Electronic Supplementary Material (ESI) for Analyst.

Supplemental Document

Method for Determining Resin Cure Kinetics with Low-Frequency Raman Spectroscopy

Robert V. Chimenti,[*a,b] Alexandra M. Lehman-Chong,[b,c] Alyssa M. Sepcic,[d] Jamison D. Engelhardt, [a,b] James T. Carriere,[e] Kayla A. Bensley,[a] Adam Markashevsky,[d] Jianwei Tu,[b] Joseph F. Stanzione, III,[b,c] and Samuel E. Lofland[a,b]

a. Department of Physics & Astronomy, Rowan University, 201 Mullica Hill Rd., Glassboro, NJ 08028, United States
b. Advanced Materials & Manufacturing Institute (AMMI), Rowan University, 201 Mullica Hill Rd., Glassboro, NJ 08028, United States
c. Department of Chemical Engineering, Rowan University, 201 Mullica Hill Rd., Glassboro, NJ 08028, United States
d. Department of Mechanical Engineering, Rowan University, 201 Mullica Hill Rd., Glassboro, NJ 08028, United States
e. Coherent Inc., 850 East Duarte Road, Monrovia, California 91016, United States

*Corresponding author:

Prof. Robert V. Chimenti

Rowan University

101D Science Hall

201 Mullica Hill Dr.

Glassboro, NJ 08028

856-256-4366

chimenti@rowan.edu

Table S.1 Summary of kinetic fit results for DA-2 resin system

Resin	Light Intensity (mW/cm^2)	Chemical				Structural				c	MSR
		α_u	k	n	SSE	α_u	k	n	SSE		
DA-2	1.02	0.79	0.20	4.24	0.58	0.51	0.26	3.00	0.75	1.41	0.0002
DA-2	1.02	0.81	0.13	4.40	0.45	0.51	0.16	3.00	0.11	1.43	0.0002
DA-2	1.08	0.80	0.12	4.30	0.92	0.50	0.16	2.90	0.14	1.43	0.0003
DA-2	0.76	0.79	0.09	4.30	0.59	0.51	0.12	3.00	0.14	1.39	0.0001
DA-2	0.76	0.79	0.12	4.25	0.70	0.51	0.18	3.10	0.13	1.41	0.0002
DA-2	0.76	0.77	0.09	3.96	0.67	0.50	0.13	2.90	0.15	1.40	0.0002
DA-2	0.50	0.75	0.08	3.70	0.68	0.50	0.09	2.80	0.18	1.40	0.0001
DA-2	0.50	0.76	0.08	3.90	0.83	0.50	0.09	2.80	0.20	1.39	0.0001
DA-2	0.50	0.76	0.08	3.90	0.64	0.51	0.12	3.10	0.17	1.40	0.0001
DA-2	0.22	0.70	0.04	3.00	1.05	0.49	0.05	2.60	0.32	1.39	0.0002
DA-2	0.22	0.69	0.04	2.94	1.00	0.49	0.05	2.60	0.32	1.38	0.0001
DA-2	0.23	0.69	0.03	3.00	1.66	0.48	0.04	2.50	0.39	1.36	0.0002

Table S.2 Summary of kinetic fit results for EPON 828 resin system

Resin	Temperature (°C)	Chemical				Structural				c	MSR
		α_u	k	n	SSE	α_u	k	n	SSE		
EPON 828	185.80	0.82	0.00143	1.08	46.22	0.48	0.00752	1.00	3.50	1.59	0.0225
EPON 828	181.20	0.82	0.00173	1.30	85.35	0.53	0.00720	2.08	0.44	1.56	0.0132
EPON 828	180.50	0.85	0.00297	1.24	72.44	0.62	0.00601	1.42	0.60	1.32	0.0110
EPON 828	180.80	0.88	0.00229	1.17	10.76	0.44	0.00455	1.47	0.16	1.99	0.0019
EPON 828	175.30	0.86	0.00215	1.07	5.65	0.40	0.01252	1.79	0.50	2.13	0.0381
EPON 828	175.10	0.90	0.00328	1.44	7.12	0.46	0.00691	1.64	0.07	1.95	0.0013
EPON 828	180.50	0.86	0.00415	1.45	42.86	0.59	0.03279	2.46	0.09	1.49	0.0131
EPON 828	176.80	0.90	0.00316	1.53	3.05	0.45	0.00750	1.46	0.40	1.90	0.0031
EPON 828	174.50	0.90	0.00280	1.29	15.56	0.54	0.00623	1.68	0.07	1.66	0.0023
EPON 828	180.00	0.88	0.00224	1.29	24.35	0.57	0.00667	1.79	0.08	1.55	0.0040

Table S.3 Summary of kinetic fit results for PBE resin system.

