Supporting Information

Super-Tough Self-Healable Multiphasic Supramolecular Plastic via Sequence-Biased Statistical Copolymerization

Woojin Lee[a,b], *Yeong Jun Yu*[c], *Haisu Kang*[d], *Sung Hyun Kwon*[e], *Seung Geol Lee*[e,f], *Jae Woo Chung*[c,*], *and Seung-Yeop Kwak*[a,b,g,*]

[a] Department of Materials Science and Engineering, Seoul National University, 1 Gwanak-ro, Gwanak-gu, Seoul 08826, Republic of Korea

[b] Institute of Engineering Research, Seoul National University, 1 Gwanak-ro, Gwanak-gu, Seoul 08826, Republic of Korea

[c] Department of Materials Science and Engineering, Soongsil University, 369 Sangdo-ro, Dongjak-gu, Seoul, 06978, Republic of Korea

[d] Department of Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States

[e] School of Chemical Engineering, Pusan National University, Busan 46241, Republic of Korea

[f] Department of Organic Material Science and Engineering, Pusan National University, 63 Busandaehak-ro, Geumjeong-gu, Pusan, 46288, Republic of Korea

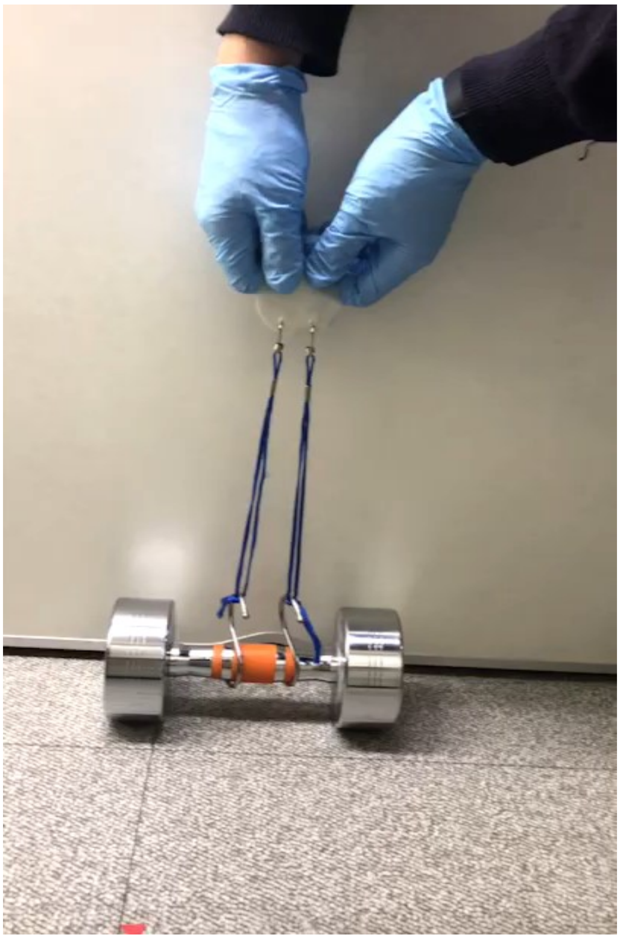
[g] Research Institute of Advanced Materials (RIAM), Seoul National University, 1 Gwanak-ro, Gwanak-gu, Seoul 08826, Republic of Korea

[*] Corresponding authors: **Jae Woo Chung (**E-mail: jwchung@ssu.ac.kr)

Tel: +82-2-828-7047, Fax: +82-2-817-8346

Seung-Yeop Kwak (E-mail: sykwak@snu.ac.kr)

Tel.: +82-2-880-8365, Fax: +82-2-885-1748



Video S1. A video file of the healed USPCD92 enduring a 5-kg dumbbell without any subtle deformation. This video displays the mechanical robustness of healed USPCD92 disk (treated at 50 °C for 10 min) sample when subjected to a high tensile loading. Remarkably, the healed USPCD92 bulk disk lifted a 5-kg dumbbell while maintaining its healed state and original shape.

