Supplemental Materials

Terpene- and Terpenoid-based Polymeric Resins for Stereolithography 3D Printing

Andrew C Weems[a], Kayla R Delle Chiaie [a], Joshua C Worch [a], Connor J Stubbs [a], Andrew P Dove [a]

[a]School of Chemistry, University of Birmingham, Birmingham, United Kingdom, B15 2TT

Methods

Synthesis of Limonene Prepolymer: Limonene (1.0 g, 7.3 mmol) and pentaerthritol tetrakis(3-mercaptopropionate) (PETMP) (0.76 g, 1.6 mmol) were added to a rbf in a 1:1 ratio and dissolved in 10% wt acetone. To this solution was added 1.5% wt photoiniator (Irgacure 819), dissolved by stirring and then irradiated for 4 h at room temperature. The solution was concentrated, dissolved in ethyl acetate, and washed with 1 M HCl. The prepolymer was isolated and used as an oligomer for resin synthesis.

Synthesis of Linalool Prepolymer: Linalool (1.00 g) and PETMP (0.76 g) were added to a vial along with acetone (0.66 g) and mixed until a homogenous solution was produced. To this, Irgacure 819 photoinitiator (0.079 g) was added. The prepolymer solution was irradiated with 365 nm light for 4 h. The solution was concentrated, dissolved in ethyl acetate, and washed with 1 M HCl. The prepolymer was isolated and used as an oligomer for resin synthesis.

Geraniol Prepolymer: Geraniol (1.00 g) and PETMP (0.76 g) were added to a vial along with acetone (0.66 g) and mixed until a homogenous solution was produced. To this, Irgacure 819 photoinitiator (0.079 g) was added. The prepolymer solution was irradiated with 365 nm light for 4 h. The solution was concentrated, dissolved in ethyl acetate, and washed with 1 M HCl. The prepolymer was isolated and used as an oligomer for resin synthesis.

Nerol Prepolymer: Nerol (1.00 g) and PETMP (0.76 g) were added to a vial along with acetone (0.67 g) and mixed until homogenized. To this vial, Irgacure 819 photoinitiator (0.081) g was added and mixed until solubilized. The prepolymer solution was irradiated with 365 nm light for 4 h. The solution was concentrated, dissolved in ethyl acetate, and washed with 1 M HCl. The prepolymer was isolated and used as an oligomer for resin synthesis

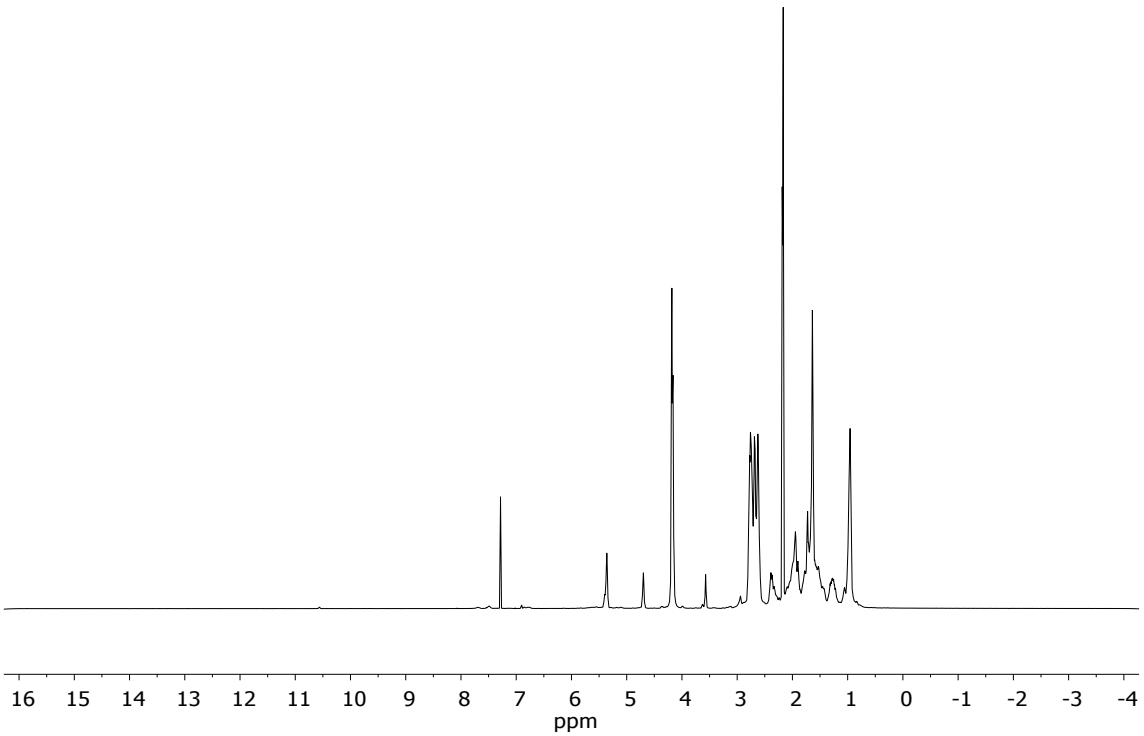

Figure S1. ^{1}H NMR spectrum of limonene prepolymer ($CDCl_3$, 400 MHz, 300 K).

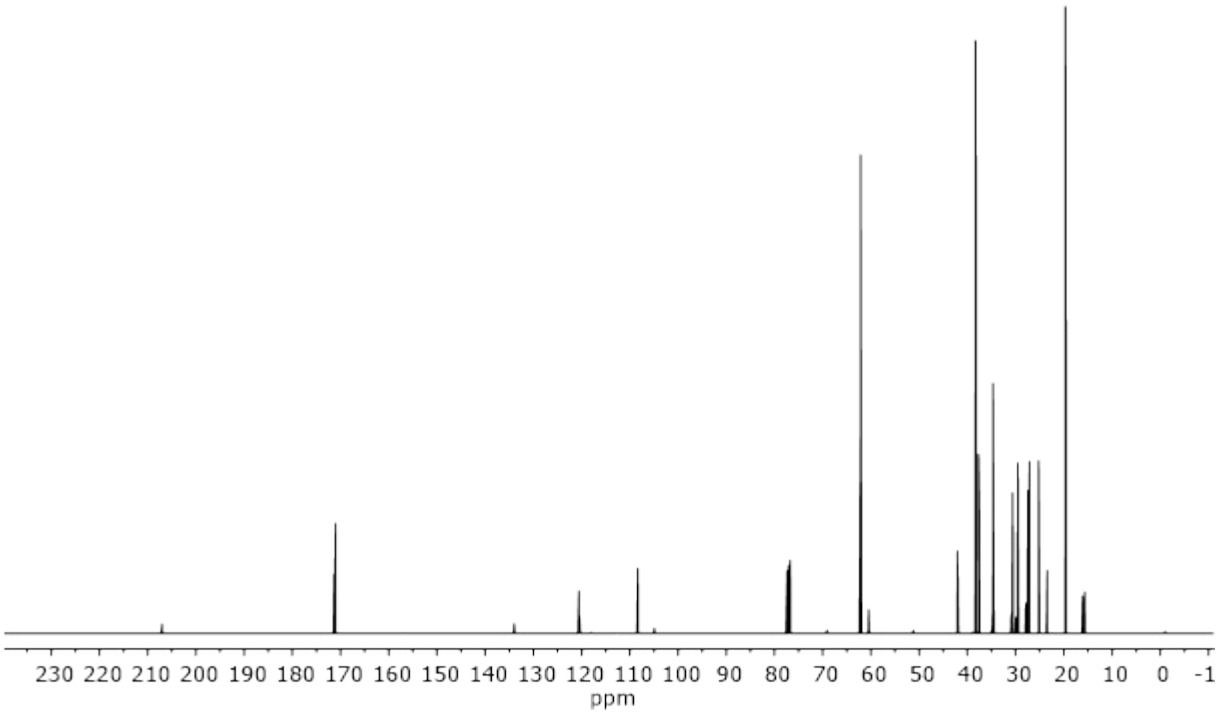

Figure S2. ^{13}C NMR spectrum of limonene prepolymer ($CDCl_3$,100 MHz, 300 K).

