

RSC Advances



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



Journal Name

ARTICLE

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

M. Schmitt^a

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

The analysis of photo-induced polymerization of bulk materials is a very important aspect of scientific and industrial researches and applications. Thereby interactions between the initiator, the monomer and the light source have to be considered which are hardly/not investigated. But for example novel UV-light source based on LED technology are in the progress of development. Hence the need of such kinetic analyses increases to investigate multiple energy and intensity dependent influencing factors like the quantum yield of the primary radical formation and reactivity's towards double bonds or inhibitors. Within this contribution a dose and wavelength dependent procedure will be firstly described in detail which allows analysing the kinetic of photo-curing and solidification of multifunctional liquid acrylic esters without solvent. Thereby photo-polymerizations induced by three different model resins containing commercial well-known initiators are in situ monitored by a *Raman* UV-vis system and analysed in detail. This novel procedure bases on an absolute and spectral calibrated fibre optical receiver which is part of the *Raman* UV-vis setup. Multiple influences of the absorbed photons on e.g. the kinetic length of the chain reaction are presented/demonstrated. For example higher yields can be achieved by less energetic and less intense irradiation.

1. Introduction

The free radical polymerization is a very familiar method leading to polymers. So, multiple investigations to analyse the reaction respective kinetic in solution can be found in literature.¹⁻¹⁰ But the photo-polymerization is an efficient method for fast production of cross-linked polymers from liquid resins/monomers without solvents.^{11, 12} Solved-free (= bulk) photo-polymerisation is used for the construction of materials and coatings. Our research focus on the photo-polymerisation of multifunctional monomers for example as used for printing applications.¹³⁻¹⁷ Nowadays, "printing" is not only a coating procedure; it ranges from coating for example journal/images by UV-printing¹⁸ (off-set, flexo) or ink-jet printing to construction e.g. by photo-lithography¹⁹ or 3D printing²⁰. This topic naming multiple applications and advantages was recently reviewed with the focus on LED technology.²¹ Characterization of the kinetic of photo-induced polymerization in bulk is also from scientific aspects an interesting and most important topic.^{6, 13, 15, 22-29} Some aspects which have to be analysed are the identification of the energy/intensity relations resulting in an effective radical formation, including e.g. the quantum yield determination and analyses of the triple state, of the radical reactivity towards acrylate

double bonds or inhibition compounds. The presented way to perform energy and intensity variations of the light source may help to analyse these and further effects. Considering application such as 3D printing or UV-printing the properties of known/used initiators are far from perfect. Multiple problems in aspects of health and/or of efficiency exist.³⁰⁻³⁷ In the past one process constant within the interplay between initiators, monomer and light sources was the light source. For example for printing applications like off-set or flexo printing a mercury mid-pressure lamp was the only applicable light source (power in the range of 200 W cm⁻¹, high intensity in UV-range). Such complex systems are hardly/not investigated because analysing the kinetic of polymerization/solidification without solvent is a challenging problem especially if practical orientations are proposed. Nowadays and in the future the light source is/will be an additional adjustable parameter. LED technology can be considered as well-established in the visible range²¹. In the UV-range LED's are still in the progress of development. Due to multiple advantages of LED²¹ technology curing units basing on LED are purchasable even today, for example high power LED up to 7 W cm⁻¹ at 365 nm ± 6 nm³⁸. This wavelength is smaller than the onset of absorbance of a number of established initiators and some resins²⁸. At the moment no LED's with comparable intensities exist in the main/strong absorption range of most initiators located below 365 nm. Hence the initiators and the initiator monomer combinations cannot be characterized and new systems cannot be developed but "new photo-initiating systems and strategies"²¹ have to be developed. This lack can be removed by the techniques and procedures presented within the

^a Dr. Michael Schmitt, Saarland University, Campus B 2 2, 66123 Saarbrücken, Germany mic.schmitt@mx.uni-saarland.de.

† Electronic Supplementary Information (ESI) available: The supplementary information contains additional equations and visualizations of all measurements. See DOI: 10.1039/x0xx00000x

following study: Recently an UV-vis **solidification** monitoring system¹⁴ and the combination *Raman* and the UV-vis monitoring system were firstly introduced/discovered^{16,17}. The combination of the *Raman* with the UV-vis system, Scheme 1, leads to the possibility to investigate the efficiency of initiators in detail. For the present study this system is further varied by a spectral and absolute calibrated light source³⁹. For absolute calibration an absolute and spectral calibrated receiver for large amount of photons is used. The recently developed procedure will also be explained within the manuscript. The combination of a linear variable filter, LVF and a band pass filter leads to the possibility to vary the energy with comparable intensity and to vary the intensity with constant energy by filter combinations and by frequency variation. The main objective of the presented study is a detailed analysis of the novel experimental setup/technique including dose and energy relations leading to e.g. kinetic lengths of the chain reaction and different efficiencies. The demonstration of the complex but easily implementable procedure takes place on the hand of three commercial available well-known and often used initiators. The first one benzophenone⁴⁰, BP, is a non-fragmenting, Norrish type II initiator, normally used together with a co-initiator⁴¹. The second one 2-hydroxy-2-methylpropiophenone, DMHA, is versatile highly efficient liquid photo-initiator which is used to initiate the photo-polymerization of chemically unsaturated prepolymers⁴². The third one 2,4,6-trimethylbenzoyl-diphenylphosphine oxide, TPO-L, is also a highly reactive/efficient liquid photo-initiator. DMHA and TPO-L react via light absorption, critical activation and cleaving of a fragile carbon carbon bound, Norrish type I initiator. The model resin is a well-defined but multifunctional inhibitor containing printable acrylic ester monomer mixture which is applicable e.g. as lacquer/finish for off-set printing. To summarize the contribution contains the development and the demonstration for wavelength and intensity dependent experimental analysis on the hand of a *Raman* UV-vis setup. This includes a detailed analysis of the measured data that means the *Raman*, the UV-vis and the dimensions of the cured solid. An uttermost important aspect is the identification of the signal curing correlations of the UV-vis system even in the "influenced" wavelength range. Recently only the reflection on the fused silica to resin interface was analysed, no.3 in Scheme 1. Additionally a cascading effect of 45° incident angle e.g. of the *Raman* UV-vis setup is clearly proven for (semi-)transparent resins. Due to the absolute and spectral

calibrated light source together with the novel data analysis the measurement system have to potential to enhance the analysis of photo-induced polymerizations in bulk not only for application aspects but also for practical and theoretical studies concerning kinetic, quantum yields (quantum yield for triplet, quantum yield of radical formation or radical reactivity towards acrylate double bonds or inhibition species) and band gap effects (if using semiconductor based initiators^{13,16,17}).

2. Experimental

2.1 Materials

The resin was a well-defined 2 to 3 mixture of trimethylolpropantriacylate, TMPTA, and bisphenol A diglycidyl ether diacrylate, BAGdA, exactly (1-methylethylidene) bis[4,1-phenyleneoxy(2-hydroxy-3,3-propanediyl)] diacrylate received from Rahn AG, Zürich, Swiss ($\rho = 1.148 \text{ g mL}^{-1}$). The number of double bonds n_{DB} can be calculated by eqn. (1), compare to supporting information, with known mass m_{total} ,

$$n_{DB} = \frac{N_{DB}}{N_A} = \left(\frac{3 \cdot 0.4}{M_{TMPTA}} + \frac{2 \cdot 0.6}{M_{BAGdA}} \right) m_{total} = \frac{m_{total} \text{ mol}}{153.23 \text{ g}} \quad (1).$$

The three initiators investigated within this study, Table 1, were also purchased from Rahn AG. The initiators were added/mixed prior to the first measurement in/with the monomer.

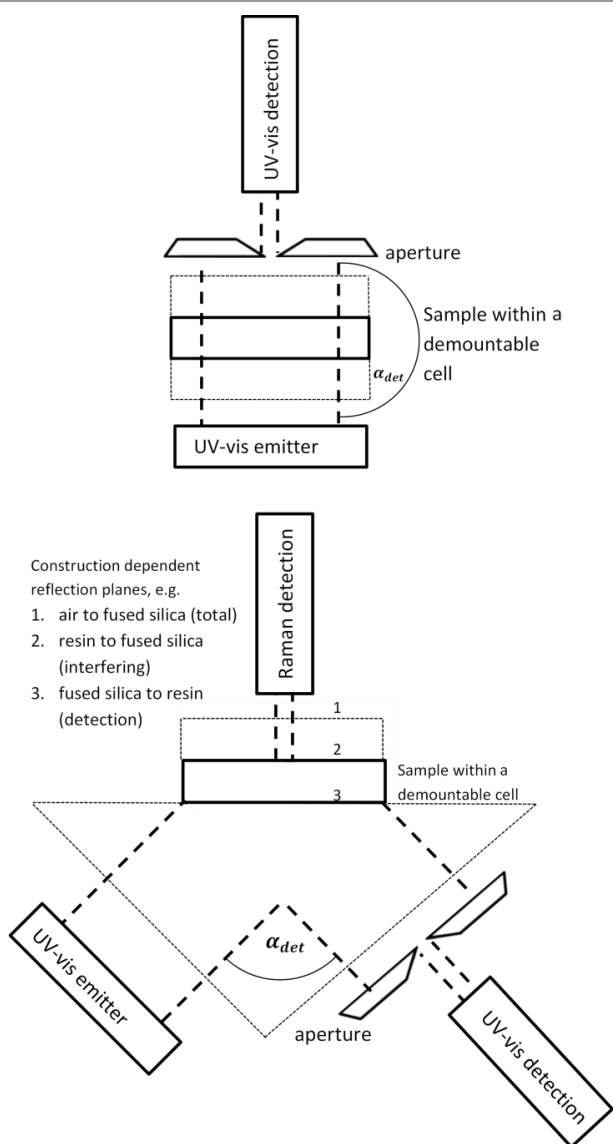
2.2 UV-vis and irradiation

The transmission measurements of the compounds solved in isopropyl alcohol, iPA, were performed with a Carry50 Bio, Agilent, Waldbronn, Germany, Figure S3. For all other experiments a modular, spectral and absolute calibrated fibre optical system was used. The detection unit was a MultiSp Desktop/USB system, tec5 AG, Oberursel, Germany equipped with a MCS FFT-CCD diode array detector, Carl Zeiss, Oberkochen, Germany. The back-thinned FFT-CCD Chip S7031-1006S, 1024x64 Pixel was fabricated by Hamamatsu Photonics K.K., Herrsching am Ammersee, Germany. For coupling a 74-UV collimating lens and an optical fibre (core diameter 0.4 mm) UV-VIS XSR solarization-resistant QP400-2-SR-BX from Ocean Optics GmbH, Ostfildern, Germany were used. The fibre optical detector was connected with a PVC-housing containing a 0.15 mm pinhole or an absorptive neutral density ND = 3 (NE30A), Thorlabs Inc, Newton, New Jersey, USA.

