

**A Fully Biomass Content Monomer from Itaconic Acid and Eugenol to Build Degradable Thermosets via Thiol-ene Click Chemistry**

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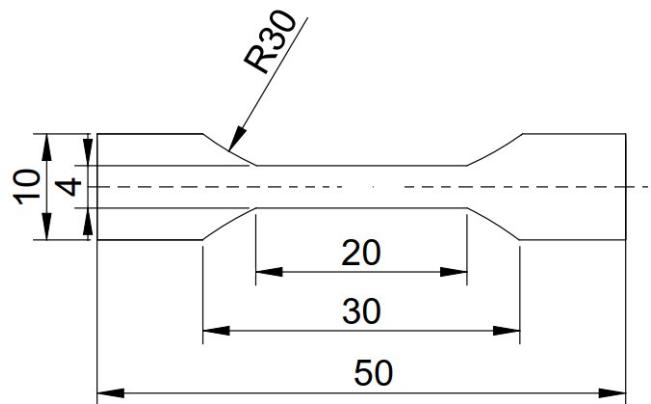
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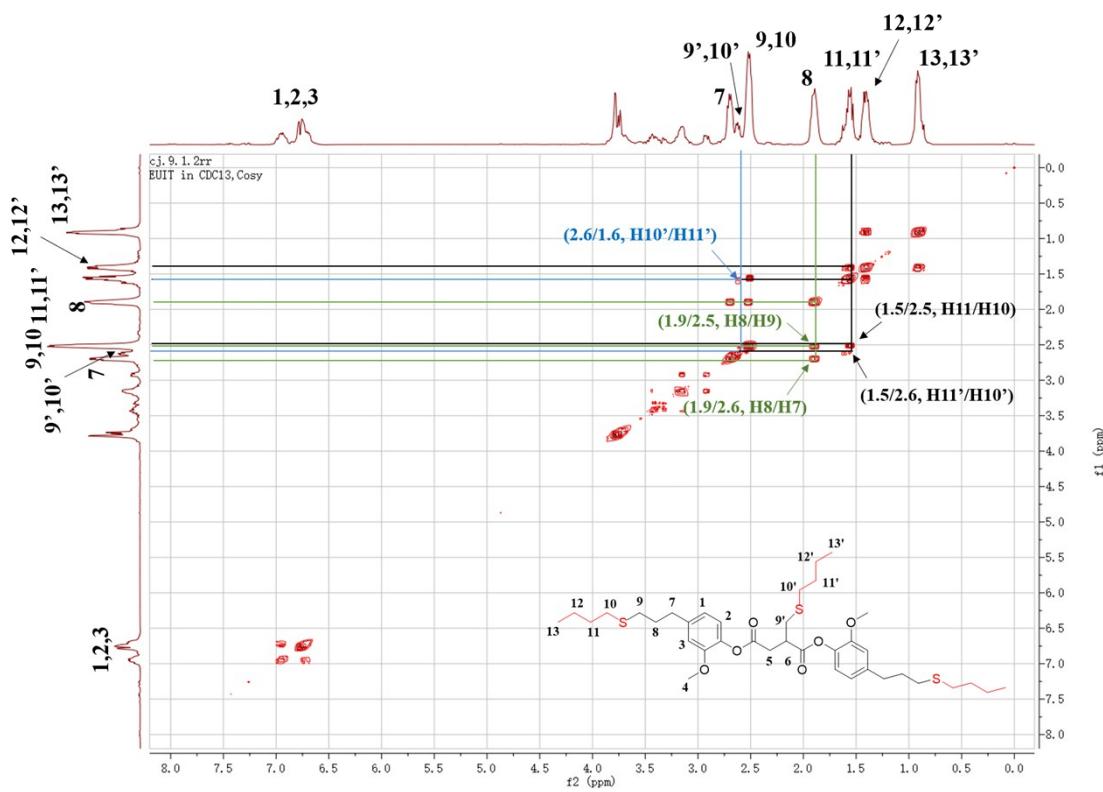
**Table S1.** The biobased allyl compound monomers and the  $T_g$ , mechanical properties, and biomass content of allyl compound of thiol-ene crosslinking network structures

