

Supplementary Information

Comprehensive itaconic acid-based vitrimers via one-pot inverse vulcanization

*Zhongkai Guo,^a Xuwei Jiao,^a Kailun Wei,^a Jianqiao Wu^{*b} and Jun Hu^{*a}*

^aBeijing Advanced Innovation Center for Soft Matter Science and Engineering, Beijing University of Chemical Technology, North Third Ring Road 15, Chaoyang District, Beijing 100029, China.

^bCollege of Materials and Chemical Engineering, Chuzhou University, Chuzhou, Anhui Province, 239000, China.

***Corresponding Authors**

Email: jhu@mail.buct.edu.cn (Jun Hu), wujianqiao1012@163.com (Jianqiao Wu).

The supporting information includes 11 pages, 3 tables and 9 figures.

Contents

1. Characterization	S3
2. Supplementray Figures	S5
Figure S1.....	S5
Fgiure S2.....	S5
Figure S3.....	S6
Figure S4.....	S6
Figure S5.....	S7
Figure S6.....	S7
Figure S7.....	S7
Figure S8.....	S8
Figure S9.....	S8
3. Supplementray Tables.....	S9
Table S1.....	S9
Table S2.....	S10
Table S3.....	S11

1. Characterization

Differential scanning calorimeter (DSC): DSC test was carried out using TADSC 250 with nitrogen purge of 50 mL.min⁻¹, temperature range from -40°C to 180°C, and heating rate of 10°C min⁻¹. The samples were approximately 5 mg and sealed in aluminum sample crucibles.

Thermogravimetric analysis (TGA): The thermal stability was measured by using a thermogravimetric analyzer (TGA, TA-Q50) under nitrogen from room temperature to 800°C at a heating rate of 10°C min⁻¹.

X-Ray diffraction (XRD): XRD measurements were conducted on a Bruker D8 ADVANCE instrument using Cu K α radiation ($\lambda=1.54178$ Å). The scanning was performed on a diffraction range (2θ) of 5-80° with a scanning speed of 10° min⁻¹.

Fourier transform infrared spectroscopy (FTIR): FTIR spectra were recorded on a spectrophotometer (Nicolet iS5). All samples were scanned from 4000 to 500 cm⁻¹.

Tensile test: Tensile stress-strain curves were obtained by using a universal testing machine (ETM504C, Hubei Wance Test Machine Co. Ltd., China) according to ASTM D882 standard. Dog-bone samples were used for the test. The crosshead speed was 10 mm per min, and the gauge length was 17 \pm 2 mm. The average values with error bar of all mechanical data were obtained after 5 times tests for every sample.

Hardness: Hardness measurements were performed on a D type Digital Shore Durometer. Same thickness of 1mm was applied to all the samples, and 7 times tests for each sample were conducted.

Dynamic mechanical analysis (DMA): Dynamic mechanical properties were measured by using a dynamic mechanical analyzer (DMA, TA-Q800) in tension mode. The sample with a dimension of 30 mm \times 5 mm \times 1 mm was scanned from -50 to 80°C at a heating rate of 5°C/min. The amplitude was set at 10 μ m and the frequency was 1 Hz.

Stress relaxation test: Stress relaxation was measured by using DMA (TA-Q800). The sample dimension was 30 mm \times 5 mm \times 1 mm. The sample was heated to the appointed temperature and soaked for 10 min with a static force (0.001 N). After that, an instantaneous strain of 2% was forced to the material. The stress and modulus were detected until it achieved equilibrium.

Physical recycling: The sample pieces were gathered and put into a mold on a press vulcanizer at 140°C at 20 tons pressure to form a new film. The new film was used to prepare dumbbell-shaped samples with similar size to original ones for the tensile test.

Welding test: Two pieces were assembled into an “L” pattern, and then welded in an oven at 140°C for 1 h. A slight weight was applied on the sample to offer a pressure.

Repairing test: The sample was cracked using a knife and repaired at an oven at 140°C. A glass slide was added on the sample to offer a small pressure. The repairing process was monitored by using an optical microscope (UPT200I).

Chemical degradation: The rectangular sample of 30 mg was immersed in ethylene glycol/dimethylformamide (EG/DMF, 0.1 g/mL, 2 mL), dithiothreitol/dimethylformamide (DTT/DMF, 0.001 g/mL, 2 mL), and EG/DTT/DMF (0.1 g/mL EG and 0.001 g/mL DTT in 2 mL DMF) at 140°C in an oven. By weighting the dry sample at different time, the degradation kinetics were obtained.