TABLE 1 Investigated initiators and amount within the sample.

brand name	name	formula	M [g mol ⁻¹]	maximum of absorbance ^c [nm]	$n_{ini}/n_{c=c}$ [mol%]	weight content [%]
Genocure*BP ^a Irgacure*BP ^b	benzophenone	C ₁₃ H ₁₀ O	182.22	254	1.05	1.25
Genocure*DMHA ^a Darocur *1173 ^b	2-hydroxy-2-methylpropiophenone	C ₁₀ H ₁₂ O ₂	164.20	247/277	0.95	1.02
Genocure*TPO-L ^a Irgacure*TPO-L ^b	2,4,6-trimethylbenzoyl-diphenylphosphine oxide	C ₂₂ H ₂₁ O ₂ P	348.37	380	0.89	2.01

^a Rahn AG (deliverer). ^b BASF. ^c manufacturer specifications.



SCHEME 1 UV-vis curing transmission (top) and *Raman* UV-vis geometry (bottom). The fused silica windows and the prism are marked by thin broken lines. If the geometry is alternated (e.g. by using IR transparent material) the FT-*Raman* system can also be replaced by a FT- or disperse IR spectrometer (compare also to section 1 within the supporting information).

This unit can be connected with a *Raman* UV-vis¹⁶ (45° geometry ($\alpha_{det} = 90^\circ$)) or a UV-vis sample cell (90° geometry ($\alpha_{det} = 180^\circ$), transmission, aligned) for monitoring the photo induced polymerization of bulk acrylic esters, Scheme 1. For illumination, the cells were also connected via optical fibre (core diameter 0.4 mm) to a Perkin Elmer optoelectronics xenon flash light (LS-FX) FX 1160 (maximum output 0.5 J flash⁻¹,

regular 370 mJ flash⁻¹, ≈ 25 W light output, 8 μ s flash⁻¹, 66.6 Hz). The light source is modified in the way that a linear variable filter and a UG11 filter can be used simultaneously without alternation of the beam path. Both were purchased from Ocean Optics GmbH, Ostfildern, Germany. The linear variable filter, LVF-HL, is an adjustable bandpass filter with the working range of 300 to 750 nm. A specific correction function $A_c(\lambda)$ exists for the detector,

$$E(\lambda) = n(\lambda)_{\text{photon}} \times \frac{h \times c}{\lambda} = n(\lambda)_{\text{counts}} \times A_c(\lambda) \times \frac{h \times c}{\lambda} \quad (2),$$

which was computed by a sophisticated statistical procedure³⁹, Table S1. This function can be used to calculate the average photon number $n(\lambda)_{\text{photon}}$ e.g. in Hz m⁻² and the irradiance $E(\lambda)$ e.g. in W m⁻² using only the count number $n(\lambda)_{\text{count}}$ per array of the fully illuminated detection area. The function itself is well-defined above 310 nm. Below 310 nm eqn. (3) is used,

$$A_c(\lambda) = A_c(310\text{nm}) \left(\frac{\lambda - 176\text{nm}}{310\text{nm} - 176\text{nm}} \right)^2 \quad (3),$$

to consider a reduction in the quantum yield of the detection unit. The function $A_c(\lambda)$ is valid if the detection area of the collimation lens (0.41 mm² ($\approx 75\%$) to 1.23 mm² (100%)) is sufficiently *uniform* illuminated. The xenon flash light is too intensive to be determinable without filter or pinhole neither within an aligned ("transition") nor within the *Raman* UV-vis setup, Scheme 1. The scaling procedure will be described in subsection "Calculation of the intensity and energy of the irradiated light" (3.6). The light using the ND3 filter or the 0.150 mm pinhole differs by a factor of 1/32 to 1/42. This value is in the range of the differences in area, compare the Table 3³⁹ of contribution dealing with the detailed characterization of this fibre optical receiver. An additional proving of the uniform illumination is performed for an aligned setup and will be part of a further research report.

2.3 *Raman* UV-vis cure monitoring

The sample cell of the *Raman* UV-vis system consist of PVC-housing containing a fused silica isosceles right angle prism and two plugs for the collimator lens or the UV-vis detection Scheme 1 bottom and Figure 2 in the reference¹⁶. The plugs are positioned at the centre of the smaller planes to allow illuminating and UV-vis detecting in $\alpha_{det} = 90^\circ$ geomet. (angle of incidence = angle of detection = 45°). The larger (top) plane can be covered with a fused silica window (1 mm). Scheme 1 bottom. At the centre of this plane, in-between the cover and the prism the liquid samples were placed. The 0.05 mm thickness was ensured by using a distance holder. Thickness accuracy was controlled as explained within the discussion by quantitative *Raman* spectroscopy (3.5). $A_c(\lambda)$

samples were sufficiently transparent to avoid heating due to the absorption of the 1064 nm Laser (1 W) from the Multiram FT-Raman spectrometer (Bruker Optic, Eislingen, Germany). For every vibrational band determination four Raman spectra (6 cm⁻¹ resolution, average spectrum of 20 measurements, ≈ 1 min measuring time) of the samples were recorded in back-reflection, Scheme 1, vertical through the cover during light-off phases (in general after every 2.000 flashes). UV-vis data were recorded/averaged during the illumination with 10-4 flashes. This recently introduced automatic Raman UV-vis system¹⁶ has the unique ability to monitor both the double bond content (deep curing by Raman) and solidification (area curing by UV-vis). Before the present study the analysis of the UV-vis data was only performed for wavelength ranges in which the sample contains strong absorbers leading to non-disturbed reflection at the fused silica to resin interface, no. 3 in Scheme 1. But in this study it will be shown that all wavelength ranges with sufficient illumination intensity can be analysed, see subsection "Analysis of the UV-vis signal to curing correlation" (3.3). After solidification the still liquid monomer is removed by washing with ethanol and the size of the solid, Figure S1, was determined from images of the SM Z800 stereomicroscope coupled with a DS-2Mv CCD camera by the imaging software NIS Elements D, 3.00 from Nikon GmbH, Düsseldorf, Germany.

2.4 Data processing Raman

The Raman data were fitted by multiple pseudo-Voigt functions $PV(\tilde{\nu})$,

$$F(\tilde{\nu}) = \sum PV_i(\tilde{\nu}) \quad (4),$$

$$PV(\tilde{\nu}) = area \cdot (\eta \cdot g(\tilde{\nu}) + (1 - \eta) \cdot l(\tilde{\nu})) \quad (5),$$

$$g(\tilde{\nu}) = \frac{4\sqrt{\ln(2)}}{\omega\sqrt{\pi}} \cdot \exp\left(-4 \cdot \ln(2) \cdot \left(\frac{\tilde{\nu} - v_{peak}}{\omega}\right)^2\right) \quad (6),$$

$$l(\tilde{\nu}) = \frac{1}{\pi} \cdot \frac{0.5 \cdot \omega}{(\tilde{\nu} - v_{peak})^2 + (0.5 \cdot \omega)^2} \quad (7),$$

to obtain the *area* of each vibrational band especially the one of the double bonds at around 1635 cm⁻¹. The parameters ω , v_{peak} , and $0 \leq \eta \leq 1$ correspond to the full width at half maximum, the peak position (in cm⁻¹) and the relation between the Gaussian shape, equation (6), and the Lorentzian shape, equation (7), which is individually calculated for every band. The specific curve shapes of the relative double bond *area* ($C=C_{acrylic}$ to $C=C_{aromatic}$) as function of the irradiated light ("time") for the Raman data were analysed by modified Gompertzian functions (k rate constant, t_s shift time),

$$f(t) = b - a \cdot \exp\left(-\exp(-k \cdot (t - t_s))\right) \quad (8),$$

$$t_i = \frac{k \cdot t_s - \ln(1.5 + 0.5 \cdot \sqrt{5})}{k} \quad (9),$$

$$t_f = 2 \cdot \frac{k \cdot t_s - \ln(1.5 - 0.5 \cdot \sqrt{5})}{k} - t_i \quad (10),$$

which allows for automatic computation of the time when the reaction starts, t_i , (affected by inhibition and oxygen) and the time when the reaction is essentially completed, t_f (the

system is solidified). The term $1-a/b$ (from limit value consideration) denotes the relative final monomer content M for Raman measurements. Details concerning the Raman analysis like aspects of noise reduction may be found in literature.^{13, 15-17, 28} Due to the used filters the UV-vis data cannot be analytically fitted¹⁶, compare to subsection "Analysis of the UV-vis signal to curing correlation" (3.3).

3. Results and Discussions

This "Results and Discussions" section can be divided in three main parts. The analysis of the sample and "light sources" (3.1) together with the experimental curing results (3.2) are the requirements for the analysis of the novel experimental and analytical technique (3.3-3.6). The utilization of a FT-Raman unit is not been mandatory. The vibrational band analysis was performed to verify the UV-vis signal curing correlations (3.3). A second focus is on the calculation of the absolute number of absorbed photons (3.6) using the computed properties of the samples and the "light sources". The detailed analysis is only possible if geometric and experimental influencing factors are considered (3.4 and 3.5). Resin-initiator-light source relations for these model samples were computed and summarized within the last part (3.7-3.8). These sections also contain different possibilities to visualize/analyse the results. All experimental details concerning the reactivity of the initiators may be found within Table S2, Table S4 and Table S5.

3.1 Analysis of the samples and the "light sources"

UV-vis emission. The intensities passing the linear variable filter (≈ 100 spectra), the UG11, the linear variable plus UG11 filter (≈ 100 spectra) and without filter are collected in 180° geometry (aligned, Scheme 1 top), Figure S2, to allow the calculation of the irradiation to be possible. Before applying the sample onto the Raman UV-vis prism, Scheme 1 bottom, the total reflected light $I_{tr}(\lambda)$ was measured. Linear scaling (C) to match with the aligned spectra and comparing with the xenon light spectrum without filter $I_{Xe,r}(\lambda)$ allows calculating the absolute transmission $T_{ill}(\lambda)$,

$$T_{ill}(\lambda) = \frac{I_{tr}(\lambda) \cdot C}{I_{Xe,r}(\lambda)} \quad (11),$$

which will be used to compute the absolute irradiation $I_{abs}(\lambda)$, see subsection "Calculation of the intensity and energy of the irradiated light" (3.6), Figure 1.

