Supporting Information for

Composition-Property Engineering of Bio-Derived UV-Curable Acrylate Oligoester Resins for Tuneable Mechanics in 3D Printing

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Table S1. Composition of the synthesized resins

			Diacid		Diol		
Class	Sample[a]	% completion[b]	IA(eq)	SA(eq)	1,2-PDO(eq)	1,4-BDO(eq)	1,8-ODO(eq)
PDO	100:0	78	1.0	0.0	1.45	-	-
	90:10	76	0.9	0.1	1.45	-	-
	80:20	76	0.8	2.0	1.45	-	-
	70:30	77	0.7	0.3	1.45	-	-
	60:40	78	0.6	0.4	1.45	-	-
	50:50	76	0.5	0.5	1.45	-	-
BDO	100:0	80	1.0	0.0	-	1.45	
	90:10	89	0.9	0.1	-	1.45	-
	80:20	89	0.8	2.0	-	1.45	-
	70:30	89	0.7	0.3	-	1.45	-
	60:40	86	0.6	0.4	-	1.45	-
	50:50	87	0.5	0.5	-	1.45	-
ODO	100:0	86	1.0	0.0	-	-	1.45
	90:10	88	0.9	0.1	-	-	1.45
	80:20	88	0.8	2.0	-	-	1.45
	70:30	89	0.7	0.3	-	-	1.45
	60:40	91	0.6	0.4	-	-	1.45
	50:50	91	0.5	0.5	-	-	1.45

[a] Sample names based on the % ratio of diacid composition. The 50:50 sample contains 50% itaconic and 50% succinic acid of diacid composition.
[b] Percent completion (% completion) was measured using titration with KOH as outlined in ASTM D7253.

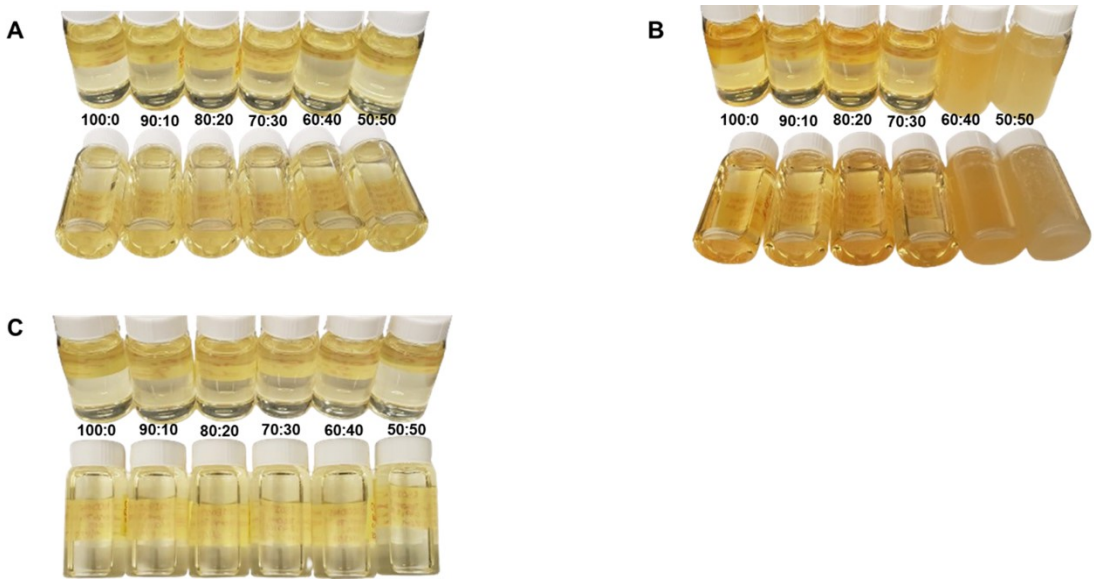

Figure S1. Photographs of mixed resins containing PDO (A), BDO (B), and ODO (C).

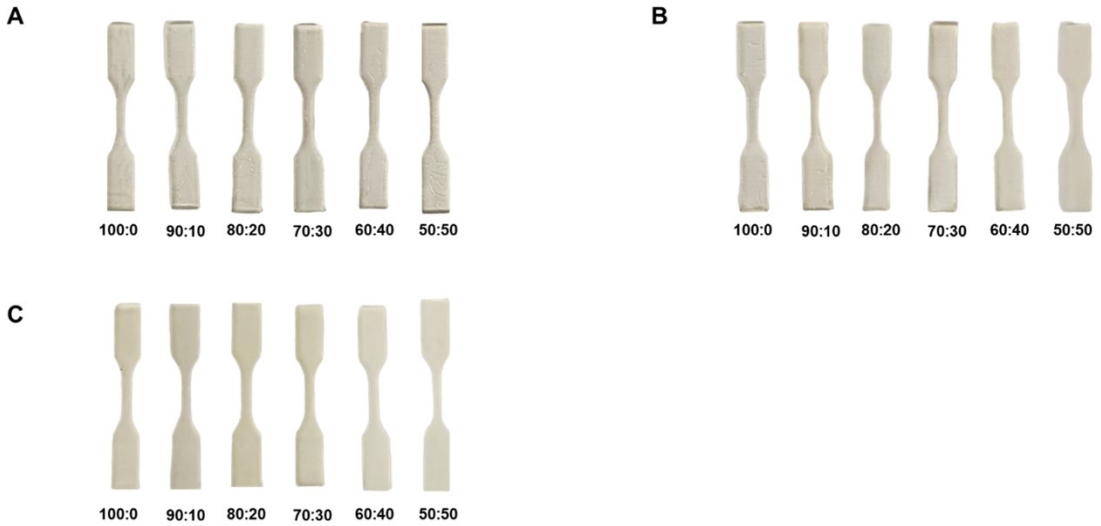

Figure S2. Molded dogbone static tensile testing specimens containing PDO (A), BDO (B), and ODO (C).