2. Supplementary Figures

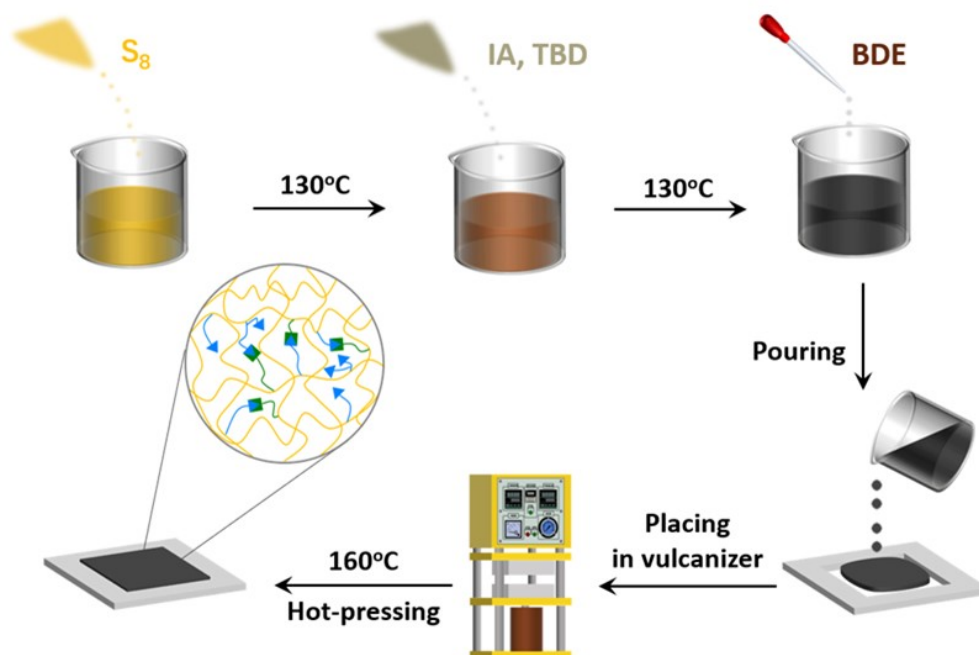


Fig. S1 Schematic illustration of the preparation of the itaconic acid-based vitrimers from S₈, IA, TBD and BDE through one-pot method.

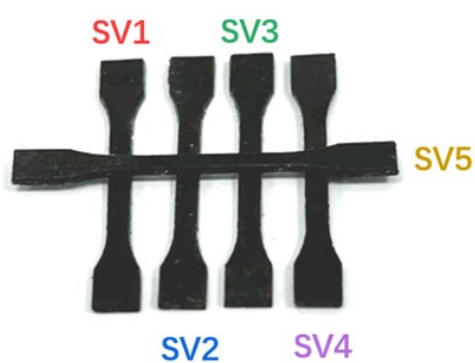


Fig. S2 Photograph of the as-prepared itaconic acid-based vitrimers (SV1 to SV5).

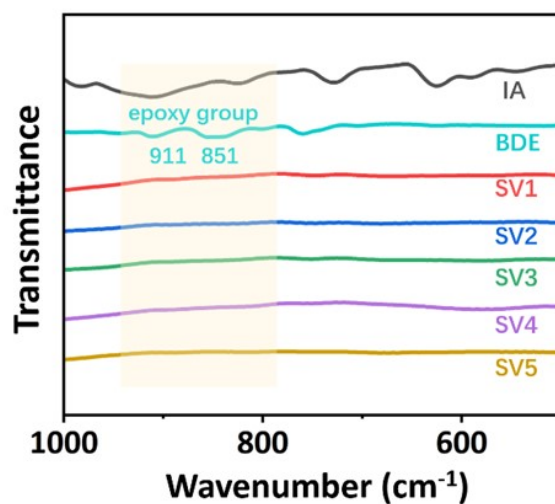


Fig. S3 FTIR spectra of IA, BDE, and itaconic acid-based vitrimers (SV1 to SV5) in the range of 500-1000 cm^{-1} . The signals at 905/853 cm^{-1} were assigned to epoxy groups from BDE.