The wide (upper quartile minus lower quartile) of the irradiation light passing the linear variable filter is with 11 nm + 2 nm so small that refractive index influences (Sellmeierian equation)⁴³ can be neglected. In this way multiple "light sources" with similar and known intensity and energy were realized, Figure 1.

UV-vis transmission and curing transmission. Determination of the absorbance in non-absorbing solvents (pure iPA) took place to verify the positions given by the distributor, Table 1. For BP and DMHA an additional absorption at ≈ 340 nm ($A = 0.8$; ≈ 1.1) was monitored for 1 M solution, Figure S3. For these solutions the absorbance is larger than 1 below 300 nm

For 1 M TPO-L solution the absorbance is larger than 1 below 340 nm. For 0.1 M solution a maximum at around 300 nm was monitored. Transition UV-vis solidification experiments, Scheme 1 top, (thickness 0.05 mm) were performed to determine the optical absorption of the initiators and the resin and to compute the absorbed light dose. Only one measurement per sample resulting in solid polyacrylic esters of around 7.0 mm diameter was performed so that no further analysis will be presented. Following to these real time solidification measurements TLO-L which also has the strongest absorbance within the investigated wavelength range, Figure S3, result in the fastest photo-polymerisation of the used acrylic ester mixture. The wavelength dependent measurements firstly presented within this study can be used to analyse some of the influencing factors (in addition to absorbance) like quantum yield for triplet, quantum yield of radical formation or radical reactivity towards acrylate double bonds. The spectral correction procedure firstly introduced in 2011¹⁴ to remove the effects of differences in reflection and

refractive index if measuring with the fibre optical system with and without sample was performed to determine the relative absorption of the initiators and of the resin, Figure 2 and Figure S4. Thereby the relation between the transmitted intensity with $I(\lambda)$ and without sample $I_r(\lambda)$ was analytically analysed by eqn. (12),

$$\frac{I(\lambda)}{I_r(\lambda)} = A(\lambda) = a + b \cdot \lambda + c \cdot \lambda^2 \quad (12),$$

in the range in which no absorbance takes place ($> 400/450$ nm). This procedure leads to the relative absorption $A_b(\lambda)$,

$$A_b(\lambda) = \frac{I_r(\lambda) - I(\lambda) \cdot A(\lambda)}{I_r(\lambda)} \quad (13).$$

Dependencies from a number of not exactly controlled experimental parameters are likely which can be reduced/crosschecked by combining these results with the ones of the transmission experiments, Figure S3.

TABLE 2 Summary of the raw data of all measurements.

sample	median [nm]	Raman t_i [10 ³ fl.]	Raman t_f [10 ³ fl.]	M_{∞} [%]	UV-vis $t_{i,1}$ [10 ³ fl.]	UV-vis $t_{i,2}$ [10 ³ fl.]	UV-vis $t_{1/2,2}$ [10 ³ fl.]	area [mm ²]	storage period [d]
BP _{FL} ^a	333.5	65.1	94.1	62.7	54.06	73.80		4.34	0.24
BP _{UG11}	317.5			100.0				0	0.00
DMHA _{FL} ^a	333.5	2.9	13.8	47.7	4.48	13.28	22.4	17.81	0.00
DMHA _{UG11}	317.5	7.2	18.8	54.5	7.99	7.99	10.2	12.72	5.99
DMHA _{UG11}	317.5	9.3	15.4	53.7	8.28	8.28	9.6	14.39	0.09
DMHA _{LVF}	312.0	46.4	66.6	61.9	37.39	37.39	43.8	6.25	0.19
DMHA _{LVF+G11}	312.5	70.9	73.9	72.8	65.80	65.80	78.0	0.97	0.98
DMHA _{LVF+G11}	333.0	40.6	59.8	57.1	37.60	37.60	47.0	7.72	1.31
DMHA _{LVF}	333.5	17.9	39.2	51.1	18.99	18.99	29.2	10.75	1.15
DMHA _{LVF}	333.5	19.1	36.3	53.4	18.33	18.33	29.0	12.29	2.25
DMHA _{LVF}	349.0	26.4	49.8	53.3	26.90	26.90	42.9	9.78	3.25
DMHA _{LVF}	368.0			100.0				0	2.05
TPO-L _{FL} ^a	333.5	0.70	2.43	51.3	0.83	0.83		10.82	0.00
TPO-L _{FL} ^a	333.5	0.88	2.26	53.8	0.90	1.49	2.6	14.56	13.71
TPO-L _{UG11}	317.5	1.33	11.89	51.9	2.70	2.70	8.4	20.3	12.76
TPO-L _{UG11}	317.5	1.40	8.48	48.6	2.71	5.21	9.6	21.1	2.98
TPO-L _{UG11}	317.5	1.67	8.88	52.8	2.63	4.60	8.4	20.9	5.67
TPO-L _{LVF+UG11}	307.0	20.2	39.0	60.1	21.23	21.23	28.3	8.8	1.66
TPO-L _{LVF+UG11}	312.5	10.6	29.7	54.8	13.01	19.65		10.6	13.87
TPO-L _{LVF+UG11}	344.5	17.0	37.9	56.8	17.58	17.60	27.9	12.51	14.94
TPO-L _{LVF+UG11}	344.0	26.6	44.7	60.5	21.10	21.10		11.6	2.84
TPO-L _{LVF+UG11}	364.0	26.5	42.2	58.9	29.93	29.92	51.2	8.29	1.96
TPO-L _{LVF+UG11}	364.5	43.6	56.0	63.3	33.66			8.42	14.84
TPO-L _{LVF}	307.0	7.2	16.9	55.7	9.10	9.10	12.0	8.45	0.86
TPO-L _{LVF}	312.5	4.2	17.2	53.6	6.59	8.36	10.4	12.67	14.71
TPO-L _{LVF}	345.5	7.0	17.0	54.0	7.67	7.67	11.2	14.44	14.85
TPO-L _{LVF}	345.5	8.6	21.9	56.1	10.70	12.76	19.6	10.8	2.74
TPO-L _{LVF}	368.0	5.5	15.6	57.0	6.26	7.14	12.5	15.83	1.83
TPO-L _{LVF}	369.0	6.9	15.6	55.4	7.00	7.00	11.6	12.79	15.72
TPO-L _{LVF}	403.0	17.5	36.0	57.0	14.76	14.76	40.0 ^c	13.81	5.79
TPO-L _{LVF}	403.0	12.2	26.5	55.1	13.10	13.10	30.0 ^c	13.84	15.99
TPO-L _{LVF}	424.0			100.0				0	5.94

^a Only wavelengths < 450 nm are considered for the flash light without filter (resulting in a median of 333.5 nm). The total energy is around 115 Wm⁻². The measurement without filter of the TPO-L containing sample was performed with 200 flashes in-between the Raman measurements.

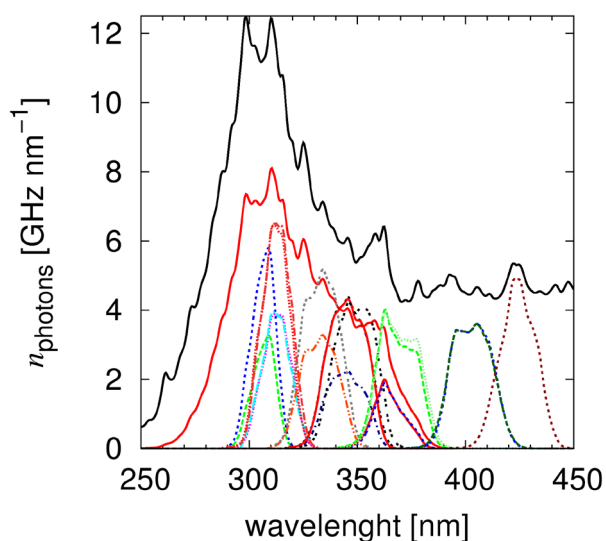


FIGURE 1 Calculated irradiated number of photons per nm for the different filter combinations. The illuminations with the highest impact of the UG11 filter are the measurements performed with the LVF-HL ≈ 370 nm.

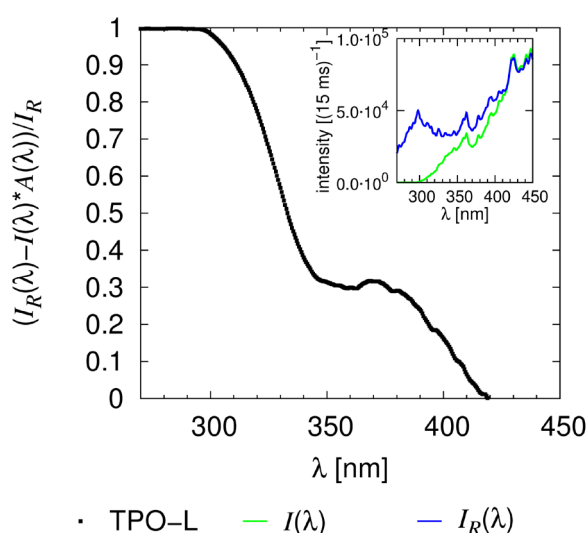


FIGURE 2 Relative absorption of the resin containing 2wt% TPO-L ($d = 0.05$ mm), compare also with Figure S4.

3.2 Experimental results of the Raman UV-vis Curing experiments

Wavelength dependent curing experiments were performed with irradiations passing the UG11 filter, the linear variable filter (different positions), the linear variable filter and the UG11 filter and no filter at all, Figure 1. Every Raman spectrum was analysed by the procedure described in subsection (2.4). The *area's*, eqn. (4) to eqn. (7), from the Raman spectra which were collected for every step in irradiation were averaged. These time/flash dependent *area's* were analysed by eqn. (8) resulting in the final t_f the initial time t_i , and the final monomer content M_∞ , Figure 3. The UV-vis data were analysed as explained within the next subsection (3.3). The median of the illumination light is used for sample nomenclature of the data e.g. within Table 2. The procedure to

calculate the median is explained in subsection "Calculation of the intensity and energy of the irradiated light" (3.6). The raw data presented in Table 2 clearly demonstrate that the TPO-L as cleavable photo-initiator is the most reactive initiator. The initiator benzophenone which works through electron transfer, triple state quenching,⁴⁴ results in low yield and is the slowest initiator by far.