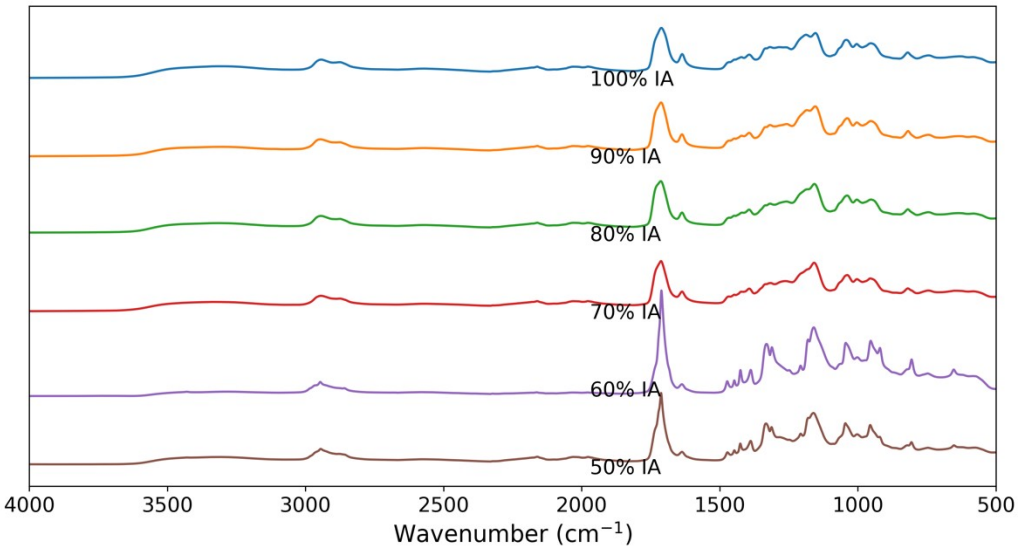

Figure S3. FTIR spectra of BDO-containing oligoesters.

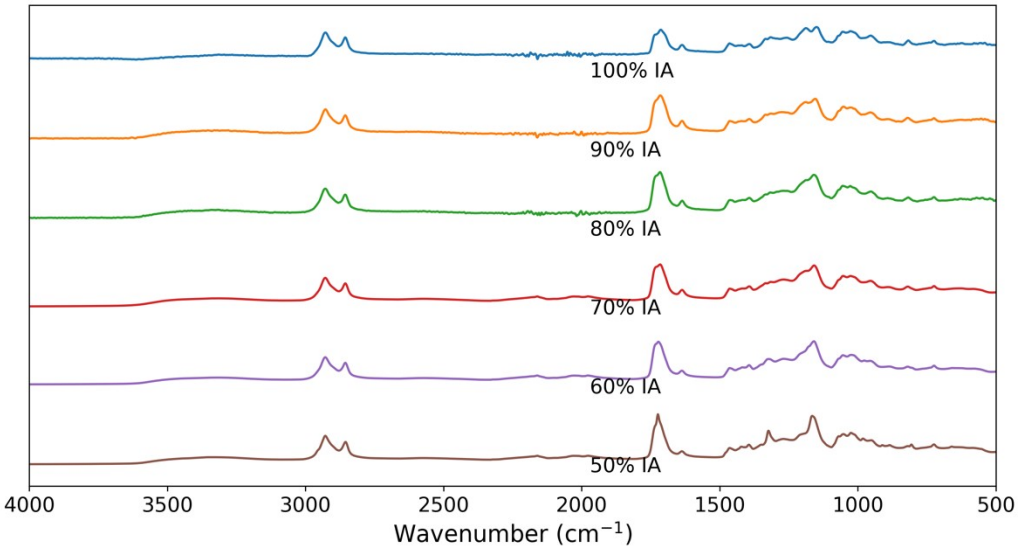

Figure S4. FTIR spectra of ODO-containing oligoesters.

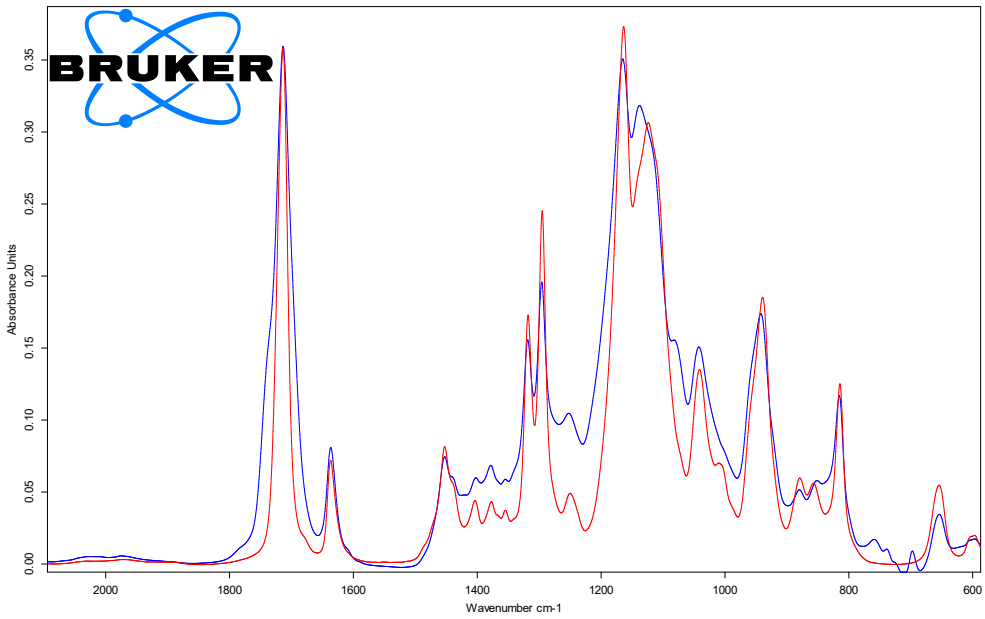

Figure S5: TEGDMA (red) and PDO,100:0 (blue) before polymerization, showing that the PDO,100:0 spectrum, is dominated by TEGDMA peaks. The C=O peak is broader due to overlapping with acid C=O from itaconic acids.

