

## Supporting Information for

### Method to analyse energy and intensity dependent photo-curing of acrylic esters in bulk

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#### 1. Comment to UV-vis, RT-IR and Raman

The measuring system within the manuscript deals with the combination of a UV-vis and a Raman system. It may be helpful to highlight some advantages/drawbacks of the proposed analytic technique. The UV-vis solidification monitoring system can be used as standalone system even for non-transparent system (effect was proven within the main manuscript) or in combination with a vibrational band monitoring system like Raman or IR (both disperse or FT systems). Every photo-induced experiment needs a light source so that only an optical receiver is the necessary condition for a UV-vis solidification monitoring system. The effect is proven to be analysable in transmission and refection. Some differences between IR and Raman are explained in M. Schmitt, *Macromol. Chem. Phys.*, 2012, **213**, 1953-1962. The strong and baseline separated C=O and C=C vibrational bands are a main advantage of the FT-Raman system. Additionally for Raman and UV-vis the same window material can be used and the *Raman* system is quantitative and works in back reflection.

#### 2. Calculation of $n_{DB}$

The number of double bound can be calculated using the amount of substance of the compounds.

$$n_{DB} = 3 \cdot n_{TMPTA} + 2 \cdot n_{BAGdA} \quad (\text{Equation S1})$$

The weights of samples lead to correlations with the amounts of substances.

$$0.6 = \frac{m_{BAGdA}}{m_{total}} = \frac{n_{BAG} \cdot M_{BAGdA}}{m_{total}} \quad (\text{Equation S2})$$

$$0.4 = \frac{m_{TMPTA}}{m_{total}} = \frac{n_{TMPTA} \cdot M_{TMPTA}}{m_{total}} \quad (\text{Equation S3})$$

$$\frac{0.4 \cdot m_{total}}{M_{TMPTA}} = n_{TMPTA} \quad (\text{Equation S4})$$

$$\frac{0.6 \cdot m_{total}}{M_{BAGdA}} = n_{BAGdA} \quad (\text{Equation S5})$$

Hence the number of double bounds can be computed.

$$n_{DB} = \frac{N_{DB}}{N_A} = \left( \frac{3 \cdot 0.4}{M_{TMPTA}} + \frac{2 \cdot 0.6}{M_{BAGdA}} \right) m_{total} = \frac{m_{total} \text{ mol}}{153.23 \text{ g}} \quad (\text{Equation S6})$$



### 3. Additional figures

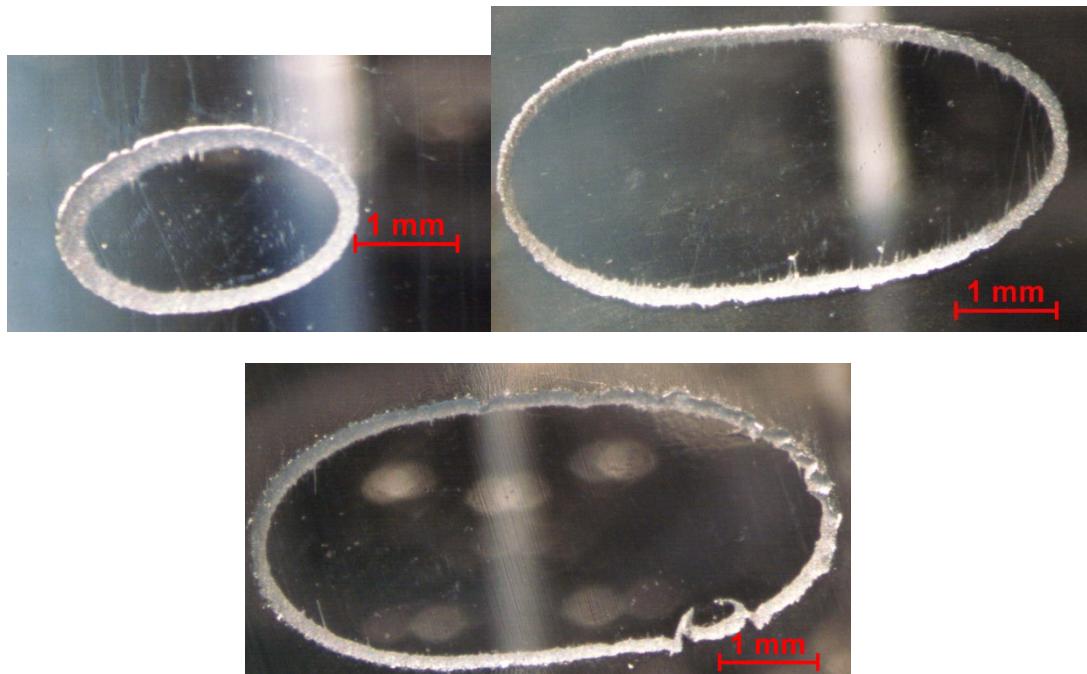


FIGURE S1 Images of selected cured solids using the *Raman* UV-vis setup. Shown are resin with BP cured without filter (top left), resin with DMHA cured with line filter median 368 nm (top right) and resin with TOP-L cured with line filter median 400 nm (bottom).

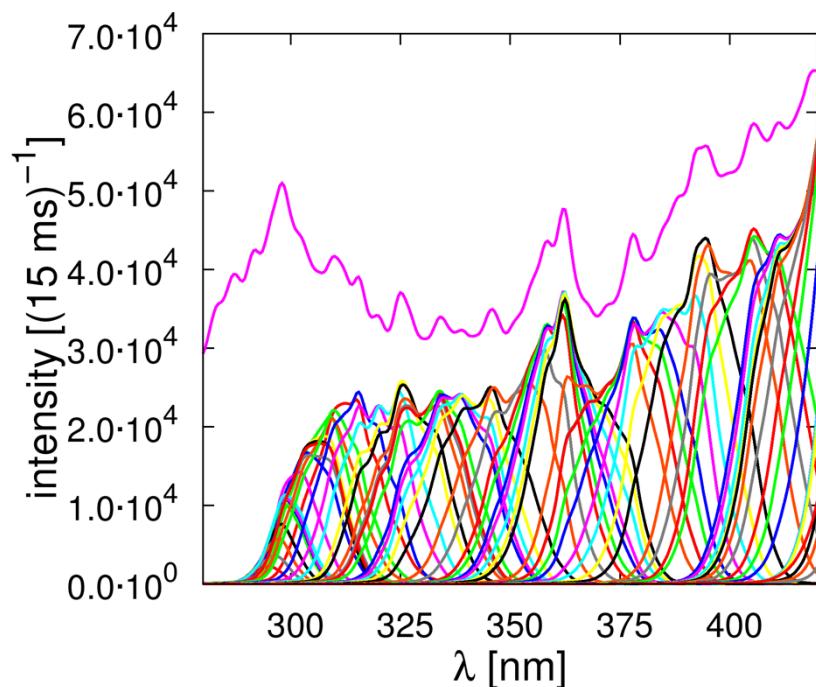


FIGURE S2 Spectrum of the xenon arc light and the spectra at different positions of the linear variable filter. These spectra (measured in transmission, 180° geometry, aligned) are used to scale the spectra of the line filter positions measured in 90° total reflection.

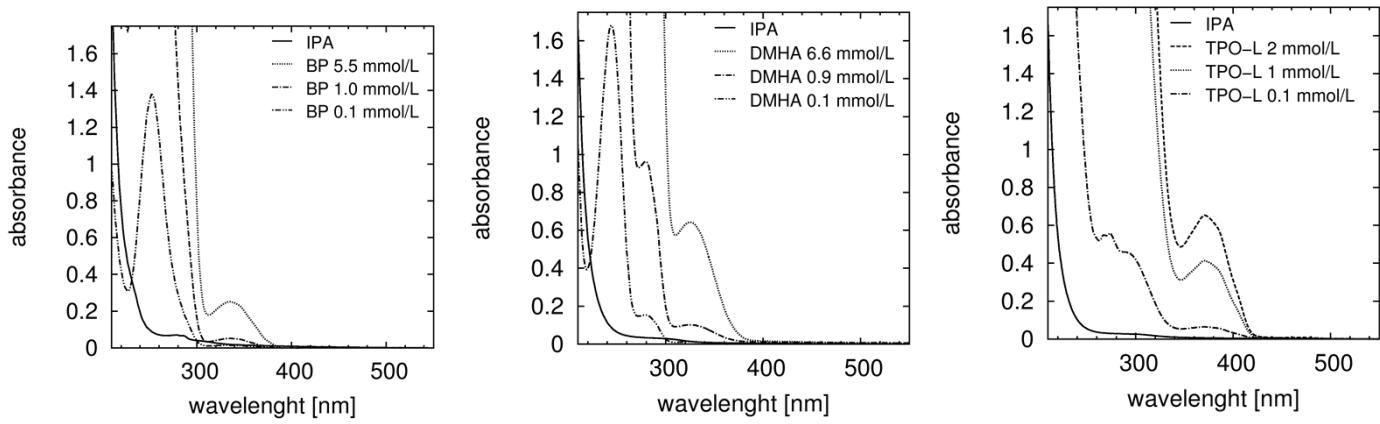


FIGURE S3 Absorbance of the initiator solutions in iPA. TPO-L results in the best absorbance relative to the concentration.

