

Supporting information for: Estimating the Photodissociation Quantum Yield from PLP-SEC Peak Heights

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1 Experimental details for the measurement of the ratio of PLP-SEC peak heights

An overview of all initial conditions for PLP of *n*-butyl acrylate (*n*BuA) and the corresponding experimental results for the ratio of the peak heights of the SEC trace is given in Table S1. For each pulse energy, an experimentally recorded SEC trace is shown in Figure S1.

Table S1: Experimental results for PLP of *n*BuA at 306 K and varying E_{pulse} ; initial conditions: $[\text{DMPA}]_0 = 3 \cdot 10^{-3} \text{ mol L}^{-1}$, $[\textit{n}\text{BuA}]_0 = 6.91 \text{ mol L}^{-1}$, $\nu = 500 \text{ s}^{-1}$.

Entry	E_{pulse} [mJ]	Number of pulses [-]	h_1/h_2
1	1.5	200	0.895
2	2.5	100	0.989
3	3.5	80	1.228
4	4.5	65	1.419
5	6	40	1.626

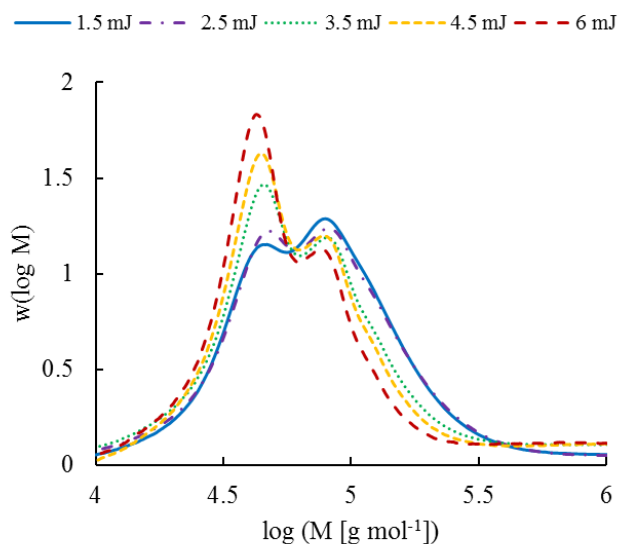


Figure S1: Experimentally recorded SEC traces for PLP of *n*BuA at various pulse energies; conditions: see Table S1.

2 Model details for the simulation of the ratio of PLP-SEC peak heights

2.1 Reactions and model parameters

In Table S2 the reactions considered in the kinetic Monte Carlo (*k*MC) model to simulate the PLP-SEC trace and, hence, the PLP-SEC peak heights are listed. The model parameters for the *in silico* testing of the method with the parameters having values reflecting typical orders of magnitude (column 3) and the parameters for the *in silico* application to MMA (column 5) are also shown. Similarly, the parameters are given for the actual application of the method to PLP of *n*BuA (column 4). The concentration of radicals generated at the laser pulses, $\Delta[R_0]$, is calculated via Equation (2; main text) with the input value of Φ for the theoretical evaluation and the value estimated via regression analysis to the peak heights of *n*BuA PLP at 306 K given in entry 1 of Table S2. For each laser pulse, $\Delta[R_0]$ is calculated taking into account the decreasing photoinitiator concentration.

Note that intermolecular chain transfer can be neglected at the low monomer conversions considered in this work.¹⁻⁴ Moreover, due to the low temperature (306 K), β -scission of MCRs can safely be neglected.^{1,5} In addition, as illustrated by the coinciding lines in Figure S2 (full green line: $k_{trM,e} = 0 \text{ L mol}^{-1} \text{ s}^{-1}$, $k_{trM,m} = 0 \text{ L mol}^{-1} \text{ s}^{-1}$; dotted black line: $k_{trM,e} = 8.0 \cdot 10^{-1} \text{ L mol}^{-1} \text{ s}^{-1}$, $k_{trM,m} = 2.8 \cdot 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$ (ref. ⁶)), chain transfer to monomer can also be neglected in the present work.