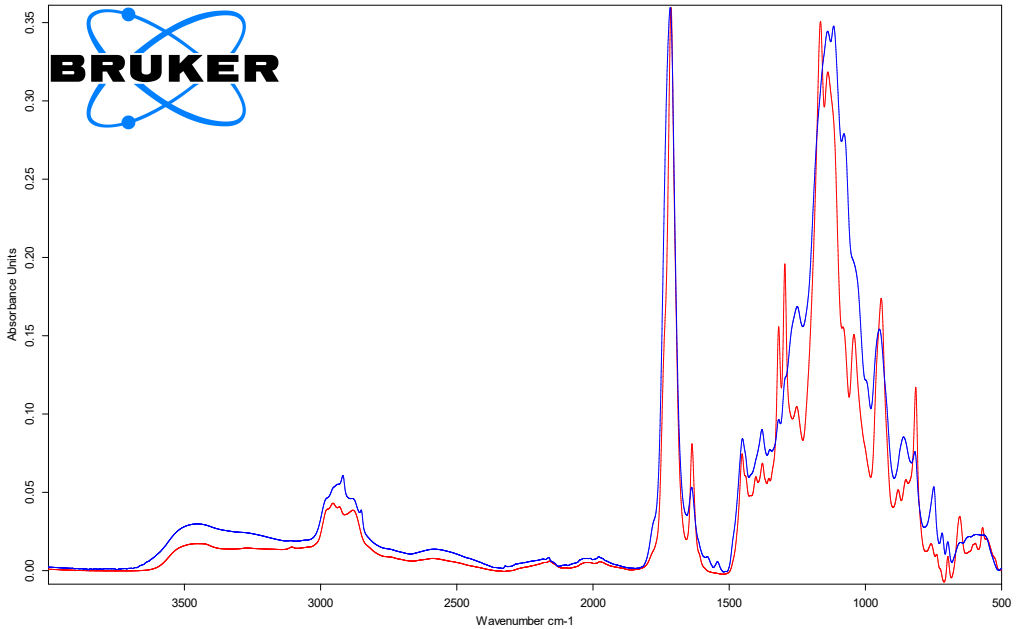

Figure S6: Spectrum of PDO-100:0 showing significant changes in all peaks in the pre- (red) and post-crosslinking (blue) spectra. Note that spectra have been normalized to the C=O peak.

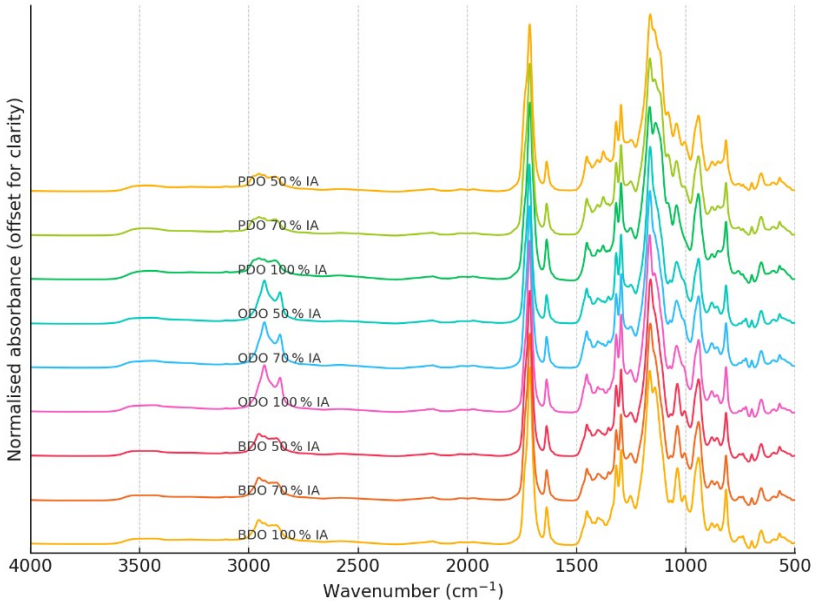

Figure S7. Stacked Fourier-transform infrared (FTIR) absorbance spectra (4000 – 500 cm^{-1}) of the pre-polymer resins before photo cross-linking.

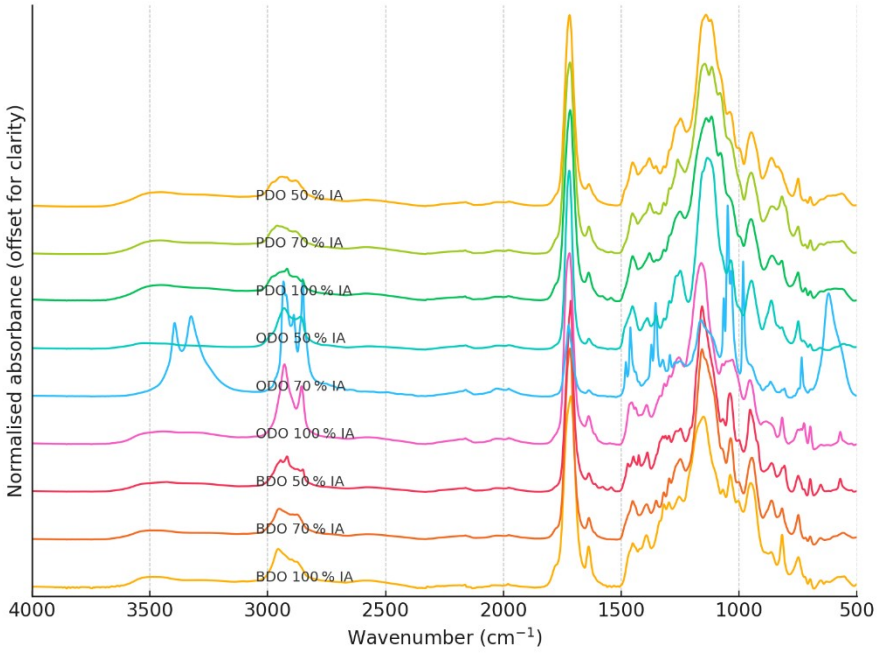

Figure S8. Stacked Fourier-transform infrared (FTIR) absorbance spectra (4000 – 500 cm^{-1}) of the post-polymer after photo cross-linking.

Table S2. Fourier-transform infrared (FTIR) quantification of the degree of double bond conversion during photo-polymerization.

sample	C=C pre	C=O pre	C=C/C=O pre	C=C post	C=O post	C=C/C=O	post/ pre ratio	%DC
PDO,100:0	1.234	13.238	0.093	0.569	15.24	0.037	0.401	59.9
PDO,70:30	0.95	13.091	0.073	0.52	15.91	0.033	0.450	55.0
PDO,50:50	0.929	14.287	0.065	0.365	15.70	0.023	0.358	64.2
BDO,100:0	1.532	16.235	0.094	1.185	21.09	0.056	0.595	40.5
BDO,70:30	1.066	13.859	0.077	0.513	15.84	0.032	0.421	57.9
BDO,50:50	1.107	14.07	0.079	0.289	14.71	0.020	0.250	75.0
ODO,100:0	1.144	12.41	0.092	0.709	15.95	0.044	0.482	51.8
ODO,70:30	1.102	12.491	0.088	0.311	13.32	0.023	0.265	73.5
ODO,50:50	1.016	12.548	0.081	0.248	13.36	0.019	0.229	77.1

Note: Peak areas at ≈1640 cm^{-1} (C=C stretching) and ≈1730 cm^{-1} (C=O stretching) were integrated for both the pre-polymer and the post-photocured polymers. The C=C/C=O area ratio provides a normalized measure of remaining vinyl groups; its decrease upon curing is expressed as the post-to-pre ratio, from which the percentage degree of double bond conversion (%DC) was calculated.