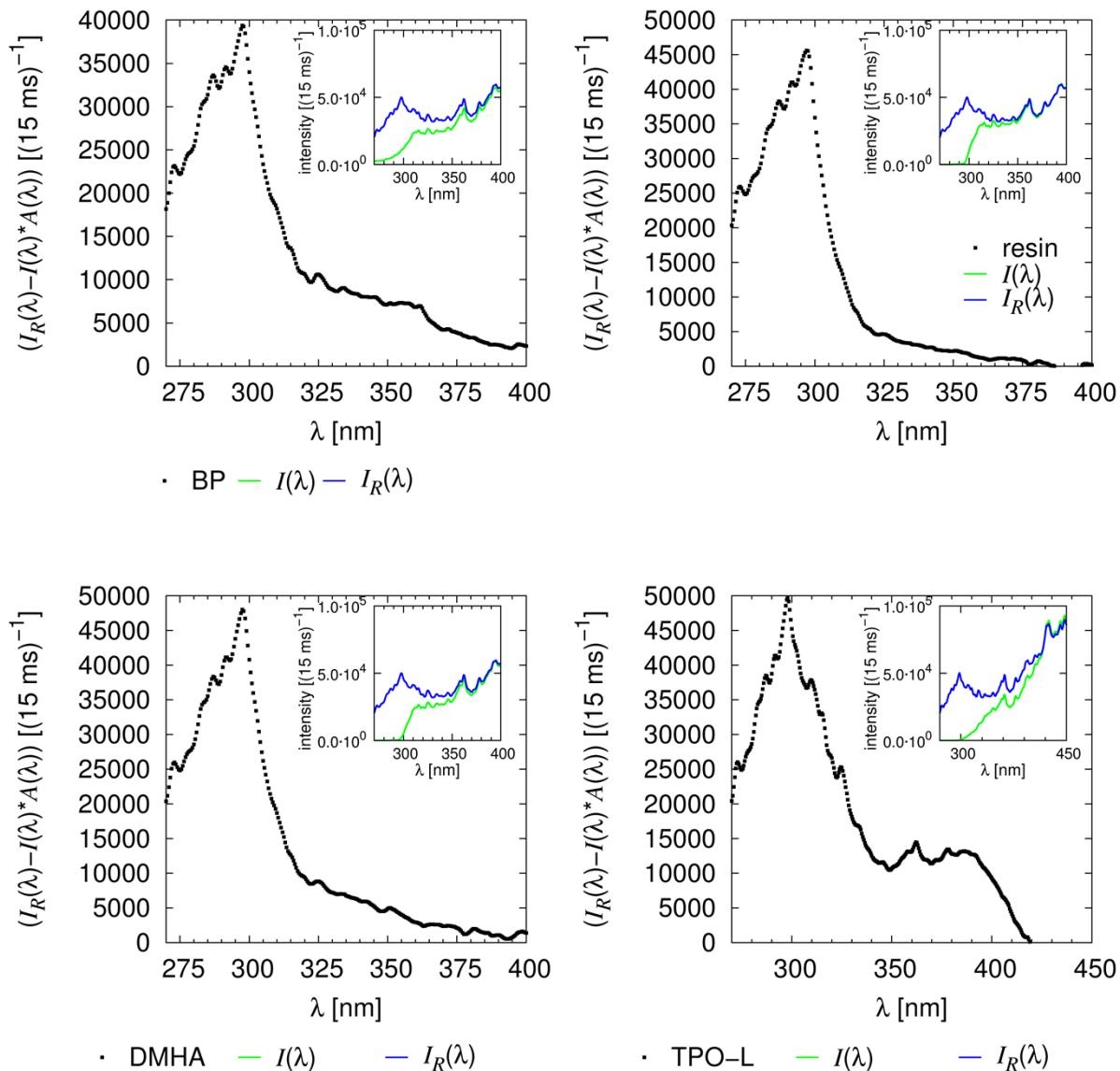


FIGURE S4 Absorption of the compounds with a film thickness of 0.05 mm. The relative absorption is obtained by additional division with  $I(\lambda)$ .

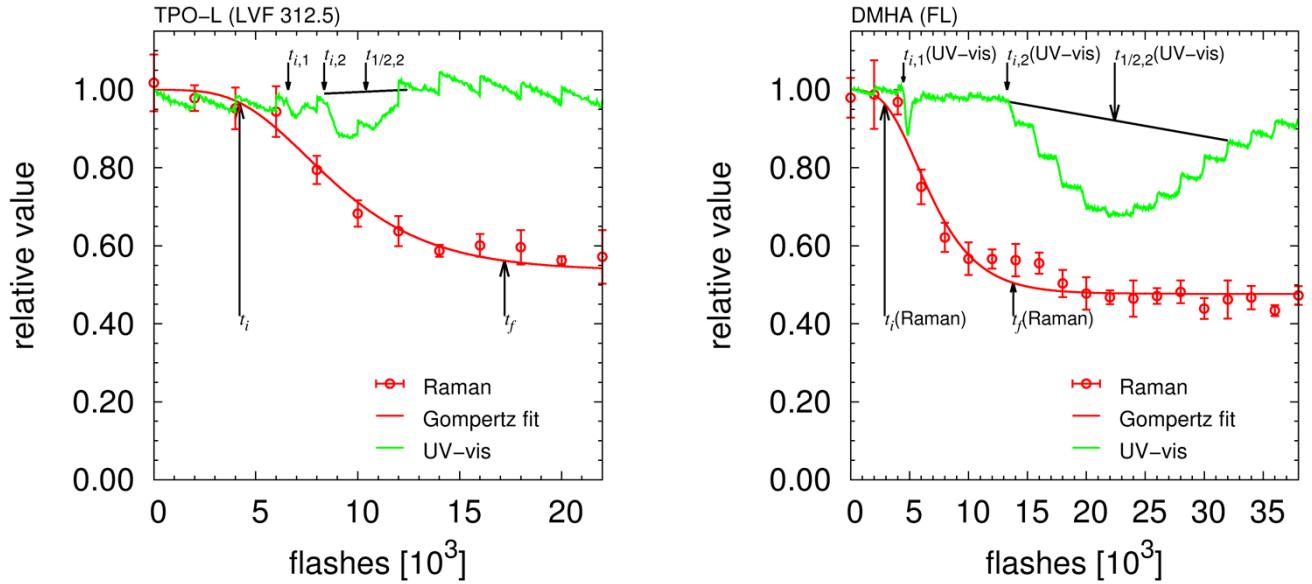


FIGURE S5 Visualisation of the relation between the monomer conversion and the detected UV-vis signal variations. All determined “times” are marked within the figure.