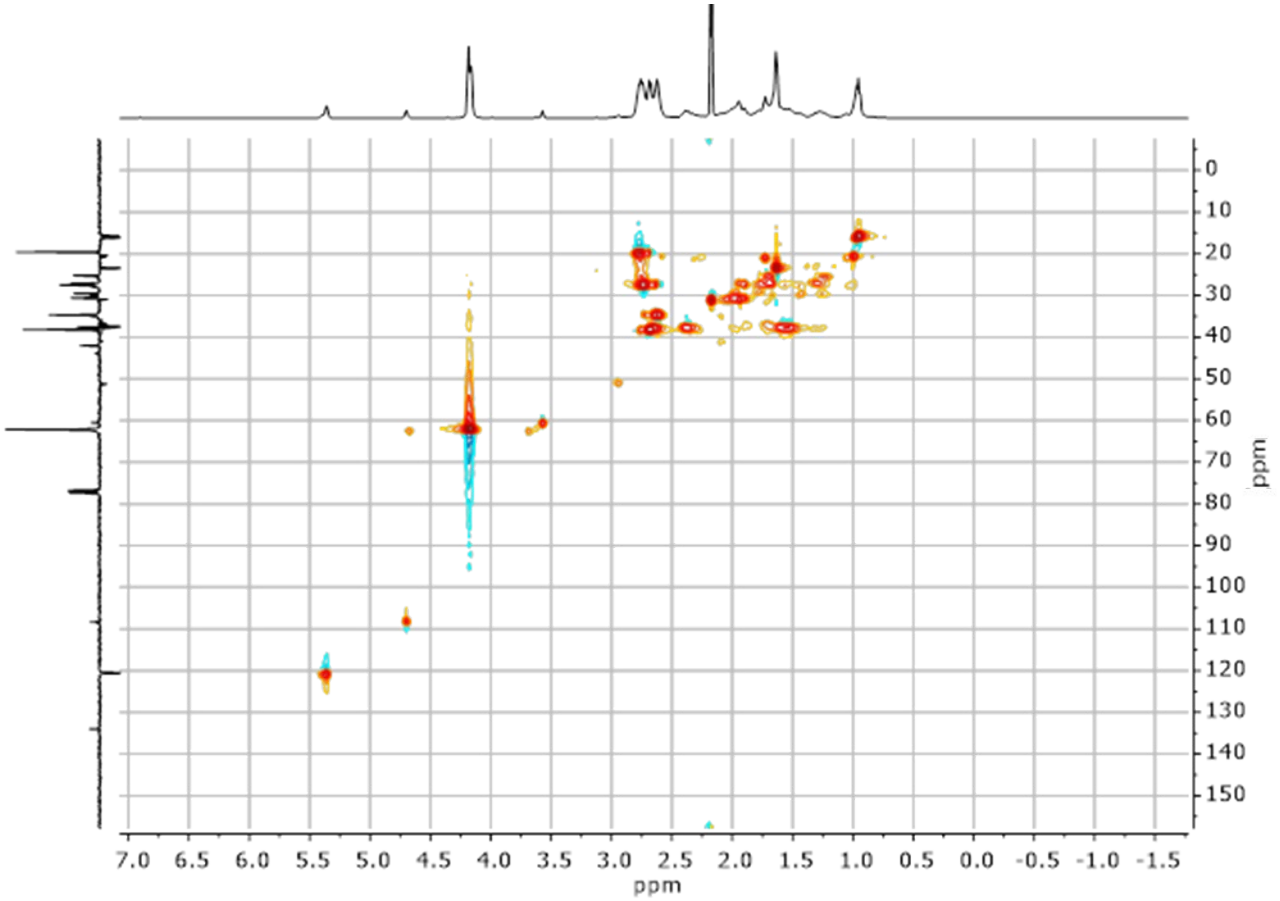

Figure S3. HSQC NMR spectrum of limonene prepolymer ($CDCl_3$, 400 MHz, 300 K).

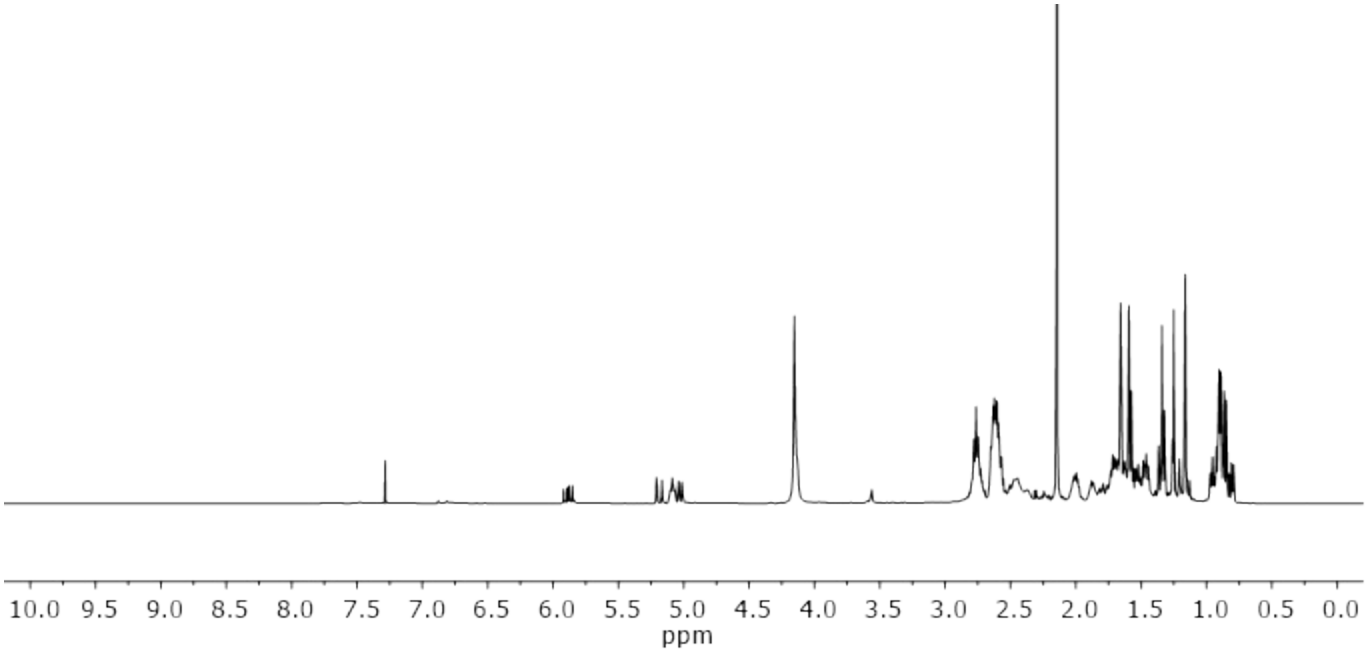

Figure S4. ^{1}H NMR spectrum of linalool prepolymer ($CDCl_3$, 400 MHz, 300 K).

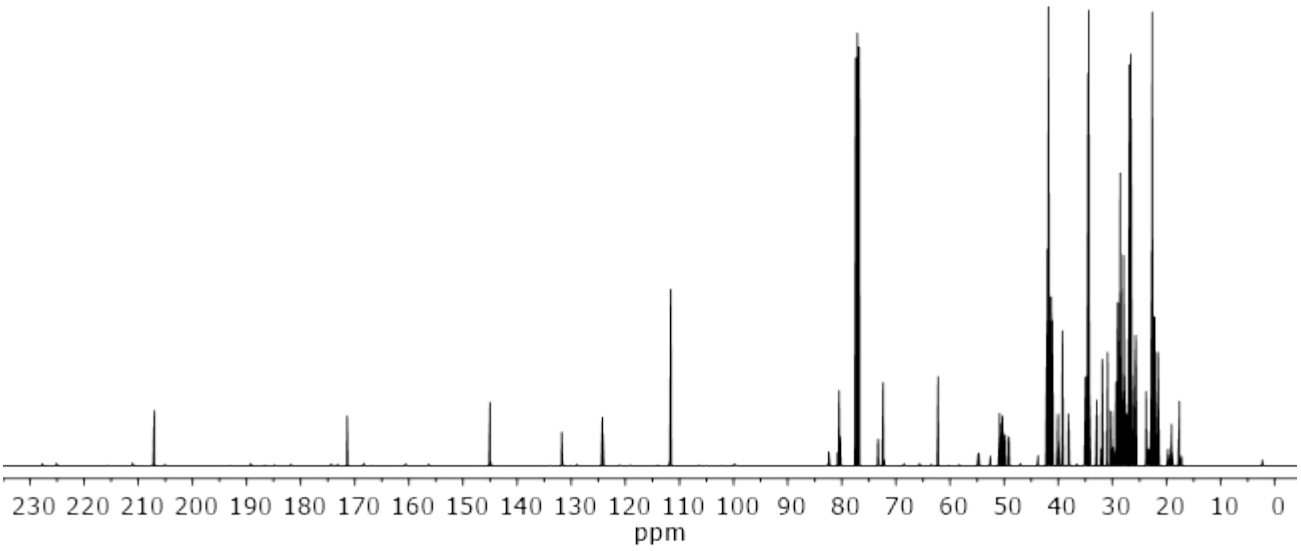

Figure S5. ^{13}C NMR spectrum of linalool prepolymer ($CDCl_3$, 100 MHz, 300 K).