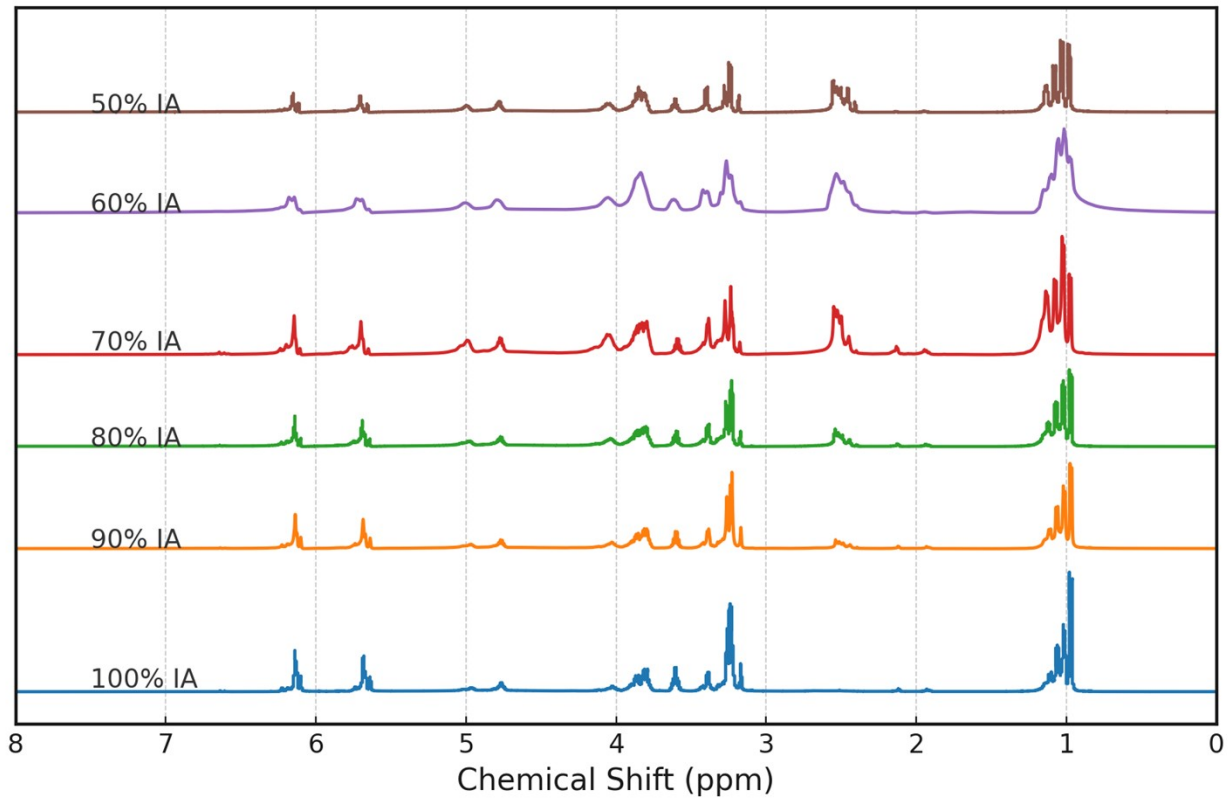

Figure S9. ^{1}H NMR spectra of PDO-containing oligoesters.

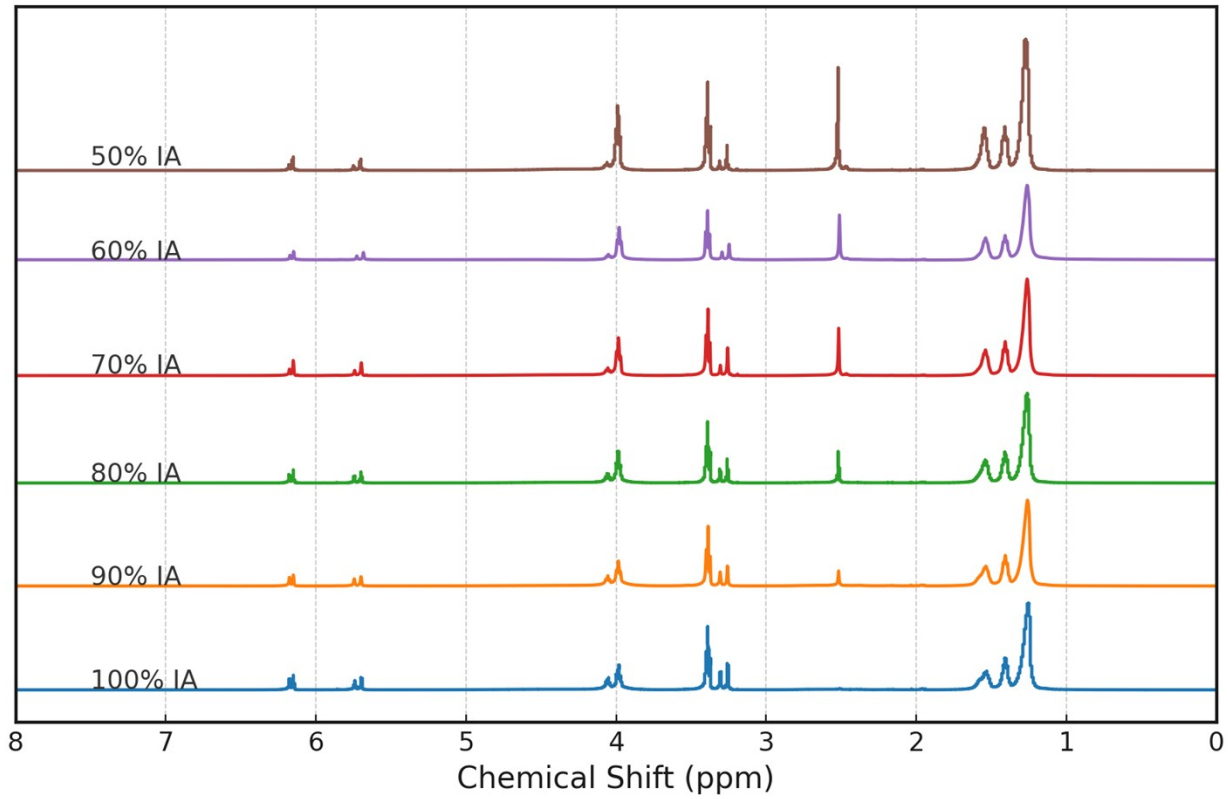

Figure S10. ^{1}H NMR spectra of ODO-containing oligoesters.

