Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Simultaneously achieving superior foldability, mechanical strength and toughness for transparent healable polysiloxane films through building hierarchical crosslinked networks and dual dynamic bonds

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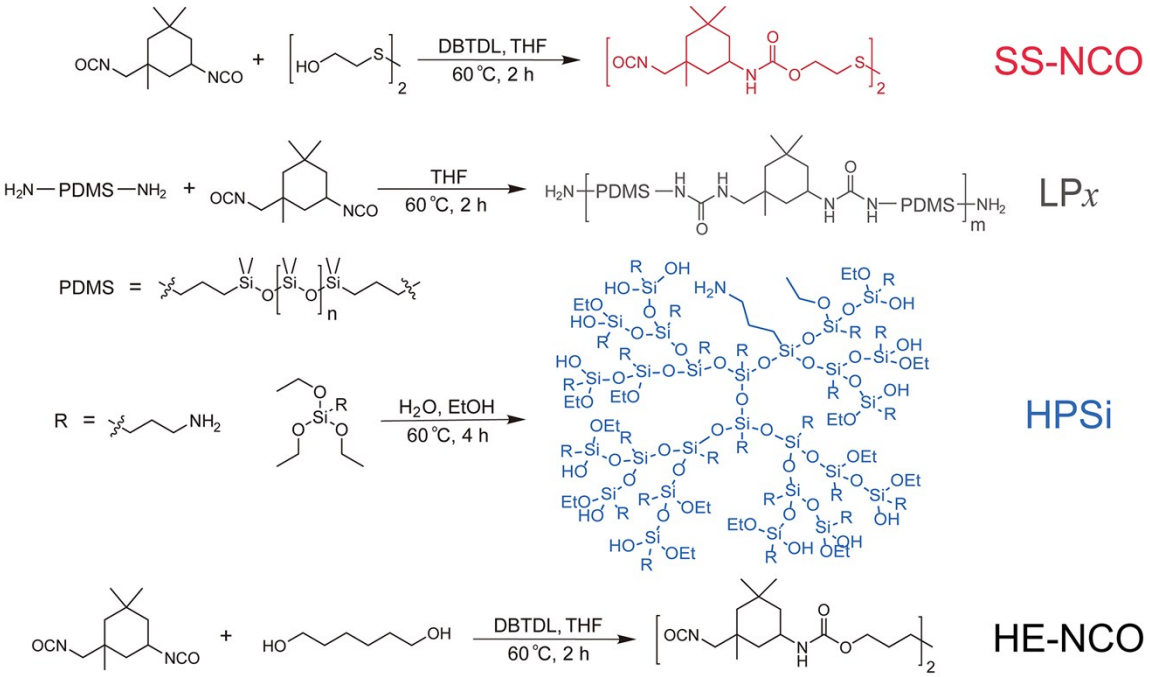

Scheme S1 Synthetic routes of SS-NCO, LP*x*, HPSi and HE-NCO.

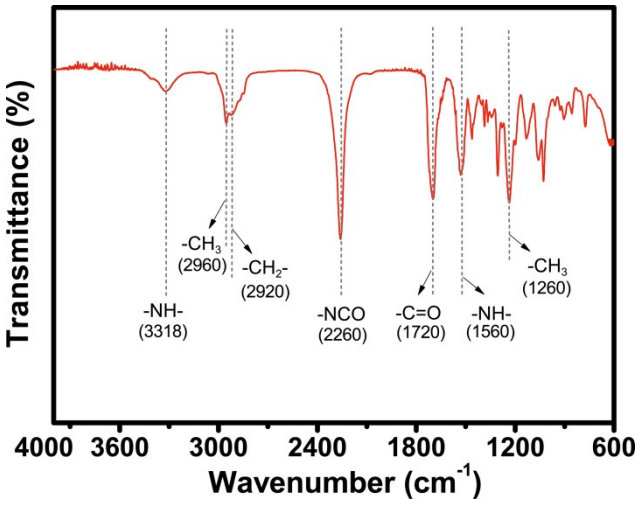

Fig. S1 FTIR spectrum of SS-NCO.