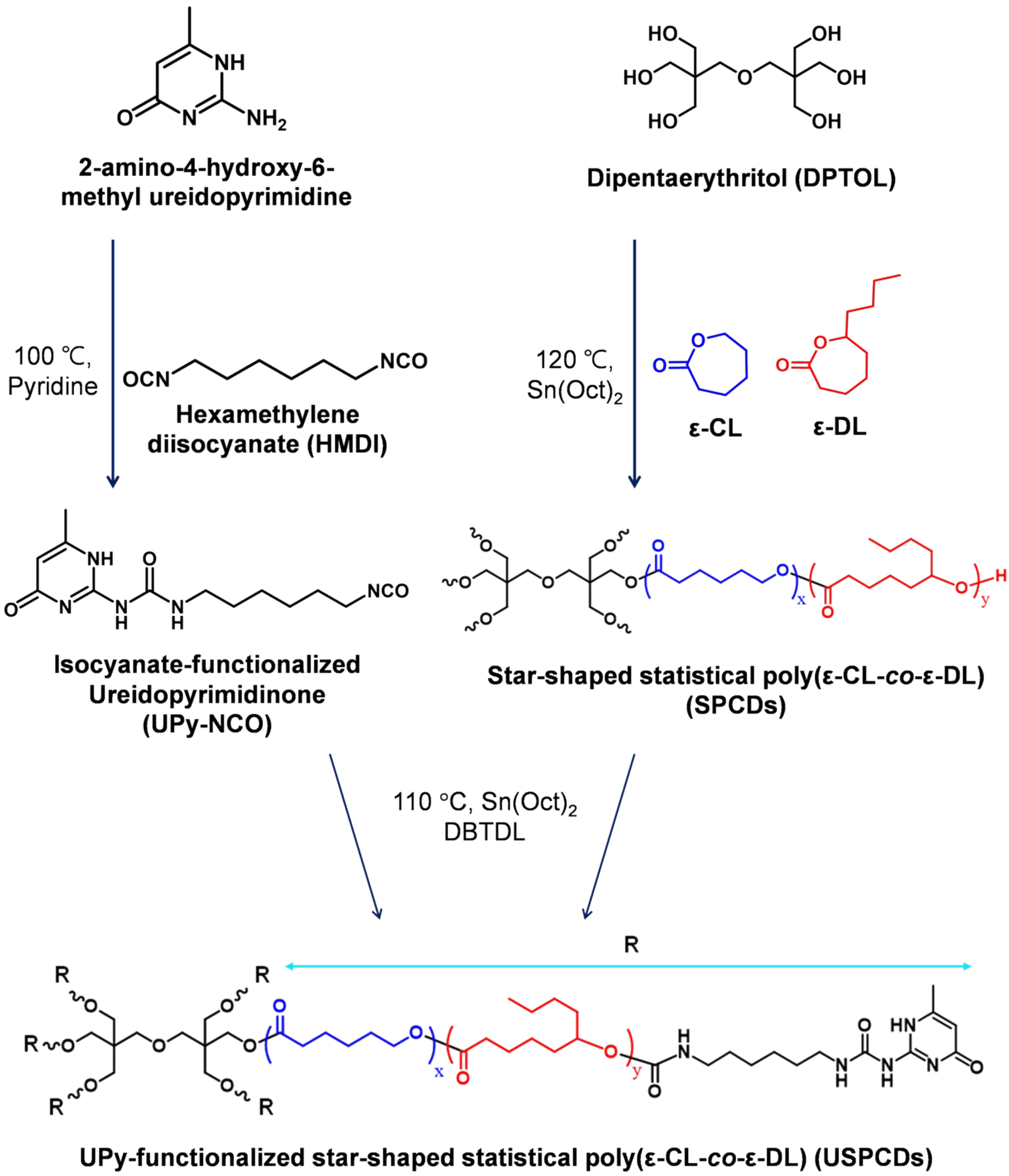


Figure S1. Synthetic routes for UPy-NCO, star-shaped poly(ε-caprolactone-*co*-ε-decalactone)s (SPCDs), and UPy-end functionalized star-shaped poly(ε-caprolactone-*co*-ε-decalactone)s (USPCDs).