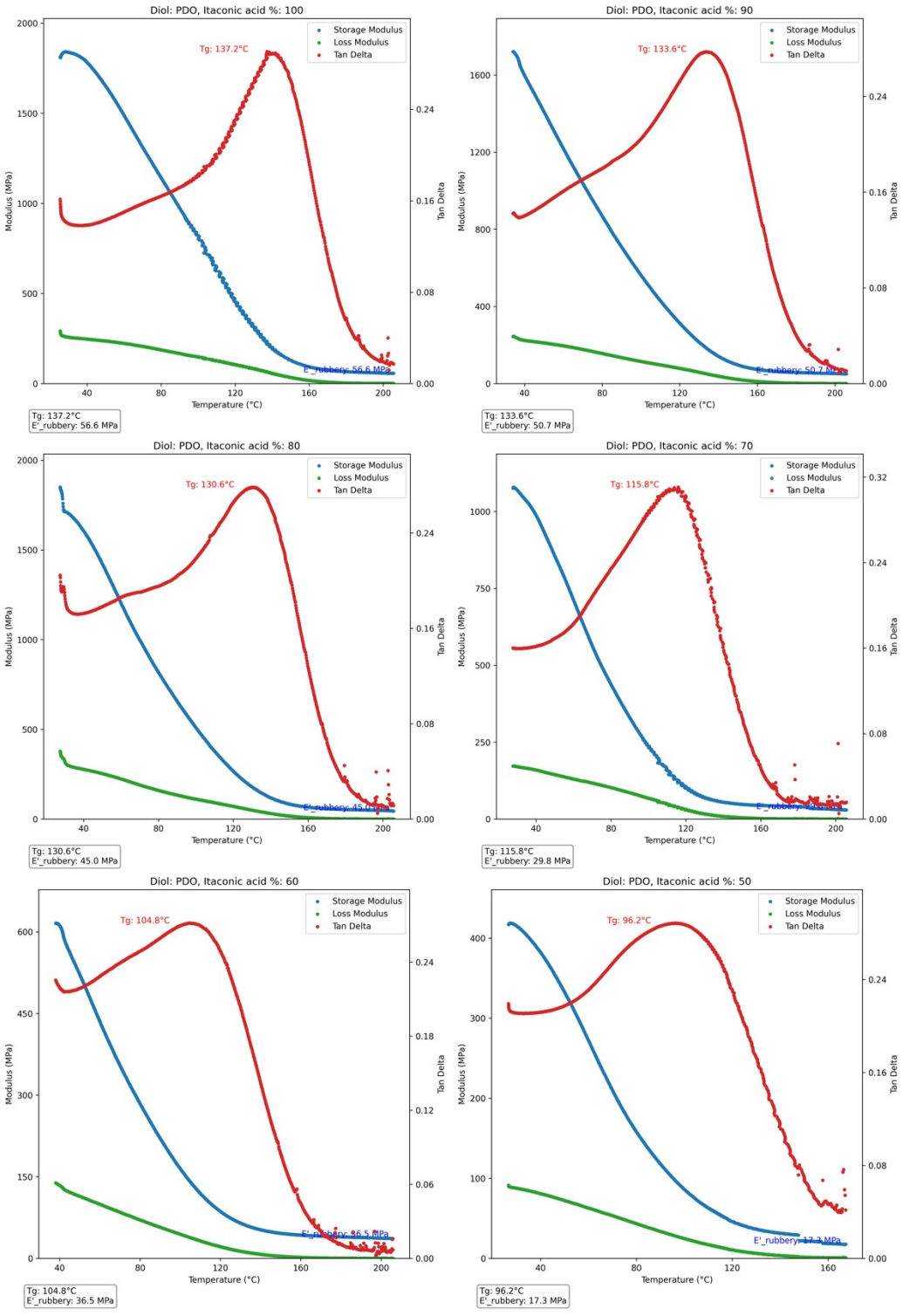

Figure S11. DMA plots of PDO-containing thermoset resins.