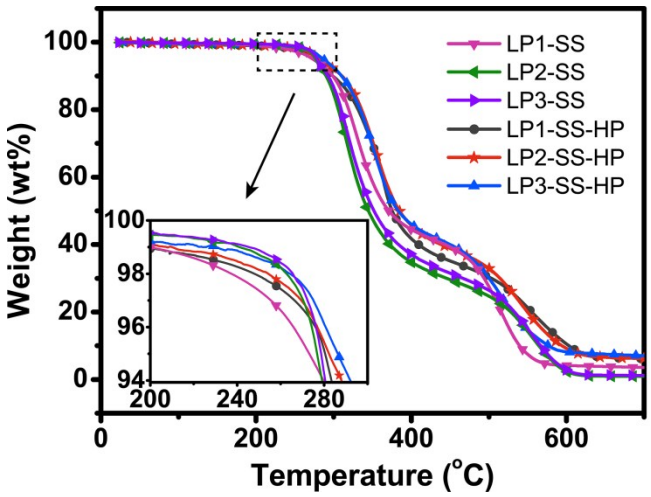

Fig. S2 TGA curves of LP*x*-SS-HP and LP*x*-SS under N_2 atmosphere.

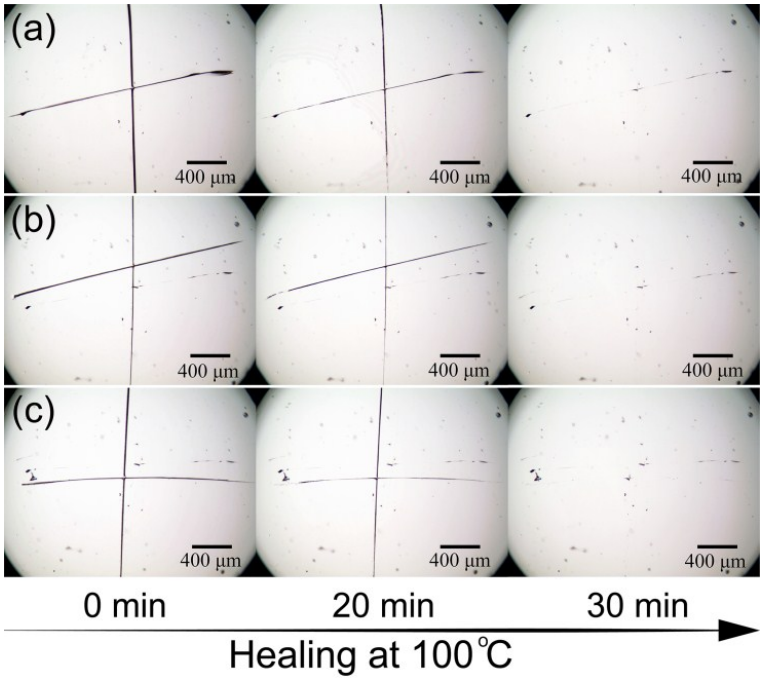

Fig. S3 Digital images during the scratch healing process on the same location of LP2-SS-HP film left in air for 24 h before starting self-healing (a: the 1st healing process; b: the 2nd healing; c: the 3rd healing process).

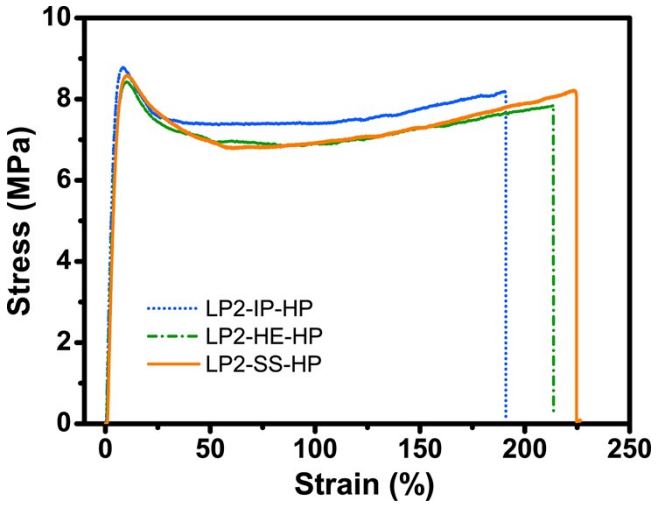

Fig. S4 Tensile stress–strain curves of LP2-IP-HP, LP2-HE-HP and LP2-SS-HP films.

