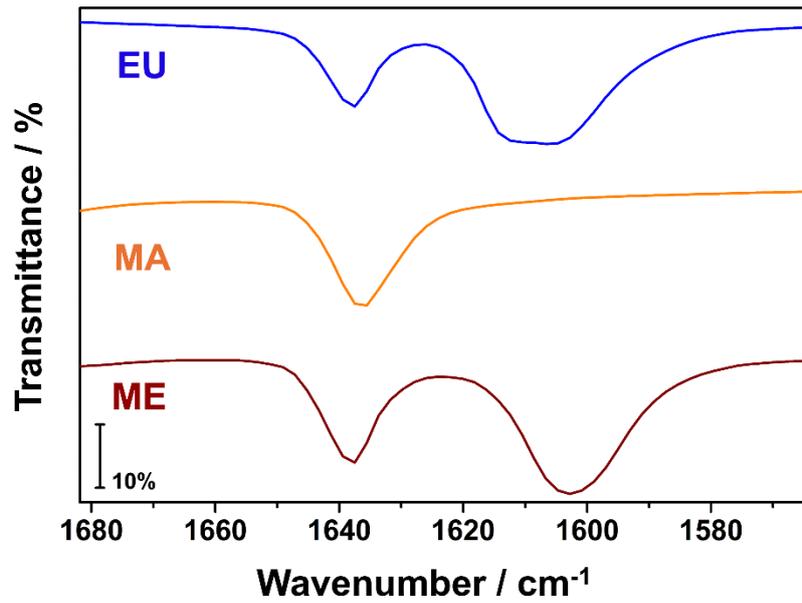# Supplementary information

Exploring Thiol-Ene and Thiol-Methacrylate Reactions in the Production of Renewable Materials from Methacrylated Eugenol

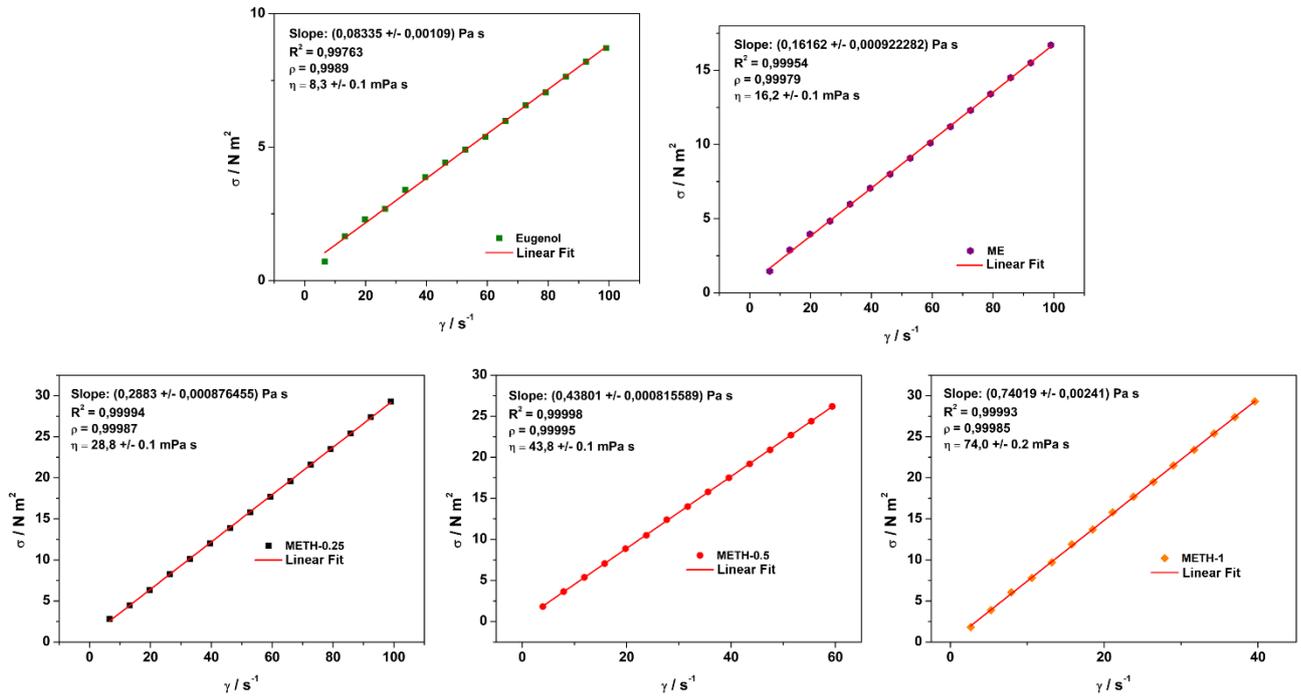Gabriel Iago dos Santos, [a] Caroline Gaglieri, [a] Fernanda Barreto dos Santos, [a] Sabrina Moises Moreno, [a] Gilbert Bannach, *[a]

