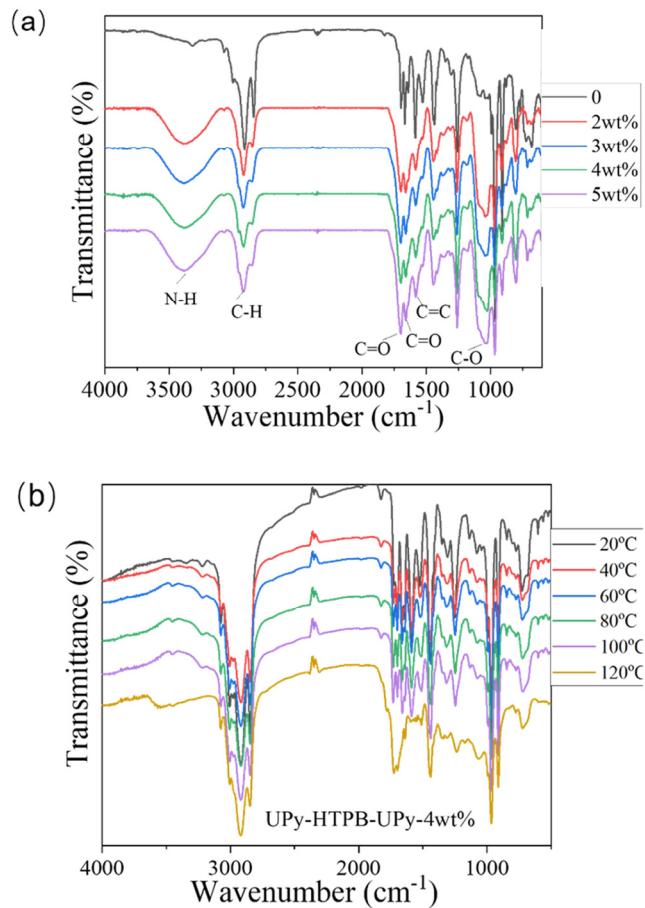


Figure S2. (a) FTIR spectra of C-UPy-HTPB-UPy-*n*wt% films with different weight content of photo initiator (*n* = 0%, 2%, 3%, 4% and 5%); (b) FTIR spectra of UPy-HTPB-UPy-4wt% at different temperatures.

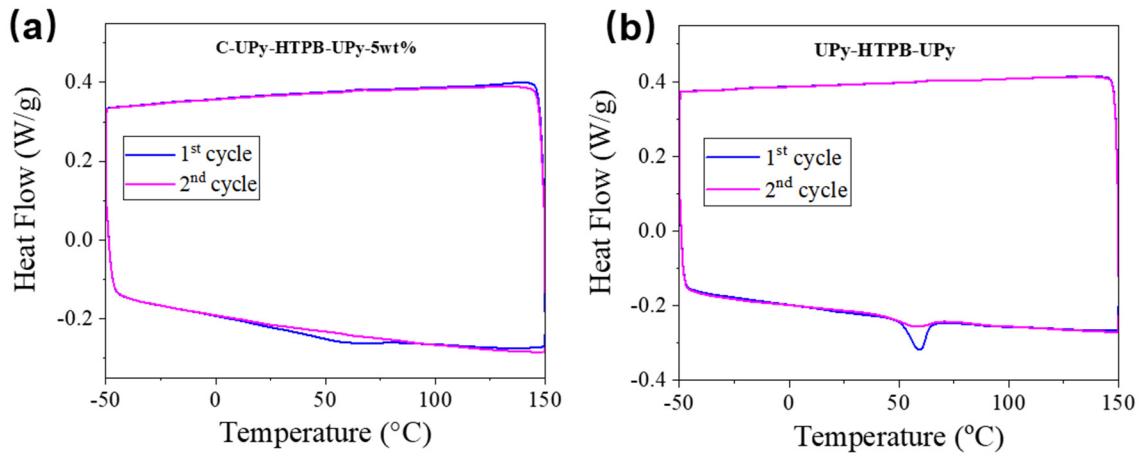


Figure S3. DSC results of (a) C-UPy-HTPB-UPy-5wt% and (b) UPy-HTPB-UPy.