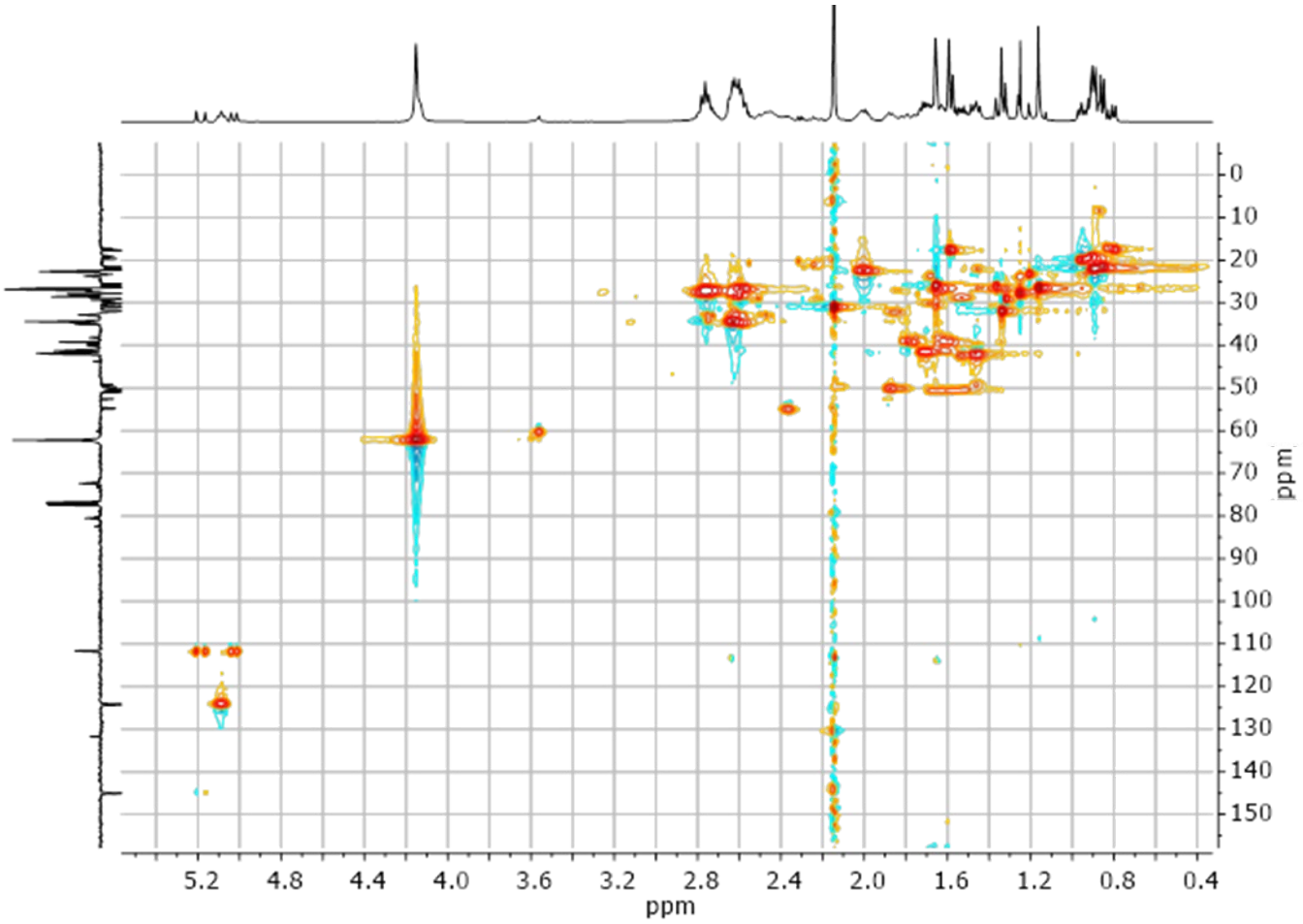

Figure S6. HSQC NMR spectrum of linalool prepolymer ($CDCl_3$, 400 MHz, 300 K).

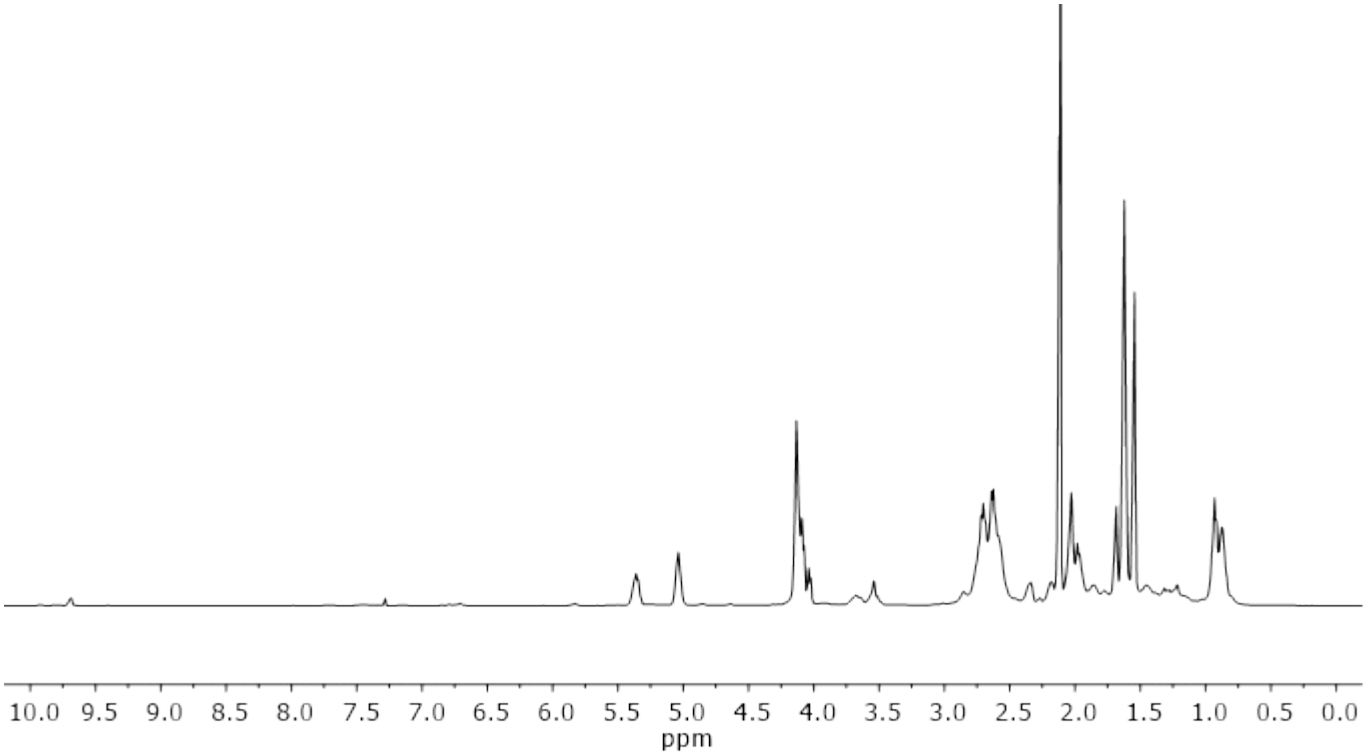

Figure S7. ^{1}H NMR spectrum of nerol prepolymer ($CDCl_3$, 400 MHz, 300 K).

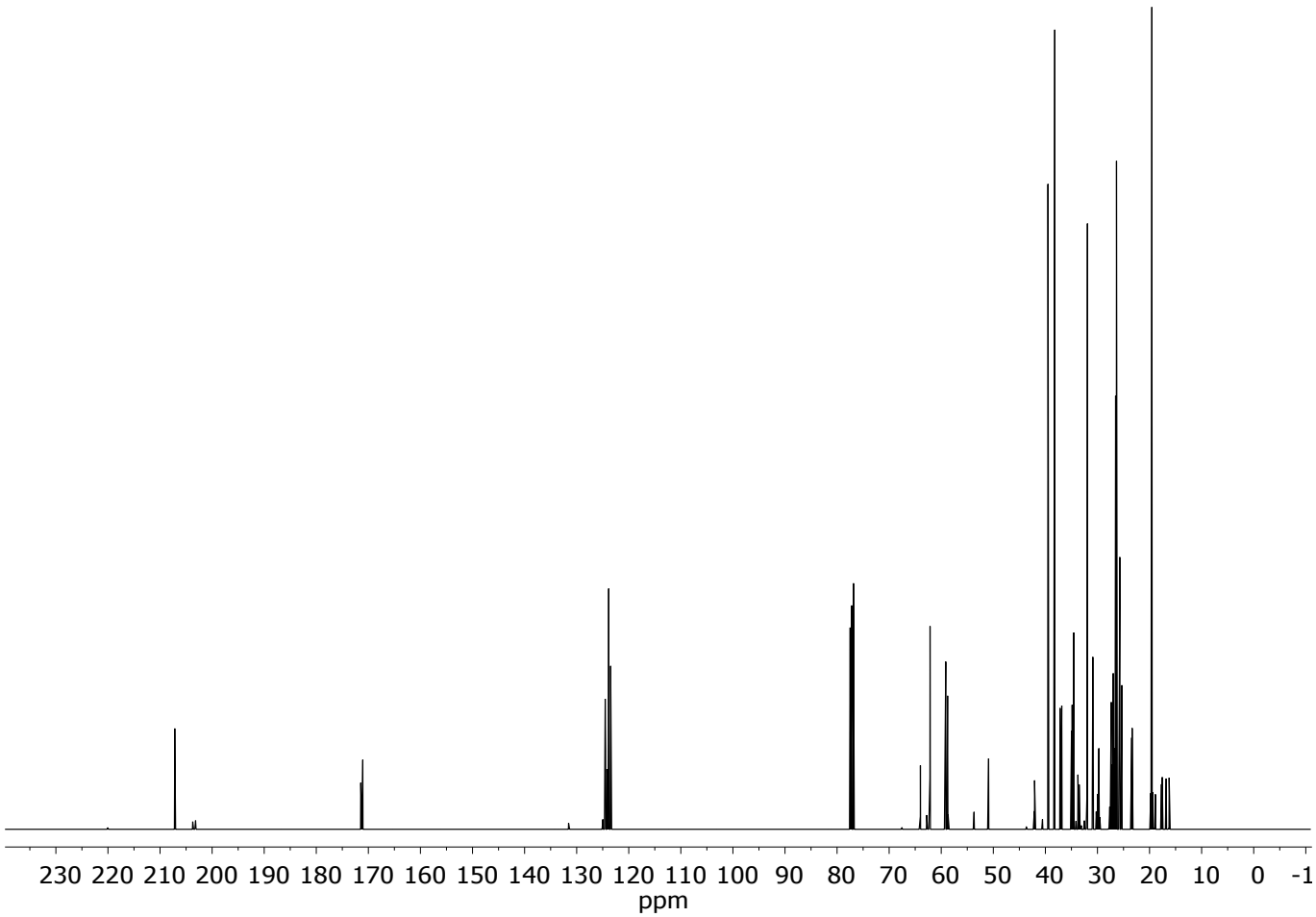

Figure S8. ^{13}C NMR spectrum of nerol prepolymer ($CDCl_3$, 100 MHz, 300 K).