[a] São Paulo State University (UNESP), School of Sciences, Bauru

Fig. S1 Magnification of the MIR spectra of eugenol (EU), methacrylic anhydride (MA), and methacrylated eugenol (ME), highlighting the C=C bonds region.

Fig. S2 Linear regression used to determine the dynamic viscosity of all samples analysed.
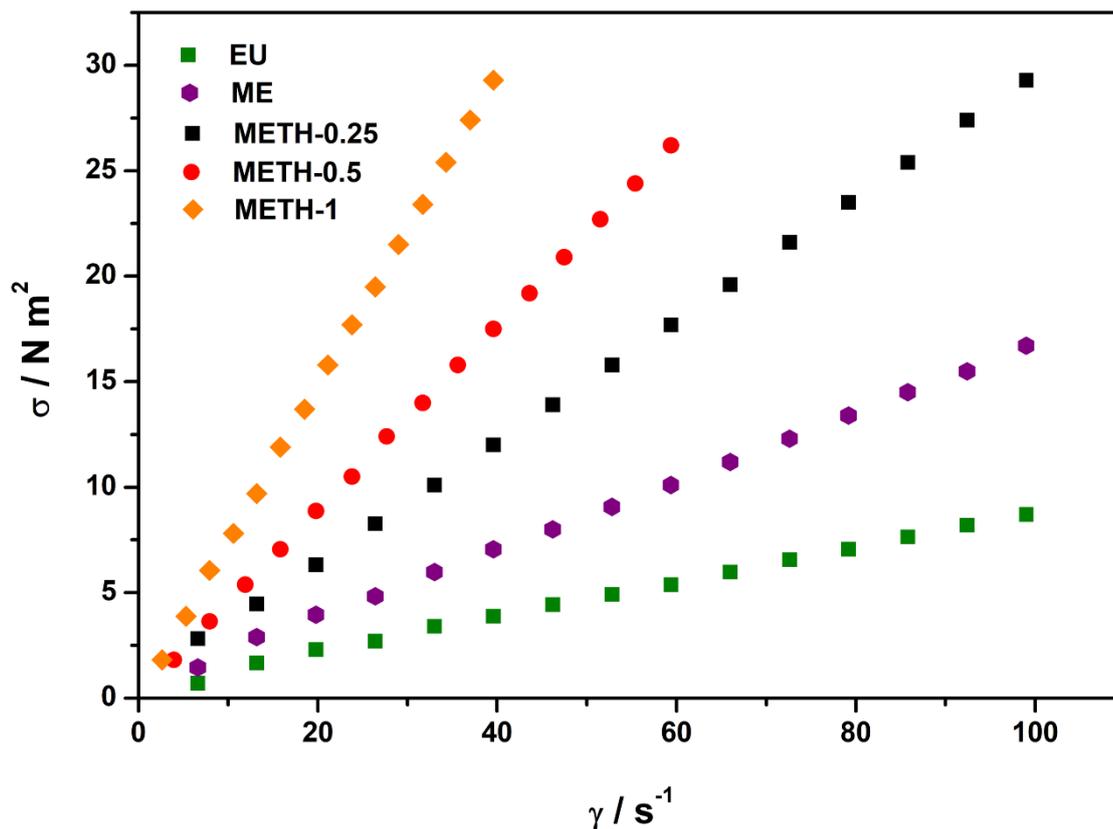
Fig. S3 Shear stress versus shear rate curves for the precursors and resins studied.

Table S1 Mass fraction of each component of the formulated resin.

	Mass fraction		
Resin	**ME**	**PETMP**	**TPO**
METH-0.25	0.77	0.20	0.03
METH-0.5	0.64	0.33	0.03
METH-1	0.47	0.50	0.03

Equations for the determination of DB_T, SH_T, DB_R, and DB_{ASP}.