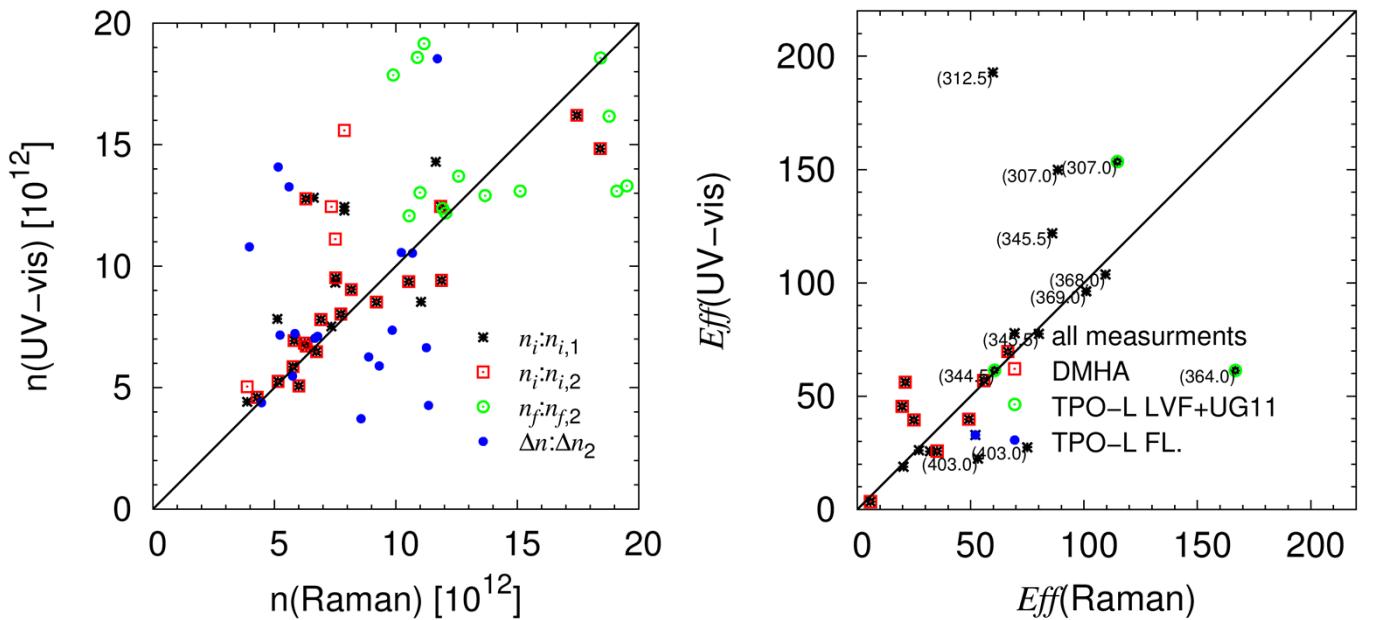


FIGURE S6 Visualisation of the relation between the monomer conversion and the detected UV-vis signal variations. The deep (Raman) curing is strongly influenced by the depth of penetration which is reduced within the resin absorbance range, compare to the efficiency figure.

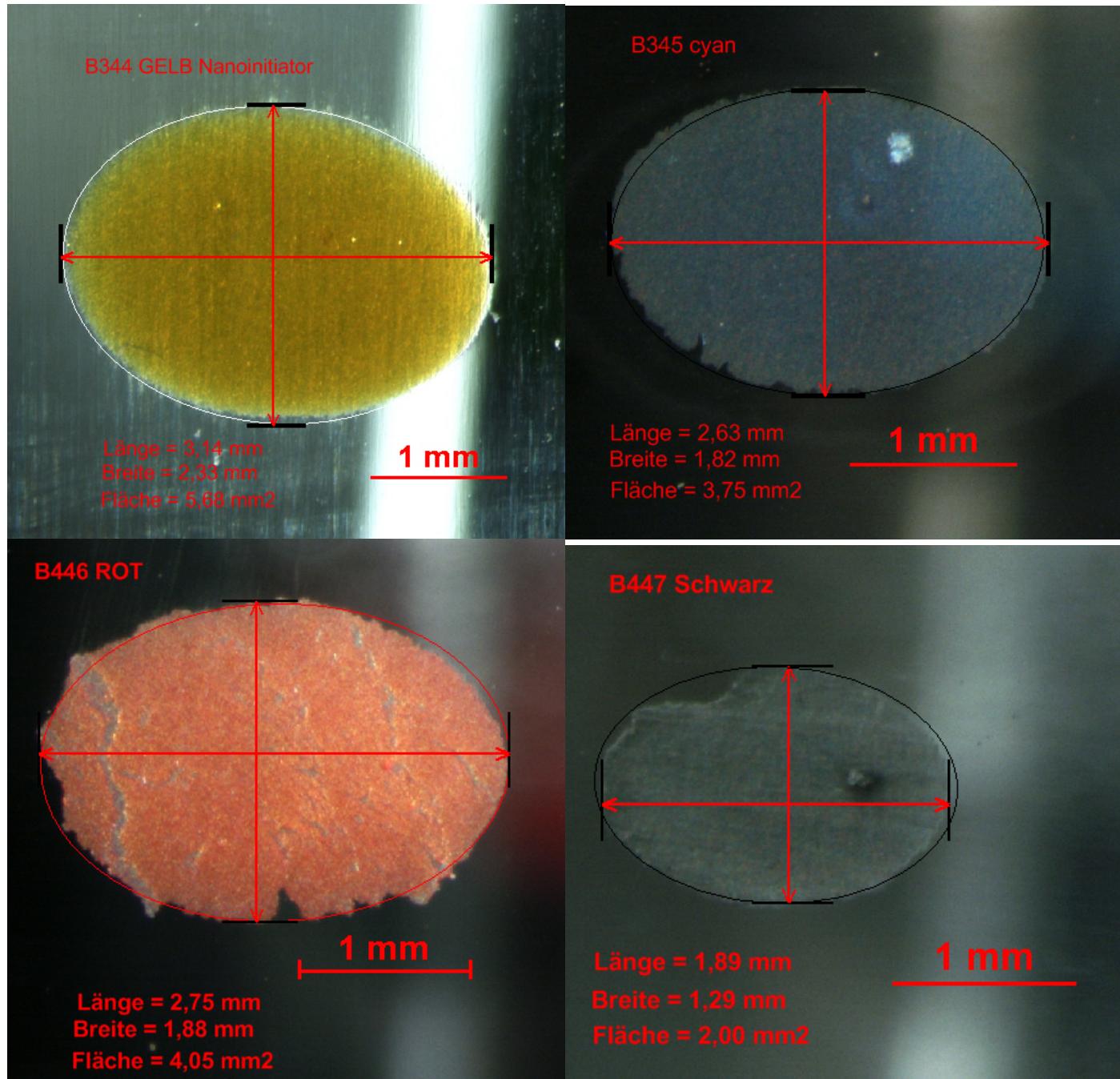


FIGURE S7 Images of selected cured non-transparent solids using the *Raman* UV-vis setup. Shown are highly pigmented UV-printable resin cured by N-ZnO as initiator (low yield initiator).

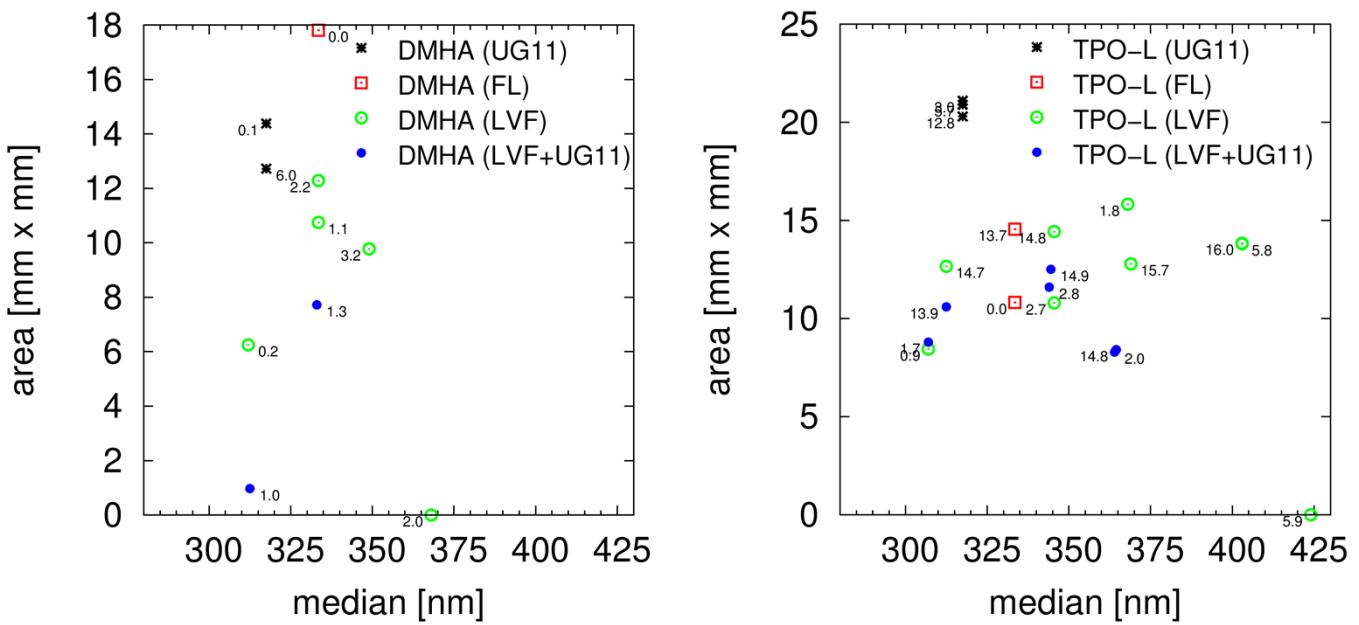
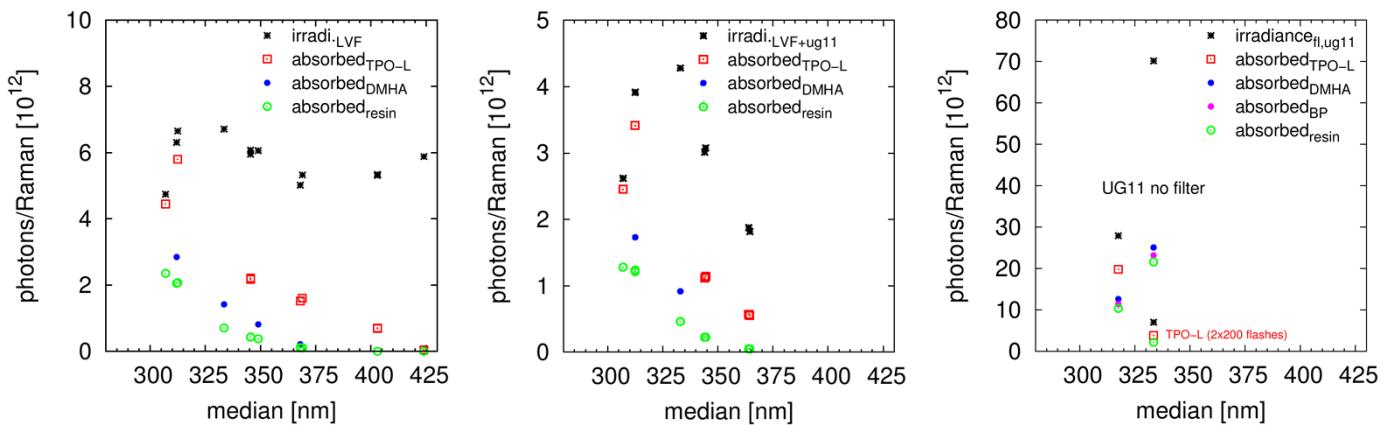