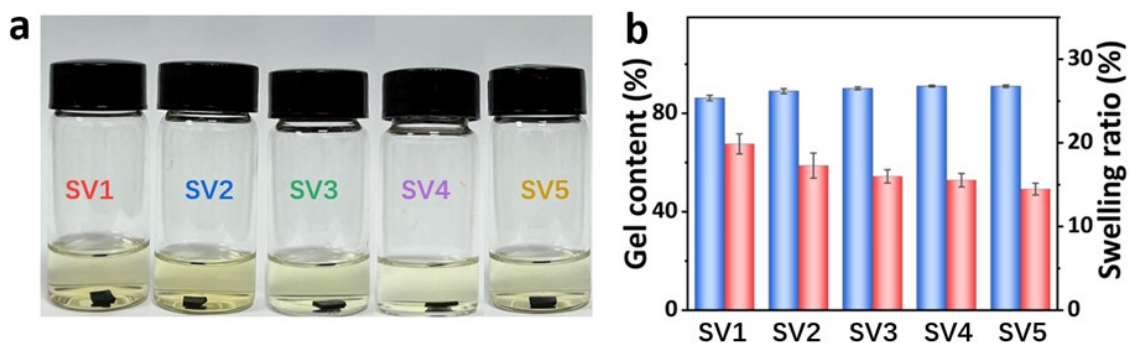


Fig. S4 (a) Digital photos of itaconic acid-based vitrimers (SV1 to SV5) after soaking in acetone for 20 h. (b) The bar graph of gel content and swelling ratio of SV1 to SV5.

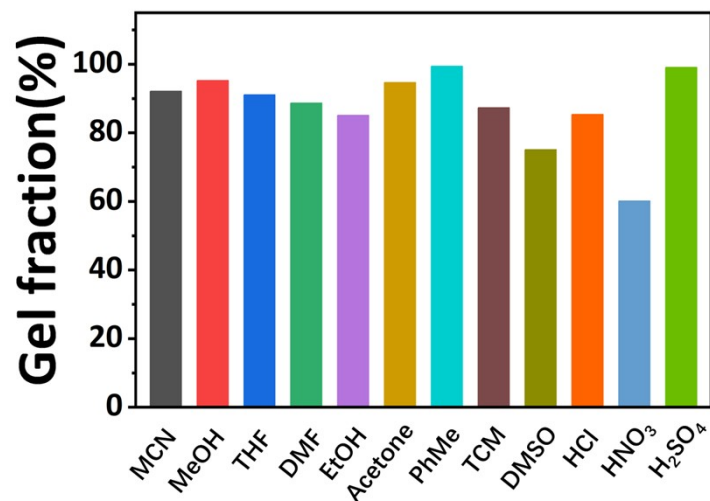


Fig. S5 Gel fraction of SV5 after soaking in 12 different solvents for 7 days.



Fig. S6 Digital photos of the polysulfides without addition of BDE (Poly(S-IA)).

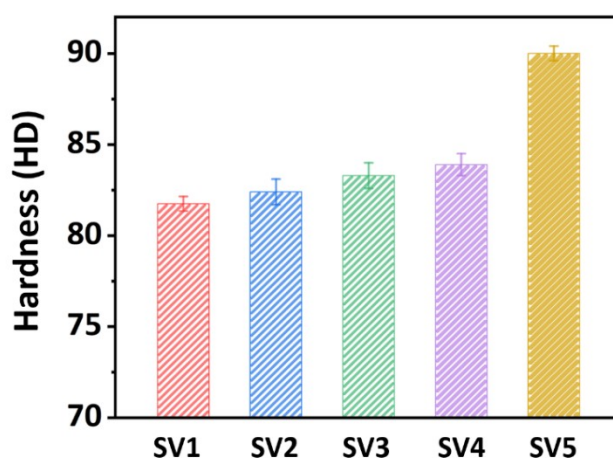


Fig. S7 Hardness of the itaconic acid-based vitrimers (SV1 to SV5)

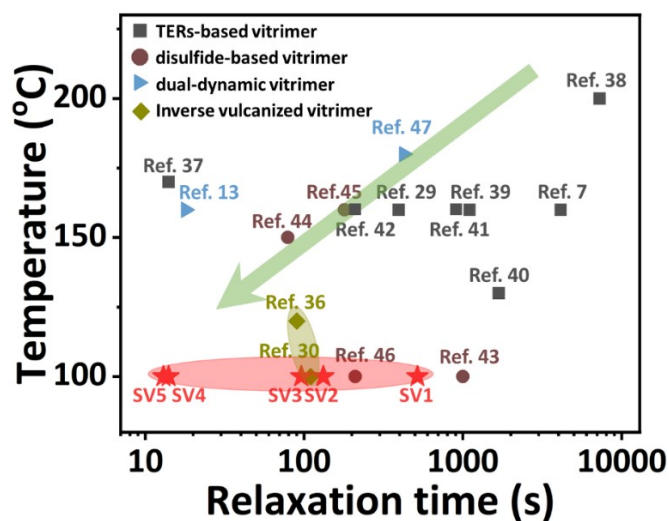


Fig. S8 Comparison of stress relaxation time between this work and other reported polysulfides and biobased vitrimers.

