Lipoic acid-based vitrimer-like elastomer

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Figure S1-1. <sup>1</sup>H-NMR spectra (600 MHz, CDCl<sub>3</sub>) of EG-CV-10



Figure S1-2. <sup>1</sup>H-NMR spectra (600 MHz, CDCl<sub>3</sub>) of EG-CV-20



Figure S1-3. <sup>1</sup>H-NMR spectra (600 MHz, CDCl<sub>3</sub>) of EG-CV-30



Figure S2-1. <sup>1</sup>H-NMR spectra (600 MHz, CDCl<sub>3</sub>) of EG-CV-20 and EG-CV-20-LA



Figure S2-2. <sup>1</sup>H-NMR spectra (600 MHz, CDCl<sub>3</sub>) of EG-CV-30 and EG-CV-30-LA



Figure S3. FTIR of EG, EG-CV-X, EG-CV-X-LA, and LAVE



Figure S4. Gel content of LAVE



Figure S5-1. Oscillatory rheology measurements of EG-CV-20-LA and LAVE20



Figure S5-2. Oscillatory rheology measurements of EG-CV-30-LA and LAVE30



Figure S6-1. Tensile stress-strain curves of the native and healed LAVE20



Figure S6-2. Tensile stress–strain curves of the native and healed LAVE30



Figure S7-1. Cycling test of LAVE20



Figure S7-2. Cycling test of LAVE30

Table S1. Composition	of the reaction mixtures u	used for the synthesis of E	G-CV-X
1		2	

EG	εCL	δVL	$Sn(Oct)_2$
(g)	(g)	(g)	(g)
0.233	4.28	3.75	0.015
0.233	8.56	7.50	0.015
0.233	12.84	11.25	0.015
	EG (g) 0.233 0.233 0.233	EGεCL(g)(g)0.2334.280.2338.560.23312.84	EGεCLδVL(g)(g)(g)0.2334.283.750.2338.567.500.23312.8411.25

Samples	Mn*	$Mw^*$	Đ*	Mw (NMR) <sup>+</sup>	$Mw$ (theo) <sup>^</sup>
	(g mol <sup>-1</sup> )	(g mol <sup>-1</sup> )		(g mol <sup>-1</sup> )	(g mol <sup>-1</sup> )
EG-CV-10	3100	6800	2.22	2702	2226
EG-CV-20	4200	9700	2.31	4849	4482
EG-CV-30	6000	17100	2.83	6798	6656
EG-CV-10-LA	3900	5500	1.42	2889	2514
EG-CV-20-LA	5100	5500	1.06	4530	4770
EG-CV-30-LA	7800	10900	1.40	7731	6944

Table S2 Molecular weights of EG-CV-X and EG-CV-X-LA

\*determined by GPC in CHCl<sub>3</sub> at 35 °C and calibrated against near-monodisperse PS; <sup>+</sup> determined by <sup>1</sup>H-NMR using end-of chain proton signal at 3.6 ppm vs. main chain proton signal at 4.0 ppm; <sup>^</sup> determined by theoretical calculation based on the ratios of M/I.

Samples	$T_{\rm deg}^{\ddagger}$ (°C)	$T_{\rm m}^{\pm}$ (°C)	$T_{c}^{\pm}(^{\circ}\mathrm{C})$
EG-CV-10	245	13	-5
EG-CV-20	179	15	-2
EG-CV-30	260	18	-1
EG-CV-10-LA	264	11	-10
EG-CV-20-LA	275	16	-5
EG-CV-30-LA	282	18	-4
LAVE-10	393	13	-13/-9
LAVE-20	399	12	-12
LAVE-30	403	13	-13/-10

Table S3. Thermal characteristics of EG-CV-X, EG-CV-X-LA, and LAVE

<sup>‡</sup> The temperature corresponds to the maximal decomposition rate observed in TGA using a rate of 10 °C min<sup>-1</sup>; <sup>±</sup> determined by differential scanning calorimetry measurements using heating and cooling rates of 10 °C min<sup>-1</sup>.

Samples	Young's Modulus (MPa)	Stress at Max. Load (MPa)	Strain at Max Load (%)
LAVE-10	1.73	0.34	25
LAVE-20	1.60	0.69	62
LAVE-30	1.82	1.41	180

## Table S4. Mechanical properties of LAVE