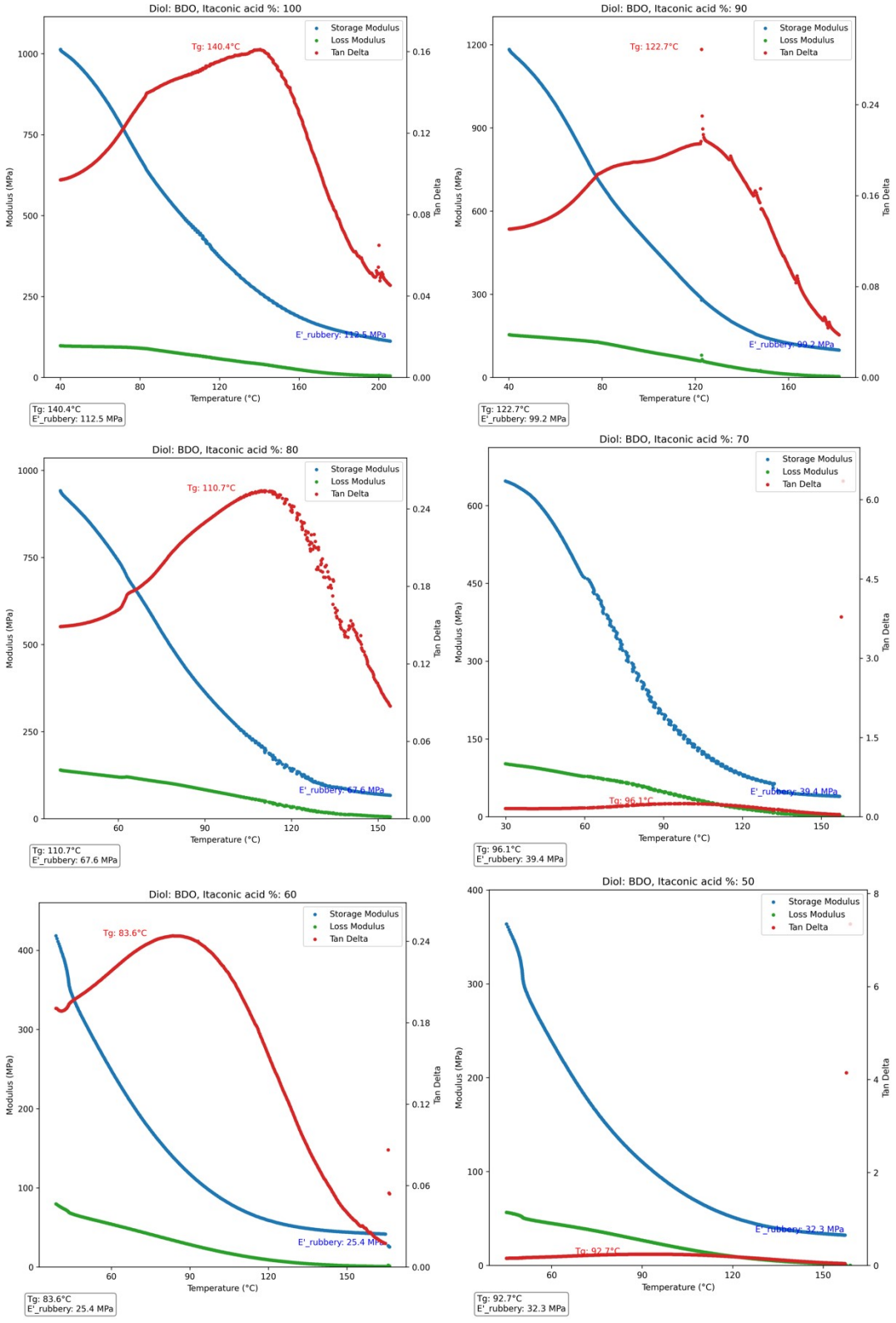

Figure S12. DMA plots of BDO-containing thermoset resins.

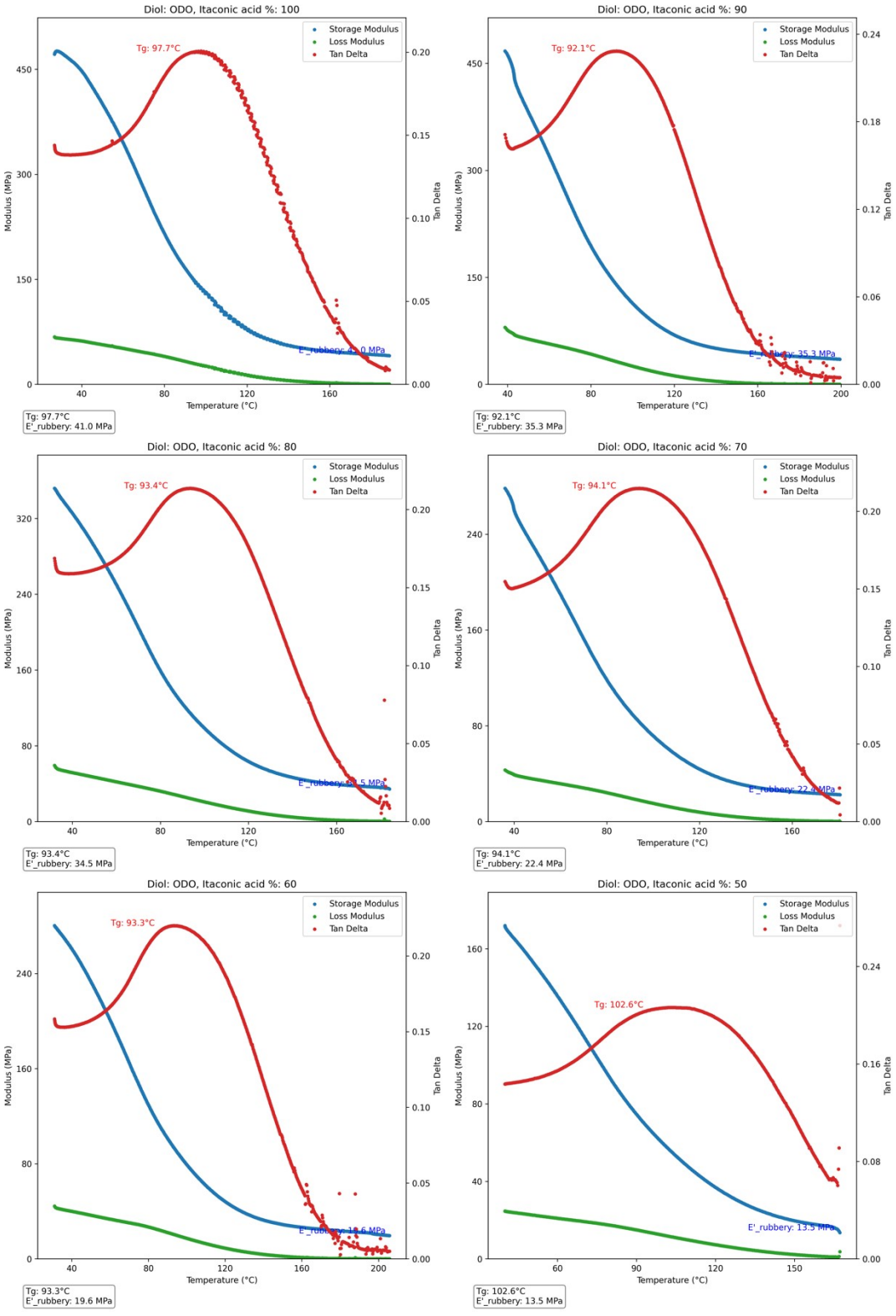

Figure S13. DMA plots of ODO-containing thermoset resins.

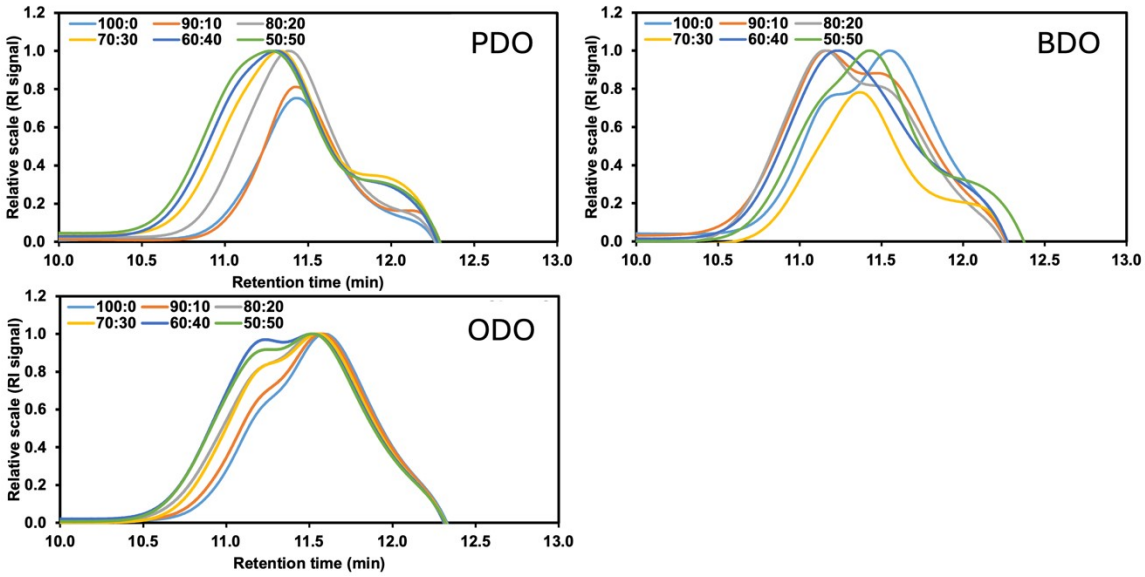

Figure S14: Plots of each oligoester's SEC chromatogram.