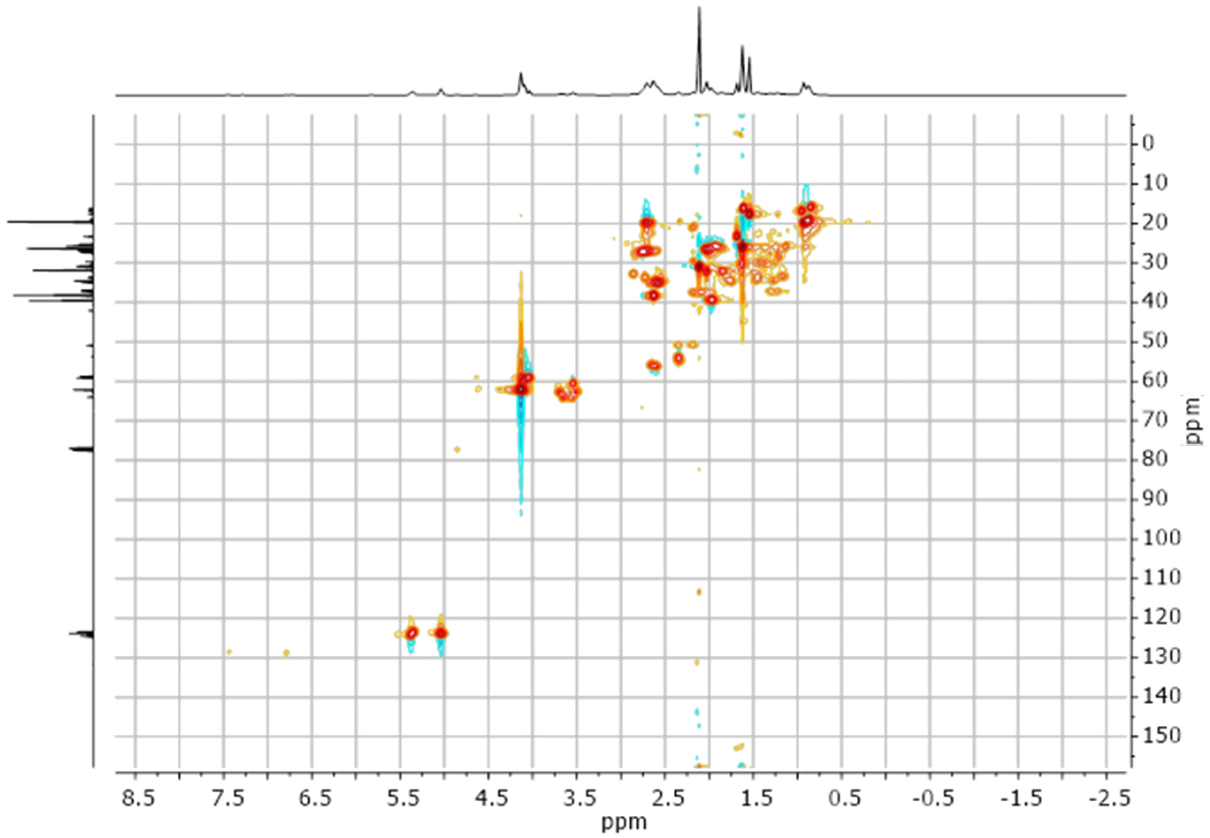

Figure S9. HSQC NMR spectrum of nerol prepolymer ($CDCl_3$, 400 MHz, 300 K).

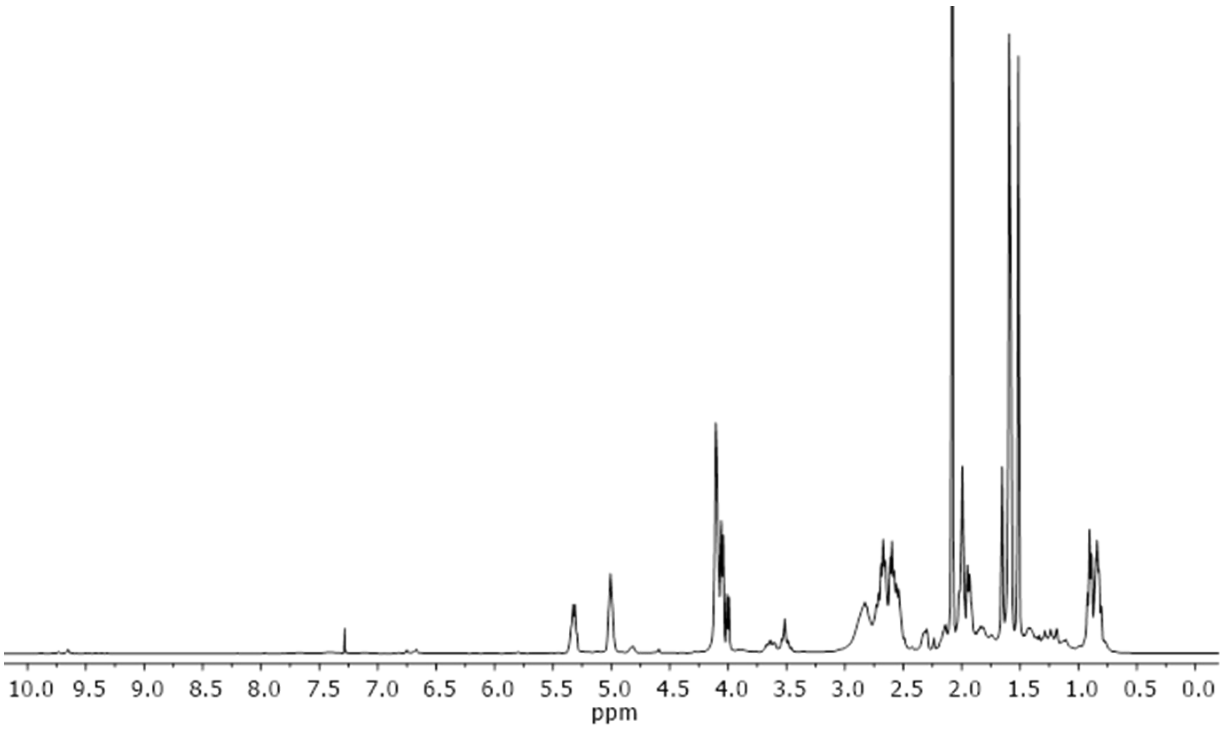

Figure S10. ^1H NMR spectrum of geraniol prepolymer ($CDCl_3$, 400 MHz, 300 K).