As ME provides all double bonds of the system (allylic and methacrylic), the total of double bonds (DB_T) was calculated from Eq. S1.

$$DB_T = \frac{m_R \times F_{ME}}{MM_{ME}} \times 2$$

Eq. S1

Where m_R is the mass of the resin, F_{ME} is the mass fraction of ME (Table S1), MM_{ME} is the molar mass of ME (232.28 g mol^{-1}), and the number 2 corresponds to two C=C bonds present in ME.

Considering that the thiol amount depends on the double bonds (allylic and methacrylic), the total number of moles of S-H sites (SH_T) was calculated by using Eq.2:

$$SH_T = \frac{m_R \times F_{S-H}}{MM_{S-H}} \times 4$$

Eq. S2

Where F_{S-H} is the mass fraction of the thiol PETMP in the respective formulation (Table S1), and MM_{S-H} is the molar mass of PETMP (488.66 g mol^{-1}).

The total number of moles of double bonds reacted (DB_R) was determined using Eq. S3.

$$DB_R = DB_T \times \frac{C_{C=C}\%}{100}$$

Eq. S3

Where $C_{C=C}\%$ is the MC value obtained by MIR, after 120 s of UV exposure.

The total number of moles of double bonds reacted by ASP (thiol-ene or thiol-methacrylate) was determined from Eq. S4, assuming that each thiol site (SH) reacts stoichiometrically with one C=C double bond, and that the formation of disulfides as a side reaction is negligible.

$$DB_{ASP} = SH_T \times \frac{C_{S-H}\%}{100}$$

Eq. S4

Where $C_{S-H}\%$ is the conversion of SH groups determined by MIR, after 120 s of UV exposure.
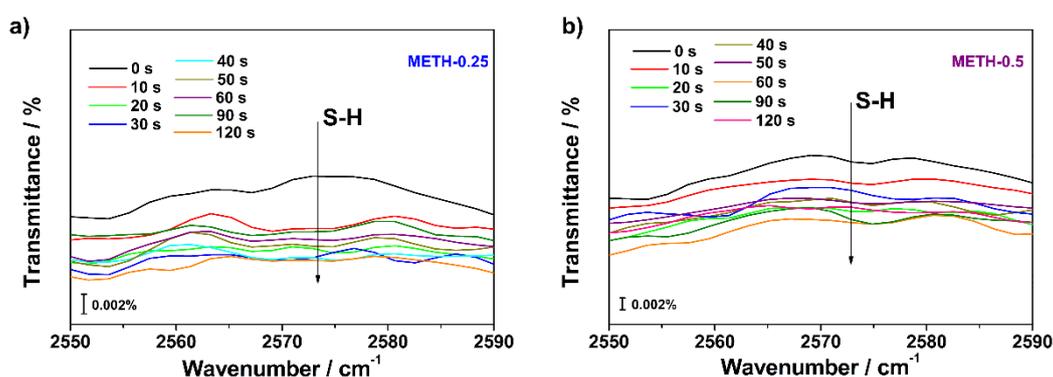
Fig. S4 Magnification of the MIR spectra of the systems a) METH-0.5 and b) METH-0.25 to highlight the S-H band during photopolymerization.
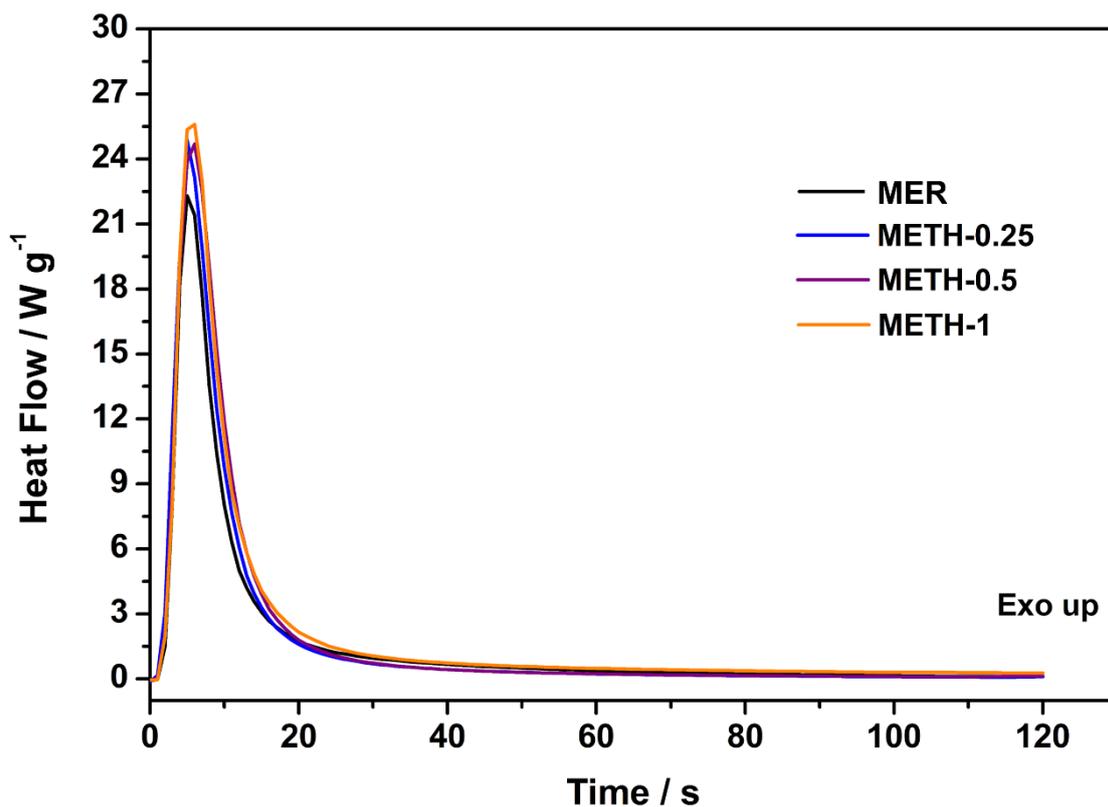
Fig. S5 Photo-DSC curves for each formulated resin.