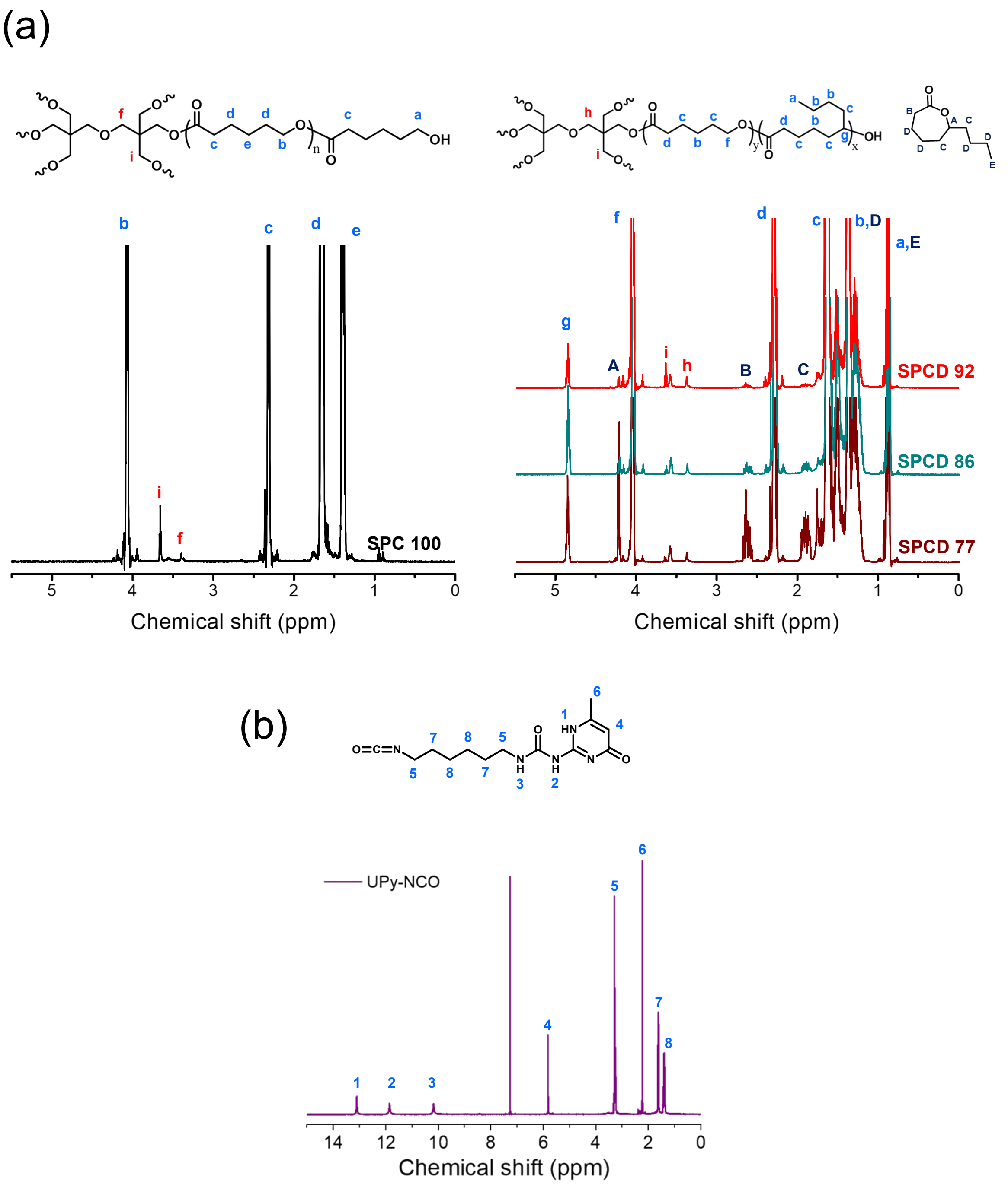


Figure S2. [1]H NMR spectra of a) SPCD100 (black line), USPCD92 (red line), USPCD86 (dark cyan line), USPCD77 (brown line), and b) UPy-NCO with proton resonance peak assignment.

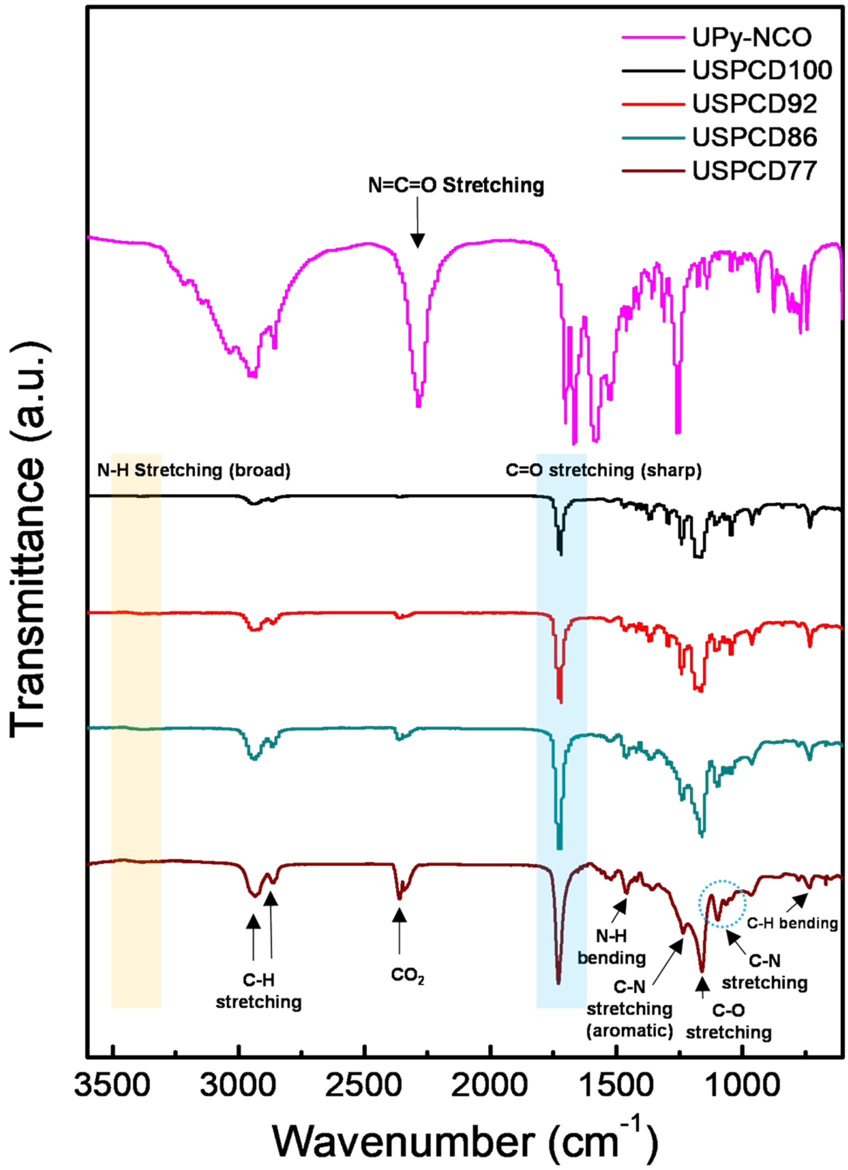


Figure S3. ATR FT-IR spectra of the prepared USPCD series.