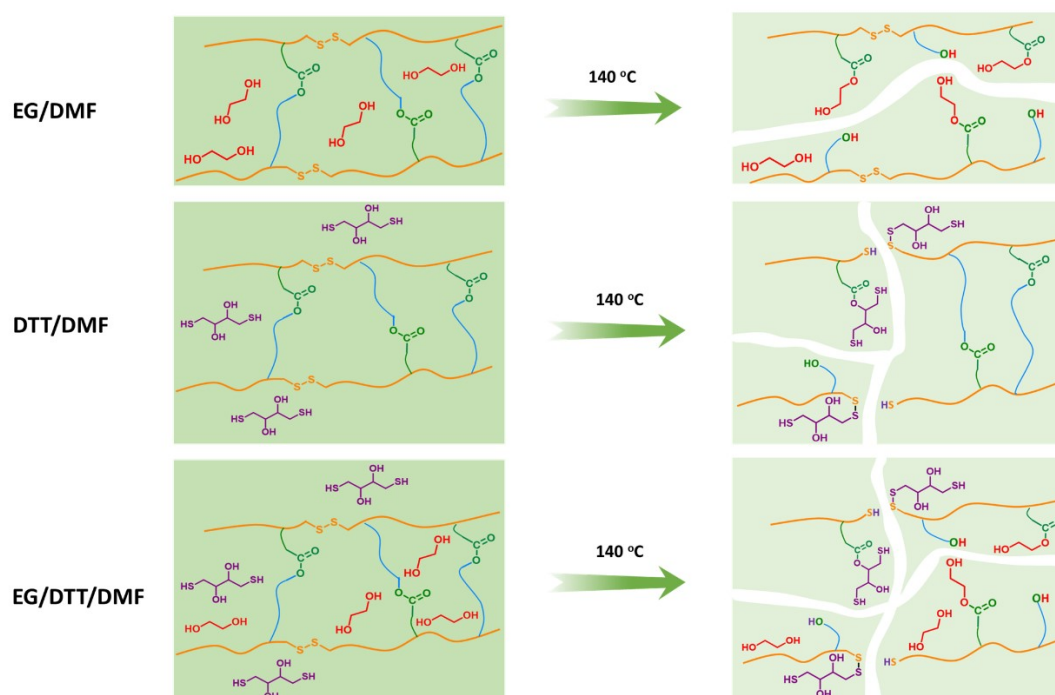


Fig. S9 The proposed degradation mechanism of SV5 in ethylene glycol/dimethylformamide (EG/DMF), dithiothreitol/dimethylformamide (DTT/DMF), and EG/DTT/DMF at 140°C.

3. Supplemtray Tables

Table S1 Gel contents of SV1-SV5 and other reported biobased vitrimers/cross-linked polysulfides.

Entry	Sample	Solvent	Gel content (%)	Reference
1	Biobased vitrimers Oz-L/Se-EP	Ethanol/acetone (1:1)	83-90	[6]
2	Biobased vitrimers ESO/GL	Acetonitrile	89-91	[7]
3	Biobased vitrimers CO/IPDI/IPI	DMF	97-99	[12]
4	Biobased vitrimers IA/TMP/DGEBA	Tetrahydrofuran	96-100	[19]
5	Biobased vitrimers DGEAC/SA/GL	Dichloromethane	90-99	[29]
6	Polysulfide polymers S ₈ /DIB	DMF	80	[25]
7	Polysulfide vitrimers S8/Span-80/BADGE	Tetrahydrofuran	64-84	[30]
8	Polysulfide polymers S ₈ /MA-St	Toluene and chloroform	78, 81	[31]
9	Polysulfide polymers S ₈ /Castor oil	Chloroform	79	[32]
10	Polysulfide polymers S ₈ /Soybean oil/Biochar	Acetone	87	[33]
11	Itaconic acid-based polysulfide vitrimers SV1-SV5	Acetone	86-91	This work

Table S2 Relaxation time of SV1-SV5 and other reported polysulfide, biobased vitrimers, traditional TERs-based vitrimers and traditional disulfide-based vitrimers.