Name	Chemical structure	$T_g$ (°C)	Tensile strength (MPa)	Biomass content of allyl compound	reference
EUIT/4SH		74.0	58.6	100.0%	This work
EUIT/3SH		53.1	26.2		
EUIT/2SH		27.2	6.5		
pA4E-S4P		4.4	2.5	46.6%	1
pA4Y-S4P		24.4	18.2	51.9%	
aSA		0.8	2.7	62.4%	
a3HBA		-7.1	1.8	62.4%	
a4HBA		5.5	3.7	62.4%	2
aGenA		-5.7	2.7	55.1%	
aGalA		-7.4	2.1	50.3%	
IDA-co-TMPTMP		15.8	7.8	45.9%	3
DADG-PS4P		8.1	0.5	66.4%	4

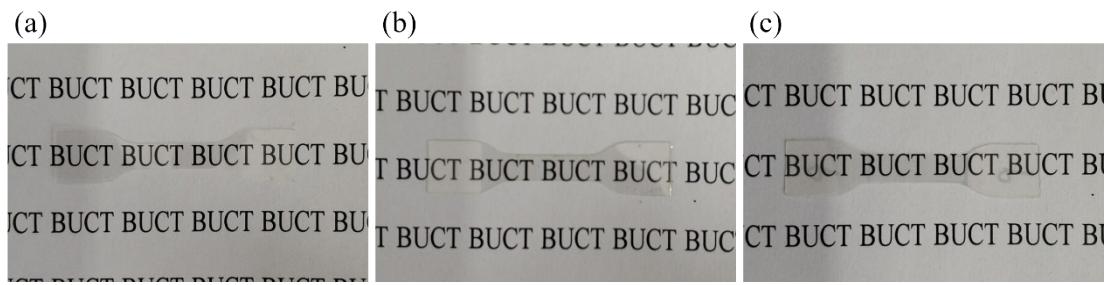
ISODIAL	<chem>C=CCO[C@H]1[C@H](CO)[C@@H](O)C1OCC=O</chem>	-2	2.0	63.7%	5
EAE	<chem>C=CCOC(=O)c1ccc(cc1)OC=O</chem>	-2.4	2.1	79.9%	6
DIA	<chem>C=CCOC(=O)C/C=C\CC(=O)OC=O</chem>	8.6	4.7	60.9%	
TEGBMP-co-TAQA	<chem>C=CCOC(=O)C[C@H]1[C@H]2[C@H]3[C@H]1OC(=O)OC=O[C@H]2OC(=O)OC=O[C@H]3OC=O</chem>	-18	Nd	40.1%	7
TMPTMP-co-TAQA		43	~39		
1,6-HDT-co-TAQA		48	~30		
2,3-BDT-co-TAQA		51	~50		
1,2-EDT-co-TAQA		65	~40		



**Figure S1.** The sample size for tensile testing (unit: mm)



**Figure S2.** The H-H COSY NMR spectra of EUIT-nBM



**Figure S3.** Visualization images of (a) EUIT/4SH, (b) EUIT/3SH, and (c) EUIT/2SH

**Table S2.** Degradation time for EUIT/S<sub>n</sub>H with different sodium hydroxide solution at room temperature and 90 °C

Sample	EUIT/2SH	EUIT/3SH	EUIT/4SH
Degradation conditions	N/A <sup>a</sup>	N/A <sup>a</sup>	N/A <sup>a</sup>
1 M NaOH (25 °C)			

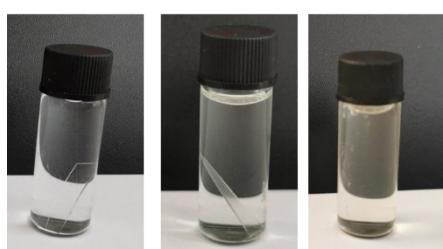
6 M NaOH (25 °C)	>2 months <sup>b</sup>	>2 months <sup>b</sup>	>2 months <sup>b</sup>
1 M NaOH (90 °C)	300 min	420 min	480 min
6 M NaOH (90 °C)	30 min	120 min	120 min

a. Two months in solution and no degradation occurred. b. Time when some degradation occurred (5% weight loss).

