# Electronic supplementary information for: "From *n*-Butyl Acrylate Arrhenius Parameters for Backbiting and Tertiary Propagation to *β*-scission via Stepwise Pulsed Laser Polymerization"

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## S1 Experimental details

The pulsed laser polymerization (PLP) experiments combined with size exclusion chromatography (SEC) analysis were carried out for a "low" (303-323 K) and "high" temperature (383-413 K) range selecting *n*-butyl acrylate (*n*BuA) as monomer. In all PLP experiments the conversion of *n*BuA was maintained low (*e.g.* 2-3%) by varying the number of pulses. The details of the PLP experimental conditions, *i.e.* frequency, pulse number and solvent volume fraction, in the "low" and "high" temperature range are summarized in **Table S1** and **Table S2** respectively. **Table S3** and **Table S4** contain the $k_{p,app}$ data.

**Table S1: Low temperature (303-323 K) PLP experimental details**

| Frequency (Hz) | Pulse Number | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Temperature = 303 K | | | Temperature = 313 K | | | Temperature = 323 K | | |
| | Solvent fraction | | | Solvent fraction | | | Solvent fraction | | |
| | **0** | **0.5** | **0.75** | **0** | **0.5** | **0.75** | **0** | **0.5** | **0.75** |
| 10 | 50 | 65 | 90 | 35 | 60 | 80 | 30 | 55 | 70 |
| 20 | 60 | 75 | 100 | 45 | 70 | 90 | 40 | 70 | 80 |
| 30 | 70 | 85 | 120 | 55 | 80 | 105 | 50 | 85 | 95 |
| 40 | 80 | 95 | 140 | 65 | 90 | 120 | 60 | 100 | 110 |
| 50 | 90 | 105 | 160 | 75 | 100 | 135 | 70 | 115 | 125 |
| 60 | 100 | 115 | 180 | 85 | 110 | 150 | 80 | 130 | 140 |

**Table S2: High temperature (383-413 K) PLP experimental details**

| Frequency (Hz) | Pulse Number | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Temperature = 383 K | | | Temperature = 393 K | | | Temperature = 403 K | | | Temperature = 413 K | | |
| | Solvent fraction | | | Solvent fraction | | | Solvent fraction | | | Solvent fraction | | |
| | **0** | **0.5** | **0.75** | **0** | **0.5** | **0.75** | **0** | **0.5** | **0.75** | **0** | **0.5** | **0.75** |
| 1 | 15 | 20 | 24 | 14 | 18 | 22 | 12 | 16 | 18 | 10 | 14 | 18 |
| 10 | 35 | 45 | 55 | 30 | 40 | 50 | 25 | 30 | 35 | 20 | 25 | 30 |
| 20 | 45 | 55 | 65 | 40 | 50 | 60 | 35 | 40 | 45 | 30 | 35 | 40 |
| 30 | 55 | 65 | 75 | 50 | 60 | 70 | 45 | 50 | 55 | 40 | 45 | 50 |
| 40 | 65 | 75 | 85 | 60 | 70 | 80 | 55 | 60 | 65 | 50 | 55 | 60 |
| 50 | 75 | 85 | 95 | 70 | 80 | 90 | 65 | 70 | 75 | 60 | 65 | 70 |

**Table S3: $k_{p,\,app}$ obtained using first inflection point data from low temperature (303-323 K) PLP experiments**

| Frequency (Hz) | $k_{p,app}$ (L mol$^{-1}$ s$^{-1}$) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | T = 303 K | | | T = 313 K | | | T = 323 K | | |
| | Solvent fraction | | | Solvent fraction | | | Solvent fraction | | |
| | **0** | **0.5** | **0.75** | **0** | **0.5** | **0.75** | **0** | **0.5** | **0.75** |
| **10** | 3404 | 3175 | 2468 | 4442 | 3477 | 2825 | 5017 | 3886 | 3043 |
| **20** | 5272 | 3900 | 3297 | 5784 | 4605 | 3719 | 6749 | 5366 | 4038 |
| **30** | 6242 | 4971 | 3877 | 7174 | 5478 | 4457 | 7717 | 6175 | 5030 |
| **40** | 6994 | 6134 | 4990 | 7593 | 6602 | 5176 | 7916 | 6996 | 5737 |
| **50** | 7370 | 6725 | 5909 | 8114 | 7520 | 6213 | 8599 | 8031 | 6917 |
| **60** | 8361 | 7820 | 6728 | 8872 | 7972 | 6958 | 9258 | 8786 | 7458 |

**Table S4: $k_{p,\,app}$ obtained using first inflection point data from high temperature (383-413 K) PLP experiments**

| Frequency (Hz) | $k_{p,app}$ (L mol$^{-1}$ s$^{-1}$) | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | T = 383 K | | | T = 393 K | | | T = 403 K | | | T = 413 K | | |
| | Solvent fraction | | | Solvent fraction | | | Solvent fraction | | | Solvent fraction | | |
| | **0** | **0.5** | **0.75** | **0** | **0.5** | **0.75** | **0** | **0.5** | **0.75** | **0** | **0.5** | **0.75** |
| **10** | 2172 | 1586 | 1296 | 1619 | 1170 | 914 | 1187 | 854 | 796 | 829 | 594 | 534 |
| **20** | 4427 | 2852 | 2158 | 2676 | 2208 | 1938 | 1997 | 1914 | 1350 | 1513 | 1378 | 1097 |
| **30** | 5416 | 4467 | 2991 | 3967 | 2783 | 2320 | 2839 | 2351 | 2093 | 1947 | 1870 | 1920 |
| **40** | 6060 | 4778 | 4143 | 4936 | 3865 | 3289 | 3331 | 3041 | 2978 | 2566 | 2402 | 2290 |
| **50** | 7366 | 5667 | 5189 | 5637 | 4706 | 4276 | 4035 | 3422 | 3927 | 3166 | 2921 | 2733 |