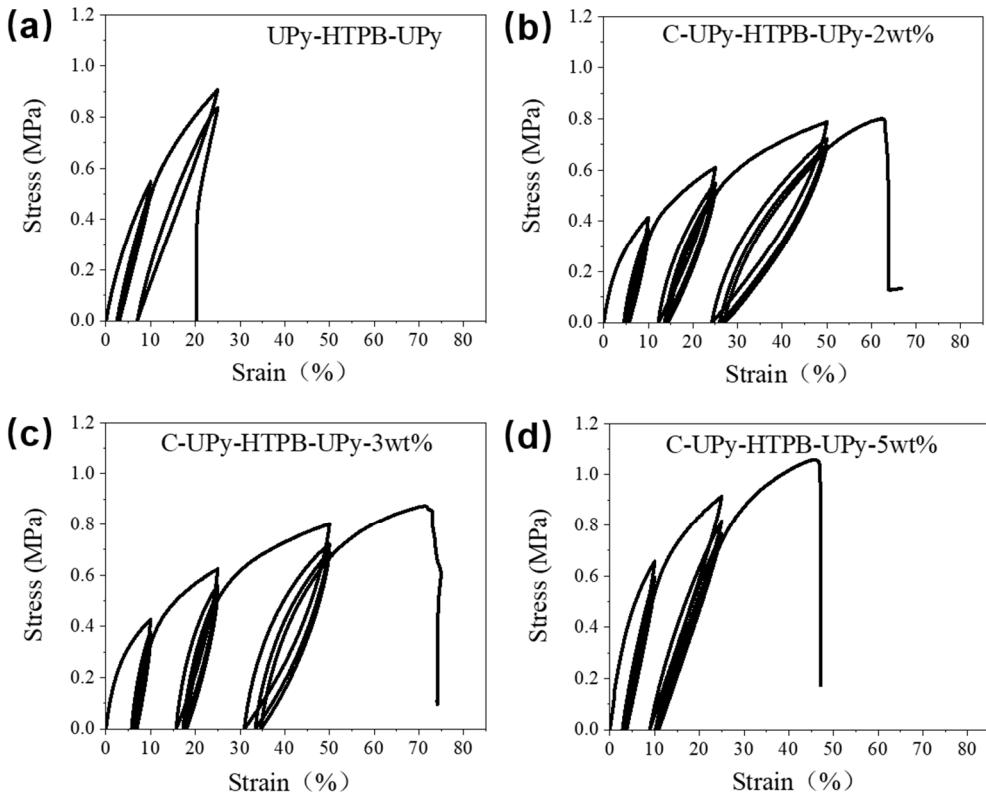


Figure S4. Cyclic uniaxial tension results of (a) UPy-HTPB-UPy and (b)-(e) C-UPy-HTPB-UPy-*n*wt% to 10%, 20%, 50%, and finally 70% strain (three cycles at each prescribed strain) (all samples were cross-linked under 25 W 365 nm UV light for 2 h).