Table S2 Photo-DSC results for all resins, including total enthalpy involved in photopolymerization (ΔH_T), polymerization ratio (R_p) at the time of the exothermic peak, as well as the time of the exothermic peak (PT).

Resin Name	ΔH_T / J g^{-1}	R_p / s^{-1}	PT / s
MER	194.1	6.7	61
METH-0.25	207.3	9.7	60
METH-0.5	219.0	10.5	53
METH-1	233.8	10.6	24

Table S3 Data relating to temperature ranges (θ), mass loss values (Δm), peak temperatures (T_p), maximum degradation rate temperature (T_{MDR}), and maximum degradation rate (MDR) associated with each mass loss stage of the polymers.

Step	Sample	PMER	PMETH-0.25	PMETH-0.5	PMETH-1
1st	θ/ °C	144.0-348.0	179.0-287.0	191.0-284.0	214.0-497.0
	Δm / %	14.9	4.2	3.4	81.3
	T_p/ °C	308.0 ↑; 366.0 ↑	229.0 ↑	---	393.0 ↑; 456.0 ↑
	T_{MDR}/ °C	244.0	264.0	---	362.0; 431.0
	MDR/ % min⁻¹	0.7	0.4	---	9.1; 5.7
2nd	θ/ °C	348.0-466.0	287.0-490.0	284.0-487.0	497.0-680.0
	Δm / %	59.3	76.9	73.9	17.9
	T_p/ °C	449.0 ↑	358.0 ↑; (408.0-478.0)ᵃ	(396.0-463.0)ᵃ	552.0 ↑
	T_{MDR}/ °C	430.0	339.0; 360.0; 398.0; 406.0; 417.0	339.0; 378.0; 389.0; 398.0; 414.0; 421.0	543.0; 552.0
	MDR/ % min⁻¹	17.1	1.7; 3.9; 7.5; 7.7; 7.9	2.7; 7.2; 7.2; 7.2; 6.4; 6.4	3.1; 3.0
3rd	θ/ °C	466.0-637.0	490.0-652.0	487.0-667.0	---
	Δm / %	24.8	17.9	22.2	---
	T_p/ °C	526.0 ↑	552.0 ↑	555.0 ↑	---
	T_{MDR}/ °C	525.0	547.0	553.0	---
	MDR/ % min⁻¹	2.8	2.7	3.0	---