3.3 Analysis of the UV-vis signal to curing correlation

Recently it was demonstrated that the light within strong absorbing ranges of the sample which is reflected at the prism to resin interface can be automatically analysed resulting in the area solidification analysis of the system, Scheme 1.¹⁶ Due to the linear variable filter and the tested initiators such unaffected ranges do not exist in this study. Nevertheless, the CCD detector monitored up to two irregular deviations for reflected light, Figure 3. The number of measurements was too small so that all of the presented hypotheses within this subsection have to be verified by future experimental and theoretical studies. Only a manual determination of two initial times $t_{i,1}$, $t_{i,2}$ and the "half effect" time $t_{1/2,2}$ was possible. The last one is used to calculate the final time respective the final absorbed photon number $n_{f,2}$,

$$n_{f,2} = n_{i,2} + 2 \cdot (n_{1/2,2} - n_{i,2}) \quad (14).$$

In general the first irregular deviation $t_{i,1}/n_{i,1}$ is measured at the start of or before the Raman observation that means is well-correlated with the initial time for the Raman measurements, Figure 3, Figure S5, Figure 4. Both UV-vis signals were clearly recognisable for measurements with high number of absorbed photons (TPO-L UG11, DMHA FL) and in the cases of strong resin absorbance (TPO-L < 312.5 nm) Table 2. Then the first effect is less wide and intense than the second UV-vis signal, Figure 3, Figure S5. But at the moment no one-to-one correlation between the initial times of the UV-vis $t_{i,1}$ and $t_{i,2}$ and the Raman observations t_i can be proven beyond doubt. The same is valid for photo-polymerisation efficiency Δn ,

$$\Delta n = n_f - n_i \quad (15),$$

Figure S5, Figure 3. For wavelength ranges smaller than 350 nm the efficiency Δn of the UV-vis data are smaller than the one of the Raman data and for ranges larger than 350 nm vice versa. This implies that the penetration depth which significantly influence the Raman measurement (deep curing) have a smaller impact on the UV-vis setup. Hence the UV-vis signal variation is even for these (partially) transparent wavelength ranges a suitable probe to monitor the curing of a thin layer. Two aspects which may influence the comparability of the data are different local position, compare to subsection (3.4), and different resolutions of the equipment (resolution Raman = 2000 flashes \ll 40 flashes = resolution UV-Vis). But the present study confirms without any doubt that the variation in the UV-vis signal is correlated with the photo-induced polymerization of the resin. This is the most important point of this subsection.

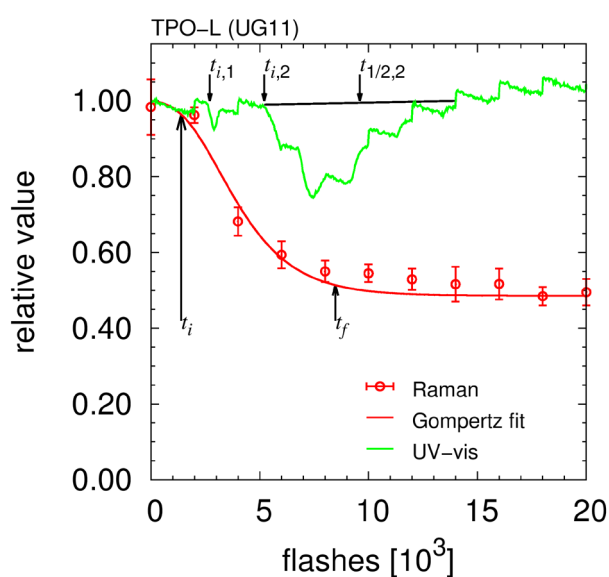


FIGURE 3 Visualisation of the relation between the monomer conversion and the detected UV-vis signal variations. All determined “times” are marked within the figure, compare also to Figure S5.

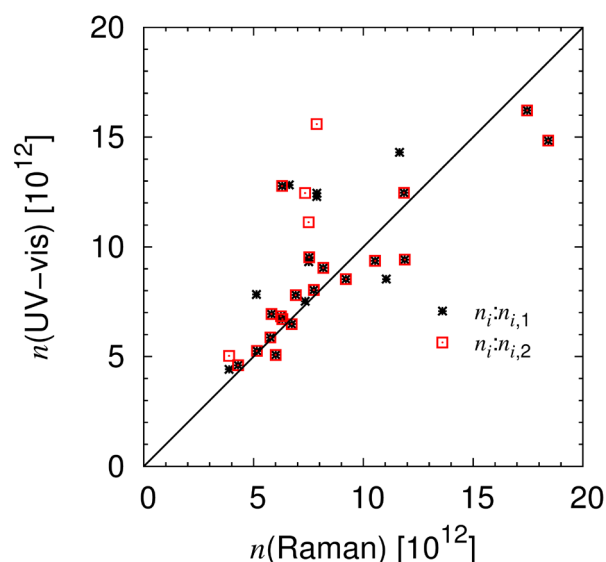


FIGURE 4 Initial times for the *Raman* and the UV-vis setup. The calculated initial times in number of absorbed photons are presented which are proportional to the number of flashes, compare also to Figure S6.

To emphasize the 45° ($\alpha_{det} = 90^\circ$) reflection UV-vis setup, Scheme 1, is even applicable for transparent systems but its main advantage is the fact that non-transparent systems like highly pigmented system are analysable.

Additionally the change in refractive index which causes the signal variation is correlated with the solidification of the system and the UV-vis equipment has a better resolution with 40 flashes (possible down to 1 flash) than the *Raman* equipment (2000 flashes). Additionally the UV-vis systems allows performing real-time (this detector down to 3 ms) of multiple data points (every 0.5 nm). The fact that not only some values (wavelength) specifically vary during the measurements is an significant advantage of the UV-vis unit in

comparison to any vibrational band sensitive technique like disperse infrared (810 cm^{-1})^{23, 24} or Raman spectroscopy (1635 cm^{-1}).[‡] Further the UV-vis setup, Scheme 1, is not restricted to transmission experiments. Both 45° ($\alpha_{det} = 90^\circ$) and 90° ($\alpha_{det} = 180^\circ$) were measured and analysed. The “always” present light source can be used for curing and monitoring. Last but not least the fused silica is much easier to handle/clean than materials transparent for IR-radiation. By varying the construction a similar UV-vis receiver can also be connected with any *real-time* IR spectrometry, compare also to the supporting information.

3.4 Analysis geometry effects of the setup

Geometry effects: position. Analysis of the data, Table 2, confirms that the *Raman* and UV-vis positions are within the area of maximal intensity. The measurement of the DMHA containing system with an irradiation median of 312.5 nm results in an area of 0.97 mm^2 . The measurable signal changes both for the UV-vis and the *Raman* setup. This fact clearly underlines the good match between the UV-vis and the *Raman* measuring position. This is also the position of maximal intensity which will be less influenced by reflection effects, compare with the influence of the incidence angle, see below.

Geometry effects: volume. For quantum yield calculation the number of double bonds have to be known. Hence the detection volume has to be specified. Due to the illumination Scheme 1 bottom, the volume is considered as a 45° prism (height 0.05 mm) whereby the diameter of the base area ranges from around $\approx 0.15\text{ mm}$ (Laser) to 0.20 mm (collected by the pinhole). For the calculations, Figure 4, the minimal diameter is chosen. Then the amount of sample/double bonds within the curing volume can easily be calculated from the data by eqn. (1). Note that for quantum yield calculation the uncertainty in the area is without any impact (photon number is in Hz m^{-2}). The consumed double bond are calculated by multiplying with the conversion ($1 - M_\infty$), Table 2. Note that also the double bond content for every position in time can be determined by eqn. (8).

Geometry effects: incidence angle. In ideal case the incidence angle of the irradiation with 45° leads to an elliptical cured solid with the well-defined aspect ratio of $2^{-0.5}$. Within the first presentation of the *Raman* UV-vis system¹⁶ a second curing area was described which was monitored for high-yield initiators (or huge number of flashes) by testing sufficient transparent resins. This second curing area is affected by the light total-reflected at the cover window air interface, no.1 in Scheme 1. The detailed analysis of the areas within this study leads to the fact that a cascading effect of the irradiated light within semi-transparent systems influences the dimension of the cured solid significantly even if no second curing are exist. For visualization a theoretical incident angle θ_i is calculated by eqn. (16),

$$\sin(\theta_i) = \frac{2 \cdot a}{2 \cdot b} \quad (16)$$

TABLE 3 Example of measured and calculated dimensions of/for the solids after curing.

	2a [mm]	2b [mm]	area measured [mm ²]	area calculated [mm ²]	theoretical incident angle [°]
TPO-L 307 nm	2.65	4.02	8.45	8.37	41.2
TPO-L (+UG11) 307 nm	2.76	4.01	8.80	8.70	43.5
TPO-L 312 nm	2.86	5.64	12.67	12.67	30.5
TPO-L (+UG11) 312 nm	2.90	4.59	10.06	10.45	39.2
DMHA 312 nm	1.97	4.06	6.25	6.28	29.0
TPO-L (+UG11) 364.5 nm	2.30	4.7	8.42	8.49	29.3
TPO-L (14.9 d) 364.5 nm	2.7	5.88	14.44	12.47	27.3
cyan ^a	1.82	2.63	3.75	3.76	43.8
magenta ^a	1.88	2.75	4.05	4.06	43.1
yellow ^a	2.33	3.14	5.68	5.76	47.9
key ^a	1.29	1.89	2.00	1.92	43.0

^a These example measurements for non-transparent resins may be found within the supporting information, Figure S7.

The area A_{ell} can also be calculated with determined axis a and b ,

$$A_{ell} = \pi \cdot a \cdot b \quad (17),$$

to prove the geometric form of the cured solid, Table 3. The results confirm that the first curing area is elliptical. If the system is sufficient transparent a cascading effect, such as light (multi-) reflected at the resin to fused silica interfaces, no. 2 in Scheme 1, is clearly recognizable by the theoretical incident angle $\ll 45^\circ$. For non-transparent systems (CMYB; highly filled resins) respective within the absorption range of the monomer/polymer for example experiment TPO-L (+UG11) 307 nm the effect does not exist. By analysing the data even a distinction between the absorption effectivity of the DMHA and the TPO-L relative to the one of the resin are possible. Hence the measured areas are strongly influenced by reflections on the resin to fused silica interface, no. 2 in Scheme 1. The geometry of the solid is most likely also influence by the wide of the beam relative to the sections of the linear variable filter. Concerning the area analysis also effects of variances in layer thickness cannot be separated, see section "Fine correction of the layer thickness and resin aging" (3.5). Nevertheless the area of the cured solid, Figure S8, Table 2, can be used to predict the effectivity of the initiator for low-intensity illumination in combination with the cascading effect if the total number of flashes for the experiment is similar, Table S2. From practical aspects this lower intensity in combination with the effects of the (semi-) transparency leads to the possibility to identify highly reactive

systems. These systems lead to an effective reaction with low photon flux (power). Hence the overall curing process of industrial applications may be optimised by the variation of the exposition time.