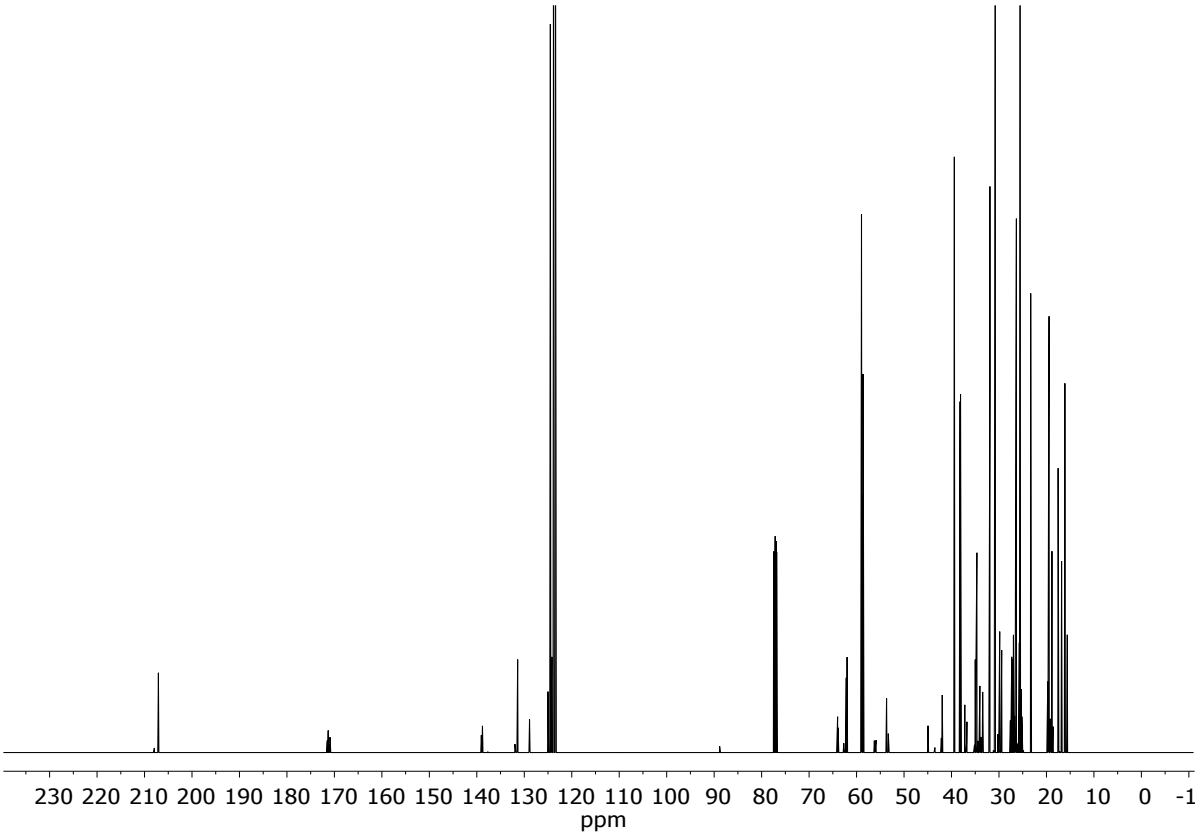

Figure S11. ^{13}C NMR spectrum of geraniol prepolymer ($CDCl_3$, 100 MHz, 300 K).

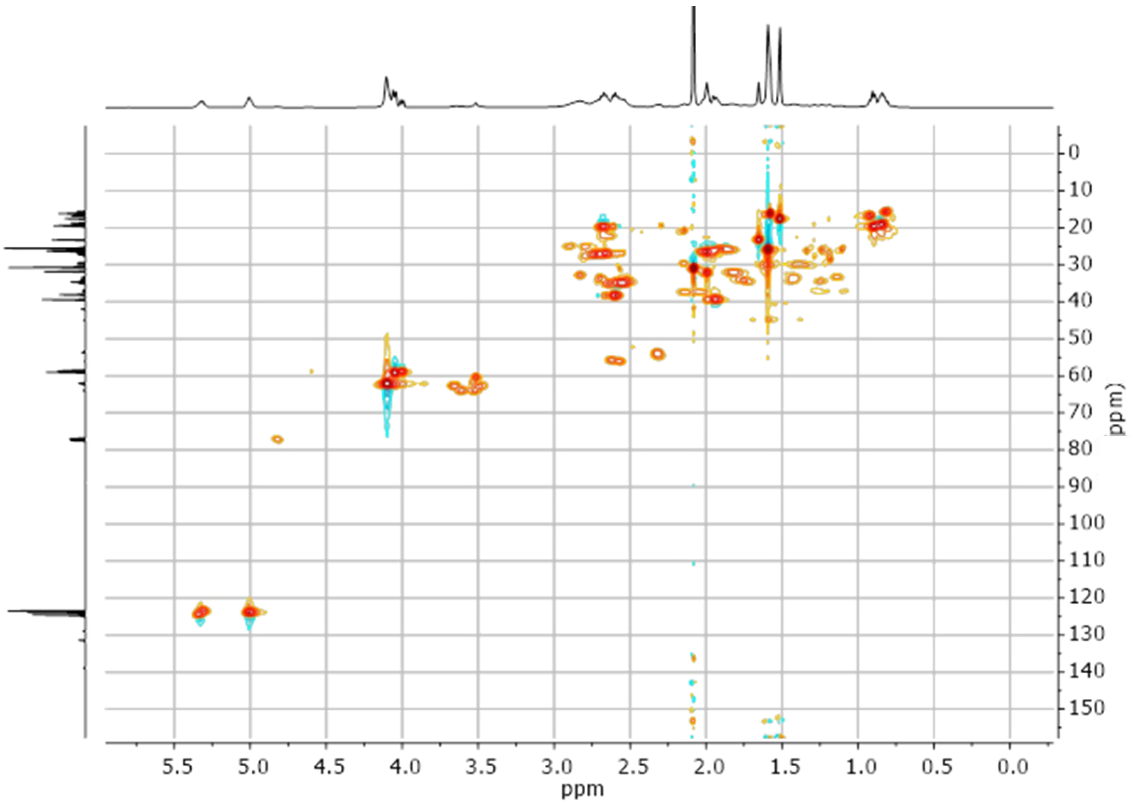

Figure S12. HSQC NMR spectrum of geraniol prepolymer ($CDCl_3$, 400 MHz, 300 K).

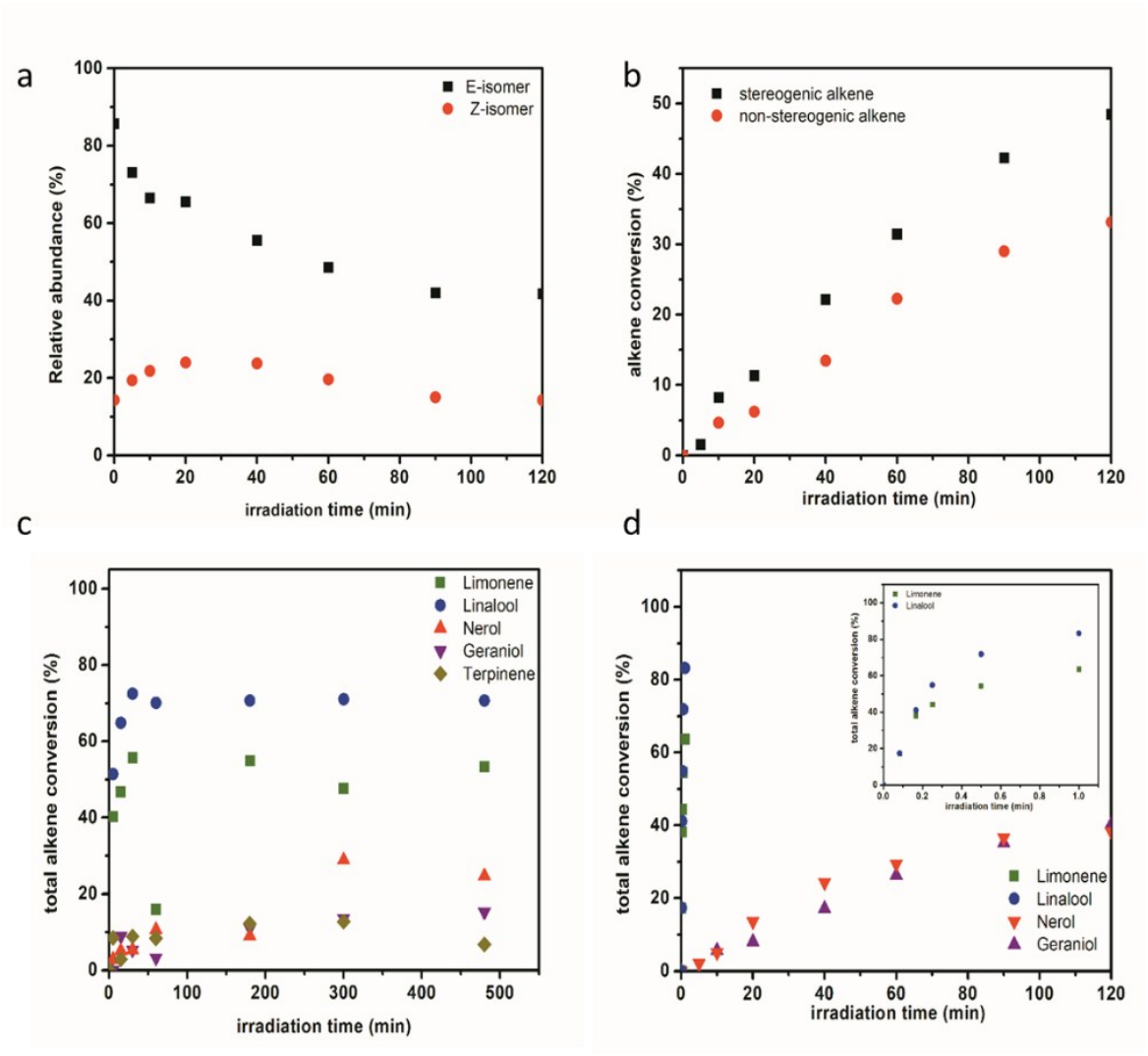

Figure S13. Alkene conversion vs. irradiation time for a) relative percentage of the E- and Z-alkene isomer for the polymerization of geraniol, b) consumption of the stereogenic and non-stereogenic alkenes in geraniol over time, c) total alkene conversion over time for different terpene monomers (2:1 alkene:thiol) during the formation of the prepolymers, and d) total alkene conversion over time for different terpene monomers (1:1 alkene:thiol). (Irradiated with 365 nm light).