It should be further reminded, as explained in the main text, that the current modeling strategy with an explicit treatment of the chemical reactions with the DMPA radical fragments does not require the introduction of a chemical initiator efficiency.

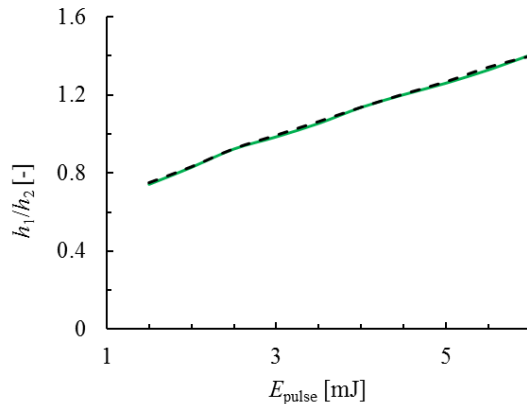


Figure S2: Illustration of the negligible effect of chain transfer to monomer on h_1/h_2 for PLP of $n\text{BuA}$ under the conditions considered in this work (Table S1); full green line: $k_{\text{trM,e}} = 0 \text{ L mol}^{-1} \text{ s}^{-1}$, $k_{\text{trM,m}} = 0 \text{ L mol}^{-1} \text{ s}^{-1}$; dotted black line: $k_{\text{trM,e}} = 7.9 \cdot 10^{-1} \text{ L mol}^{-1} \text{ s}^{-1}$,⁶ $k_{\text{trM,m}} = 2.7 \cdot 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$; ⁶ model parameters: Table S2 (column 4).

Chain length dependent (apparent) termination kinetics are taken into account and expressed as:

$$k_t^{\text{app}}(i, i) = k_t^{\text{app}}(1, 1) i^{-\alpha_S} \quad i \leq i_c \quad (\text{S.1})$$

$$k_t^{\text{app}}(i, i) = k_t^{\text{app}}(1, 1) i_c^{-\alpha_S + \alpha_L} i^{-\alpha_L} \quad i > i_c \quad (\text{S.2})$$

$$k_t^{\text{app}}(i, j) = [k_t^{\text{app}}(i, i) k_t^{\text{app}}(j, j)]^{0.5} \quad (\text{S.3})$$

with α_S , α_L and i_c equal to 0.85, 0.16 and 30 (theoretical evaluation (Figure 2, 3 in the main text) and application to $n\text{BuA}$ (Figure 4 in the main text); parameters *cf.* ref. ⁷) or α_S , α_L and i_c equal to 0.65, 0.15 and 100 (*in silico* application to MMA (Figure S3); parameters *cf.* ref. ⁸).

Non-instantaneous quenching at the end of a PLP experiment is accounted for in agreement with ref.⁹

Table S2. Basic reaction scheme to simulate low temperature PLP initiated by DMPA, including a listing of the model parameters used for the theoretical evaluation of the method (only orders of magnitude) and the actual application to *n*BuA at 306 K, for which intermolecular chain transfer and β -scission can be neglected based on literature data¹⁻⁵, and for which chain transfer to monomer can also be neglected, as demonstrated above. The model parameters for the *in silico* application to PLP of MMA are also listed.