↑ = Exothermic peak. ᵃ Exotherm.
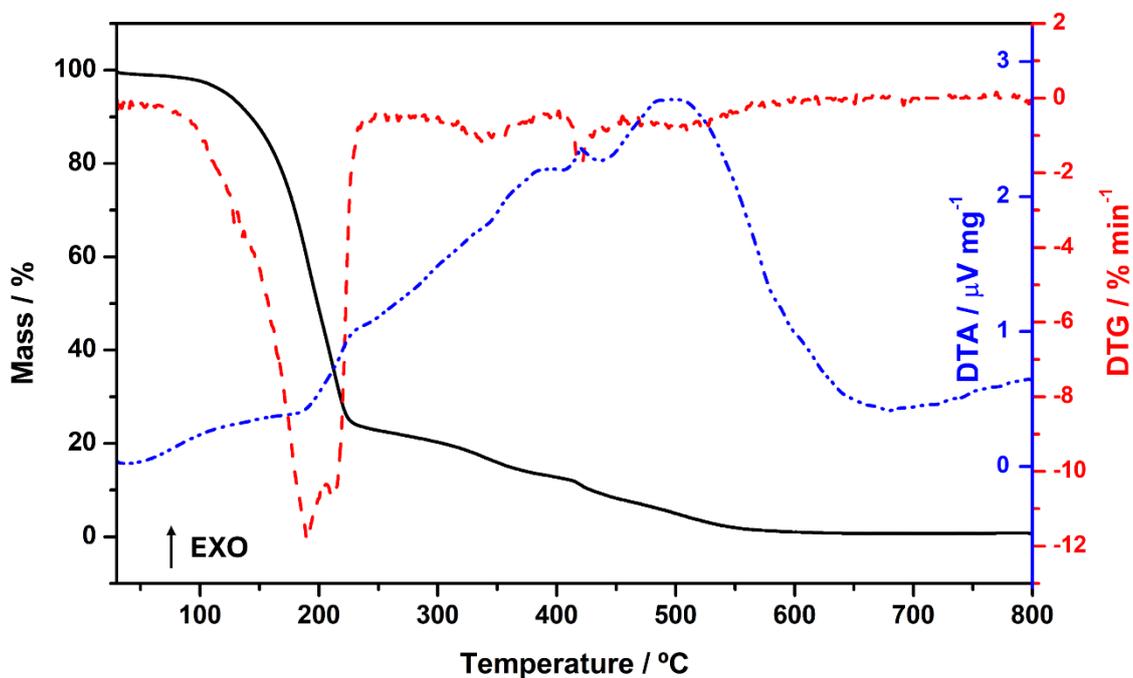
**Fig. S6** TG/DTG-DTA curves for ME.

Table S4 Data relating to temperature ranges (θ), mass loss values (Δm), peak temperatures (T_p), maximum degradation rate temperature (T_{MDR}), and maximum degradation rate (MDR) associated with each mass loss stage of ME.

Step	Sample	ME
1st	θ/ °C	30.0-78.0
	Δm / %	1.4
	T_p/ °C	---
	T_{MDR}/ °C	---
	MDR/ % min⁻¹	---
2nd	θ/ °C	78.0-253.0
	Δm / %	75.9
	T_p/ °C	188.8 ↓; 231.0 ↑
	T_{MDR}/ °C	129.4; 190.1; 210.3
	MDR/ % min⁻¹	3.4; 11.8; 10.6
3rd	θ/ °C	252.8-400.8
	Δm / %	9.9
	T_p/ °C	(345.9-398.2)[a]
	T_{MDR}/ °C	336.8
	MDR/ % min⁻¹	1.16
4th	θ/ °C	400.8-624.8
	Δm / %	11.9
	T_p/ °C	498.3 ↑
	T_{MDR}/ °C	509.8
	MDR/ % min⁻¹	0.9