3.5 Fine correction of the layer thickness and resin aging

The further analysis of the data without correction led to a confliction result that the curing of the DMHA containing resin (using UG11) started earlier but was finished later 6 days after preparation. Hence, in this case the layer thickness has to be considered. Fortunately, the used *Raman* setup allows controlling the accuracy of the layer thickness by comparing the computed intensities of the maximum of the double bond vibrational band I at 1635 cm^{-1} before the first irradiation. These intensities are more or less randomly distributed in time whereby for the resins containing TPO-L the average value is $\langle I \rangle = 0.038 \pm 0.004$ for the first measurement cycle ($t < 6\text{ d}$) and for the second measurement cycle $\langle I \rangle = 0.036 \pm 0.002$ ($t > 12.5\text{ d}$). Considering the results of the curing experiment using the UG11 filter it can be assumed that the resin is slightly aged. For the two measurements of the DMHA contacting resin with UG11 filter the difference in *Raman* intensity is $\Delta I = 0.012$ which corresponds to a significant thickness variation. For moderate/sufficient absorbed photons the correction of the final amount n_f and the initial amount n_i , by eqn. (18)

$$n_f = \frac{\langle I \rangle}{I} (n_{f,0} - n_i) + n_i \quad (18),$$

leads to a higher accuracy of the measured curing behaviour, see section "Intensity and energy relations of the initiators" (3.7).

3.6 Calculation of the intensity and energy of the irradiated light

The absolute and spectral calibration of the fibre optic detector led to a correction function $A_c(\lambda)$, eqn. (2), which is valid if the whole detection area is illuminated by a uniformly distributed light source³⁹ and correlates the count number of the detection unit with the photon number per array. Within the cited publication the specific energy is calculated by trapeze formula,

$$value = 0.5 \cdot \sum (value(\lambda_i) + value(\lambda_{i-1})) \cdot (\lambda_i - \lambda_{i-1}) \quad (19).$$

Here the number of photons is calculated by trapeze formula. The general technique to transfer/calculated necessary spectra was described within the cited publication in detail.³⁹ First of all the spectra of the illumination xenon light source passing a ND3-filter (aligned geometry) and a pinhole (0.15mm) are recorded. Note that the effective beam wide (diameter of the cured solids) for the aligned geometry is 0.3 mm broader due to difference in the constructing/distances, Scheme 1. The pinhole spectrum is multiplied by a scalar factor to match with the ND3 spectrum within the transmission range. A detailed study is in preparation which deals with the aligned transition UV-vis setup, Scheme 1 top, and the area distribution of the irradiation light source. First evaluations prove that the intensity of the used xenon flash light is sufficiently uniform, distributed within the receiver detection "area"³⁹.

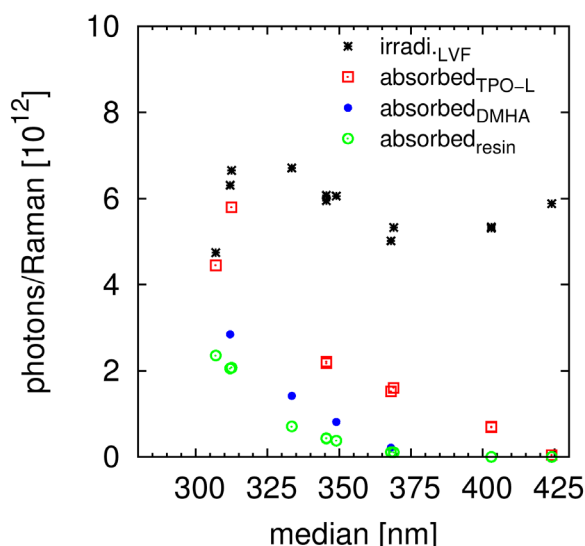


FIGURE 4 Overview of the incident irradiation n_{ill} and the absorbed photons n for the initiators and the resins during one cycle of irradiation between the Raman measurements (LVF-HL). Compare also to the illuminations within Figure S9. The number of photons is relative to calculated illumination area, Table 3.

Also no variations in the energy distribution were observable within this “area” (the relative count numbers between different wavelengths do not change). Hence the absolute irradiation $I_{abs}(\lambda)$ is allowed to be calculated simply by multiplying with the correction function $A_c(\lambda)$, eqn. (2), Figure 4,

$$I_{abs}(\lambda) = n(\lambda)_{counts} \times A_c(\lambda) \quad (20).$$

The number of irradiated photons effecting the photopolymerization is influenced by the cascading effect = multi-reflection on the resin to fused silica interfaces (3.4). But it can be assumed that within the centre of the cured solid the effect is relatively small. Hence, absolute photon dependent analysing of the border regions with the 45° ($\alpha_{det} = 90^\circ$) setup, Scheme 1, is not possible. Within the detection area the xenon flash-light source (25 W light output) illuminated the sample with 115 W m^{-2} (176 nm to 990 nm). Due to the energy distribution the value corresponds $77 \text{ W m}^{-2} = 1.32 \cdot 10^{20}$ photons $\text{s}^{-1} \text{m}^{-2}$ for wavelength smaller than 450 nm. Following to Fouassier *et al*, 1993,⁶ a 80 W cm^{-1} (Hg mid-pressure lamp) leads to 10^{22} photons $\text{s}^{-1} \text{m}^{-2}$. The presented calculation leads to reasonable results because the used resin without added initiator is not curable by the xenon lamp (< 140.000 flashes) whereas a 0.05 mm thick layer is solidified after some runs through our 100 W cm^{-1} (1.5 kW Hg mid-pressure lamp) lab curing unit.

Calculation of the number of absorbed photons. It is well known that in general for a transition from the highest occupied molecular orbital to an unoccupied molecular orbital one photon is necessary. Hence it is reasonable to analyse the measurements on the hand of the absorbed photons per array $n(\lambda)$,

$$n(\lambda) = I_{abs}(\lambda) \cdot T_{ill}(\lambda) \cdot A_b(\lambda) = n_{ill}(\lambda) \cdot A_b(\lambda) \quad (21),$$

where $I_{abs}(\lambda)$, $A_b(\lambda)$, $T_{ill}(\lambda)$ and $n_{ill}(\lambda)$ are the calculated absolute irradiation, the relative absorption, the absolute transmission and the incident irradiation/ photon number, Table 4. By comparing the absolute absorbed number of photons which is calculated from $n(\lambda)$ by eqn. (19), the significance/effect of the number of incident photons is reduced. Hence effects of molecular effectiveness can be monitored. Within Figure 4 the absolute absorbed numbers of photons for the initiators and for the resin are presented.

The absorption efficiency of the monomer/polymer may be differ from the one of the initiators but the resin definitively reduce the number of photons absorbable by the initiator as proven by comparing Table S4 with Table S5. Most data discussed within the manuscript are corrected with a maximal influence of the resins, e.g. the relative absorption efficiency AE , last two columns in Table 4. The parameter with the highest critical impact (and the largest experimental workload), on the absorbed photons is the absolute irradiation $I_{abs}(\lambda)$, eqn. (20). But this procedure has only to be performed once if the functionality of the light source is carefully monitored. For the presented results the linear variable filter leads to an illuminated energy of $6.2 \pm 1.1 \text{ W m}^{-2}$ and the linear variable filter plus the UG11 filter to an irradiation of $3.6 \pm 1.3 \text{ W m}^{-2}$. The average wide of the illumination is $11 \text{ nm} \pm 2 \text{ nm}$, Figure 1, Table S6.

3.7 Intensity and energy relations of the initiators

The analysis of the data will focus on the Raman measurements. Details concerning the UV-vis monitoring are part of the subsection “Analysis of the UV-vis signal to curing correlation” (3.3). If a maximal optical absorption influence of the resin is assumed the variances of the data are smaller, see Table S4 and Table S5. But the tables within the supplemental materials contain all calculated results. The data obtained with maximal influence of the resin on the absorption are summarized in Table 5. Due to the limited number of measurements the detailed analysis mainly focused on the results of TPO-L.

Effect of inhibition on n_i . For bulk polymerization of commercial monomers the chain reaction is usually inhibited by storage stabilizers (hydroquinone monomethyl ether, MEHQ) and/or oxygen.^{41, 44} Thereby the created radicals react with inhibitor/oxygen until overcompensation or consumption of the inhibiting species. Reworded, the radical concentration is nearly zero and the termination rate is very high R_t . All steps leading to inhibition species not resulting in chain reactions (within the solidification time) are defined as terminated which are for example midchain radicals²⁸. For a discontinuous irradiation the number of radicals R can be increased if one flash leads to sufficient radicals (high Rate R_i by a huge number of photons) or if the reaction is slow/stable enough (> 15 ms) to accumulate the radicals describable by an average radical balance B_A ,

$$B_A = \frac{dR}{dt} = R_{INI} - R_t \quad (22)$$

TABLE 4 Integrals of the calculated incident irradiation n_{ill} , E_{ill} and relative absorptions of initiators n_{INI} , E_{INI} and resin n_{res} , E_{res} .