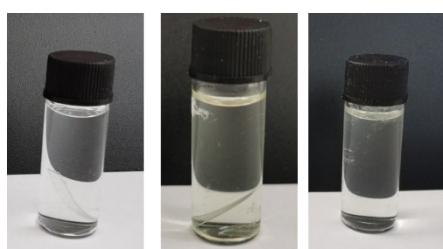
#### The degradation of EUIT/2SH at 90 °C for 30 min



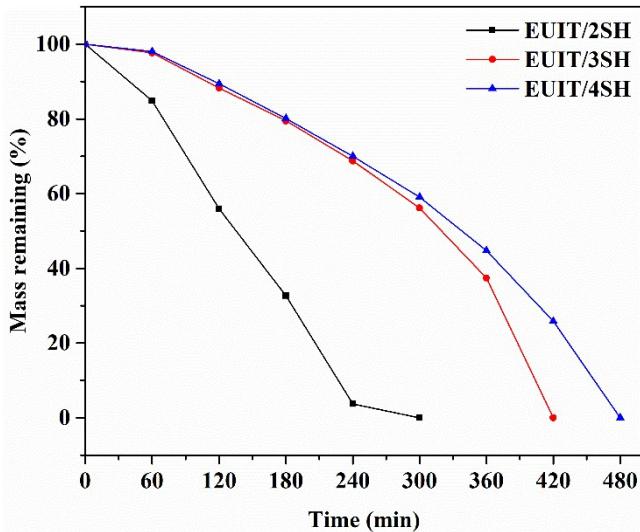
#### The degradation of EUIT/3SH at 90 °C for 120 min



#### The degradation of EUIT/4SH at 90 °C for 120 min



**Figure S4.** Degradation of the thiol-ene crosslinked networks at 90 °C at 6M NaOH



**Figure S5.** The weight loss studies of EUIT/SH (1M at 90 °C)

## References

1. S. Aoyagi, T. Shimasaki, N. Teramoto and M. Shibata, *European Polymer Journal*, 2018, **101**, 151-158.
2. G. Yang, S. L. Kristufek, L. A. Link, K. L. Wooley and M. L. Robertson, *Macromolecules*, 2016, **49**, 7737-7748.
3. T. S. Kristufek, S. L. Kristufek, L. A. Link, A. C. Weems, S. Khan, S.-M. Lim, A. T. Lonnecker, J. E. Raymond, D. J. Maitland and K. L. Wooley, *Polymer Chemistry*, 2016, **7**, 2639-2644.
4. T. Yoshimura, T. Shimasaki, N. Teramoto and M. Shibata, *European Polymer Journal*, 2015, **67**, 397-408.
5. T. Modjinou, D.-L. Versace, S. Abbad-Andallousi, N. Bousserrhine, J. Babinot, V. Langlois and E. Renard, *ACS Sustainable Chemistry & Engineering*, 2015, **3**, 1094-1100.
6. J. Dai, S. Ma, L. Zhu, S. Wang, L. Yang, Z. Song, X. Liu and J. Zhu, *Polymer*, 2017, **108**, 215-222.
7. L. A. Link, A. T. Lonnecker, K. Hearon, C. A. Maher, J. E. Raymond and K. L. Wooley, *ACS Appl Mater Interfaces*, 2014, **6**, 17370-17375.