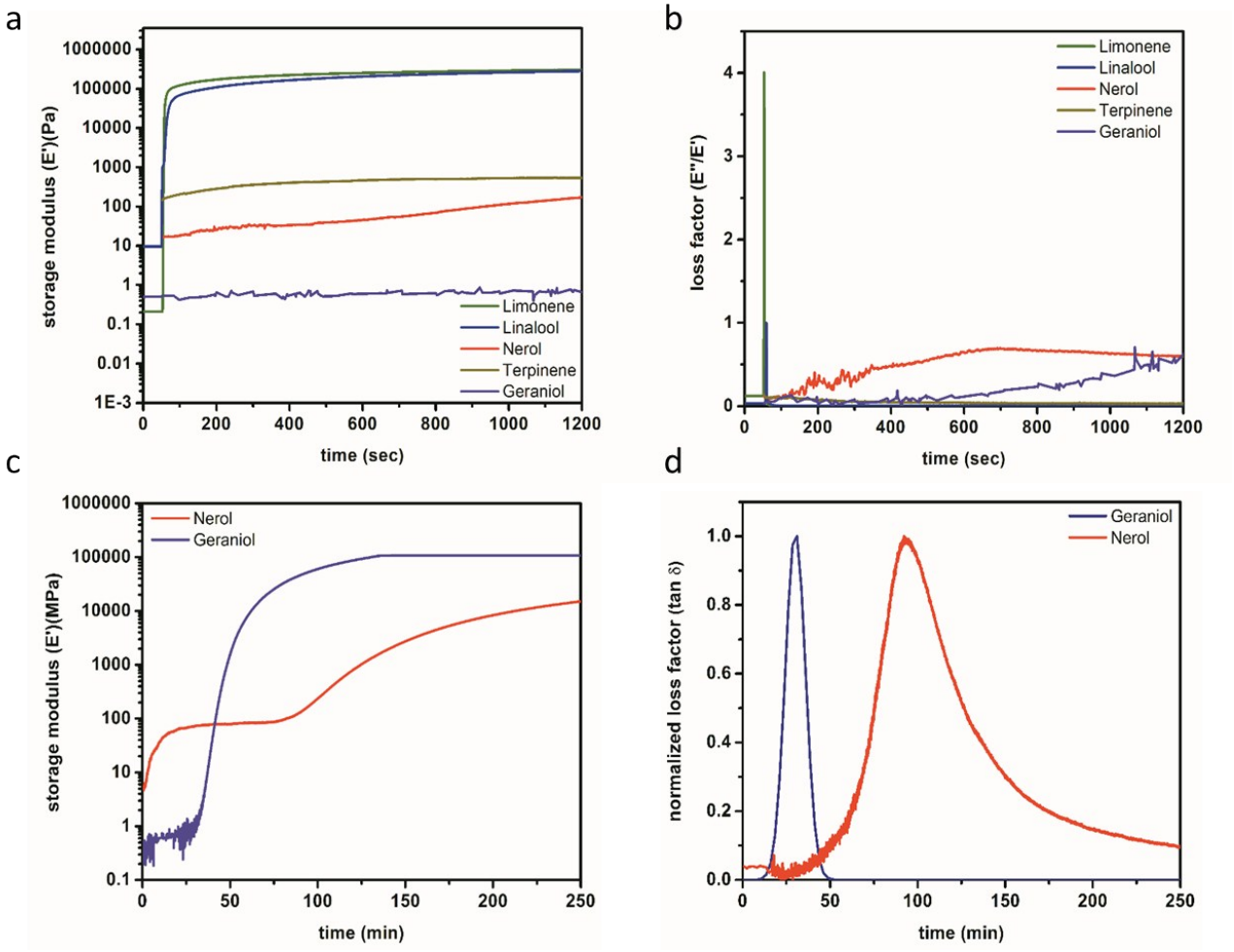

Figure S14. Photorheology of monomer resin systems over the initial 1200 s irradiation (a-b) and for nerol and geraniol over an extended 3.5 h irradiation (c-d), displaying the storage moduli of the networks (a,c) and the normalized loss moduli with peaks indicating phase transition times (b,d).

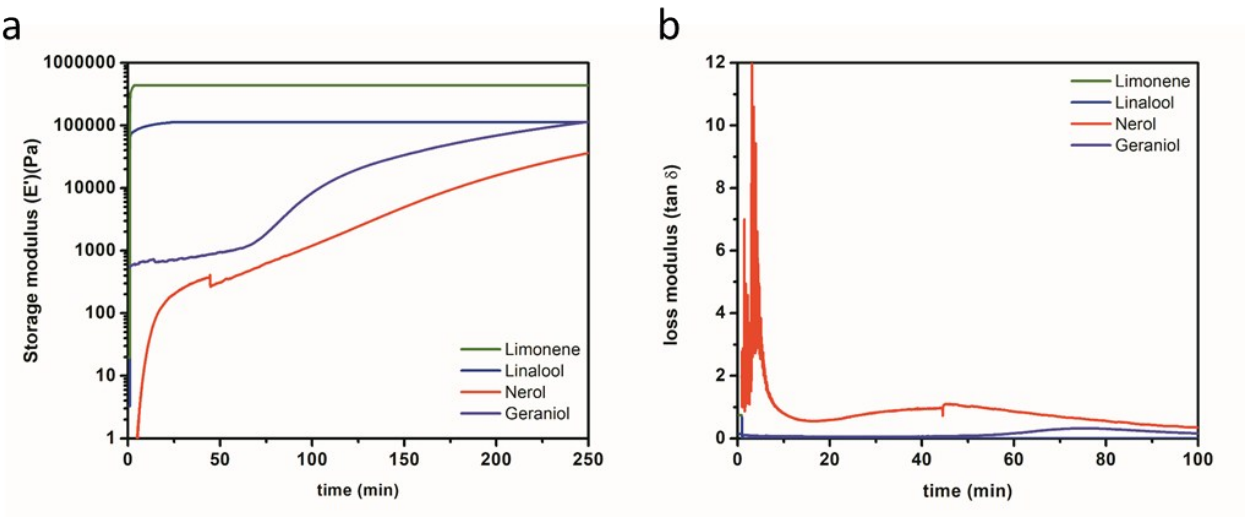

Figure S15. Photorheology of prepolymer resin systems over 3.5 h irradiation, displaying the storage moduli of the networks (a) and the normalized loss moduli with peaks indicating phase transitions (b).

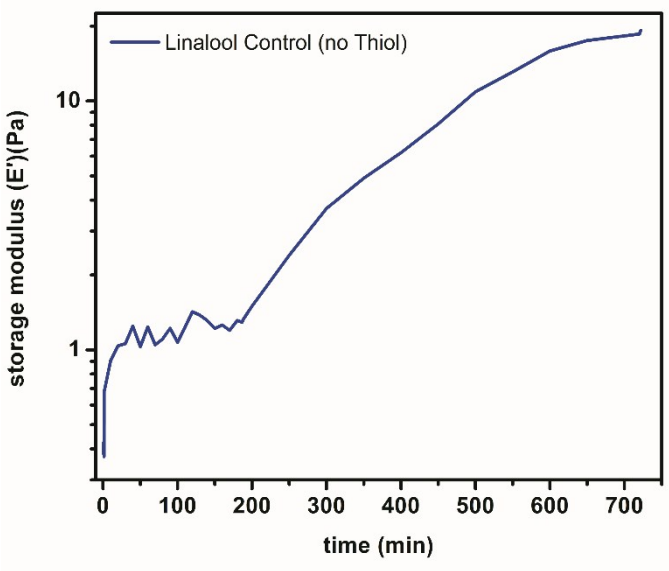

Figure S16. Photorheology of linalool monomer with only 1.5% wt photoinitiator added, irradiated over 3.5 h, displaying the storage moduli of the mixture.

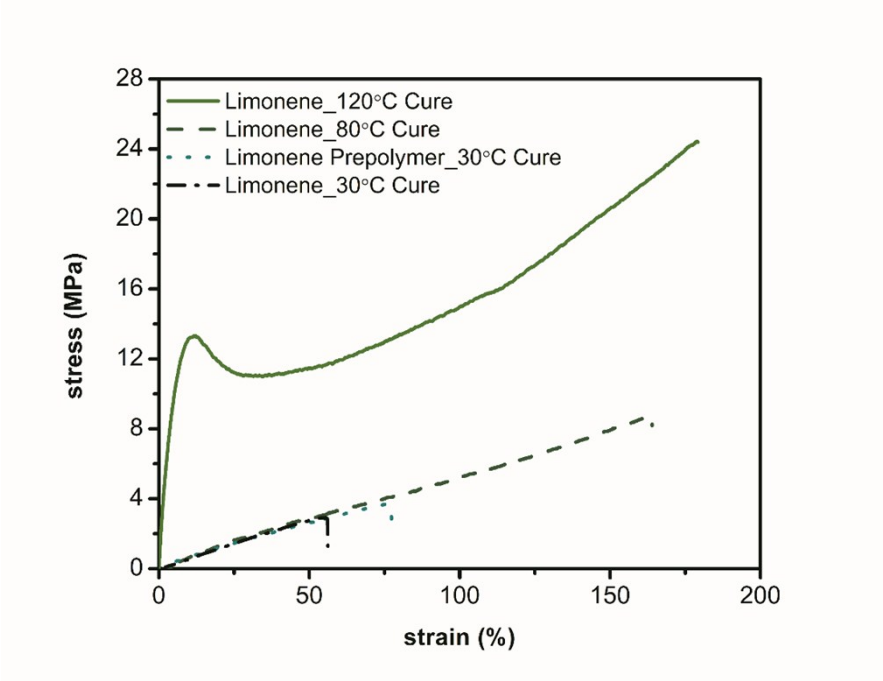

Figure S17. Representative tensile stress-strain curves for limonene polymer films as a function of post-polymerization treatment temperatures, all conducted over 12 h. Tensile testing was conducted at room temperature at 5 mm/min.