sample	median [nm]	n_{ill} [10 ⁹ p s ⁻¹]	E_{ill} [W m ⁻²]	n_{INI} [10 ⁹ p s ⁻¹]	E_{INI} [W m ⁻²]	n_{res} [10 ⁹ p s ⁻¹]	E_{res} [W m ⁻²]	$\frac{n_{INI}}{n_{ill}}$	$\frac{n_{INI} - n_{res}}{n_{ill}}$
BP _{FL} ^a	333.5	2337.9	77.83	772.1	29.63	719.5	27.71	0.33	0.02
BP _{UG11}	317.5	930.4	32.80	379.9	14.26	345.0	12.99	0.41	0.04
DMHA _{FL} ^a	333.5	2337.9	77.83	836.0	31.80	719.5	27.71	0.36	0.05
DMHA _{UG11}	317.5	930.4	32.80	420.4	15.64	345.0	12.99	0.45	0.08
DMHA _{UG11}	317.5	930.4	32.80	420.4	15.64	345.0	12.99	0.45	0.08
DMHA _{LVF}	312.0	210.2	7.58	94.9	3.45	68.4	2.49	0.45	0.13
DMHA _{LVF+UG11}	312.5	130.5	4.70	57.6	2.09	41.2	1.50	0.44	0.13
DMHA _{LVF+UG11}	333.0	142.6	4.82	30.5	1.04	15.4	0.52	0.21	0.11
DMHA _{LVF}	333.5	223.6	7.55	47.2	1.60	23.7	0.80	0.21	0.11
DMHA _{LVF}	333.5	223.6	7.55	47.2	1.60	23.7	0.80	0.21	0.11
DMHA _{LVF}	349.0	201.9	6.51	27.1	0.88	12.6	0.41	0.13	0.07
DMHA _{LVF}	368.0	167.2	5.11	7.1	0.22	3.7	0.11	0.04	0.02
TPO-L _{FL} ^a	333.5	2337.9	77.83	1276.7	46.63	719.5	27.71	0.55	0.24
TPO-L _{FL} ^a	333.5	2337.9	77.83	1276.7	46.63	719.5	27.71	0.55	0.24
TPO-L _{UG11}	317.5	930.4	32.80	660.4	23.95	345.0	12.99	0.71	0.34
TPO-L _{UG11}	317.5	930.4	32.80	660.4	23.95	345.0	12.99	0.71	0.34
TPO-L _{UG11}	317.5	930.4	32.80	660.4	23.95	345.0	12.99	0.71	0.34
TPO-L _{LVF+UG11}	307.0	87.3	3.20	81.8	3.00	42.7	1.58	0.94	0.45
TPO-L _{LVF+UG11}	312.5	130.4	4.69	113.7	4.10	40.4	1.47	0.87	0.56
TPO-L _{LVF+UG11}	344.5	102.5	3.35	38.0	1.25	7.6	0.25	0.37	0.30
TPO-L _{LVF+UG11}	344.0	100.4	3.28	37.2	1.22	7.5	0.25	0.37	0.30
TPO-L _{LVF+UG11}	364.0	62.5	1.93	19.1	0.59	1.7	0.05	0.31	0.28
TPO-L _{LVF+UG11}	364.5	60.6	1.87	18.5	0.57	1.6	0.05	0.31	0.28
TPO-L _{LVF}	307.0	158.1	5.81	148.3	5.45	78.5	2.91	0.94	0.44
TPO-L _{LVF}	312.5	221.7	7.98	193.3	6.97	69.0	2.51	0.87	0.56
TPO-L _{LVF}	345.5	202.4	6.60	73.9	2.42	14.5	0.48	0.36	0.29
TPO-L _{LVF}	345.5	198.4	6.47	72.4	2.37	14.3	0.47	0.36	0.29
TPO-L _{LVF}	368.0	167.2	5.11	50.7	1.55	3.7	0.11	0.30	0.28
TPO-L _{LVF}	369.0	177.6	5.41	53.6	1.64	3.6	0.11	0.30	0.28
TPO-L _{LVF}	403.0	177.0	4.94	22.9	0.65	0.0	0.00	0.13	0.13
TPO-L _{LVF}	403.0	178.0	4.97	23.4	0.66	0.0	0.00	0.13	0.13
TPO-L _{LVF}	424.0	196.0	5.20	1.5	0.04	0.0	0.00	0.01	0.01

^a Only wavelengths < 450 nm are considered for the flash light without filter. The total energy is around 115 Wm⁻². The measurement without filter of the TPO-L containing sample was performed with 200 flashes between the Raman measurements.

The differences in initial times (= photon number) n_i , Table 5, Figure S10 and Figure S11, cannot doubtlessly assign to a physical/chemical property of the system. The storage period influenced by manual mixing of the system defiantly influences the inhibition period. This effect has a higher impact for *Raman* analysis (deep curing) of the measurements performed using LVF-HL plus UG11 filter like TPO-L median = 344 nm respective = 364 nm, Figure 4. The absorbance by the resin does not result in consumption of the inhibitor because n_i increases for wavelength smaller than the onset of the monomer absorbance. The analyses performed with maximal resin correction leads for the TPO-L with LVF to a nearly complete compensation of the monomer absorption, Figure 4. Additional experimental studies focusing on the inhibition period have to be performed for doubtless free conclusions and to calculate reactivates of the initiators towards inhibitor compounds.

Effect of wavelength/intensity on photo-polymerization efficiency.

The photo-polymerization efficiency Δn is defined as the absorbed number of photons to cure the monomer, eqn. (15). Effects which are considered/removed as good as possible are the resin absorbance, the differences in illuminated number of photons, the inhibition and the thickness variance. A significant difference can be observed between the flashlight and the UG11 measurements of TPO-L. This effect is without any doubt dependent from the number of absorbed photons per Raman measurements, Figure S9. Thereby the experiments with the flashlight (higher energy per flash) are recorded with 200 flashes per *Raman* steps and the ones with the UG11 filter were performed with 2000 flashes. Hence an accumulation of the radicals as assumed within the previous subsection took place leading to a more than *optimal* amount of radicals (enhanced amount of side reactions, reduced reactivity towards acrylic double bonds, lower kinetic length of the chain

reaction). This intensity related effects, Figure 3 and Figure 4, can also be demonstrated by comparing the LVF TPO-L measurement 307 and 312 nm (the one with and without UG11 filter) and the ≈ 370 nm measurement with and without UG11 filter, Table 4, Figure 1. The efficiency significantly increase with increasing wavelength median (linear variable filters) up to absorbance onset of TPO-L ≈ 410 nm, Figure 4 and Figure S3. Thereby resins absorbance and illumination differences are remove/strongly reduced so that an effective cleaving and/or a more selective reaction of the fragmentation intermediate are likely. A higher selectivity of "low energetic", low concentration benzoyl radicals was reported if the radicals are generated from surface modified N-ZnO particles¹⁶. Low excited radicals seems to result in a smaller amount of side reactions like the formation of midchain radicals than the same radicals produced by cleaving of e.g. α,α -dimethoxy- α -phenylacetophenone²⁸. Within the cited ESR based study the curing rates of the model initiators (molecular and particular) were strongly different.

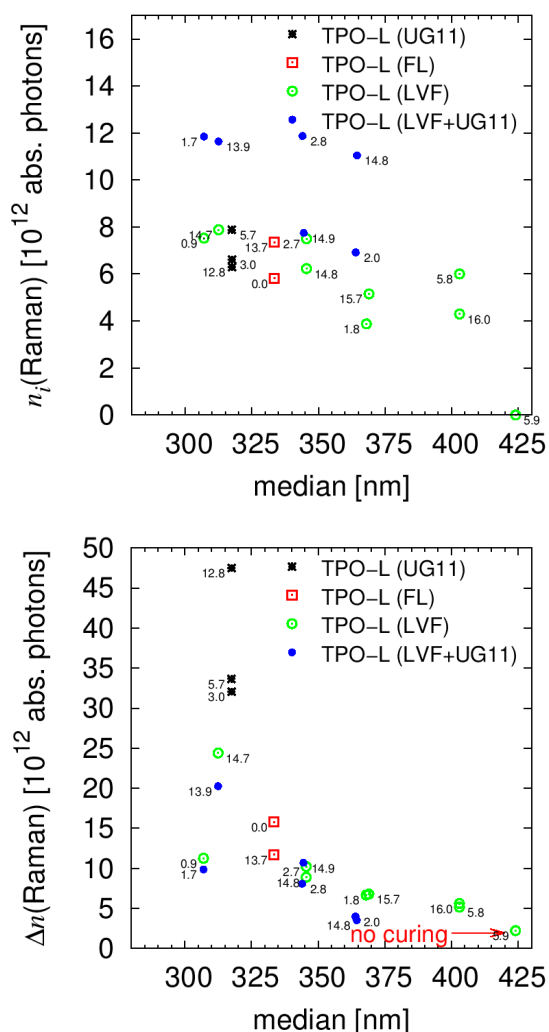


FIGURE 4 Visualization of the relations between the illumination wavelength and the absorbed photon number to compensate the inhibition and to cure the resin (efficiency, eqn. (15)), compare also to Table 5 and Figure S10, Figure S11. The storage period is labelled within the figure. The storing times have no simple correlation with the curing results, compare to the LVF+UG11 measurements.

Nevertheless the difference in the radical content (intensity) may not influence the monitored selectivity for midchain radical formation. Further studies can be interesting to optimize the selectivity and efficiency of chain reactions in bulk systems. Such controlling and monitoring of radical selectivity/activity are normally not considered for industrial applications but as the results in this study confirms may be important to optimize the whole procedure. The desired objective is an optimal curing result with the smallest amount of power (number of photons) leading to well-defined solids (low amount of side reactions) and reproducible properties of the polymeric product. Both initiators DMHA and TPO-L are highly reactive in the range up to the measured onsets in absorbance, Figure S3. The study further clearly confirms that overcompensation of the inhibitor (whereby the inhibitor is not fully consumed) as monitored for the UG11 measurements of TPO-L, Table 5, leads to a significant higher number of necessary photons to cure the resin. Such overcompensation within the centre of the curing area of course leads also to larger solids, Table 2, whereby it can be assumed that the kinetic length of the chain reaction (3.8) will be strongly dependent from the position relative to the maximal irradiation. Such effects may result in inhomogeneities in the final product.

To summarize the presented technique allow calculating, separating and analysing inhibition period and chain reaction. Together with the intensity and energy variation of the irradiation multiple influencing factors of the photopolymerisation in bulk may be investigated. The number of measurements analysed in detail is too small for further well-founded hypotheses but all results are accessible within Table S2, Table S4 and Table S5.

3.8 Kinetic lengths of the chain reaction, quantum yields and efficiencies

Average kinetic length of the chain reaction and quantum yields. If the inhibitors are not overcompensated as monitored for high photon flux, compare to the previous subsection, the presented experimental technique allows separating the initial period from the chain reaction. Hence, the minimal and maximal kinetic length of the chain reaction, CL , can be calculated by eqn. (22), Table S4, Table S5, Table 4,

$$\frac{N_{DB}}{n_f} \leq CL \leq \frac{N_{DB}}{\Delta n} \quad (23).$$

The maximal length $CL(max)$ corresponds to the average number of propagation steps for one initialization event quantum yield. Generally the length has to be as large as possible. The differences in the consumed number of double bonds N_{DB} are similar for all cured samples so that conclusion concerning the initiation potential remain the ones of the previous subsection. For chain lengths of free radical polymerization of multifunctional acrylate no literature value exist (the solid is cross-linked) but free radical polymerization of cyclohexyl acrylate (monofunctional) led to chain length of 1120²⁹ which is larger but in the same range as the computed kinetic lengths of the chain reaction, Table 4.