↑ = Exothermic peak. ↓ = Endothermic peak [a] Exotherm.
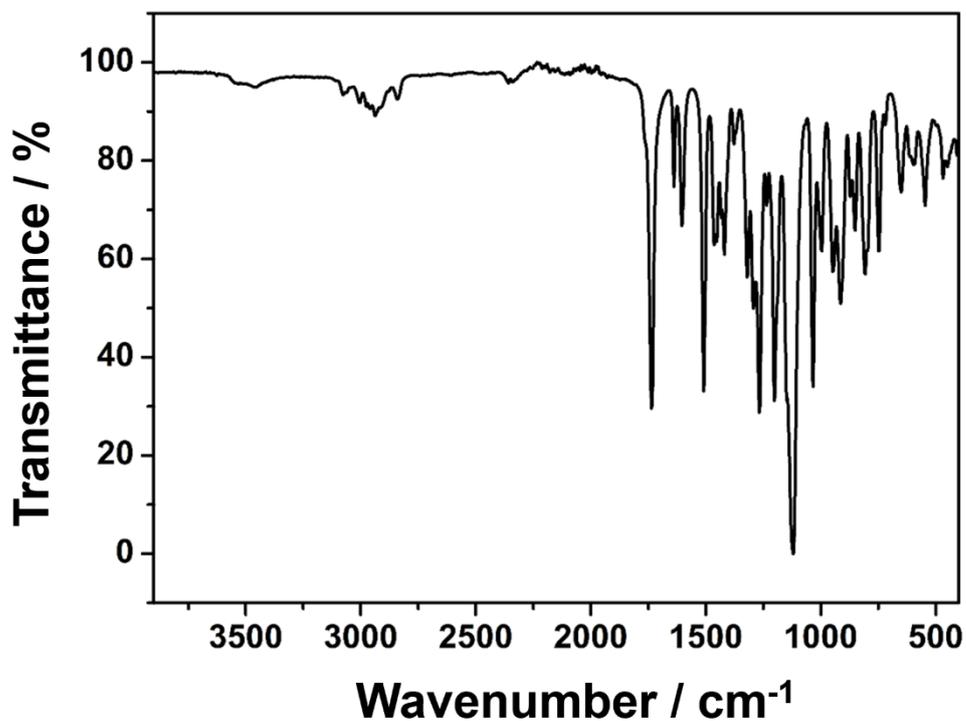
Fig. S7 MIR spectrum for the condensate collected after heating the PMETH-0.5 sample.

Homopolymerization resulting structure   **Thiol-ene/methacrylate resulting structure**
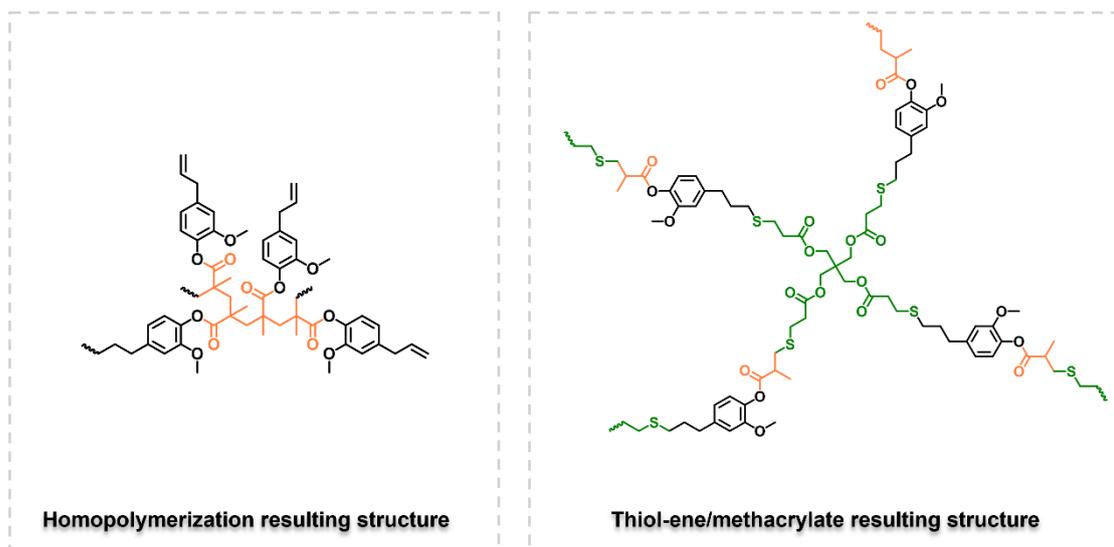
Fig. S8 Illustration of the structures resulting from homopolymerization and thiol-ene/methacrylate ASP reactions.

Table S5 Working curves for METH-0.25, METH-0.5, and METH-1 resins.

Resin Name	E_c / mJ cm^{-2}	D_p / μm	R^2
METH-0.25	5.01	413.29	0.99
METH-0.5	5.38	503.49	0.99
METH-1	5.16	470.41	0.99