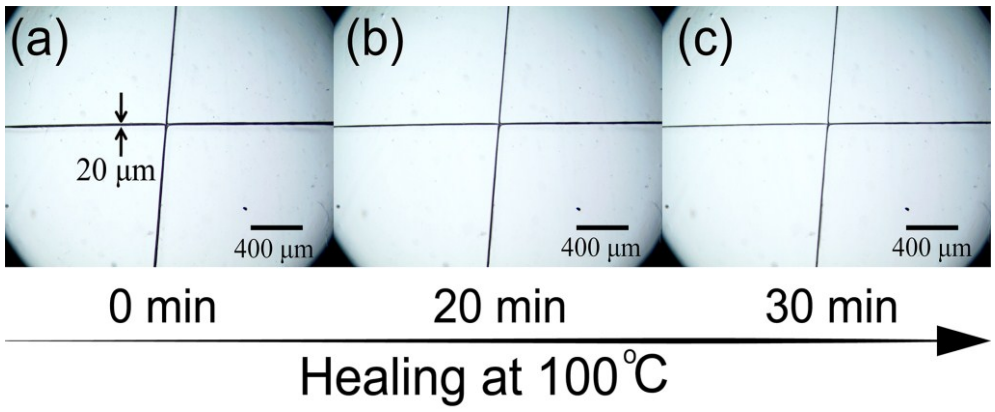

Fig. S5 Digital images during the healing process of LP2-IP-HP film.

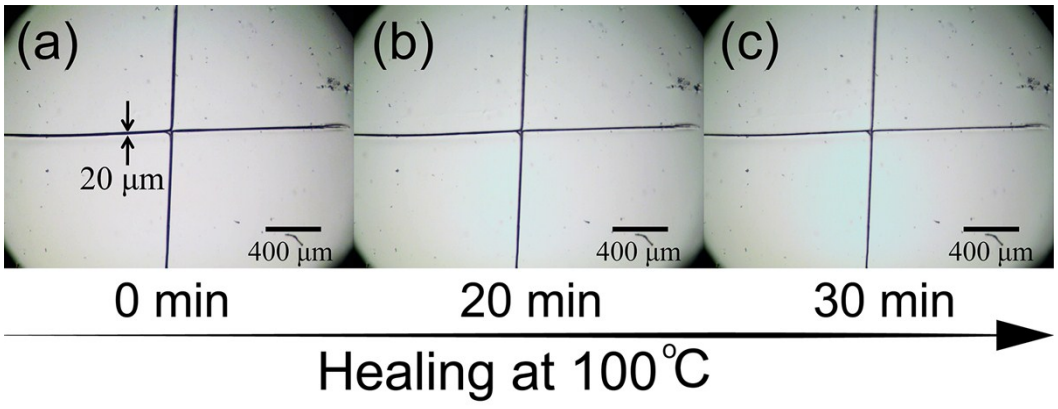

Fig. S6 Digital images during the healing process of LP2-HE-HP film.