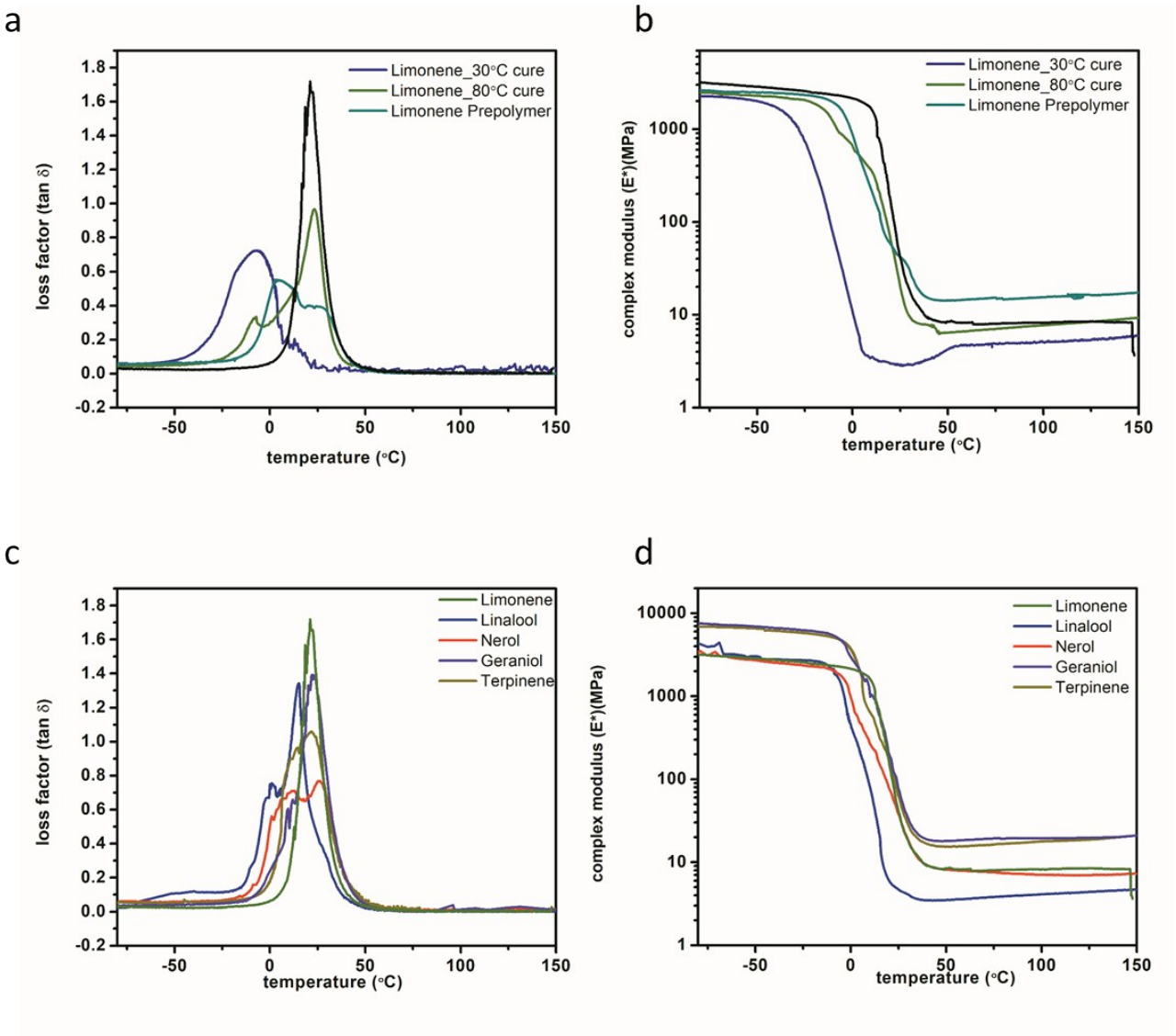

Figure S18. Dynamic mechanical analysis (DMA) of limonene networks (a,b) as a function of different curing conditions and of monomer systems (c,d) cured at 120 °C for 12 h. Phase transitions as determined by tan *δ* (a,c) and complex moduli (b,d) of the networks are displayed. (n=3)

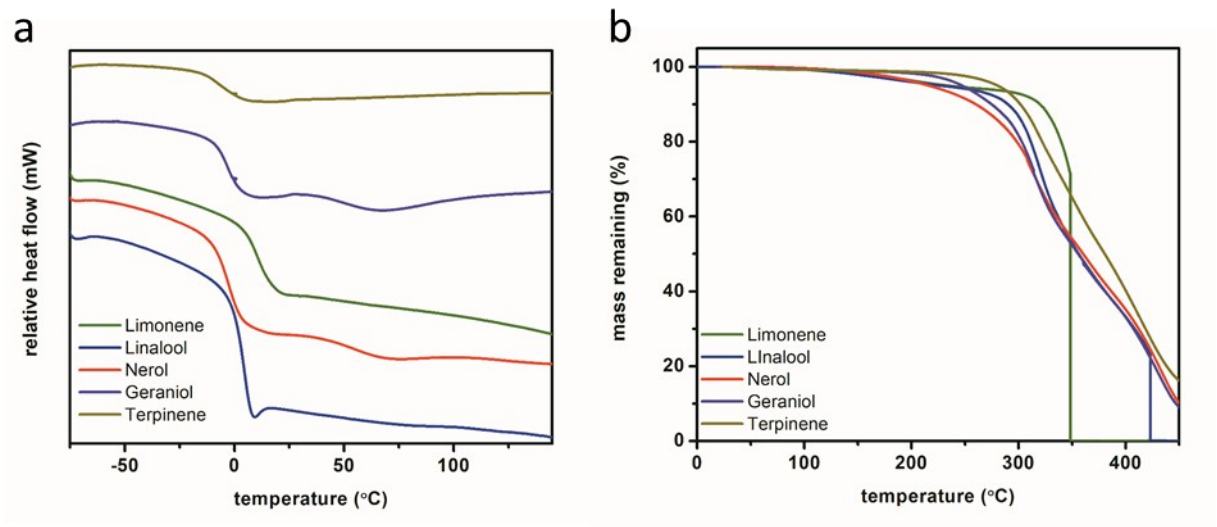

Figure S19. Differential scanning calorimetry (DSC, a) and thermogravimetric analysis (TGA, b) thermograms for monomer-based polymer networks.

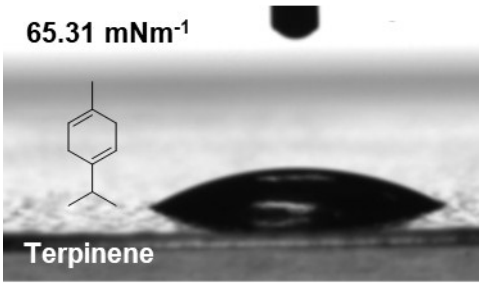

Figure S20. Contact angle pictograph of terpinene surface during water contact angle.

