

Supporting information

Recent advances in radical polymerization of biobased monomers in aqueous dispersed media

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Green metrics calculations:

- Atom economy: measure of the amount of starting materials that ends up as useful products.

$$\% \text{ atom economy} = \frac{\text{Molecular Weight (MW) of desired product}}{\sum \text{MW of reactants}} \times 100$$

- E-factor: measure of the amount of waste produced in a process.

$$E - \text{Factor} = \frac{\text{mass of total waste}}{\text{mass of desired product}}$$

- Carbon efficiency: measure of the amount of carbon atoms in the starting materials that ends up in the desired product.

$$\text{Carbon efficiency} = \frac{\sum \text{mass of C in the desired product}}{\sum \text{mass of C of reactants}} \times 100$$

- Reaction mass efficiency: measure of the efficiency with which reactant mass ends up in the desired product.

$$\text{Reaction mass efficiency} = \frac{\text{mass of isolated product}}{\sum \text{mass of reactants}} \times 100$$

- Biobased carbons: measure of the amount of renewable carbon in the final monomer.

$$\text{Renewable carbons} = \frac{\sum \text{biobased atoms of C}}{\sum \text{total atoms of C}} \times 100$$

For all the reactions, the work-up procedure is not taken in account. E-factor, C-efficiency and RME are calculated from experimental results considering the yield given in the articles and they are based on mass conservation.

Synthesis of soybean methacrylate (SBMA) from oleic soybean oil (**Figure S1**)[1]:

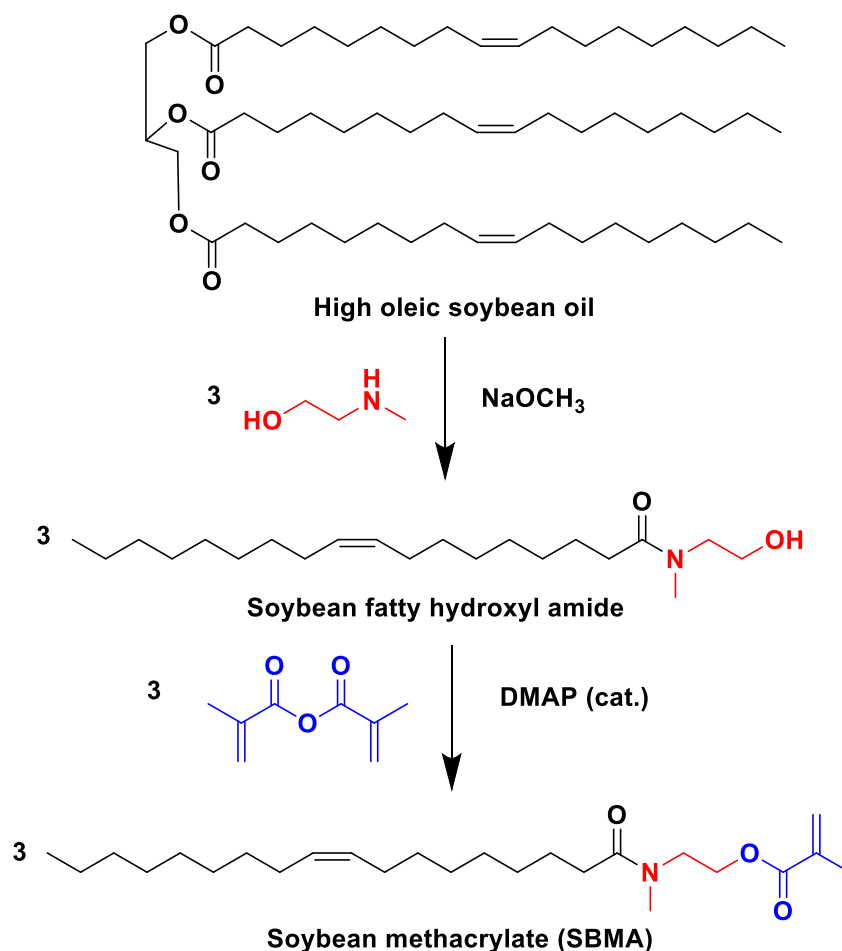


Figure S1: Synthesis of soybean methacrylate (SBMA) from oleic soybean oil.

Step 1:

Step 1	HOSO	N-methylethanolamine	NaOCH ₃	SFHA	Yield	AE	E-factor	C-efficiency	RME
MW (g/mol)	884.78	75.07	54.01	339.56					
Equivalents	1.0	3.9	0.1	3					
nb of C per molecule	57	3	1	21					
m (g)	101.45	33.26	0.43						
n (mol)	0.115	0.443	0.008						
m exp (g)				113.30					
n exp (mol)				0.334					
					0.97	0.864	0.193	0.891	0.838

Ethanolamine could be biobased (produced from the fermentation of L-serine).