TABLE 5 Summary of the calculated numbers of absorbed photons, the Raman Δn chain length and the relative absorption efficiency with maximal influence of the monomer absorbance, compare also Table S4, Table S5.

sample	median [nm]	Δn Raman [10^{12} p]	Δn 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]	storage period [d]	Raman Δn chain length	$AE(min)$ [%]
BP _{FL} ^a	333.5	22.6		51.3	42.6	58.2	0.24	94	2.2
BP _{UG11}	317.5						0.00		3.7
DMHA _{FL} ^a	333.5	21.8	36.8	5.1	7.8	23.2	0.00	117	5.0
DMHA _{UG11}	317.5	11.3	4.3	8.2	9.0	9.0	5.99	261	8.1
DMHA _{UG11}	317.5	8.6	3.7	10.5	9.4	9.4	0.09	244	8.1
DMHA _{LVF}	312.0	9.3	5.9	18.4	14.8	14.8	0.19	198	12.6
DMHA _{LVF+G11}	312.5	0.8 ^b	6.5	17.5	16.2	16.2	0.98	1763	12.6
DMHA _{LVF+G11}	333.0	4.5	4.4	9.2	8.5	8.5	1.31	526	10.6
DMHA _{LVF}	333.5	5.7	5.5	6.3	6.7	6.7	1.15	630	10.5
DMHA _{LVF}	333.5	5.8	7.2	6.7	6.5	6.5	2.25	117	10.5
DMHA _{LVF}	349.0	5.2	7.2	5.8	5.9	5.9	3.25	261	7.2
DMHA _{LVF}	368.0						2.05		2.1
TPO-L _{FL} ^a	333.5	15.8		5.8	6.9	6.9	0.00	159	23.8
TPO-L _{FL} ^a	333.5	11.7	18.5	7.3	7.5	12.5	13.71	219	23.8
TPO-L _{UG11}	317.5	47.5	51.3	6.3	12.8	12.8	12.76	60	33.9
TPO-L _{UG11}	317.5	32.1	40.0	6.6	12.8	24.6	2.98	95	33.9
TPO-L _{UG11}	317.5	33.6	35.1	7.9	12.4	21.8	5.67	80	33.9
TPO-L _{LVF+UG11}	307.0	9.9	7.4	11.9	12.5	12.5	1.66	256	44.8
TPO-L _{LVF+UG11}	312.5	20.3		11.6	14.3	21.6	13.87	131	56.2
TPO-L _{LVF+UG11}	344.5	10.7	10.5	7.7	8.0	8.0	14.94	204	29.7
TPO-L _{LVF+UG11}	344.0	8.1		11.9	9.4	9.4	2.84	275	29.6
TPO-L _{LVF+UG11}	364.0	4.0	10.8	6.9	7.8	7.8	1.96	600	27.8
TPO-L _{LVF+UG11}	364.5	3.5		11.0	8.5		14.84	521	27.9
TPO-L _{LVF}	307.0	11.3	6.6	7.5	9.5	9.5	0.86	200	44.1
TPO-L _{LVF}	312.5	24.4	7.6	7.9	12.3	15.6	14.71	107	56.1
TPO-L _{LVF}	345.5	8.9	6.3	6.2	6.8	6.8	14.85	293	29.3
TPO-L _{LVF}	345.5	10.2	10.6	7.5	9.3	11.1	2.74	274	29.3
TPO-L _{LVF}	368.0	6.7	7.0	3.9	4.4	5.0	1.83	389	28.1
TPO-L _{LVF}	369.0	6.8	7.1	5.1	5.3	5.3	15.72	358	28.2
TPO-L _{LVF}	403.0	5.2	14.1	6.0	5.1	5.1	5.79	579	12.9
TPO-L _{LVF}	403.0	5.6	13.3	4.3	4.6	4.6	15.99	404	13.2
TPO-L _{LVF}	424.0								0.8

^a Only wavelengths < 450 nm are considered for the flash light without filter. The total energy is around 115 Wm⁻². The measurement without filter of the TPO-L containing sample was performed with 200 flashes between the Raman measurements.

Efficiencies. Especially for practical application the kinetic length of the chain reaction is not sufficient to characterize the efficiency of an initiator-resin-light source combination. The relative absorption efficiency AE ,

$$\frac{n_{INI}-n_{res}}{n_{ill}} \leq AE \left(\leq \frac{n_{INI}}{n_{ill}} \right) \quad (24),$$

takes the absorbance of the system into consideration and therefore combines the information within Figure 4. The minimal relative absorption efficiency $AE(min)$ corresponds to the maximal influence of the resin as discussed within the manuscript, Table S5. Especially for light sources with a narrow wavelength range this relative absorption efficiency will eminently influence the curing result of the initiator. For the used geometry, Scheme 1 bottom, $AE(max)$'s larger than 0.85 results in a reduced the cascading effect = more real incident angles Table 3. Hence, the value describes a process dependent balance between deep/(through) and area curing.

Different efficiency like the irradiation corrected efficiency Eff can be defined by eqn. (25),

$$Eff = CL \cdot AE = Eff_{n_{ill}}/n_{ill} = Eff_{n_{INI}}/n_{INI} \quad (25),$$

which is especially interesting if we are able to choose the illumination wavelength with similar photon flux. Otherwise the relative efficiencies to the irradiated n_{ill} and the absorbed number of photons n_{INI} leads to a weighting and can be interesting to optimize desired processes. Considering the resin absorbance six efficiencies for both $CL(max)$'s by eq. (24) and eqn. (25) exist, Scheme S1. Thereby the irradiation corrected efficiency Eff is independent from the resin absorbance/correction, Figure S12. This is a clear contrast to most values for which a maximal influence of the monomer/polymer absorbance (\neq maximal values) and a minimal influence may be calculated by Table S4, Table S5 and Table S2.

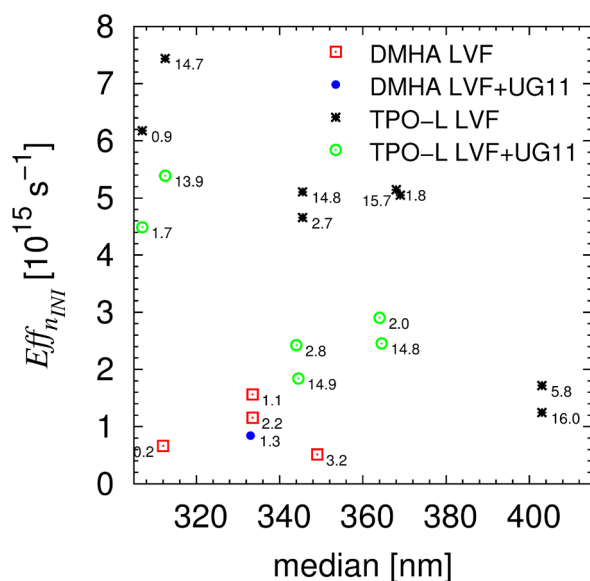


FIGURE 5 Relative efficiencies $Eff_{n_{INI}}$ with maximal resins correction of the performed experiments with linear variable filter and linear variable filter plus UG11.

Within Figure S12 the irradiation corrected efficiency Eff for every initiator are visualized whereas within Figure 5 the efficiency relative to $Eff_{n_{INI}}$ is presented which results in more application near conditions. Even for the irradiation corrected efficiency Eff the most effective reaction took place for the lowest number of photon at around 365 nm. The differences between $Eff_{n_{INI}}$, Figure 5, of the measurements with and without UG11 filter clearly demonstrate the advantage of this visualization that increased light intensities lead to a larger efficiency values. The initiator TPO-L is very efficient in the range of 350 nm even though the relative absorption efficiency is more than 20%/50% smaller, Figure 5 and Figure S12, than below 320 nm. From authors opinion further/faster experiments have to be performed to verify/falsify the presented hypotheses or to conclude further hypotheses especially concerning the reactivity of DMHA. After the presented verification of the UV-vis signal variation the aligned setup, Scheme 1, in combination with a LVF-UV-HL (230-500 nm) filter can be used to obtain faster result.

4. Conclusions

This study can be divided in the presentation of the experimental and analytical technique, the model experiments and the outlook/impact on the resin-initiator-light source relations.

The *Raman* UV-vis curing equipment is a combined monitoring system of photo-induced polymerization. It was proven within this study that the variations in the UV-vis signal are correlated with the reaction even for influenced wavelength ranges (by scattering, interfering reflection). Hence the UV-vis 45° ($\alpha_{det} = 90^\circ$) reflection setup, Scheme 1 bottom, can be used as standalone system without *Raman* detection unit to measure the solidification of even highly pigmented systems, Table 2,