Resin	Light Intensity (mW/cm^2)	Chemical				Structural				c	MSR
		α_u	k	n	SSE	α_u	k	n	SSE		
PBE	1.01	0.76	0.01	1.80	1.92	0.40	0.02	2.00	0.24	1.95	0.0003
PBE	1.04	0.78	0.01	1.60	2.54	0.39	0.02	1.70	0.29	2.01	0.0004
PBE	1.00	0.83	0.02	2.40	2.11	0.40	0.03	2.00	0.34	2.01	0.0003
PBE	0.73	0.77	0.01	1.90	2.11	0.38	0.01	1.50	0.30	1.97	0.0004
PBE	0.74	0.79	0.01	1.80	2.82	0.40	0.02	1.90	0.40	1.98	0.0004
PBE	0.75	0.78	0.01	1.70	2.76	0.39	0.01	1.40	0.36	1.97	0.0004
PBE	0.48	0.77	0.01	1.80	4.47	0.39	0.02	1.90	0.38	1.98	0.0009
PBE	0.50	0.79	0.01	2.00	3.19	0.39	0.01	1.60	0.46	2.01	0.0004
PBE	0.49	0.80	0.01	2.10	3.70	0.39	0.01	1.30	0.50	1.97	0.0004
PBE	0.49	0.80	0.01	2.20	4.86	0.39	0.01	1.60	0.48	1.94	0.0005
PBE	0.53	0.78	0.01	1.65	2.48	0.39	0.01	1.40	0.44	1.98	0.0003
PBE	0.22	0.80	0.01	3.00	12.21	0.44	0.01	2.40	1.55	1.94	0.0007
PBE	0.21	0.83	0.01	2.54	8.37	0.40	0.01	1.80	1.10	1.99	0.0003
PBE	0.21	0.82	0.01	2.90	15.46	0.41	0.01	2.10	1.72	1.96	0.0005

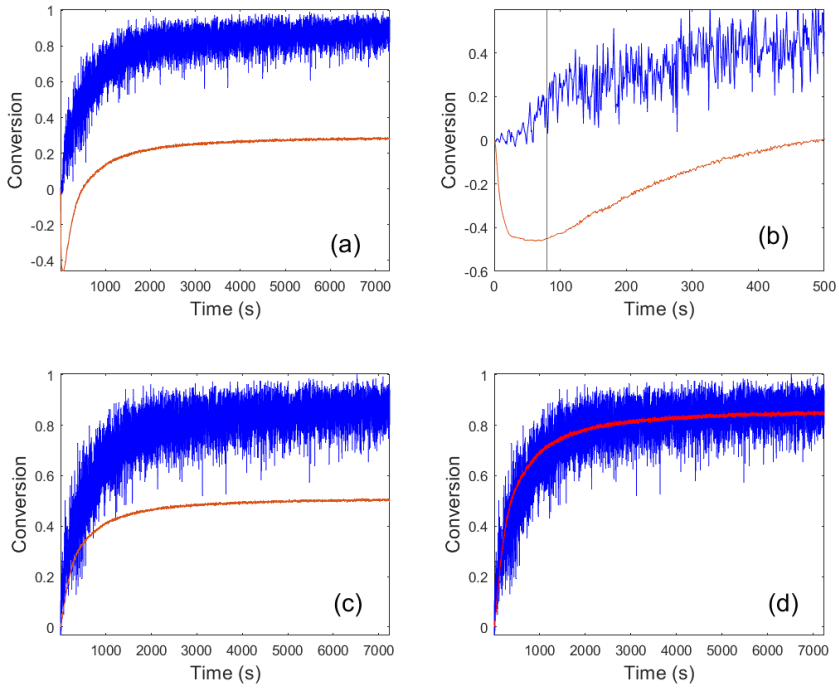

Figure S.1 Chemical (blue) and structural (red) conversion kinetics of an EPON 828 resin thermally cured at 180 °C. Complete kinetic profiles (a), first 500s of the cure with the vertical black line indicating the inflection point in structural kinetics, recalculated conversion profiles after truncation (c), and an overlay of the chemical conversion kinetics and the structural kinetics scaled by c = 1.68 (d).

During many of the EPON 828 cure kinetics experiments, there was an initial dip in the structural conversion region, which was not reflected in the chemical conversion kinetics. We hypothesize that this is due to an initial drop in viscosity (modulus) when the sample was rapidly heated from room temperature to 180 °C. Further rheological studies are needed to test this hypothesis, which is beyond the scope of this study. To accurately calculate the proportionality constant, *c*, when necessary, the kinetics data was truncated to remove the initial dip. Figure S.1 shows a representative example of the workflow for an EPON 828 resin thermally cured at 180 °C. The initial data shown in Figure S.1a shows an overlay of the chemical and structural conversion, with Figure S.1b showing a zoomed-in view of the dip with the black line indicating the truncation point at 80 s. All truncation points were determined by visual inspection and typically ranged from ~60 s – ~100 s. Figure S.1c shows the overlays of the recalculated conversion data post-truncation, and figure S.1d shows the overlays after the structural data was scaled by c = 1.68.