FIGURE S8 Measured areas of the solids after the curing experiments. The cascading effect seems to be confirmed by the reduction in the area for smaller wavelength even through e.g. for DMHA (LVF 335.5) the number of absorbed photons increased, Figure S7. From author opinion the areas only lead to uncertain results concerning the effectiveness of the initiators within the maximal, the computable intensity.



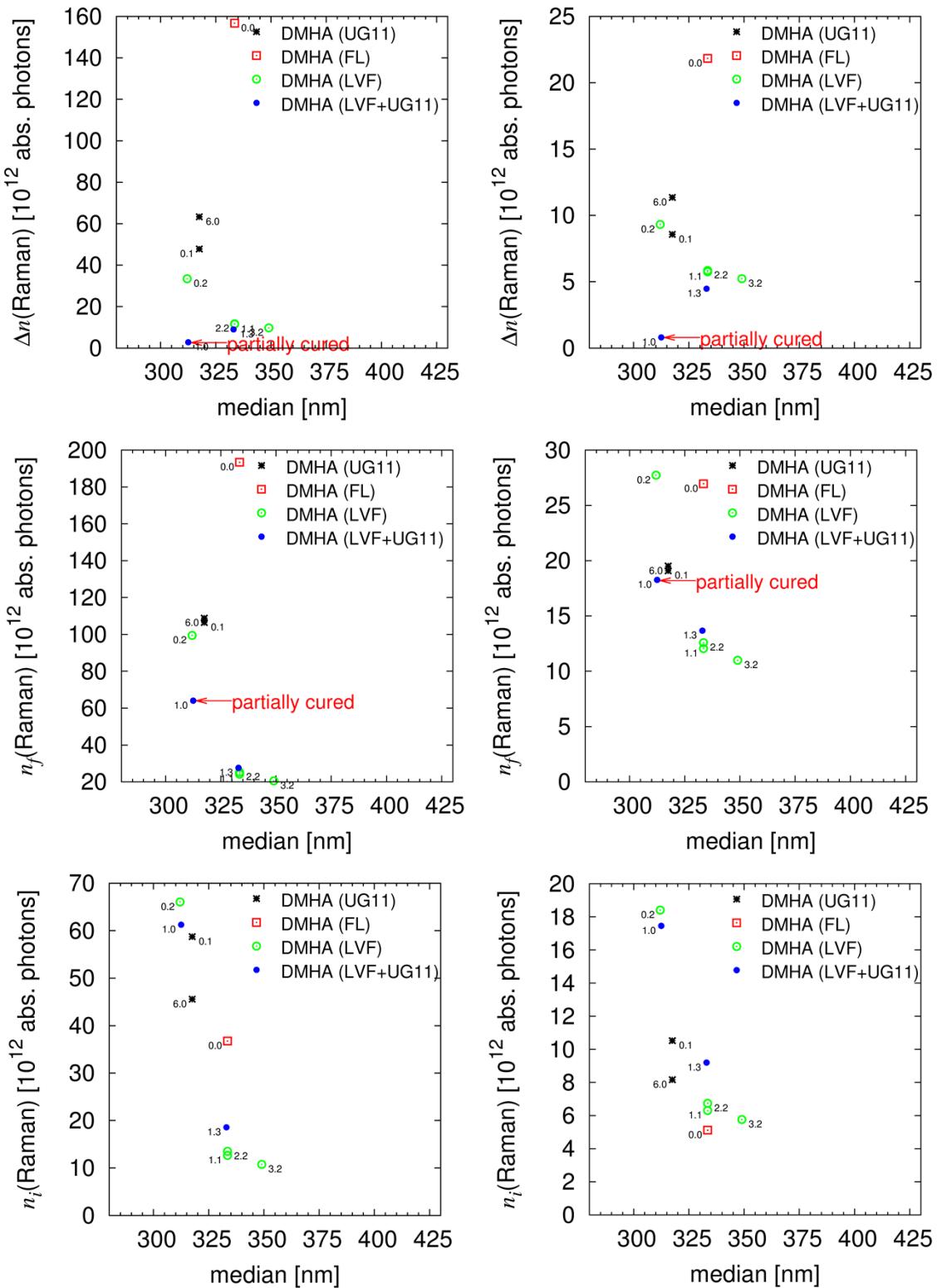


FIGURE S10 Analysis of the resin curing initiated by DMHA. On the left hand side the Raman data of the absolute absorbed photons without resin absorbance is presented, on the right hand side with maximal influence of the resin absorbance.