Reaction	Equation	Theoretical evaluation (Figure 2, 3) Φ [-] or k [(L mol ⁻¹) s ⁻¹]	<i>n</i> BuA 306 K (Figure 4) Φ [-] or k [(L mol ⁻¹) s ⁻¹]	MMA 306 K (Figure S3) Φ [-] or k [(L mol ⁻¹) s ⁻¹]
Photodissociation ^[a]	$DMPA \xrightarrow{h\nu, \Phi} R_{0,e}^I + R_{0,e}^{II}$	0.5	0.42 (this work; estimated)	0.42
Chain initiation ^[b]	$R_{0,e}^I + M \xrightarrow{k_{p,I}} R_{1,e}$	10 ⁴	2.0 10 ⁴	4.1 10 ²
Propagation	$R_{i,e} + M \xrightarrow{k_{p,e}} R_{i+1,e}$	10 ⁴	2.0 10 ⁴ [10]	4.1 10 ² [11]
	$R_{i,m} + M \xrightarrow{k_{p,m}} R_{i+1,e}$	10 ¹	1.4 10 ¹ [7]	-
Backbiting ($i \geq 3$)	$R_{i,e} \xrightarrow{k_{bb}} R_{i,m}$	10 ²	1.9 10 ² [7]	-
Termination ^[c] ($i, j \geq 0$)	$R_{i,e} + R_{j,e} \xrightarrow{k_{t,ee}^{app}(i,j)} P_{i(+j)}(+P_j)$	10 ⁹	9.6 10 ⁸ [7]	1.5 10 ⁹ [8,d]
	$R_{i,e} + R_{j,m} \xrightarrow{k_{t,em}^{app}(i,j)} P_{i(+j)}(+P_j)$	10 ⁸	3.1 10 ⁸ [7]	-
	$R_{i,m} + R_{j,m} \xrightarrow{k_{t,mm}^{app}(i,j)} P_{i(+j)}(+P_j)$	10 ⁶	2.0 10 ⁶ [7]	-

^a: dissociation into a benzoyl and dimethoxy benzyl radical; $\Delta[R_0]$ calculated via Equation (2; main text), with both for the theoretical validation and the actual application to PLP of *n*BuA $\epsilon = 280$ L mol⁻¹ cm⁻¹, $\lambda = 351$ nm, $V = 0.2$ mL and $L = 0.52$ cm (*cf.* Experimental Section (main text)).

^b: $k_{p,I}$ can be taken equal to the plateau value for propagation with long ECRs, no propagation of $R_{0,II}$ (*cf.* ref. ⁹)

^c: chain length dependent (apparent) termination rate coefficients are considered (Equation (S.1) - (S.3); parameters: ref. ^{7, 8}); $k_t^{app}(1,1)$ is reported, taking into account a correction with a factor 2, as indicated by *e.g.* Derboven *et al.*;¹² fraction termination by recombination (δ) in agreement with literature data (column 3,4: $\delta_{ee} = 0.9$, $\delta_{em} = 0.3$, $\delta_{mm} = 0.1$ *cf.* ref ^{5, 13}; column 5: $\delta_{ee} = 0.25$ *cf.* ref. ¹⁴); $i, j = 0$: $R_{0,e}^{I/II}$ (hence termination of the propagating and non-propagating radical also taken into account)

^d: $k_{t,ee}^{app}(1,1)$ determined from its value at 353 K as reported in ref. ⁸ and an E_a of 9 kJ mol⁻¹ in agreement with ref. ¹⁵

2.2 Correction for SEC broadening

In agreement with the method described in previous work,¹⁶ the simulated log-MMD $w(\log M)$ is corrected according to the following formula to account for SEC broadening:

$$w_{SEC}(\log M) = \frac{1}{(2\pi)^{0.5} \sigma_v b} \int_0^{+\infty} \exp\left(-\frac{(\log(M) - \log(\tilde{M}))^2}{2(\sigma_v b)^2}\right) w(\log \tilde{M}) d\log(\tilde{M}) \quad (\text{S.4})$$

In this work, the SEC broadening parameter $\sigma_v b$ is taken equal to 0.05, in agreement with typical values reported in literature.^{9, 17, 18}

3 *In silico* application to PLP of MMA

In order to test if the method yields the same estimate for Φ_{diss} for other monomers, the method is applied to *in silico* PLP data of MMA at 306 K (all conditions are listed in the caption of Figure S3; in order to increase the intensity of the SEC signal, multiple samples at identical conditions may be combined before SEC analysis). These data are obtained via *k*MC simulations using the model parameters as listed in Table S2 (5th column) and a value of 0.42 for Φ_{diss} (*cf.* value estimated from PLP data of *n*BuA). In a subsequent step this data is superimposed with a random error determined via Gaussian sampling with standard deviation $\sigma = 0.3$ to mimic an experimental error of *ca.* 10%. By performing a regression analysis to the latter data an estimate for Φ_{diss} of 0.43 ± 0.07 (95% confidence interval) is obtained, with the corresponding fit shown in Figure S3. Since the obtained estimate ($\Phi_{\text{diss}} = 0.43$) is very close to the estimate obtained via regression analysis to PLP data of *n*BuA ($\Phi_{\text{diss}} = 0.42$), it has been demonstrated that in case accurate monomer-specific model parameters are used, the obtained estimate for Φ_{diss} does not depend on the selected monomer.