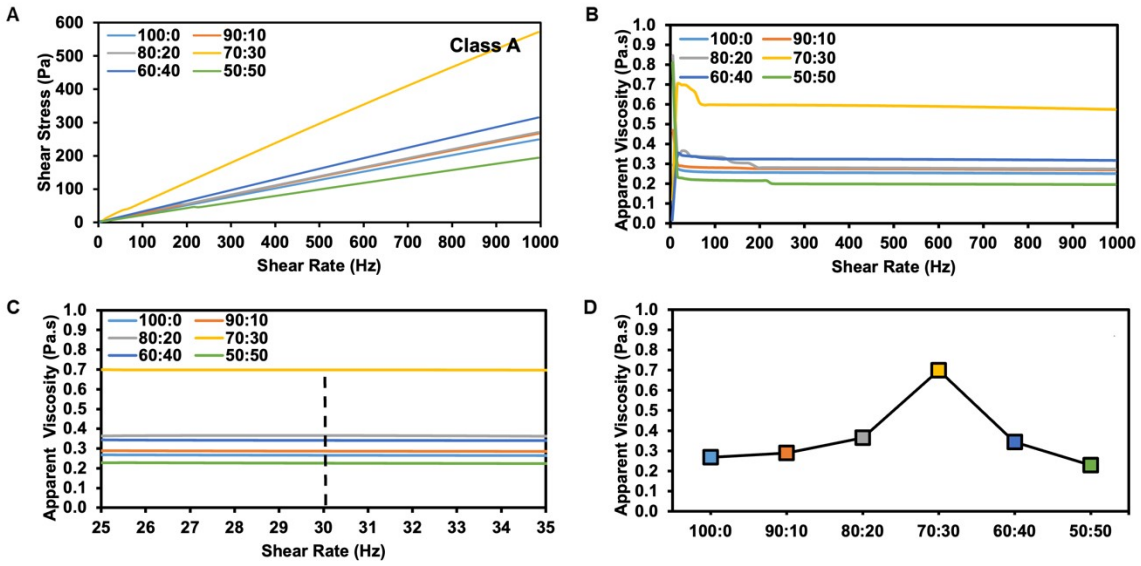

Figure S15. Rheological properties of different PDO-containing resins. **A:** Shear stress vs shear rate **B:** Apparent viscosity vs shear rate **C:** Apparent viscosity in the range of 25 – 35 shear rates. **D:** A plot of apparent viscosity comparison at 30 Hz.

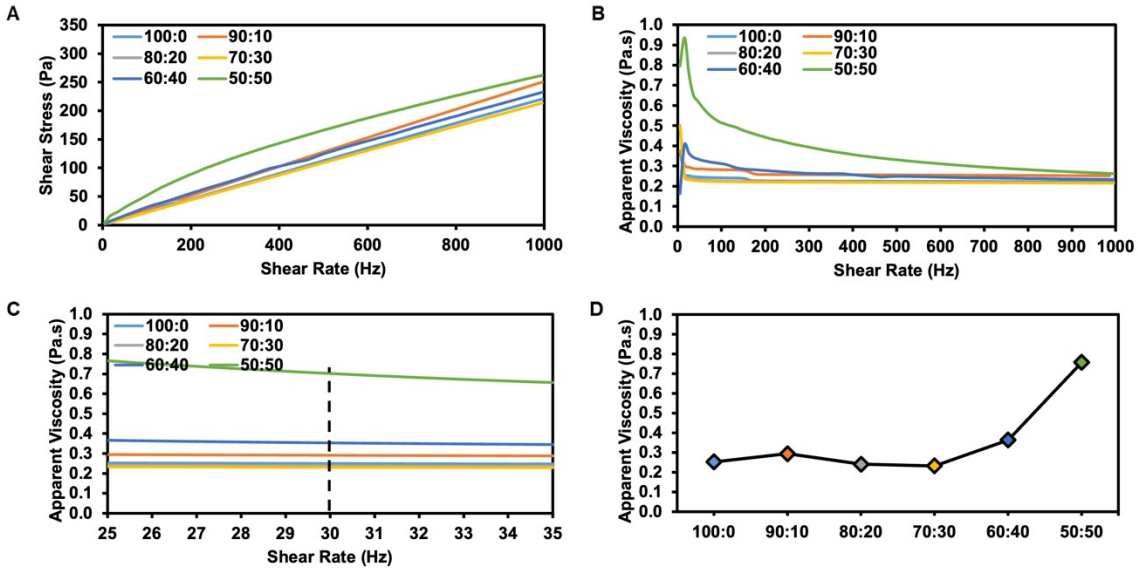

Figure S16. Rheological properties of different BDO-containing resins. **A:** Shear stress vs shear rate **B:** Apparent viscosity vs shear rate **C:** Apparent viscosity in the range of 25 – 35 shear rates. **D:** A plot of apparent viscosity comparison at 30 Hz.