Step 2:

Step 2	SFHA	Anhydride	DMAP (cat)	Water	SBMA	Yield	AE	E-factor	C-efficiency	RME
MW (g/mol)	339.56	154.17	122.17		407.34					
Equivalents	1.0	1.0	0.010		1					
nb of C	21	8	7		25					
m (g)	101.868	46.251	0.37	10						
n (mol)	0.3	0.3	0.003							
m exp (g)					122.202					
n exp (mol)					0.3					
						1	0.823	0.297	0.862	0.823

Total:

AE	E-factor	C-efficiency	RME	Renewable C
0.711	0.490	0.768	0.690	0.84

Transesterification of high oleic soybean oil (*Figure S2*)[2]:

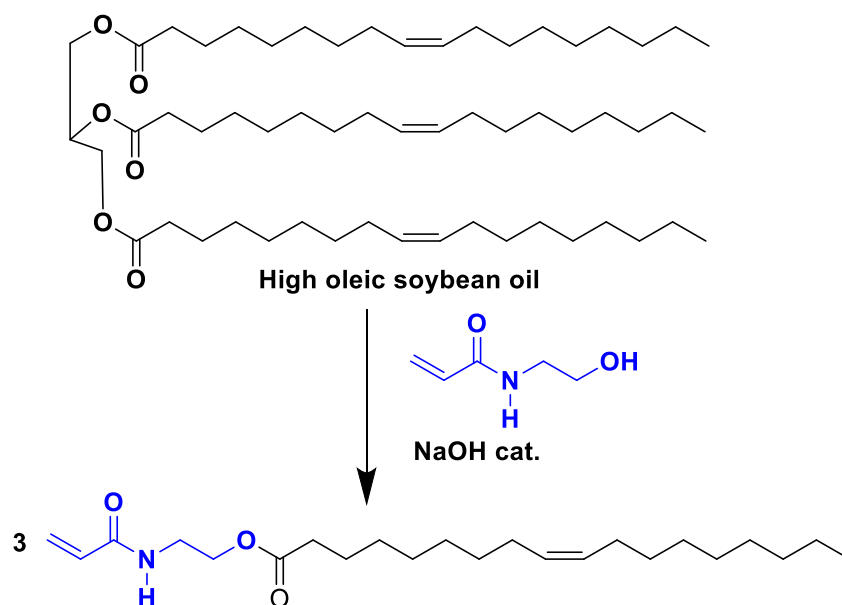


Figure S2: Synthesis of HOSBM by transesterification of high oleic soybean oil.

	HOSB	Amide	NaOH (cat)	THF	HOSB M	Yield	AE	E-factor	C-efficiency	RME	Renewable C
MW (g/mol)	884.78	115.06	40		379.31						
Equivalents	1.0	5.8	0.2		3						
nb of C	57	5	0		23						
m (g)	150.41 26	113.90 94	1.5	133.14							
n (mol)	0.17	0.99	0.0375								
m exp (g)					181.84						
n exp (mol)					60.61						
						0.94	0.73	1.19	95.23	0.68	0.87

Green metrics calculation for eugenol (**Figure S3**)[3]:

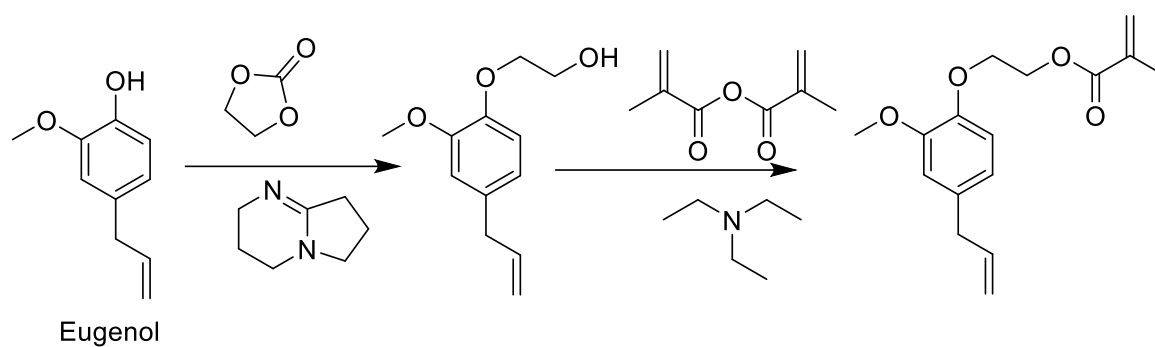


Figure S3: Functionalization of eugenol.