Figure S4. Size exclusion chromatography (SEC) traces of the prepared SPCD series.

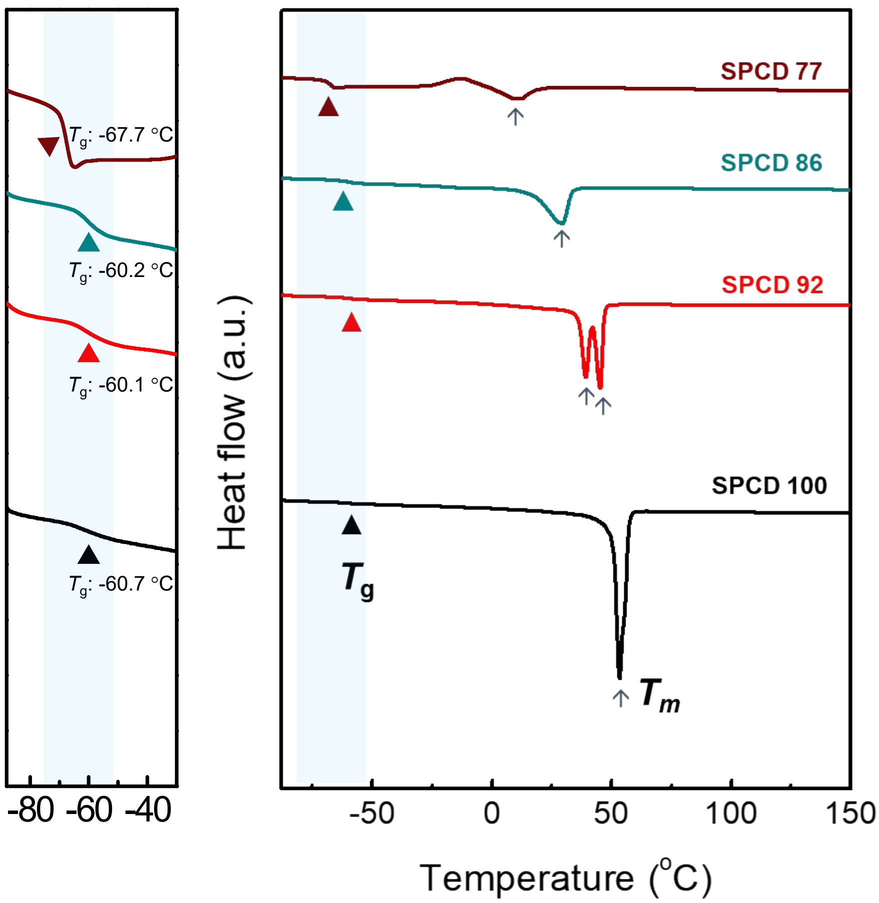


Figure S5. DSC thermograms of the SPCDs acquired during the second heating scan.