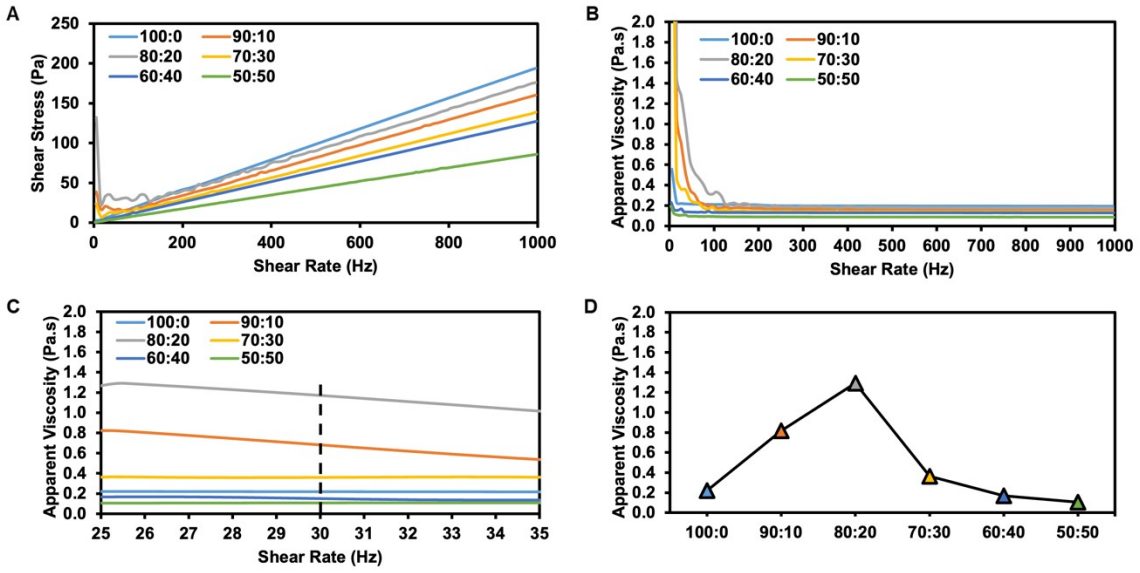

Figure S17. Rheological properties of different ODO-containing resins. **A:** Shear stress vs shear rate **B:** Apparent viscosity vs shear rate **C:** Apparent viscosity in the range of 25 – 35 shear rates. **D:** A plot of apparent viscosity comparison at 30 Hz.

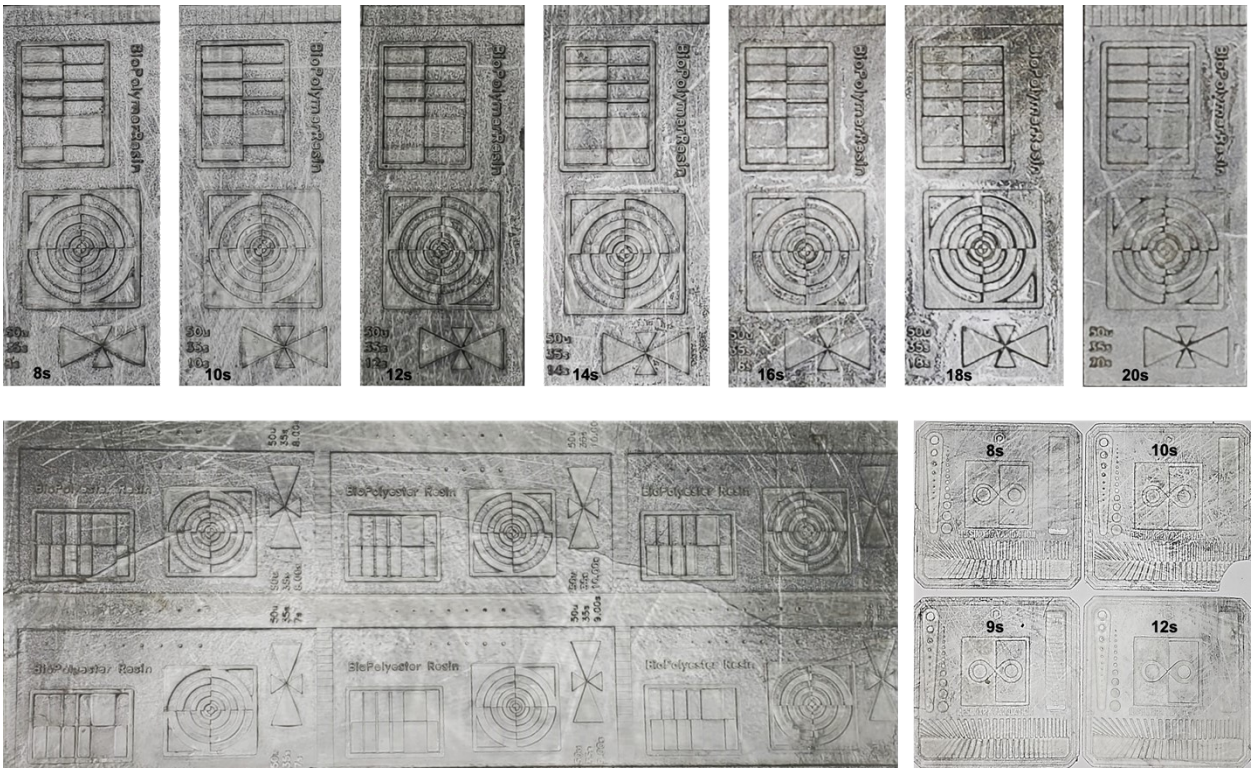

Figure S18. Exposure time result prints for PDO-containing resin, 100:0 IA:SA.

Table S3. Mechanical and printing benchmarks of commercially available LCD-MPSL Resins

Resin (LCD-MPSL)	Viscosity @ 25 °C (mPa.s)	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation at break (%)	Layer thickness (µm)	Layer exposure (s)	Bottom exposure (s)
PDO 100:0 (this work)	370	32	875-950	3.5	20	10	35
Elegoo Standard[1]	150-200	36-53	-*	14.2	50	2.5	35
Anycubic Plant-based[2]	150-350	59-70	-*	11-20	50	2.0	40
Siraya Tech Fast ABS-like[3]	110	30-32	1050-1100	7	50	2.5	30-35
Phrozen Aqua Gray-4K[4]	250-400	18	1435	1.3	50	2.3	30

Note: *Manufacturers list flexural modulus only; no tensile modulus reported.

References (for commercial resin properties)

1 Take You to the 3D Printing Material-Photopolymer Resin, https://jp.elegoo.com/blogs/3d-printer-user-guide/take-you-to-the-3d-printing-material-photopolymer-resin, (accessed 2 May 2025).
2 Resin 3D Printing, https://wiki.anycubic.com/en/filament-and-resin/resin-guide, (accessed 2 May 2025).
3 ABS-like Fast Resin TDS | For Basic Fast, https://siraya.tech/pages/abs-like-fast-resin-tds-for-basic-fast, (accessed 2 May 2025).
4 Phrozen Aqua 3D Printing Resin | Phrozen Technology: Resin 3D Printer Manufacturer, https://phrozen3d.com/products/aqua-resin, (accessed 2 May 2025).