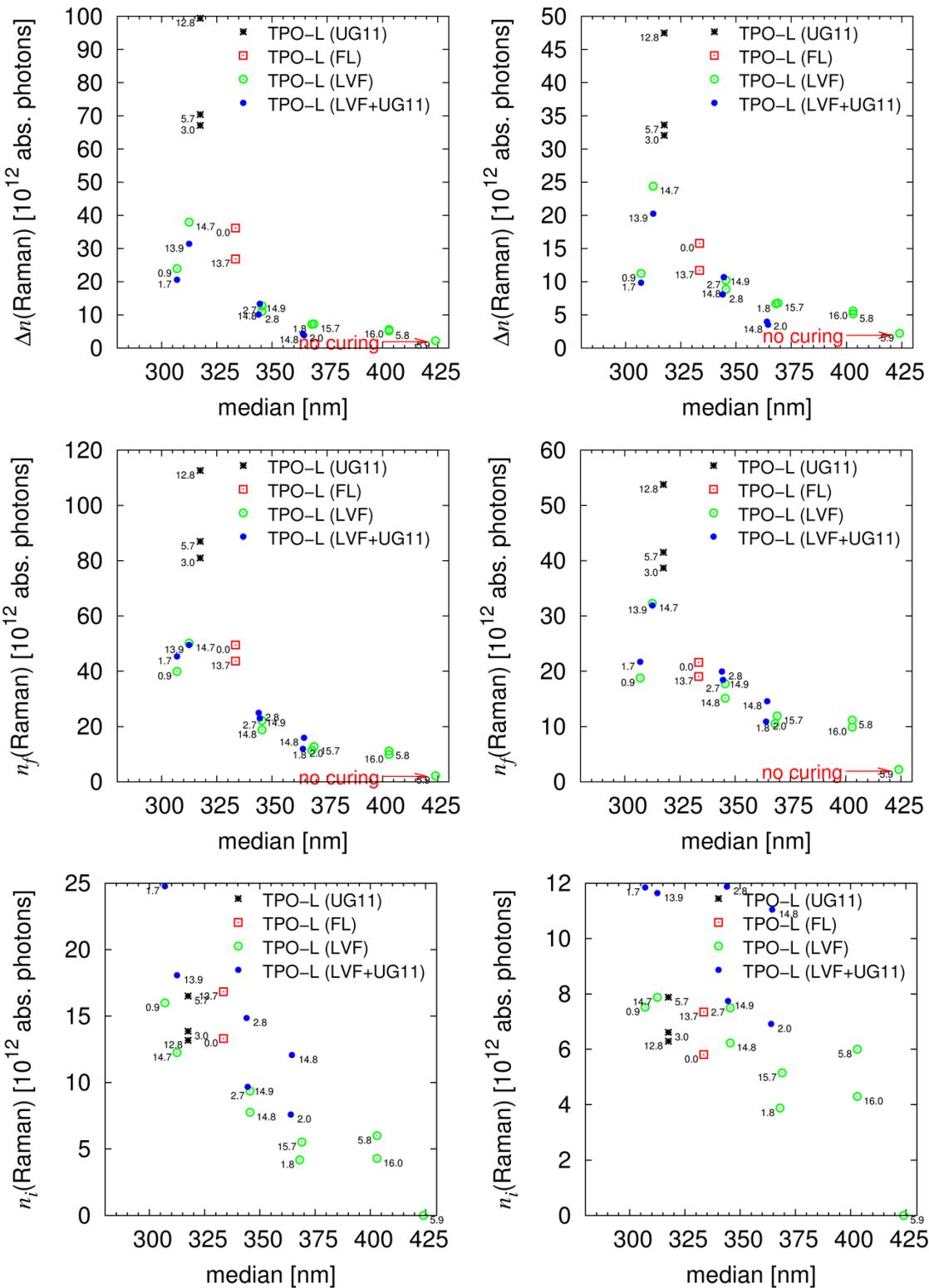


FIGURE S11 Analysis of the resin curing initiated by TPO-L. On the left hand side the Raman data of the absolute absorbed photons without resin absorbance is presented, on the right hand side with maximal influence of the resin absorbance. A significant influence of the reduced irradiation per Raman measurement (200 instead of 2.000 flashes) of the irradiation without filter is recognisable.

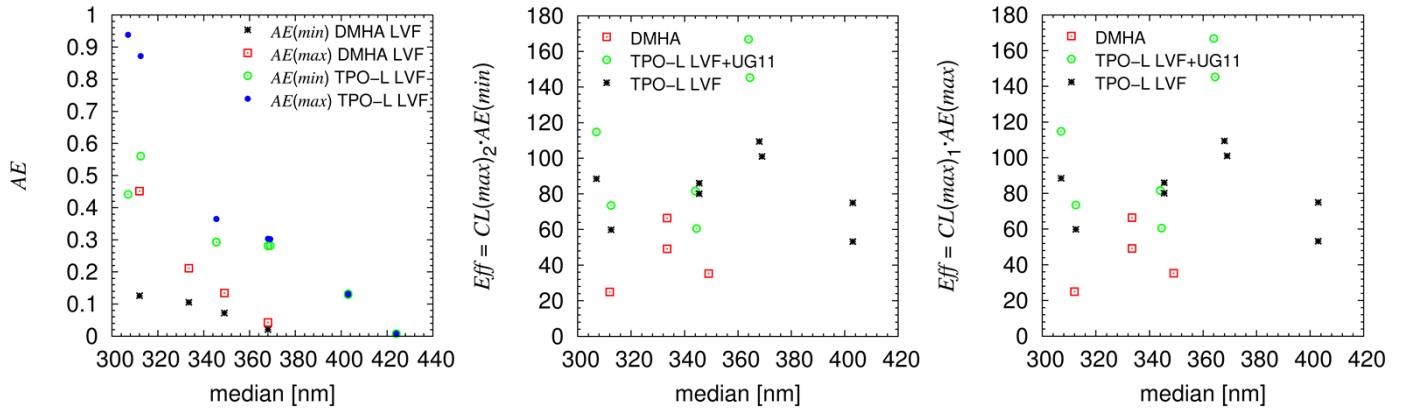


FIGURE S12 Relative absorption efficiencies  $AE$  and visualization of both ways to compute the irradiation corrected efficiency  $Eff$  from the non-corrected index 1 and the corrected maximal chain length index 2.

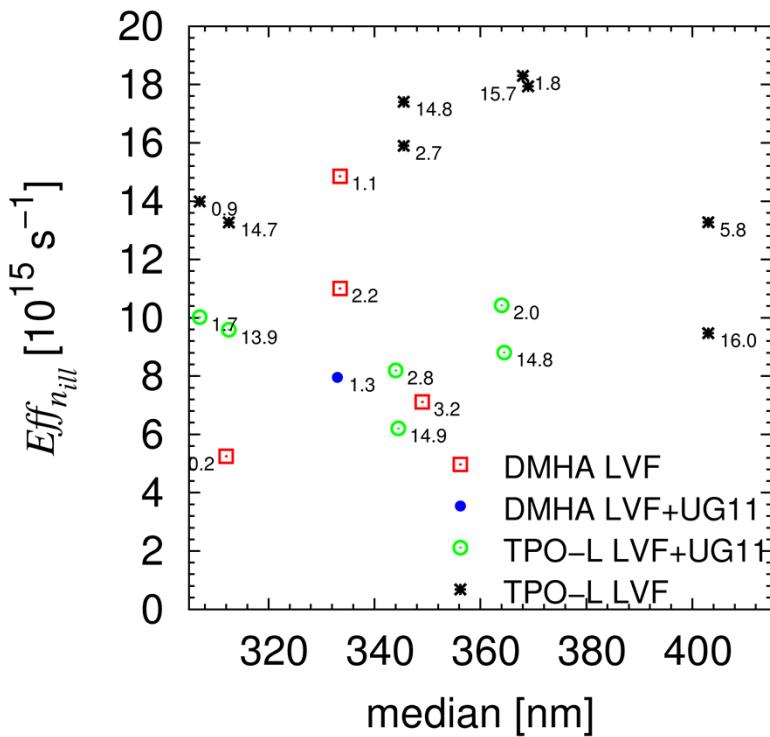


FIGURE S13 Visualization of the relative efficiencies  $Eff_{n_{ill}}$  for the performed experiments with linear variable filter and linear variable filter plus UG11.

$CL(max)_1$	$Eff = CL(max)_1 \times AE(max)$	$Eff_{n_{INI}1} = Eff \times (n_{INI} - n_{res})$
$CL(max)_2$	$Eff = CL(max)_1 \times AE(min)$	$Eff_{n_{INI}2} = Eff \times n_{INI}$
	$Eff = CL(max)_2 \times AE(max)$	$Eff_{n_{ill}} = Eff \times n_{ill}$
	$Eff = CL(max)_2 \times AE(min)$	
$CL(min)_1$		
$CL(min)_2$	...	

SCHEME S1 Overview of the possible theoretical and practical efficiencies. Non-corrected is marked by index 1 ( $AE(max)$ ) whereas the resin absorbed values are marked by index 2. Pointless relations are crossed out. 12 values can be presented.

**4. Additional Tables**

TABLE S1 Parameters of the detector specific correction function.

> 310 nm	a0	a1	a2	a3	a4	a5
	$4.40 \cdot 10^{11}$	$-3.64 \cdot 10^9$	$1.19E \cdot 10^7$	$-1.94 \cdot 10^4$	15.5	$-4.88 \cdot 10^{-3}$

TABLE S2 Summarised data of the performed measurements. Irradiation per *Raman* measurement can be calculated with the frequency (66.66 Hz) and the number of flashes per *Raman* measurement (2000 or 200 (TPO-L<sub>FL</sub>).