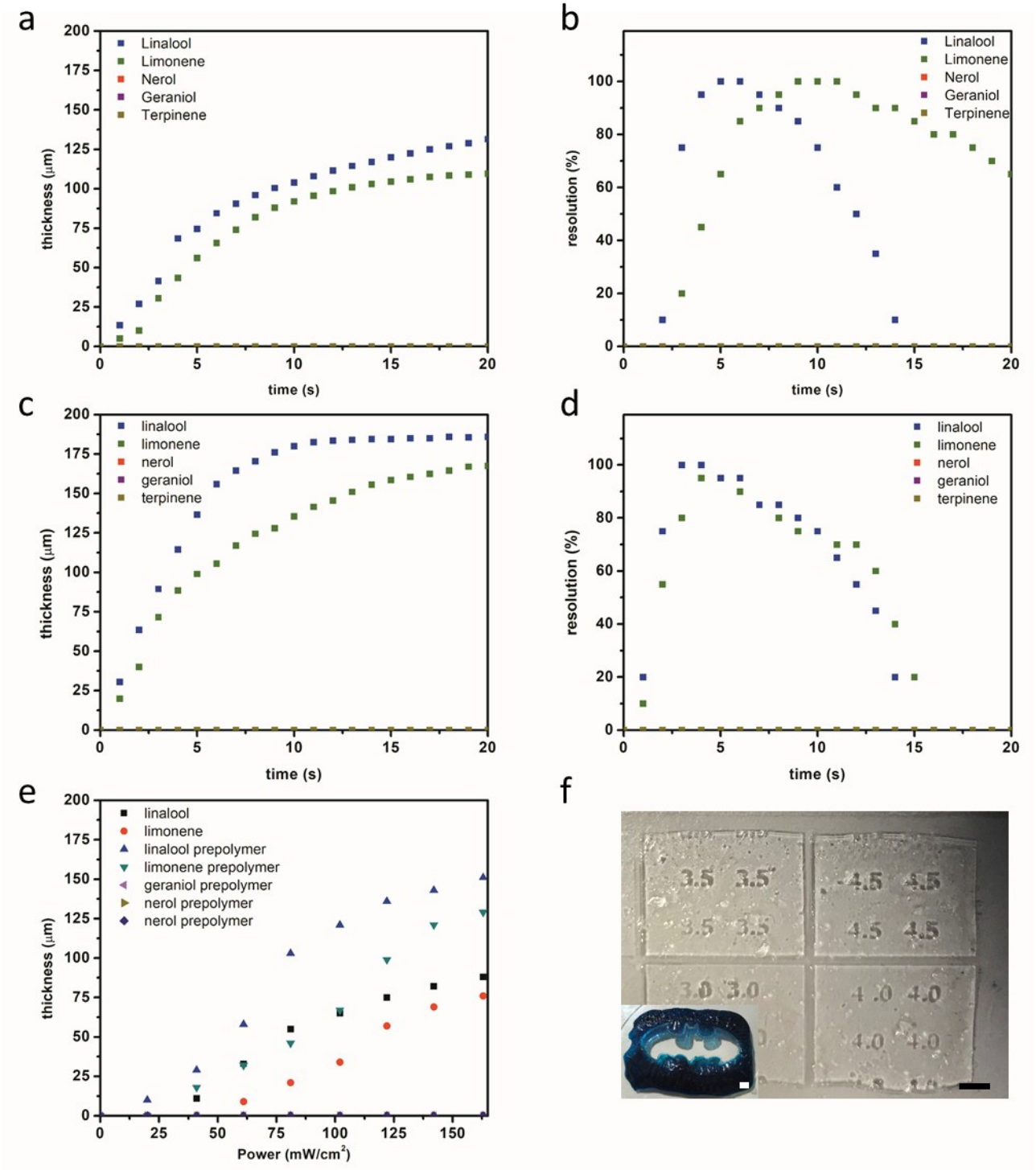

Figure S21. Digital light processing working curves of monomers (a,b) and prepolymer resins (c,d), displaying the film thickness as a function of irradiation time (a,c,e) and the semi-quantified print feature resolution as a function of irradiation time (b,d) with example features printed as representative features (f and insert, bar =260 μm).

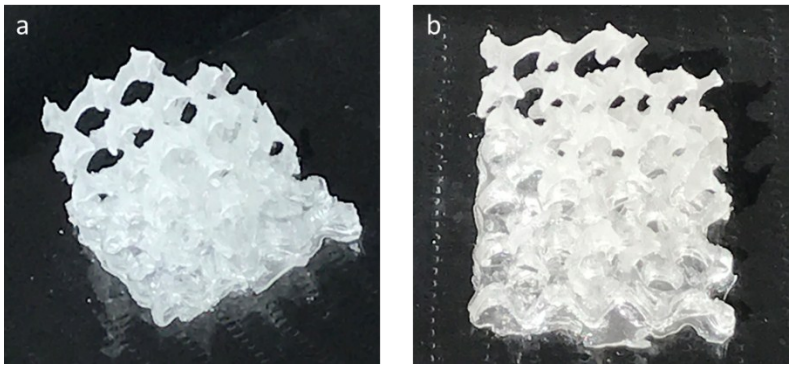

Figure S22. Cross sectioned Hart's cubes, sectional diagonally to display the pores along both the z-axis (printing axis) and those achieved in the xy plane (printing vat) of the linalool (a) and limonene prepolymer (b) resins.

Table S1. Consumption of double bonds in limonene with PETMP during irradiation at λ = 365 nm in acetone.

TIME (S)	EXO CONVERSION	ENDO CONVERSION
0	0	0
5	0.31	0.01
10	0.64	0.07
15	0.73	0.09
30	0.83	0.19
60	0.93	0.27

Table S2. Consumption of double bonds in linalool with PETMP during irradiation at λ = 365 nm in acetone.

TIME (S)	TRISUBSTITUTED CONVERSION	DISUBSTITUTED CONVERSION
0	0	0
5	0.16	0.21
10	0.39	0.48
15	0.51	0.69
30	0.69	0.81
60	0.80	0.93

Table S3. Consumption of double bonds in nerol with PETMP during irradiation at λ = 365 nm in acetone

TIME (S)	DISUBSTITUTED CONVERSION	TRISUBSTITUTED CONVERSION
0	0	0
300	0.03	0.01
600	0.07	0.03
1200	0.17	0.10
2400	0.28	0.20
3600	0.34	0.25
5400	0.43	0.31
7200	0.45	0.31

Table S4. Consumption of double bonds in geraniol with PETMP during irradiation at λ = 365 nm in acetone.

TIME (S)	DISUBSTITUTED CONVERSION	TRISUBSTITUTED CONVERSION
0	0	0
300	0.02	-0.02
600	0.08	0.05
1200	0.11	0.06
2400	0.22	0.13
3600	0.31	0.22
5400	0.42	0.29
7200	0.48	0.33

Table S5. Consumption of double bonds in limonene prepolymer with PETMP kinetics during irradiation at λ = 365 nm in acetone

TIME (MIN)	EXO CONVERSION	ENDO CONVERSION
0	0	0
5	0.54	0.13
15	0.64	0.13
30	0.74	0.20
60	0.36	-0.25
180	0.73	0.18
300	0.66	0.11
480	0.72	0.16

Table S6. Consumption of double bonds in nerol prepolymer with PETMP during irradiation at λ = 365 nm in acetone.

TIME (S)	DISUBSTITUTED CONVERSION	TRISUBSTITUTED CONVERSION
0	0	0
300	0.03	0.03
900	0.08	0.03
1800	0.09	0.02
3600	0.16	0.06
10800	0.16	0.07
18000	0.36	0.22
28800	0.34	0.15

Table S7. Consumption of double bonds in geraniol prepolymer with PETMP during irradiation at λ = 365 nm in acetone.

TIME (S)	DISUBSTITUTED CONVERSION	TRISUBSTITUTED CONVERSION
0	0	0
300	-0.02	-0.03
900	0.10	0.08
1800	0.08	0.03
3600	0.09	-0.02
10800	0.17	0.06
18000	0.22	0.06
28800	0.24	0.07

Table S8. Consumption of double bonds in linalool prepolymer with PETMP during irradiation at λ = 365 nm in acetone.

TIME (S)	TRISUBSTITUTED CONVERSION	DISUBSTITUTED CONVERSION
0	0	0
300	0.50	0.55
900	0.63	0.72
1800	0.71	0.79
3600	0.68	0.77
10800	0.69	0.77
18000	0.69	0.78
28800	0.68	0.78

Table S9. Thermal behaviour of terpene polymers as determined by DSC, DMA and TGA for monomer systems cured at 120 °C; specific testing conditions are listed in the Methods and Materials section.

TERPENE	DMA		DSC		TGA	
	Tan δ (°C)	E^* inflection point (°C)	Onset transition (°C)	Half height transition (°C)	5% mass loss (°C)	10% mass loss (°C)
LIMONENE	23.2	11.0	0.3	10.9	228.9	320.4
LINALOOL	15.1	9.4	-4.1	2.7	228.9	290.4
NEROL	11.9/25.9	15.6	-13.8	-3.3/ 51.3	216.1	206.2
GERANIOL	11.9/21.9	19.3	-15.9/29.0	-2.5/52.0	216.3	290.0
TERPINENE	21.7	11.6	-19.4	-3.2	280.4	301.6

Table S10. Water and diiodomethane contact angles, utilized to calculate dispersive and polar contributions, as well as surface free energy of spin-coated terpene polymer surfaces. (n=3)

	WATER CONTACT ANGLE (°)	**DIIODOMETHANE CONTACT ANGLE** (°)	**DISPERSIVE CONTRIBUTION** (MNM^{-1})	**POLAR CONTRIBUTION** (MNM^{-1})	**TOTAL SFE** (MNM^{-1})
LIMONENE	73.80 ± 2.97	39.26 ± 2.75	39.98	4.26	44.25
LINALOOL	49.77 ± 1.54	41.73 ± 1.78	38.73	16.82	55.55
NEROL	44.47 ± 2.98	44.05 ± 2.84	37.52	20.59	58.11
GERANIOL	38.66 ± 2.78	55.71 ± 3.81	31.04	28.24	59.28
TERPENINE*	31.31 ± 2.78	45.05 ± 2.57	36.98	28.32	65.31

Uncertainties for reaction to be calculated *under-cured version (hence increased wetting)