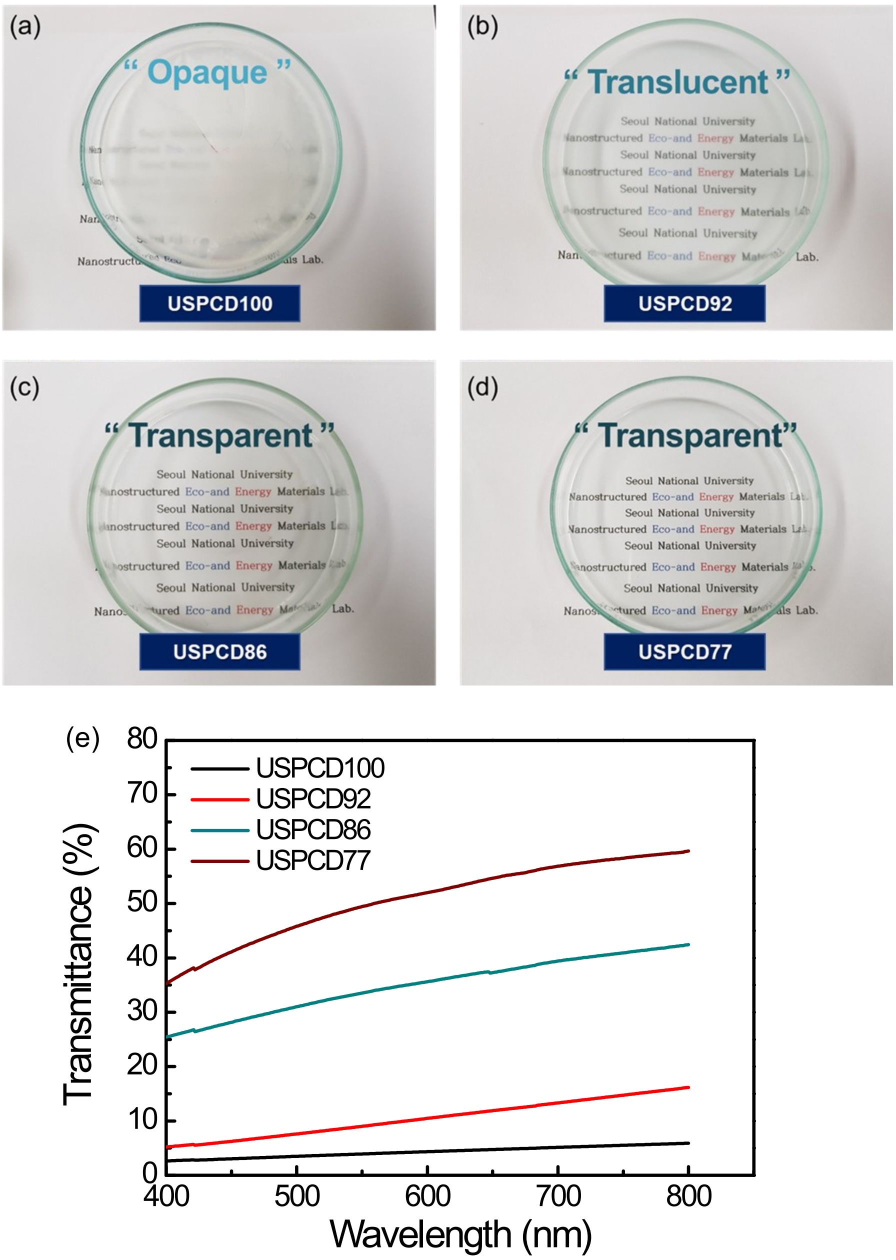


Figure S6. Photographs of solution–casted pristine films of a) USPCD100, b) USPCD92, c) USPCD86, and d) USPCD77. As the arm-chain content of ε-DL increased, a more transparent film of USPCD was formed. e) UV–vis light transmittance for the pristine USCPD series. For all the experimental samples, the sample thickness was estimated as ~ 0.5 mm.