sample	median (irradi. photons <sup>b</sup> ) [nm]	irradi. [10 <sup>9</sup> p s <sup>-1</sup> ]	irradi. [Wm <sup>-2</sup> ]	abs. dose [10 <sup>9</sup> p s <sup>-1</sup> ]	abs. dose [Wm <sup>-2</sup> ]	abs. dose (resin) [10 <sup>9</sup> p s <sup>-1</sup> ]	abs. dose (resin) [Wm <sup>-2</sup> ]	flashes	Raman <i>t<sub>i</sub></i> [10 <sup>3</sup> fl.]	Raman <i>t<sub>f</sub></i> [10 <sup>3</sup> fl.]	<i>M<sub>final</sub></i> [%]	area [mm <sup>2</sup> ]	UV-vis <i>t<sub>i,1</sub></i> [10 <sup>3</sup> fl.]	UV-vis <i>t<sub>i,2</sub></i> [10 <sup>3</sup> fl.]	UV-vis <i>t<sub>1/2,2</sub></i> [10 <sup>3</sup> fl.]	storage period [d]
BP <sub>FL</sub> <sup>a</sup>	333.5	2337.9	77.83	772.1	29.63	719.5	27.71	118000	65.1	94.1	62.7	4.34	54.06	73.80		0.24
BP <sub>UG11</sub>	317.5	930.4	32.80	379.9	14.26	345.0	12.99	78000			100.0	0				0.00
DMHA <sub>FL</sub> <sup>a</sup>	333.5	2337.9	77.83	836.0	31.80	719.5	27.71	38000	2.9	13.8	47.7	17.81	4.48	13.28	22.4	0.00
DMHA <sub>UG11</sub>	317.5	930.4	32.80	420.4	15.64	345.0	12.99	38000	7.2	18.8	54.5	12.72	7.99	7.99	10.2	5.99
DMHA <sub>UG11</sub>	317.5	930.4	32.80	420.4	15.64	345.0	12.99	38000	9.3	15.4	53.7	14.39	8.28	8.28	9.6	0.09
DMHA <sub>LVF</sub>	312.0	210.2	7.58	94.9	3.45	68.4	2.49	78000	46.4	66.6	61.9	6.25	37.39	37.39	43.8	0.19
DMHA <sub>LVF+UG11</sub>	312.5	130.5	4.70	57.6	2.09	41.2	1.50	78000	70.9	73.9	<b>72.8</b>	0.97	65.80	65.80	78.0	0.98
DMHA <sub>LVF+UG11</sub>	333.0	142.6	4.82	30.5	1.04	15.4	0.52	78000	40.6	59.8	57.1	7.72	37.60	37.60	47.0	1.31
DMHA <sub>LVF</sub>	333.5	223.6	7.55	47.2	1.60	23.7	0.80	78000	17.9	39.2	51.1	10.75	18.99	18.99	29.2	1.15
DMHA <sub>LVF</sub>	333.5	223.6	7.55	47.2	1.60	23.7	0.80	98000	19.1	36.3	53.4	12.29	18.33	18.33	29.0	2.25
DMHA <sub>LVF</sub>	349.0	201.9	6.51	27.1	0.88	12.6	0.41	98000	26.4	49.8	53.3	9.78	26.90	26.90	42.9	3.25
DMHA <sub>LVF</sub>	368.0	167.2	5.11	7.1	0.22	3.7	0.11	78000			<b>100.0</b>	0				2.05
TPO-L <sub>FL</sub> <sup>a</sup>	333.5	2337.9	77.83	1276.7	46.63	719.5	27.71	7800	0.70	2.43	51.3	10.82	0.83	0.83		0.00
TPO-L <sub>FL</sub> <sup>a</sup>	333.5	2337.9	77.83	1276.7	46.63	719.5	27.71	7800	0.88	2.26	53.8	14.56	0.90	1.49	2.6	13.71
TPO-L <sub>UG11</sub>	317.5	930.4	32.80	660.4	23.95	345.0	12.99	38000	1.33	11.89	51.9	20.3	2.70	2.70	8.4	12.76
TPO-L <sub>UG11</sub>	317.5	930.4	32.80	660.4	23.95	345.0	12.99	38000	1.40	8.48	48.6	21.1	2.71	5.21	9.6	2.98
TPO-L <sub>UG11</sub>	317.5	930.4	32.80	660.4	23.95	345.0	12.99	38000	1.67	8.88	52.8	20.9	2.63	4.60	8.4	5.67
TPO-L <sub>LVF+UG11</sub>	307.0	87.3	3.20	81.8	3.00	42.7	1.58	78000	20.2	39.0	60.1	8.8	21.23	21.23	28.3	1.66
TPO-L <sub>LVF+UG11</sub>	312.5	130.4	4.69	113.7	4.10	40.4	1.47	78000	10.6	29.7	54.8	10.6	13.01	19.65		13.87
TPO-L <sub>LVF+UG11</sub>	344.5	102.5	3.35	38.0	1.25	7.6	0.25	78000	17.0	37.9	56.8	12.51	17.58	17.60	27.9	14.94
TPO-L <sub>LVF+UG11</sub>	344.0	100.4	3.28	37.2	1.22	7.5	0.25	78000	26.6	44.7	60.5	11.6	21.10	21.10		2.84
TPO-L <sub>LVF+UG11</sub>	364.0	62.5	1.93	19.1	0.59	1.7	0.05	78000	26.5	42.2	58.9	8.29	29.93	29.92	51.2	1.96
TPO-L <sub>LVF+UG11</sub>	364.5	60.6	1.87	18.5	0.57	1.6	0.05	78000	43.6	56.0	63.3	8.42	33.66			14.84
TPO-L <sub>LVF</sub>	307.0	158.1	5.81	148.3	5.45	78.5	2.91	32000	7.2	16.9	55.7	8.45	9.10	9.10	12.0	0.86
TPO-L <sub>LVF</sub>	312.5	221.7	7.98	193.3	6.97	69.0	2.51	38000	4.2	17.2	53.6	12.67	6.59	8.36	10.4	14.71
TPO-L <sub>LVF</sub>	345.5	202.4	6.60	73.9	2.42	14.5	0.48	38000	7.0	17.0	54.0	14.44	7.67	7.67	11.2	14.85
TPO-L <sub>LVF</sub>	345.5	198.4	6.47	72.4	2.37	14.3	0.47	38000	8.6	21.9	56.1	10.8	10.70	12.76	19.6	2.74
TPO-L <sub>LVF</sub>	368.0	167.2	5.11	50.7	1.55	3.7	0.11	38000	5.5	15.6	57.0	15.83	6.26	7.14	12.5	1.83
TPO-L <sub>LVF</sub>	369.0	177.6	5.41	53.6	1.64	3.6	0.11	38000	6.9	15.6	55.4	12.79	7.00	7.00	11.6	15.72
TPO-L <sub>LVF</sub>	403.0	177.0	4.94	22.9	0.65	0.0	0.00	78000	17.5	36.0	57.0	13.81	14.76	14.76	40.0 <sup>c</sup>	5.79
TPO-L <sub>LVF</sub>	403.0	178.0	4.97	23.4	0.66	0.0	0.00	78000	12.2	26.5	55.1	13.84	13.10	13.10	30.0 <sup>c</sup>	15.99
TPO-L <sub>LVF</sub>	424.0	196.0	5.20	1.5	0.04	0.0	0.00	78000			<b>100.0</b>	0				5.94

<sup>a</sup>Only wavelengths < 450 nm are considered for the flash light without filter. The total energy is around 115 Wm<sup>-2</sup>. <sup>b</sup>pixel ≡ p. <sup>c</sup>second signal cannot be identified without any doubt.

TABLE S3 Overview fine correction of the layer thickness. Additionally, the storage periods are presented.