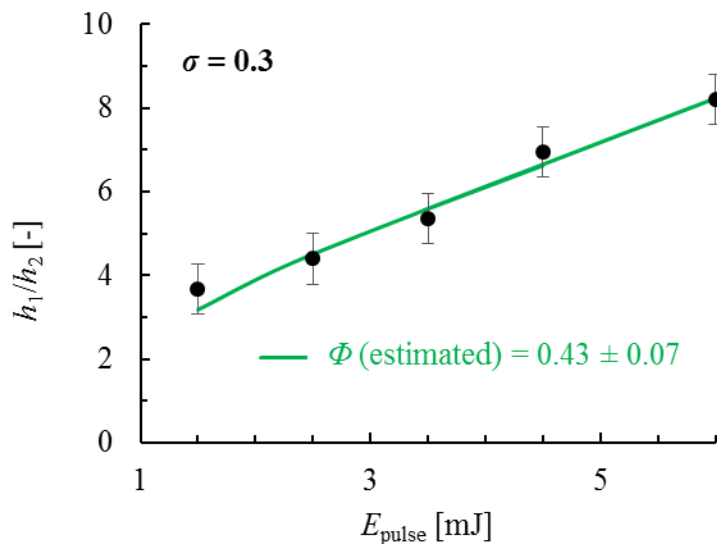


Figure S3. *In silico* application to PLP of MMA; symbols: data generated using a *k*MC model with an input value of 0.42 for Φ_{diss} (*cf.* value estimated from PLP data of *n*BuA) and all other model parameters as in Table S2 (5th column), superimposed with a random error (Gaussian sampling with standard deviation $\sigma = 0.6$ (*i.e.* an error of *ca.* 10%)); full line: model after regression analysis; conditions: $T = 306 \text{ K}$, $\nu = 10 \text{ s}^{-1}$, $[\text{DMPA}]_0 = 0.3 \text{ mmol L}^{-1}$, sample volume: 0.2 mL (optical path length: 0.52 cm), $N_{\text{pulse}} = 225$ (1.5 mJ), 150 (2.5 mJ), 120 (3.5 mJ), 100 (4.5 mJ), 70 (6mJ).

4 Sensitivity to the apparent termination reactivity

As for any method, the accuracy of the presented approach is affected by the accuracy of the model parameters. In particular, the method is most sensitive to the apparent termination reactivity $k_{t,\text{app}}(i,j)$. In this section, the effect a large error on $k_{t,\text{app}}(i,j)$ has on the estimate for Φ_{diss} is investigated.

To this purpose, a regression analysis to the same data as in Figure 3 (left; main text), *i.e.* h_1/h_2 data obtained via simulation with an input value of 0.5 for Φ_{diss} and the model parameters as listed in Table S2 (column 3) and superimposed with a Gaussian error mimicking an experimental error of *ca.* 10%, is performed. However, in the regression analysis $k_{t,\text{app}}(i,j)$ is increased with 50% compared to Table S2 (column 3). Hence, a large error of 50% is considered in this case study. An

estimate of 0.34 ± 0.04 (95% confidence interval) is obtained. The overestimation of $k_{t,app}(i,j)$ thus leads to an underestimation of Φ_{diss} . Importantly, such inaccuracies can be detected by applying the method to another monomer for which extensively studied rate coefficients are available. Indeed, provided that accurate monomer-specific model parameters are used, the same value of Φ_{diss} is obtained.

5 References

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