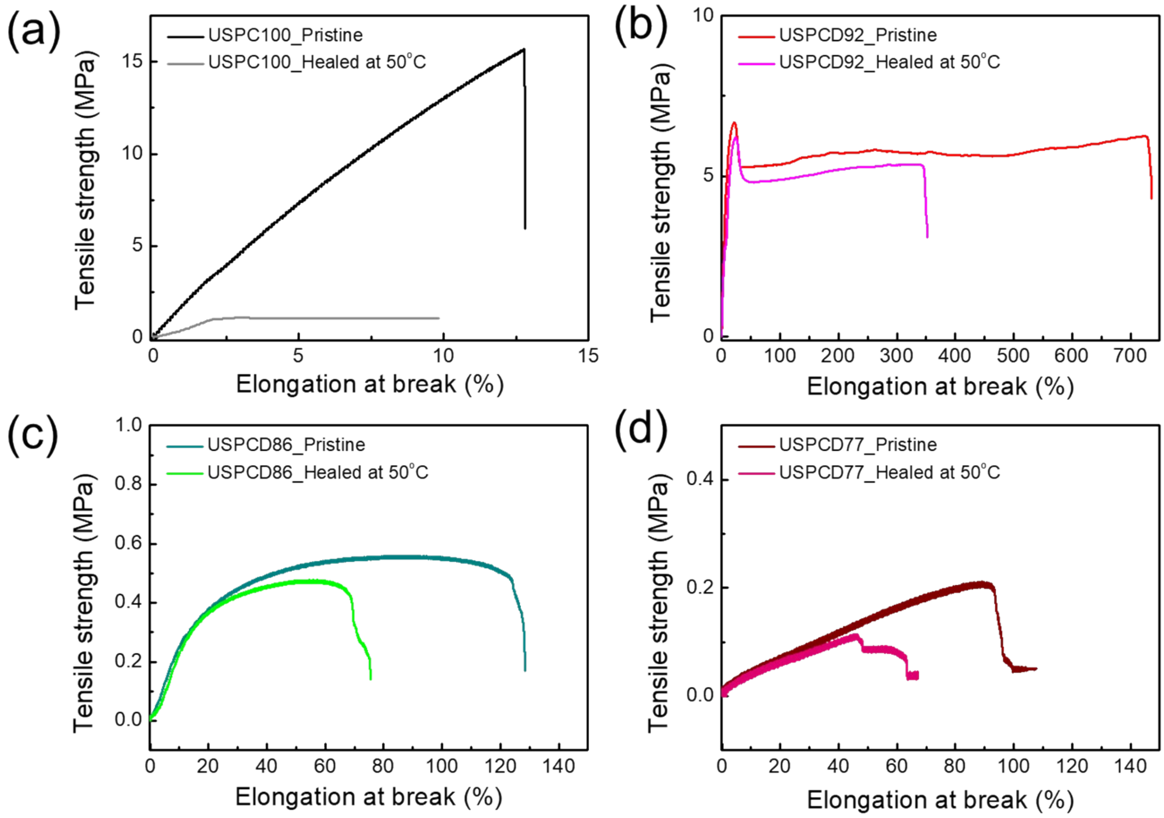


Figure S7. Representative stress−strain curves of the pristine and healed USPCDs: a) USPCD100; b) USPCD92; c) USPCD86; d) USPCD77.

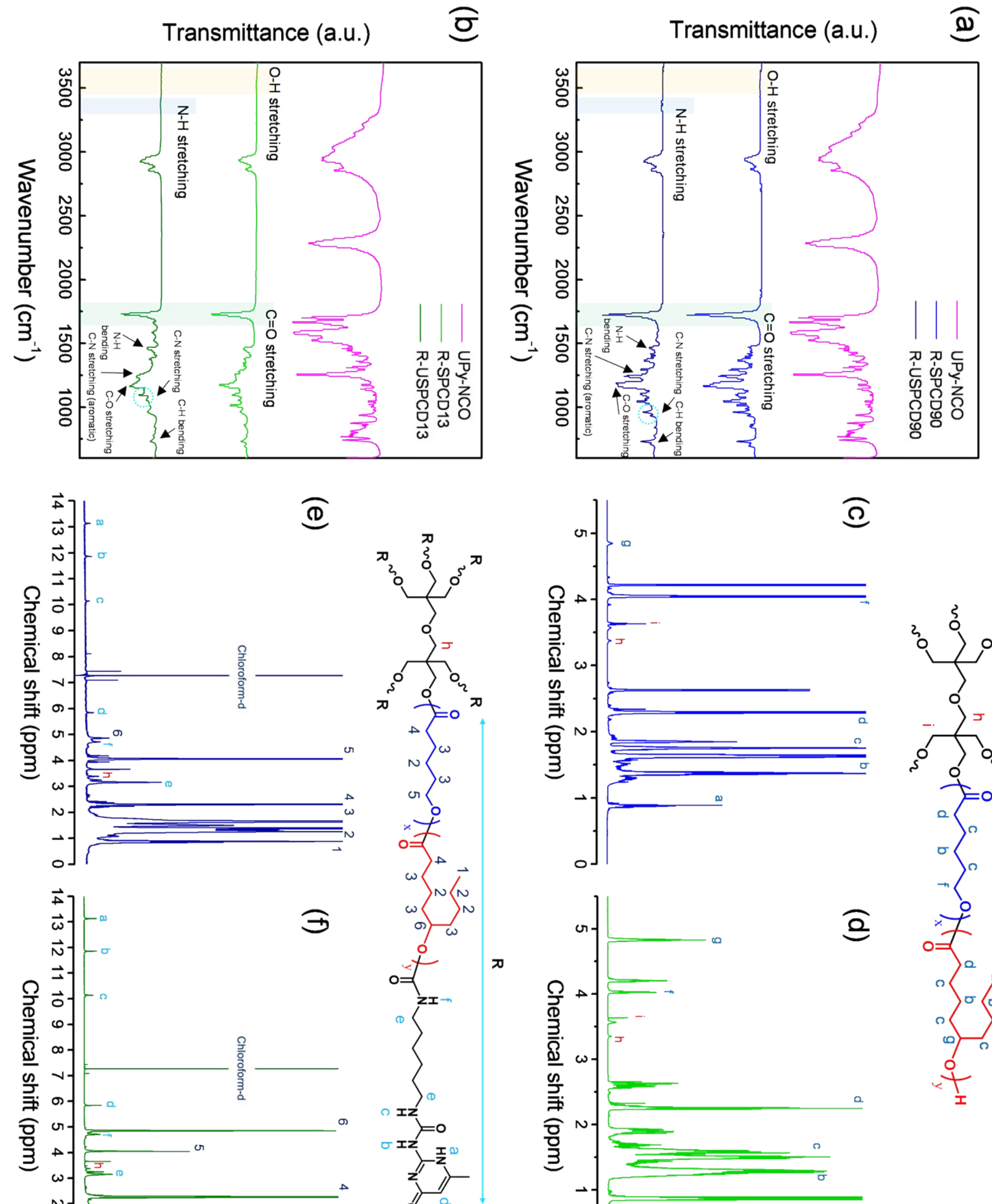


Figure S8. ATR FT-IR spectra of the synthesized a) B-SPDC90 and B-USPDC90 and b) B-SPDC13 and B-USPDC13 samples, showing their characteristic stretching peaks. ^{1}H NMR spectra of the synthesized c) B-SPDC90, d) B-SPDC13 e) B-USPDC90, and f) B-USPDC13 samples with the resonance peak assignment.