Figure S7. On the hand of wavelength and intensity dependent measurements it was proven that both systems allow performing kinetic quantification with comparable intensities for photo-induced bulk polymerization. Due to its velocity and simplicity the UV-vis setup also have the potential for online applications/monitoring during irritations for example in printing machines. Depending on the geometry the resulting UV-vis signal will be less distorted and therefore easier to analyses than in the presented case. Due to the availability of NIR-/(IR-) sensitive CCD detection units or by using a low power wolfram illumination also thermal induced polymerization will most likely be monitorable by the presented analytical technique. The UV-vis monitoring system can also be combined with any well-known monitoring system like IR (disperse or FT), disperse *Raman* system or even UV curing system for rheometers. Our own research will use the 180° UV-vis system, Scheme 1 top, as standalone technique with unique properties (especially velocity and statistical accuracy). The measuring time of a UV-vis setup is shorter than the one of the *Raman* UV-vis setup. Hence effects of storage time can be investigated/reduced. The resolution of the *Raman* data as presented in this study was usually 2000 flashes whereas the one of the UV-vis data was 40 flashes. The used UV-vis receiver can store data in the range of 30 ms and therefore even much faster processes can be distinct. Additionally to the better resolution in time the aligned UV-vis setup can vary the irradiation intensity by variation in the detection position (variation of the aperture position relative to the emitter, Scheme 1). The data analysis firstly presented within this study leads to absolute consumed monomers and absolute numbers of absorbed photons at a well-defined position of the curing setup. Hence average kinetic lengths of the chain reaction and different efficiencies were computed. The investigated model resin was a printable monomer mixture containing three different well-known initiators, Table 1. Even if only considering the absorbed number of photons (that means after removing the absorbance effects) the initiation potential TPO-L is higher than the one of DMHA. Due to the analytical approach quantum yield of radical generation, radical reactivity towards inhibitor consumption and towards acrylate double bonds may be investigated in the future. As expected benzophenone as Norrish type II initiator results in a low yield⁴⁴. Different additional results were obtained by the detailed analyses: TPO-L is not only the fastest tested initiator but also the impact of the monomer absorption is smaller than for DMHA. For this "versatile highly efficient liquid photo-initiator"⁴² the effect of resin absorption on deep curing is more pronounced. If using a LVF-UV-HL (230-500 nm) this effect of interfering absorbance can be further analysed. Interestingly the presented studies indicate that light with lower energy (up to the onset of the absorbance) or lower intensity results in larger average kinetic lengths of the chain reaction > 400, that means higher reactivity towards the acrylic double bonds. This effect basing on the accumulation of radicals could be further underlined by variation of the flash frequency for the TPO-L containing sample. The experiments without filter (200 flashes per *Raman*) results in much larger

average kinetic lengths of the chain reaction than the measurements with UG11 filter (2000 flashes per *Raman*). Hence, a dependence of the flash frequency can be suggested which results in a specific amount of produced radicals. The lifetime of these propagating radicals is larger than 15 ms, so that a more than *optimal* amount of radicals is possible. Further experiments are necessary to underline this hypothesis. All results are accessible within Table S2, Table S4 and Table S5 to allow performing future interpretations of the data.

The analytical methods as firstly presented in detail within this contribution can be essential for the development/optimization of inhibitor-resin-light source combinations. Both parts of the setup (*Raman* and UV-vis) are exchangeable/variable. For example microscopic optics results in the possibility to investigate several locally distributed factors like the mobility of propagation/inhibiting species and micro gel formation. Wavelength dependent analysis can be used to investigate quantum yield for triplet state formation or radical reactivity (difference in absorbance can be in-situ be monitored). The variability of the fibre optical system e.g. to choose the wavelengths (visible and IR) by light source and filter variations can also be combined with temperature dependent analysis (e.g. temperature variation of the sample holder and IR-free illumination with well-defined energy and known intensity). Also from aspects of application the presented study may be useful to develop LED simulations with comparable intensity which can be essential to develop selective initiators for this novel kind of light sources. For example recently 365 nm high power UV-LED curing units³⁸ achieved market readiness. Power outputs of 70 kW m⁻² (365 nm) can be emitted by using water cooled arrays of diodes.³⁸ The tested xenon flash light have an output of only around 25 W resulting in an *energy on the sample* of around 115 W m⁻² (255 nm to 950 nm) or 5 W m⁻² (367.5 nm ± 6 nm). By considering a maximal area of 24 mm² less than 0.001 % (1 ppm) of the light reaches the sample. Interestingly this is exactly the amount which was calculated in Schmitt, 2011.¹⁴ One flash corresponds to 8 µs illumination time so that the sample is exposed to 0.075 J m⁻² by the xenon light and illuminated with 0.56 J m⁻² by the high power LED array. Note that the used xenon light source is around 10² times less intensive than a commercial lab curing unit, subsection 3.6 (without considering different energy distributions). But it is relatively simple to implement different light sources (continuous emission, higher output or enhanced collecting). Even the effect of UV-B irradiation can be analysed by such equipment if an adjustable bandpass filter with a different working range like LVF-UV-HL (230-500 nm) is used. Then the effect of the resin can be investigated more in detail. At the moment such studies below 360 nm are impossible to perform by using LED radiation.

Acknowledgements

I want to thank F. Heib and R. Hempelmann for their support.

Notes and references

‡ Details concerning UV-vis, Raman and IR may be found within the supplemental material and within literature, Figure 4¹⁶.

‡‡ The formulation “overcompensation” describes the condition when during a measured reduction in the monomer content a significant amount of inhibition species is still present.

1. I. I. Abu-Abdoun and A. Aale, *Eur. Polym. J.*, 1993, **29**, 1445-1450.
2. J. Barth, M. Buback, P. Hesse and T. Sergeeva, *Macromolecules*, 2010, **43**, 4023-4031.
3. M. Buback, L. H. Garciarubio, R. G. Gilbert, D. H. Napper, J. Guillot, A. E. Hamielec, D. Hill, K. F. Odriscoll, O. F. Olaj, J. C. Shen, D. Solomon, G. Moad, M. Stickler, M. Tirrell and M. A. Winnik, *Journal of Polymer Science Part C-Polymer Letters*, 1988, **26**, 293-297.
4. M. Buback and R. A. Laemmel, *Macromol. Theory Simul.*, 1997, **6**, 145-150.
5. O. Elizalde, J. R. Leiza and J. M. Asua, *Macromolecular Symposia*, 2004, **206**, 135-148.
6. J. P. Fouassier, D. Ruhlmann and A. Erddalane, *Macromolecules*, 1993, **26**, 721-728.
7. A. J. Hoffman, G. Mills, H. Yee and M. R. Hoffmann, *J. Phys. Chem.*, 1992, **96**, 5546-5552.
8. B. Kraeutler, H. Reiche, A. J. Bard and R. G. Hocker, *Journal of Polymer Science Part C-Polymer Letters*, 1979, **17**, 535-538.
9. M. Schmitt, J. Wagner, G. Jung and R. Hempelmann, *J. Colloid Interface Sci.*, 2007, **311**, 425-429.
10. K. Prajapati and A. Varshney, *Journal of Polymer Research*, 2006, **13**, 97-105.
11. A. Endruweit, M. S. Johnson and A. C. Long, *Polym. Compos.*, 2006, **27**, 119-128.
12. M. Skrifvars, P. Niemela, R. Koskinen and O. Hormi, *J. Appl. Polym. Sci.*, 2004, **93**, 1285-1292.
13. M. Schmitt, S. Kuhn, M. Wotocek and R. Hempelmann, *Z. Phys. Chem.*, 2011, **225**, 297-311.
14. M. Schmitt, *Macromol. Chem. Phys.*, 2011, **212**, 1276-1283.
15. M. Schmitt, R. Schulze-Pillot and R. Hempelmann, *PCCP*, 2011, **13**, 690-695.
16. M. Schmitt, *Macromol. Chem. Phys.*, 2012, **213**, 1953-1962.
17. M. Schmitt, *Nanoscale*, 2015, **7**, 9532-9544.
18. K. L. Mendoza, A. Ortega and N. S. Kim, *Journal of Electronic Materials*, 2015, **44**, 784-791.
19. M. Han, W. Lee, S. K. Lee and S. S. Lee, *Sensors and Actuators a-Physical*, 2004, **111**, 14-20.
20. I. Cooperstein, M. Layani and S. Magdassi, *Journal of Materials Chemistry C*, 2015, **3**, 2040-2044.
21. C. Dietlin, S. Schweizer, P. Xiao, J. Zhang, F. Morlet-Savary, B. Graff, J.-P. Fouassier and J. Lalevee, *Polymer Chemistry*, DOI: 10.1039/C5PY00258C.
22. C. Decker and K. Moussa, *J. Appl. Polym. Sci.*, 1987, **34**, 160-1618.
23. P. M. Johnson, J. W. Stansbury and C. N. Bowman, *Macromolecular Reaction Engineering*, 2009, **3**, 522-528.

24. C. Decker and K. Moussa, *Macromol. Chem. Phys.*, 1988, **189**, 2381-2394.
25. C. Decker, K. Moussa and T. Bendaikha, *Journal of Polymer Science Part A-Polymer Chemistry*, 1991, **29**, 739-747.
26. M. D. Dickey and C. G. Willson, *AIChE J.*, 2006, **52**, 777-784.
27. A. K. O'Brien and C. N. Bowman, *Macromolecules*, 2006, **39**, 2501-2506.
28. M. Schmitt, *Analyst*, 2013, **138**, 3758-3770.
29. B. Yamada, M. Azukizawa, H. Yamazoe, D. J. T. Hill and P. J. Pomery, *Polymer*, 2000, **41**, 5611-5618.
30. G. Allegrone, I. Tamaro, S. Spinardi and G. Grosa, *Journal of Chromatography A*, 2008, **1214**, 128-133.
31. S. Aprile, E. Del Grosso and G. Grosa, *Xenobiotica*, 2011, **41**, 212-225.
32. H. Gallart-Ayala, O. Nunez, E. Moyano and M. T. Galceran, *Journal of Chromatography A*, 2011, **1218**, 459-466.
33. M. Hefnawy, *Advances in Food Protection Series A: Chemistry and Biology*, Springer VCH, 2010.
34. T. Jung, T. J. Simat and W. Altkofer, *Food Additives and Contaminants Part A-Chemistry Analysis Control Exposure & Risk Assessment*, 2010, **27**, 1040-1049.
35. T. Jung, T. J. Simat, W. Altkofer and D. Fugel, *Food Additives and Contaminants Part A-Chemistry Analysis Control Exposure & Risk Assessment*, 2013, **30**, 1993-2016.
36. A. K. Malik, C. Blasco and Y. Pico, *Journal of Chromatography A*, 2010, **1217**, 4018-4040.
37. T. Rothenbacher, M. Baumann and D. Fugel, *Food Additives and Contaminants*, 2007, **24**, 438-444.
38. Heraeus Noblelight GmbH, The Heraeus Noblelight UV-LED portfolio, 2014.
39. M. Schmitt and F. Heib, *RSC Advances* 2014, **4**, 17639-17647.
40. R. S. P. Teixeira, R. J. Correa, A. Belvino and R. S. V. Nascimento, *J. Appl. Polym. Sci.*, 2013, **130**, 2458-2467.
41. G. Moad and D. H. Solomon, *The Chemistry of Radical Polymerization*, Elsevier B.V., 2006.
42. BASF, Ciba® DAROCUR® 1173, 2014.
43. O. Paul, A. Quosig, T. Bauer, M. Nittmann, J. Bartschke, G. Anstett and J. A. L'Huillier, *Applied Physics B-Lasers and Optics*, 2007, **86**, 111-115.
44. J.-P. Fouassier, *Photoinitiation, Photopolymerization, and Photocuring: Fundamentals and Applications*, Hanser Gardner Pubns, 1995.