sample	median [nm]	$\langle I \rangle / I$	$I$ (Raman)	+-	$I(t_{0,1})$	$I(t_{0,2})$	$I(t_{0,3})$	$I(t_{0,4})$	storage period [d]
BP <sub>FL</sub>	333.5	0.988	0.03933	0.00064	0.0401	0.0386	0.0398	0.0388	0.24
BP <sub>UG11</sub>	317.5	1.013	0.03835	0.00131	0.0376	0.0369	0.0385	0.0404	0.00
mean value		0.0388	0.0012						
DMHA <sub>FL</sub>	333.5	1.153	0.02990	0.00051	0.0299	0.0301	0.0291	0.0305	0.00
DMHA <sub>UG11</sub>	317.5	<b>0.866</b>	0.03983	0.00065	0.0408	0.0399	0.039	0.0396	5.99
DMHA <sub>UG11</sub>	317.5	<b>1.247</b>	0.02765	0.00050	0.0268	0.0278	0.0279	0.0281	0.09
DMHA <sub>LVF</sub>	312.0	1.162	0.02968	0.00070	0.03	0.0296	0.0305	0.0286	0.19
DMHA <sub>LVF+UG11</sub>	312.5	1.084	0.03183	0.00080	0.0305	0.0319	0.0326	0.0323	0.98
DMHA <sub>LVF+UG11</sub>	333.0	1.028	0.03355	0.00078	0.0323	0.0342	0.0342	0.0335	1.31
DMHA <sub>LVF</sub>	333.5	<b>0.761</b>	0.04533	0.00133	0.0457	0.0473	0.0445	0.0438	1.15
DMHA <sub>LVF</sub>	333.5	0.962	0.03585	0.00041	0.0359	0.0355	0.0365	0.0355	2.25
DMHA <sub>LVF</sub>	349.0	1.027	0.03358	0.00066	0.033	0.0337	0.0346	0.033	3.25
DMHA <sub>LVF</sub>	368.0	0.915	0.03768	0.00033	0.0376	0.0378	0.0381	0.0372	2.05
mean value		0.0345	0.005						
TPO-L <sub>FL</sub>	333.5	1.090	0.03428	0.00022	0.0343	0.0342	0.034	0.0346	0.00
TPO-L <sub>FL</sub>	333.5	1.018	0.03673	0.00049	0.0364	0.0361	0.0373	0.0371	13.71
TPO-L <sub>UG11</sub>	317.5	0.951	0.03930	0.00100	0.0403	0.039	0.0378	0.0401	12.76
TPO-L <sub>UG11</sub>	317.5	0.956	0.03908	0.00023	0.0393	0.0388	0.0393	0.0389	2.98
TPO-L <sub>UG11</sub>	317.5	0.985	0.03793	0.00111	0.0372	0.0365	0.0392	0.0388	5.67
TPO-L <sub>LVF+UG11</sub>	307.0	0.891	0.04193	0.00075	0.0429	0.0411	0.0424	0.0413	1.66
TPO-L <sub>LVF+UG11</sub>	312.5	0.962	0.03885	0.00123	0.0409	0.0386	0.0377	0.0382	13.87
TPO-L <sub>LVF+UG11</sub>	344.5	1.117	0.03345	0.00027	0.0333	0.0336	0.0338	0.0331	14.94
TPO-L <sub>LVF+UG11</sub>	344.0	1.000	0.03738	0.00051	0.0369	0.0369	0.0376	0.0381	2.84
TPO-L <sub>LVF+UG11</sub>	364.0	0.973	0.03843	0.00071	0.0378	0.0388	0.0394	0.0377	1.96
TPO-L <sub>LVF+UG11</sub>	364.5	1.124	0.03325	0.00053	0.0332	0.0333	0.034	0.0325	14.84
TPO-L <sub>LVF</sub>	307.0	1.107	0.03378	0.00075	0.0349	0.0338	0.0328	0.0336	0.86
TPO-L <sub>LVF</sub>	312.5	1.005	0.03720	0.00051	0.0368	0.0373	0.0367	0.038	14.71
TPO-L <sub>LVF</sub>	345.5	0.996	0.03753	0.00106	0.0379	0.0391	0.0366	0.0365	14.85
TPO-L <sub>LVF</sub>	345.5	0.884	0.04228	0.00075	0.0413	0.0419	0.0433	0.0426	2.74
TPO-L <sub>LVF</sub>	368.0	0.935	0.03998	0.00069	0.0393	0.0394	0.0402	0.041	1.83
TPO-L <sub>LVF</sub>	369.0	1.035	0.03613	0.00144	0.0381	0.0348	0.0347	0.0369	15.72
TPO-L <sub>LVF</sub>	403.0	0.812	0.04605	0.00032	0.0463	0.0456	0.0459	0.0464	5.79
TPO-L <sub>LVF</sub>	403.0	1.117	0.03345	0.00074	0.0338	0.0323	0.0343	0.0334	15.99
TPO-L <sub>LVF</sub>	424.0	1.224	0.03053	0.00044	0.0299	0.0311	0.0304	0.0307	5.94
mean value		0.0374	0.0037						

TABLE S4 Summary of the quantum yield/ effectivity and the minimal chain length calculations without resin absorbance relative to the absorbed photons.

sample	median [nm]	$\Delta n$ Raman [ $10^{12}$ p]	$\Delta n$ UV-vis [ $10^{12}$ p]	$n_i$ Raman [ $10^{12}$ p]	$n_{i,1}$ UV-vis [ $10^{12}$ p]	$n_{i,2}$ UV-vis [ $10^{12}$ p]	consumed N(C=C) [ $10^{12}$ ] <sup>a</sup>	Raman ( $\Delta n$ ) chain length	UV-vis ( $\Delta n$ ) chain length	Raman ( $n_f$ ) chain length	UV-vis ( $n_f$ ) chain length	storage period [d]	AE(max) [%]
BP <sub>FL</sub> <sup>a</sup>	333.5	331.9		753.8	626.1	854.7	2129	6		2		0.24	33.0
BP <sub>UG11</sub>	317.5						0					0.00	40.8
DMHA <sub>FL</sub> <sup>a</sup>	333.5	156.7	263.8	36.8	56.2	166.5	2557	16	10	13	6	0.00	35.8
DMHA <sub>UG11</sub>	317.5	63.3	23.8	45.6	50.4	50.4	2962	47	124	27	40	5.99	45.2
DMHA <sub>UG11</sub>	317.5	47.8	20.8	58.7	52.2	52.2	2093	44	101	20	29	0.09	45.2
DMHA <sub>LVF</sub>	312.0	33.4	21.1	66.0	53.2	53.2	1848	55	87	19	25	0.19	45.1
DMHA <sub>LVF+UG11</sub>	312.5	2.8 <sup>b</sup>	22.9	61.2	56.9	56.9	1415	503	62	22	18	0.98	44.1
DMHA <sub>LVF+UG11</sub>	333.0	9.0	8.8	18.6	17.2	17.2	2353	261	266	85	90	1.31	21.4
DMHA <sub>LVF</sub>	333.5	11.5	11.0	12.6	13.5	13.5	3624	315	330	150	148	1.15	21.1
DMHA <sub>LVF</sub>	333.5	11.7	14.5	13.5	13.0	13.0	2731	233	189	108	99	2.25	21.1
DMHA <sub>LVF</sub>	349.0	9.8	13.4	10.8	10.9	10.9	2563	262	192	125	106	3.25	13.4
DMHA <sub>LVF</sub>	368.0						0					2.05	4.3
TPO-L <sub>FL</sub> <sup>a</sup>	333.5	36.2		13.3	15.9	15.9	2518	70		51		0.00	54.6
TPO-L <sub>FL</sub> <sup>a</sup>	333.5	26.8	42.5	16.8	17.2	28.5	2559	95	60	59	36	13.71	54.6
TPO-L <sub>UG11</sub>	317.5	99.4	107.4	13.2	26.7	26.7	2852	29	27	25	21	12.76	71.0
TPO-L <sub>UG11</sub>	317.5	67.1	83.8	13.9	26.8	51.6	3030	45	36	37	22	2.98	71.0
TPO-L <sub>UG11</sub>	317.5	70.4	73.4	16.5	26.1	45.6	2700	38	37	31	23	5.67	71.0
TPO-L <sub>LVF+UG11</sub>	307.0	20.6	15.4	24.8	26.0	26.0	2523	123	164	56	61	1.66	93.7
TPO-L <sub>LVF+UG11</sub>	312.5	31.4		18.1	22.2	33.5	2649	84		54		13.87	87.2
TPO-L <sub>LVF+UG11</sub>	344.5	13.3	13.2	9.7	10.0	10.0	2180	163	166	96	94	14.94	37.1
TPO-L <sub>LVF+UG11</sub>	344.0	10.1		14.9	11.8	11.8	2227	220		89		2.84	37.1
TPO-L <sub>LVF+UG11</sub>	364.0	4.4	11.8	7.6	8.6	8.6	2382	547	201	199	117	1.96	30.5
TPO-L <sub>LVF+UG11</sub>	364.5	3.9		12.1	9.3		1841	476		116		14.84	30.5
TPO-L <sub>LVF</sub>	307.0	23.9	14.1	16.0	20.2	20.2	2257	94	160	57	66	0.86	93.8
TPO-L <sub>LVF</sub>	312.5	37.9	11.8	12.3	19.1	24.2	2604	69	221	52	72	14.71	87.2
TPO-L <sub>LVF</sub>	345.5	11.1	7.8	7.8	8.5	8.5	2604	236	334	138	160	14.85	36.5
TPO-L <sub>LVF</sub>	345.5	12.7	13.2	9.4	11.6	13.8	2800	220	213	127	104	2.74	36.5
TPO-L <sub>LVF</sub>	368.0	7.2	7.6	4.2	4.8	5.4	2593	361	342	228	199	1.83	30.3
TPO-L <sub>LVF</sub>	369.0	7.3	7.6	5.5	5.6	5.6	2430	334	319	190	183	15.72	30.2
TPO-L <sub>LVF</sub>	403.0	5.2	14.1	6.0	5.1	5.1	2987	579	212	268	156	5.79	12.9
TPO-L <sub>LVF</sub>	403.0	5.6	13.3	4.3	4.6	4.6	2266	404	171	229	127	15.99	13.2
TPO-L <sub>LVF</sub>	424.0						0					5.94	0.8

<sup>a</sup>The computed content of initiator within the sample volume is around  $57 \cdot 10^{12}$ . <sup>b</sup>Only partially cured; calculated  $t_f$  wrong.