Step 1:

Step 1	Eugenol	Ethylene carbonate	DBN (cat)	Ethoxy eugenol	Yield	AE	E-factor	C-efficiency	RME
MW (g/mol)	164.08	88.02	124.1	208.11					
Equivalents	1.0	1.1	0.003	1					
nb of C	10	3		12					
m (g)	78.758	46.475	0.182						
n (mol)	0.48	0.528	0.00147						
m exp (g)				94.898					
n exp (mol)				0.456					
					0.95	0.796	0.322	0.857	0.757

Step 2:

Step 2	Ethoxy eugenol	Methacrylic anhydride	Triethylamine	DCM (solvent)	Ethoxy methacrylated eugenol	Yield	AE	E-factor	C-efficiency	RME
MW (g/mol)	208.11	154.17	101.12		276.14					
Equivalents	0.9	1.0	2.2		0.9					
nb of C	12	8	6		16					
m (g)	93.44	76.62	109.01	200						
n (mol)	0.449	0.497	1.078							
m exp (g)					91.75					
n exp (mol)					0.332					
						0.74	0.427	4.221	0.568	0.329

Total:

AE	E-factor	C-efficiency	RME	Renewable C
0.34	4.54	0.49	0.25	0.63

Green metrics for ISOMArAw synthesis (**Figure S4**)[4]:

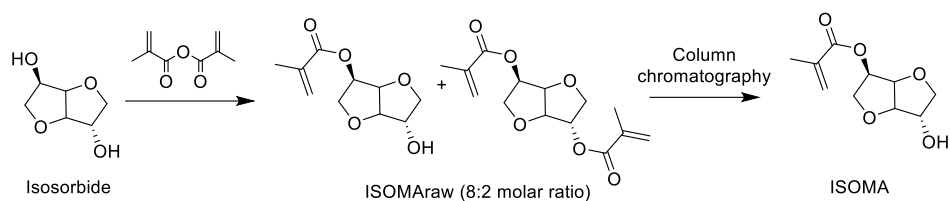


Figure S4: Synthesis of ISOMArAw and its purification.

	Isosorbide	Anhydride	4-DMAP (cat)	DCM (Solvent)	ISOMArAw	Yield	AE	E-factor	C-efficiency	RME
MW (g/mol)	146	106	122		216.4					
Equivalents	1.0	0.7	0.1		1					
nb of C	6	8	7		10.4					
m (g)	29.93	14.522	2.562	332.5						
n (mol)	0.205	0.137	0.021							
m exp (g)					24.843					
n exp (mol)					0.1148					
						0.56	0.94	14.28	0.51	0.53

$$\% \text{renewable C (ISOMA)} = \frac{6}{10} \times 100 = 60\%$$

References:

- [1] L. Yuan, Z. Wang, N. M. Trenor, and C. Tang, "Robust amidation transformation of plant oils into fatty derivatives for sustainable monomers and polymers," *Macromolecules*, vol. 48, no. 5, pp. 1320–1328, 2015, doi: 10.1021/acs.macromol.5b00091.
- [2] Z. Demchuk, W. S. J. Li, H. Eshete, S. Caillol, and A. Voronov, "Synergistic Effects of Cardanol- and High Oleic Soybean Oil Vinyl Monomers in Miniemulsion Polymers," *ACS Sustain. Chem. Eng.*, vol. 7, no. 10, pp. 9613–9621, May 2019, doi: 10.1021/acssuschemeng.9b01137.
- [3] S. Molina-Gutiérrez, A. Manseri, V. Ladmira, R. Bongiovanni, S. Caillol, and P. Lacroix-Desmazes, "Eugenol: A Promising Building Block for Synthesis of Radically Polymerizable Monomers," *Macromol. Chem. Phys.*, vol. 220, no. 14, p. 1900179, Jul. 2019, doi: 10.1002/macp.201900179.
- [4] A. Badía, A. Agirre, M. J. Barandiaran, and J. R. Leiza, "Removable Biobased Waterborne Pressure-Sensitive Adhesives Containing Mixtures of Isosorbide Methacrylate Monomers," *Biomacromolecules*, vol. 21, no. 11, pp. 4522–4531, Nov. 2020, doi: 10.1021/acs.biomac.0c00474.