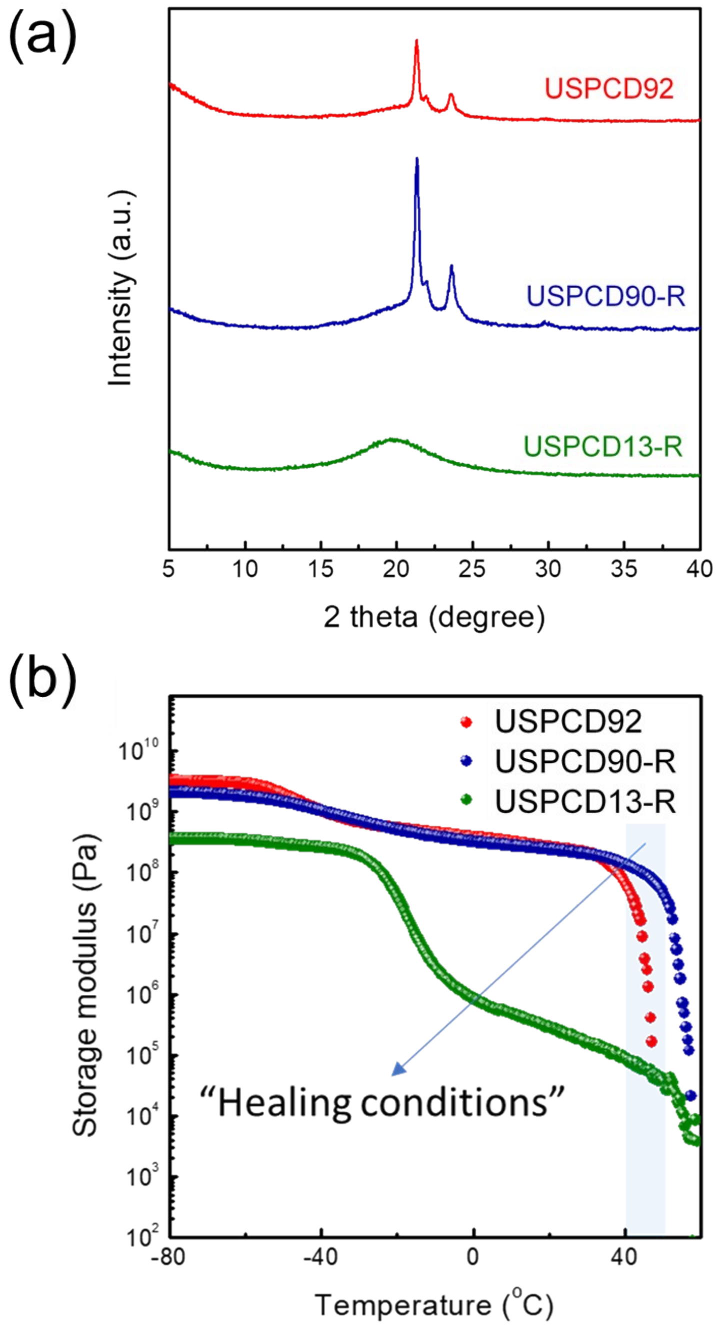


Figure S9. a) WXRD patterns of USPCD92, USPCD90-R, and USPCD13-R at room temperature. b) Storage modulus curves of USPCD92, USPCD90-R, and USPCD13-R with respect to the temperature based on DMA.

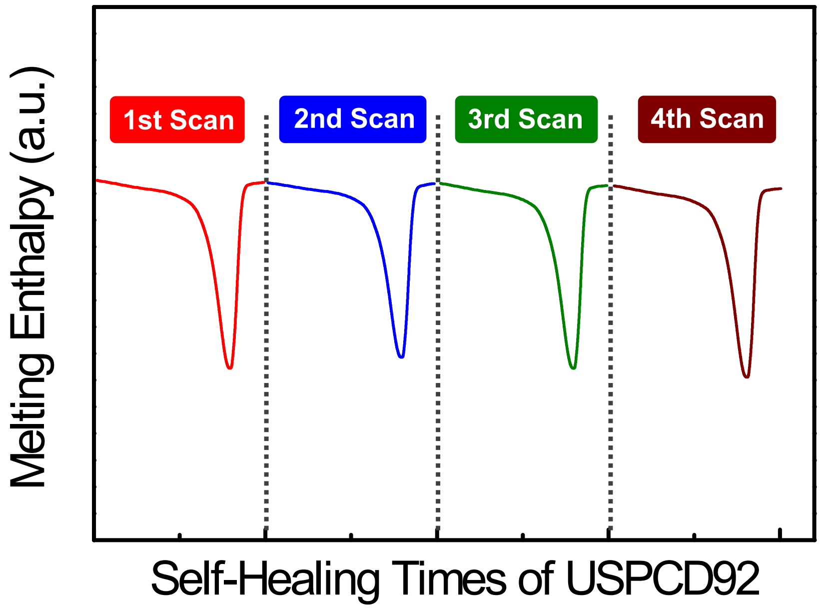


Figure S10. Recovery of crystalline melting enthalpy for USPCD92 after four DSC heating scans. Each experiment was performed after the temperature was reduced to 0 °C at a rate of 10 °C min-1 and then increased to 50 °C (i.e., self-healing temperature), followed by an isothermal step for 10 min (i.e., self-healing time).