Table S1 Typical self-healing properties of polydimethylsiloxane polymers

Sample name	Self-healing component	T_g (°C)	T_{di} (°C)	Self-healing condition	Self-healing Efficiency (%)	Photo[b]	σ_b [c] (MPa)	ε_b (%)	Ref
P1	Hydrogen bonds	--[a]	--	1 h	--	Yes	--	--	S1
P2		--	--	2 h	--	Yes	--	--	
SESi-3	Hydrogen bonds	-112.7	--	25 °C/24 h	90	Yes	0.45	400	S2
$SESi_1$	Hydrogen bonds	-118.3	--	100 °C/16 h	100	No	2.75	225	S3
Co-TIA-PDMS	Coordination bonds	<-100	<350	140 °C/24 h	52.2	Yes	1.12	560	S4
Fe-TIA-PDMS	Coordination bonds	<-90	--	60 °C/20 h	94.3	Yes	0.35	2500	S5
PDMS-Boroxine	Boroxine	65	--	70 °C/12 h	100	Yes	9.46	10	S6
Fe-Hpdca-PDMS	Coordination bonds	<-90	--	r.t./48 h	90	Yes	0.225	1880	S7
PDMS-PtL	Pt···Pt and π–π interaction	<-50	--	r.t./12 h	100	Yes	0.3	1390	S8
$Zn(OTf)_2$-PDMS	Coordination bonds	<-50	--	r.t./48 h	76	Yes	0.6	310	S9
HSE-0.65	Hydrogen bonds	-120	--	80 °C/24 h	>90	Yes	0.15	550	S10
PDMS-DA-PU	Diels–Alder reaction	--	--	140 °C/0.5 h	99	Yes	1.04	108	S11
PDMS/PCL-DA-PU-10%		--	--	80 °C/24 h	90	Yes	3.25	244	
PM2FS	Diels–Alder reaction	--	--	140 °C/0.5 h	85	Yes	0.13	35.5	S12
PM3FS		--	--	80 °C/24 h	95	Yes	0.61	50.9	
Py-PDMS-Co-0.5	Coordination bonds	-114	233	r.t./24 h	91	Yes	0.13	560	S13
$Eu(OTf)_3$-PDMS	Coordination bonds	-19.1	--	r.t./24 h	~100	No	0.2	300	S14
$Tb(OTf)_3$-PDMS		-18.1	--		~100	No	0.25	290	
PDMS-network	Vinylogous urethane	-118	--	75 °C/3 h	--	Yes	0.08	67	S15
SR-SH	Disulfide	--	--	light radiation/48 h	84	Yes	1.03	178	S16
PDMS-TFB	Imine	-117	--	25 °C/1 h	98.3	Yes	0.035	135	S17
C1	Boronic ester bonds	--	--	r.t./24 h	85	Yes	1.28	1000	S18
DAE@AS	Imine	--	--	UV-light/2 h	91	Yes	0.35	55	S19
PAPMS-25-OA-2.5	Ionic bonds	--	200	methanol and chloroform mixture	81.5	Yes	4.43	1150	S20
A_4B_2	Acylhydrazone; Hydrogen bonds	-120	--	120 °C/1 h	99	Yes	1.75	150	S21
PY-PSBTh	Lewis acid- base adduct	--	--	70 °C/1 h	--	Yes	--	--	S22
PDMS-MeNNN-Zn	Coordination bonds	-69.6	--	r.t./1 h	99.3	Yes	0.066	456	S23
PDMS-NNN-Zn		-68.7	--	r.t./24 h	100.3	Yes	0.091	230	
PDMS-PUa	Hydrogen bonds	--	--	r.t./48 h	90	Yes	0.81	551	S24
Si-A_IN30	Ionic bonds	--	--	120 °C/12 h	77	Yes	3.08	387	S25
PDMS-1	Disulfide	--	--	r.t./4 h	95	Yes	0.15	700	S26
LP2-SS-HP	Disulfide	96	282	100 °C/0.5 h	96.5	Yes	8.6	224.2	This work

a: data not given in the reference. b: "Yes" means that optical microscopic photos representing the self-healing of the sample were provided in the reference. "No" means that optical microscopic photos representing the self-healing of the sample were not provided in the reference. c: the value of the original sample without scratch.

Table S2 Tensile properties for LP2-IP-HP and LP2-HE-HP films

Film	σ_b (MPa)	ε_b (%)	E (MPa)	Toughness (MJ m^{-3})
LP2-IP-HP	8.8±0.5	191.4±4.1	196.6±12.7	14.4±0.2
LP2-HE-HP	8.5±0.4	213.8±3.1	181.2±13.5	15.4±0.3

References

[S1] N. Roy, E. Buhler, J.-M. Lehn, *Chem. Eur. J.* **2013**, 19, 8814.

[S2] A. Zhang, L. Yang, Y. Lin, L. Yan, H. Lu, L. Wang, *J. Appl. Polym. Sci.* **2013**, 129, 2435.

[S3] L. Yang, Y. Lin, L. Wang, A. Zhang, *Polym. Chem.* **2014**, 5, 153.