TABLE S5 Summary of the quantum yield/ effectivity and the minimal chain length calculations with maximal influence of the resin absorbance relative to the absorbed photons.

sample	median [nm]	$\Delta n$ Raman [ $10^{12}$ p]	$\Delta n$ UV-vis [ $10^{12}$ p]	$n_i$ Raman [ $10^{12}$ p]	$n_{i,1}$ UV-vis [ $10^{12}$ p]	$n_{i,2}$ UV-vis [ $10^{12}$ p]	consumed N(C=C) [ $10^{12}$ ] <sup>a</sup>	Raman $\Delta n$ chain length	UV-vis $\Delta n$ chain length	Raman $n_f$ chain length	UV-vis $n_f$ chain length	storage period [d]	$AE(min)$ [%]
BP <sub>FL</sub> <sup>a</sup>	333.5	22.6		51.3	42.6	58.2	2129	94		29		0.24	2.2
BP <sub>UG11</sub>	317.5						0					0.00	3.7
DMHA <sub>FL</sub> <sup>a</sup>	333.5	21.8	36.8	5.1	7.8	23.2	2557	117	70	95	43	0.00	5.0
DMHA <sub>UG11</sub>	317.5	11.3	4.3	8.2	9.0	9.0	2962	261	694	152	223	5.99	8.1
DMHA <sub>UG11</sub>	317.5	8.6	3.7	10.5	9.4	9.4	2093	244	562	110	160	0.09	8.1
DMHA <sub>LVF</sub>	312.0	9.3	5.9	18.4	14.8	14.8	1848	198	314	67	89	0.19	12.6
DMHA <sub>LVF+UG11</sub>	312.5	0.8 <sup>b</sup>	6.5	17.5	16.2	16.2	1415	1763	217	78	62	0.98	12.6
DMHA <sub>LVF+UG11</sub>	333.0	4.5	4.4	9.2	8.5	8.5	2353	526	537	172	182	1.31	10.6
DMHA <sub>LVF</sub>	333.5	5.7	5.5	6.3	6.7	6.7	3624	630	661	301	297	1.15	10.5
DMHA <sub>LVF</sub>	333.5	5.8	7.2	6.7	6.5	6.5	2731	117	70	217	199	2.25	10.5
DMHA <sub>LVF</sub>	349.0	5.2	7.2	5.8	5.9	5.9	2563	261	694	233	197	3.25	7.2
DMHA <sub>LVF</sub>	368.0						0					2.05	2.1
TPO-L <sub>FL</sub> <sup>a</sup>	333.5	15.8		5.8	6.9	6.9	2518	159		117		0.00	23.8
TPO-L <sub>FL</sub> <sup>a</sup>	333.5	11.7	18.5	7.3	7.5	12.5	2559	219	138	134	83	13.71	23.8
TPO-L <sub>UG11</sub>	317.5	47.5	51.3	6.3	12.8	12.8	2852	60	56	53	45	12.76	33.9
TPO-L <sub>UG11</sub>	317.5	32.1	40.0	6.6	12.8	24.6	3030	95	76	78	47	2.98	33.9
TPO-L <sub>UG11</sub>	317.5	33.6	35.1	7.9	12.4	21.8	2700	80	77	65	48	5.67	33.9
TPO-L <sub>LVF+UG11</sub>	307.0	9.9	7.4	11.9	12.5	12.5	2523	256	343	116	127	1.66	44.8
TPO-L <sub>LVF+UG11</sub>	312.5	20.3		11.6	14.3	21.6	2649	131		83		13.87	56.2
TPO-L <sub>LVF+UG11</sub>	344.5	10.7	10.5	7.7	8.0	8.0	2180	204	207	118	117	14.94	29.7
TPO-L <sub>LVF+UG11</sub>	344.0	8.1		11.9	9.4	9.4	2227	275		112		2.84	29.6
TPO-L <sub>LVF+UG11</sub>	364.0	4.0	10.8	6.9	7.8	7.8	2382	600	221	219	128	1.96	27.8
TPO-L <sub>LVF+UG11</sub>	364.5	3.5		11.0	8.5		1841	521		126		14.84	27.9
TPO-L <sub>LVF</sub>	307.0	11.3	6.6	7.5	9.5	9.5	2257	200	340	120	140	0.86	44.1
TPO-L <sub>LVF</sub>	312.5	24.4	7.6	7.9	12.3	15.6	2604	107	344	81	112	14.71	56.1
TPO-L <sub>LVF</sub>	345.5	8.9	6.3	6.2	6.8	6.8	2604	293	416	172	199	14.85	29.3
TPO-L <sub>LVF</sub>	345.5	10.2	10.6	7.5	9.3	11.1	2800	274	265	158	129	2.74	29.3
TPO-L <sub>LVF</sub>	368.0	6.7	7.0	3.9	4.4	5.0	2593	389	369	246	215	1.83	28.1
TPO-L <sub>LVF</sub>	369.0	6.8	7.1	5.1	5.3	5.3	2430	358	342	204	196	15.72	28.2
TPO-L <sub>LVF</sub>	403.0	5.2	14.1	6.0	5.1	5.1	2987	579	212	268	156	5.79	12.9
TPO-L <sub>LVF</sub>	403.0	5.6	13.3	4.3	4.6	4.6	2266	404	171	229	127	15.99	13.2
TPO-L <sub>LVF</sub>	424.0						0					5.94	0.8

<sup>a</sup>The computed content of initiator within the sample volume is around  $57 \cdot 10^{12}$ . <sup>b</sup>Only partially cured ;calculated  $t_f$  wrong.

TABLE S6 Additional information concerning the quartiles and the medians of the illuminations.

sample	median [nm]	lower median [nm]	upper [nm]
BP <sub>FL</sub> <sup>a</sup>	333.5	303.5	388.0
BP <sub>UG11</sub>	317.5	301.5	339.5
DMHA <sub>FL</sub> <sup>a</sup>	333.5	303.5	388.0
DMHA <sub>UG11</sub>	317.5	301.5	339.5
DMHA <sub>UG11</sub>	317.5	301.5	339.5
DMHA <sub>LVF</sub>	312.0	307.5	316.5
DMHA <sub>LVF+UG11</sub>	312.5	308.0	317.0
DMHA <sub>LVF+UG11</sub>	333.0	326.5	338.5
DMHA <sub>LVF</sub>	333.5	327.5	339.0
DMHA <sub>LVF</sub>	333.5	327.5	339.0
DMHA <sub>LVF</sub>	349.0	342.5	355.0
DMHA <sub>LVF</sub>	368.0	362.0	375.0
TPO-L <sub>FL</sub> <sup>a</sup>	333.5	303.5	388.0
TPO-L <sub>FL</sub> <sup>a</sup>	333.5	303.5	388.0
TPO-L <sub>UG11</sub>	317.5	301.5	339.5
TPO-L <sub>UG11</sub>	317.5	301.5	339.5
TPO-L <sub>UG11</sub>	317.5	301.5	339.5
TPO-L <sub>LVF+UG11</sub>	307.0	303.0	310.5
TPO-L <sub>LVF+UG11</sub>	312.5	308.5	317.0
TPO-L <sub>LVF+UG11</sub>	344.5	338.5	351.0
TPO-L <sub>LVF+UG11</sub>	344.0	339.0	351.5
TPO-L <sub>LVF+UG11</sub>	364.0	360.0	369.5
TPO-L <sub>LVF+UG11</sub>	364.5	360.5	370.0
TPO-L <sub>LVF</sub>	307.0	302.5	310.0
TPO-L <sub>LVF</sub>	312.5	308.0	317.0
TPO-L <sub>LVF</sub>	345.5 (later)	339.0	351.5
TPO-L <sub>LVF</sub>	345.5	339.5	352.0
TPO-L <sub>LVF</sub>	368.0	362.0	375.0
TPO-L <sub>LVF</sub>	369.0	363.0	376.0
TPO-L <sub>LVF</sub>	403.0	369.5	409.5
TPO-L <sub>LVF</sub>	403.0	369.5	409.5
TPO-L <sub>LVF</sub>	424.0	419.0	430.0