Entry	Sample	Dynamic bond	Catalyst	Relaxation time (s)	Reference
1	Polysulfide vitrimer S8/Span-80/MDI (S-Span-MDI-1)	Multi-sulfide	Zn(DTC) ₂	90 s (160°C)	[36]
2	Polysulfide vitrimer S8/Span-80/BADGE (BA75)	Multi-sulfide	None	110 s (110°C)	[30]
3	Biobased vitrimer ESO/GL (R = 0.5)	Ester	TBD	4118 s (160°C)	[7]
4	Biobased vitrimer DGEAC/SA/GL (V4)	Ester	None	394 s (160°C)	[29]
5	Biobased vitrimer FEP/CA/FEHBP	Ester	None	50 s (140°C)	[37]
6	Biobased vitrimer CPA/ESO (R = 1.25)	Ester	TBD	7245 s (200°C)	[38]
7	Biobased vitrimer LAE/GLU	Ester	None	1100 s (160°C)	[39]
8	TERs-based vitrimer	Ester	None	1680 s (130°C)	[40]
9	TERs-based vitrimer PE-COOH/BDE (CL-PE-720)	Ester	Zn(OAc) ₂	120 s (180°C)	[41]
10	TERs-based vitrimer PE-COOH/BDE (CL-PE-1)	Ester	Zn(OAc) ₂	900 s (160°C)	[42]
11	Biobased vitrimer ESO/APD (ESOV-24)	Disulfide	None	356 s (120°C)	[43]
12	Disulfide-based vitrimer bCC/cystamine/TREN	Disulfide	None	111 s (120°C)	[44]
13	Disulfide-based vitrimer	Disulfide	None	240 s (160°C)	[45]
14	Biobased vitrimers ESO/DAA/DTSA (ESO ₆ -SS ₃ -DAA ₃)	Disulfide	None	210 s (120°C)	[46]
15	Biobased vitrimer PA1010/CO/APD (PEAV-3)	Disulfide and ester	None	2002 s (100°C)	[13]
16	Biobased vitrimers ESO/DA/SiO ₂ (ESO/SiO ₂ -3)	Disulfide and ester	TBD	898 s (170°C)	[47]
17	Itaconic acid-based polysulfide vitrimers (SV1-SV5)	Multi-sulfide and ester	TBD	516 s (SV1, 100°C) 132 s (SV2, 100°C) 96 s (SV3, 100°C) 14 s (SV4, 100°C) 13 s (SV5, 100°C)	This work

Table S3 Tensile strength and elongation at break of SV1-SV5 and other polysulfides prepared by inverse vulcanization

Entry	Sample	Vitrimer or not	Tensile strength (MPa)	Elongation at break (%)	Reference
1	S ₈ /Span-80/BADGE (BA25, BA50, BA75, BA100)	✓	0.48	171	[30]
			1.51	215	
			6.36	167	
			13	113	
2	S ₈ /MA-St	✗	0.5	2	[31]
3	S ₈ /Span-80/MDI (S-Span-MDI-4, 3, 2, 1)	✓	0.14	35	[36]
			0.59	51.2	
			1.88	42	
			9.64	16	
4	S ₈ /lignin (LS ₈₀ , LS ₈₅ , LS ₉₀)	✗	2	0.2	[48]
			1.5	0.2	
			0.6	0.01	
5	S ₈ /fatty acids (ZPLS90, ZPLS95)	✗	2	5	[49]
			1.8	23	
6	S ₈ /oleic acid/pozzolan cements	✗	2.5	23	[50]
7	S ₈ /DA	✗	0.5	47.67	[51]
8	S ₈ /DVB/DIB (pS-DVB ₁₅ , pS-DIB ₁₅)	✗	1.2	40	[52]
			0.8	50	
9	S ₈ /DIB/TIB (poly(S-r-TIB ₃₀), poly(S-r-TIB ₅₀), poly(S-r-DIB ₃₀), poly(S-r-DIB ₅₀))	✗	19.5	1.63	[53]
			9.43	2.33	
			10.1	1.27	
			2.33	228	
10	S ₈ /DIB (poly(S-r-DIB ₅₀))	✗	18	2	[54]
			12.5	10	
11	S ₈ /DCPD	✗	6	0.1	[55]
12	S ₈ /L-tyrosine	✗	6	0.9	[56]
13	S ₈ /squalene/β-myrcene (R=5:4:1, 5:3:2)	✗	1.3	280	[57]
			0.4	330	
14	Itaconic acid-based polysulfide vitrimers (SV1-SV5)	✓	0.68	21	This work
			1.03	22	
			5.34	59.38	
			5.66	55	
			6.3	49.77	