[S4] X.-Y. Jia, J.-F. Mei, J.-C. Lai, C.-H. Li, X.-Z. You, *Chem. Commun.* **2015**, 51, 8928.

[S5] X.-Y. Jia, J.-F. Mei, J.-C. Lai, C.-H. Li, X.-Z. You, *Macromol. Rapid Commun.* **2016**, 37, 952.

[S6] J. C. Lai, J. F. Mei, X. Y. Jia, C. H. Li, X. Z. You, Z. Bao, *Adv. Mater.* **2016**, 28, 8277.

[S7] C.-H. Li, C. Wang, C. Keplinger, J.-L. Zuo, L. Jin, Y. Sun, P. Zheng, Y. Cao, F. Lissel, C. Linder, X.-Z. You, Z. Bao, *Nat Chem* **2016**, 8, 618.

[S8] J. F. Mei, X. Y. Jia, J. C. Lai, Y. Sun, C. H. Li, J. H. Wu, Y. Cao, X. Z. You, Z. Bao, *Macromol. Rapid Commun.* **2016**, 37, 1667.

[S9] Y.-L. Rao, A. Chortos, R. Pfattner, F. Lissel, Y.-C. Chiu, V. Feig, J. Xu, T. Kurosawa, X. Gu, C. Wang, M. He, J. W. Chung, Z. Bao, *J. Am. Chem. Soc.* **2016**, 138, 6020.

[S10] Y. You, W. Huang, A. Zhang, Y. Lin, *J. Polym. Sci., Part A: Polym. Chem.* **2016**, 54, 3760.

[S11] J. Zhao, R. Xu, G. X. Luo, J. Wu, H. S. Xia, *Polym. Chem.* **2016**, 7, 7278.

[S12] J. Zhao, R. Xu, G. Luo, J. Wu, H. Xia, *J. Mater. Chem. B* **2016**, 4, 982.

[S13] L. Liu, S. Liang, Y. Huang, C. Hu, J. Yang, *Chem. Commun.* **2017**, 53, 12088.

[S14] Y.-L. Rao, V. Feig, X. Gu, G.-J. Nathan Wang, Z. Bao, *J. Polym. Sci., Part A: Polym. Chem.* **2017**, 55, 3110.

[S15] T. Stukenbroeker, W. D. Wang, J. M. Winne, F. E. Du Prez, R. Nicolay, L. Leibler, *Polym. Chem.* **2017**, 8, 6590.

[S16] H. P. Xiang, M. Z. Rong, M. Q. Zhang, *Polymer* **2017**, 108, 339.

[S17] B. Zhang, P. Zhang, H. Zhang, C. Yan, Z. Zheng, B. Wu, Y. Yu, *Macromol. Rapid Commun.* **2017**, 38, 1700110.

[S18] Y. Zuo, Z. Gou, C. Zhang, S. Feng, *Macromol. Rapid Commun.* **2016**, 37, 1052.

[S19] M. Kathan, P. Kovaricek, C. Jurissek, A. Senf, A. Dallmann, A. F. Thunemann, S. Hecht, *Angew. Chem. Int. Ed. Engl.* **2016**, 55, 13882.

[S20] H. Lu, S. Feng, *J. Polym. Sci., Part A: Polym. Chem.* **2017**, 55, 903.

[S21] D.-D. Zhang, Y.-B. Ruan, B.-Q. Zhang, X. Qiao, G. Deng, Y. Chen, C.-Y. Liu, *Polymer* **2017**, 120, 189.
[S22] F. Vidal, H. Lin, C. Morales, F. Jakle, *Molecules* **2018**, 23, 405.
[S23] D. P. Wang, J. C. Lai, H. Y. Lai, S. R. Mo, K. Y. Zeng, C. H. Li, J. L. Zuo, *Inorg. Chem.* **2018**, 57, 3232.
[S24] C. Liu, C. Ma, Q. Xie, G. Zhang, *J. Mater. Chem. A* **2017**, 5, 15855.
[S25] F. B. Madsen, L. Yu, A. L. Skov, *ACS Macro Lett.* **2016**, 5, 1196.
[S26] C. Lv, K. Zhao, J. Zheng, *Macromol. Rapid Commun.* **2018**, 39, 1700686.