Table S1. Molecular characteristics of UPy-end-functionalized star poly(ε-caprolactone-co-ε-decalactone)s (USPCDs)

Sample [a]	Feed molar ratio (mmol) ([ε-CL] / [ε-DL] / [DPTOL])	DP_{arm}	Chain composition (mol%) (DP_{CL} : DP_{DL})	UPy-end functionality (%)	$M_{n,NMR}$ (g/mol)	$M_{n,GPC}$ (g/mol)	M_w/M_n
USPCD 100	180 / 0 / 1	32.33	100 : 0	92.3	24000	48500	1.45
USPCD 92	162 / 18 / 1	34.24	92 : 8	95.2	26200	43700	1.45
USPCD 86	144 / 36 / 1	33.13	86 : 14	95.1	26300	40200	1.49
USPCD 77	126 / 54 / 1	29.90	77 : 23	93.6	24700	32200	1.39

Table S2. Molecular characteristics of SPCDs

Sample	DP_{arm}	DP_{CL}	DP_{DL}	$M_{n,NMR}$ (g/mol)	$M_{n,GPC}$ (g/mol)	M_w/M_n
SPCD 100	32.33	193.98	0	22400	26500	1.62
SPCD 92	34.24	190.26	15.18	24600	31000	1.25
SPCD 86	33.13	168.54	30.24	24650	31500	1.18
SPCD 77	29.90	138.24	41.16	23040	27500	1.10

Table S3. Thermal characteristics of SPCDs

Sample	T_g (^{o}C)	T_m (^{o}C)	ΔH_m (J/g)	T_c (^{o}C)	ΔH_c (J/g)
SPCD100	-60.74	53.47	62.87	28.30	63.32
SPCD92	-60.08	39.25/45.37	39.15	16.98	46.26
SPCD86	-60.15	29.50	23.61	-14.92	30.77
SPCD77	-67.64	11.28	10.41	-	-

Table S4. Thermal characteristics of the synthesized USPCDs

Sample	T_g (°C)	T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)
USPCD100	–55.92	53.64	45.96	26.78	51.51
USPCD92	–55.12	38.87	24.67	–4.23	28.28
USPCD86	–57.94	21.93	14.61	–33.18/–23.93	12.78/3.20
USPCD77	–57.85	n.a.	n.a.	n.a.	n.a.

Table S5. Macroscopic mechanical properties of the prepared USPCDs

Sample	Tensile strength σ (MPa)	Elongation at break ε (%)	Tensile toughness η (MJ m^{-3})
USPCD100	14.35 ± 3.43	12.44 ± 1.55	0.99 ± 0.38
USPCD92	6.94 ± 0.45	722.19 ± 13.35	43.89 ± 3.97
USPCD86	0.69 ± 0.24	149.51 ± 19.60	0.79 ± 0.19
USPCD77	0.23 ± 0.10	145.21 ± 24.24	0.22 ± 0.07

Table S6. Repulsion parameters (a_{ij}) based on Flory–Huggins parameters

	M	A	B	C	H
M	25.00	26.01	25.02	28.03	50.89
A		25.00	26.27	25.39	37.48
B			25.00	28.43	51.37
C				25.00	33.91
H					25.00

Table S7. Molecular characteristics of USPCD92 and its experimental counterparts

Sample [a]	Feed molar ratio (mmol) ([ε-CL] / [ε-DL] / [DPTOL])	DP_{arm}	Chain composition (mol%) (DP_{CL} : DP_{DL})	UPy-end functionality (%)	$M_{n, NMR}$ (g/mol)
USPCD92	162 / 18 / 1	34.24	92 : 8	95.2	26200
USPCD90-R	162 / 18 / 1	34.08	90 : 10	91	26300
USPCD13-R	18 / 162 / 1	30.62	13 : 87	93	31800

Table S8. Thermal and mechanical properties of USPCD92 and its experimental counterparts

Sample [a]	T_g (°C)	T_m (°C)	ΔH_m (J/g)	Tensile strength σ (MPa)	Elongation at break ε (%)
USPCD 92	-55.12	38.87	24.67	6.94 ± 0.45	722.19 ± 13.35
USPCD90-R	-56.58	48.81	40.45	3.19 ± 0.45	7.02 ± 1.01
USPCD13-R	-44.04	-	-	0.14 ± 0.01	292.88 ± 26.11