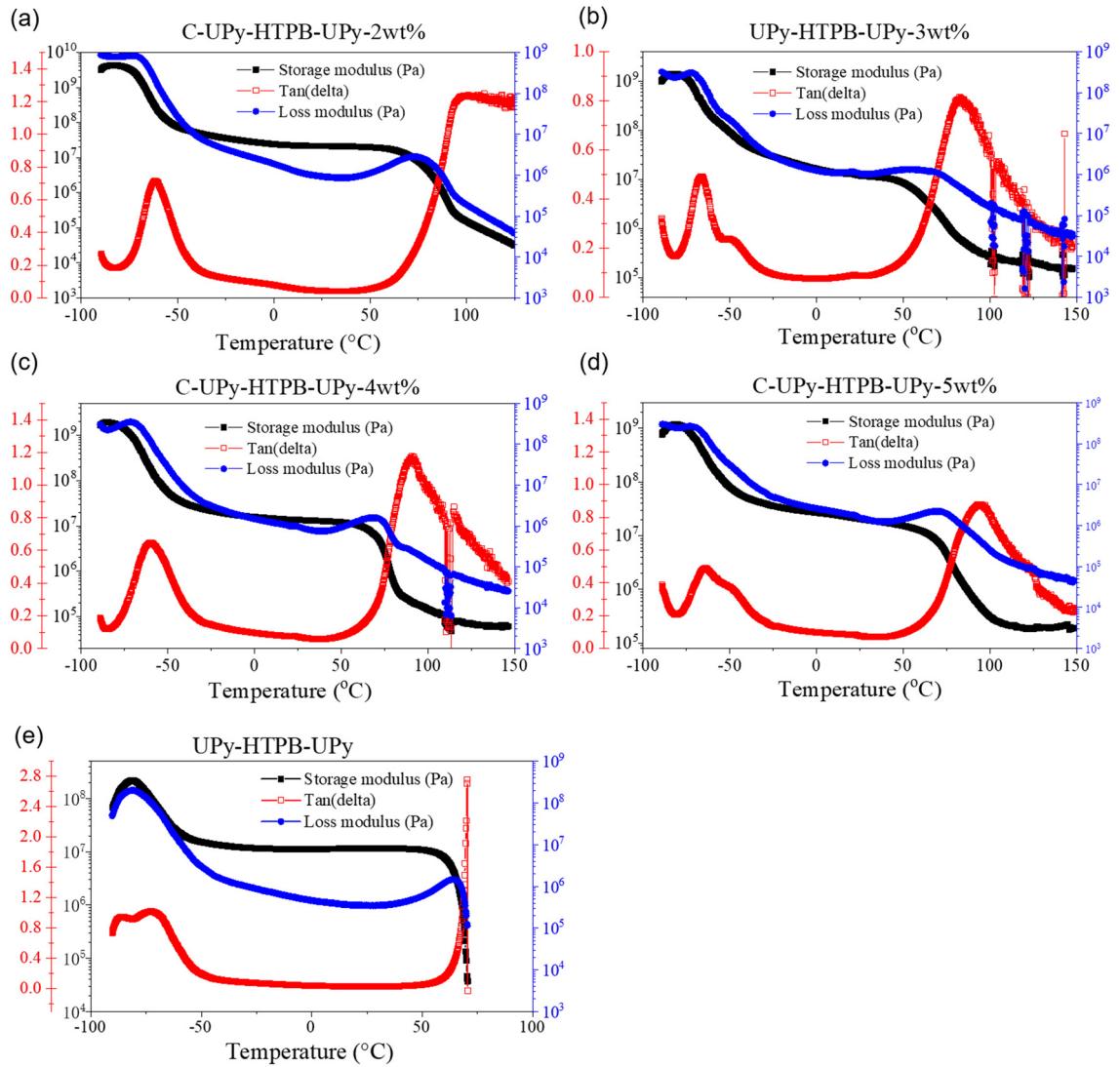


Figure S5. DMA results of (a)~(d) C-UPy-HTPB-UPy-*n*wt% (*n*=2,3,4,5) and (e) UPy-HTPB-UPy.

Table S1. Uniaxial tension to fracture of C-UPy-HTPB-UPy-*n*%.

<i>n</i>	2	3	4	5
Fracture stress σ (MPa)	0.84±0.05	0.98±0.09	1.05±0.02	1.15±0.02
Fracture strain ϵ (%)	56.7±4.2	67.9±2.7	78.1±6.96	50.1±3.0

Table S2. Shape fixation ratio (R_f) and shape recovery ratio (R_r) of C-UPy-HTPB-UPy-*n*% in three shape memory cycles carried out by DMA.

<i>n</i>	2wt%			3wt%			4wt%			5wt%		
	1 st	2 nd	3 rd	1 st	2 nd	3 rd	1 st	2 nd	3 rd	1 st	2 nd	3 rd
R_f (%)	99	99	99	95	87	77	89	83	82	81	73	82
R_r (%)	52	71	50	50	70	65	74	92	92	76	92	94

Movie S1. Demonstration of UV cross-linking in solid state at room temperature.

<https://www.youtube.com/watch?v=0r3455sb8Lg>