## S2 Correction for SEC broadening

A correction for SEC broadening is considered based on the method proposed by Buback *et al.*[1] For more details readers are referred to our previous work.[2] The log-MMD after SEC broadening is calculated as:

$$w_{SEC}(\log\ \mathrm{M}) = \frac{1}{(2\pi)^{0.5}(\sigma_{\upsilon} b)} \int_{0}^{+\infty} \exp\left( -\frac{\left(\log(M) - \log(\tilde{M})\right)^2}{2(\sigma_{\upsilon} b)^2} \right) w(\log \tilde{M})\ d\log(\tilde{M}) \qquad \text{(S1)}$$

In this work $(\sigma_{\upsilon} b) = 0.04$ is used based on literature data.[3,4]

## S3 Kinetic modeling details

The reaction scheme and associated Arrhenius parameters for PLP of *n*-butyl acrylate (*n*BuA) used in the kinetic Monte Carlo (*k*MC) simulations are summarized in **Table S5**. Literature-based parameters are used for all reactions, except for backbiting, tertiary propagation and *β*-scission as these are determined in the current work. Backbiting and tertiary propagation Arrhenius parameters are determined via regression to “low” temperature (303-323 K) $k_{\mathrm{p,app}}$ data. At these temperatures the *β*-scission reactions indicated by the dashed red box in Table S5 can be neglected. Arrhenius parameters for *β*-scission are determined in a next step via regression analysis to “high” temperature (383-413 K) $k_{\mathrm{p,app}}$ data, using the previously determined Arrhenius parameters for backbiting and tertiary propagation as input. Based on our previous work thermal self-initiation and macropropagation reactions are neglected.[5]

**Table S5** Reactions and Arrhenius parameters used in the simulations of PLP of *n*-butyl acrylate (photoinitiator DMPA) at low (303-323 K) and high temperature (383-413 K; extra dashed box).

| Entry | Reaction | Equation | *A* [(L mol$^{-1}$)s$^{-1}$] | *E*A. [kJ mol$^{-1}$] | Reference |
|---|---|---|---|---|---|
| **1** | photo-dissociation | $I_2 \xrightarrow{h\nu} R_{0,e}^{I} + R_{0,e}^{II}$ | | | 6 |
| **2** | chain initiation | $R_{0,e}^{I/III/IV} + M \xrightarrow{k_{\mathrm{p,I/III/IV}}} R_{1,e}$ | $2.4\times10^{8}$ | 17.9 | *17,b* |
| **3** | propagation[c] | $R_{i,e} + M \xrightarrow{k_{\mathrm{p,e}}} R_{i+1,e}$ | $2.2\times10^{7}$ | 17.9 | 7 |
| **4** | | $R_{i,m} + M \xrightarrow{k_{\mathrm{p,m}}} R_{i+1,e}$ | $1.94\times10^{6}$ | 30.1 | this work |
| **5** | backbiting | $R_{i,e} \xrightarrow{k_{\mathrm{bb}}} R_{i,m} \quad \mathrm{i} \geq 3$ | $5.38\times10^{7}$ | 30.6 | this work |
| **6** | *β*-scission of MCR[i] | $R_{i,m} \xrightarrow{k_{\beta}} MM_3 + R_{i-3,e}$ | $1.5\times10^{9}$ | 63.9 | this work |
| **7** | | $R_{i,m} \xrightarrow{k_{\beta}} MM_{i-2} + R_{2,e}$ | $1.5\times10^{9}$ | 63.9 | this work |
| **8** | *β*-scission of dimethoxy benzyl radical | $R_{0,e}^{II} \xrightarrow{k_{\beta\mathrm{o}}} R_{0,e}^{III} + \mathrm{MeBez}^{h}$ | $2.0\times10^{13}$ | 61.8 | 8 |
| **9** | chain transfer to monomer | $R_{i,e} + M \xrightarrow{k_{\mathrm{trM,e}}} P_i + R_{0,e}^{IV}$ | $2.9\times10^{5}$ | 32.6 | 9 |
| **10** | | $R_{i,m} + M \xrightarrow{k_{\mathrm{trM,m}}} P_i + R_{0,e}^{IV}$ | $2.0\times10^{5}$ | 46.1 | 9 |
| **11** | termination[d] | $R_{i,e} + R_{j,e} \xrightarrow{k_{\mathrm{t,ee}}^{\mathrm{app}}(i,j)} P_{i(+j)}\left(+P_j\right)$ | $1.3\times10^{10}$ | 8.4 | 10 |
| **12** | | $R_{i,e} + R_{j,m} \xrightarrow{k_{\mathrm{t,em}}^{\mathrm{app}}(i,j)} P_{i(+j)}\left(+P_j\right)$ | $4.2\times10^{9}$ | 6.6 | 10 |
| **13** | | $R_{i,m} + R_{j,m} \xrightarrow{k_{\mathrm{t,mm}}^{\mathrm{app}}(i,j)} P_{i(+j)}\left(+P_j\right)$ | $9.0\times10^{6}$ | 5.6 | 10 |
| **14** | | $R_{0,e}^{I/II/III/IV} + R_{0,e}^{I/II/III/IV} \xrightarrow{k_{\mathrm{t,00}}^{\mathrm{app}}} P_0$ | $1.3\times10^{10}$ | 8.4 | *e* |
| **15** | | $R_{0,e}^{I/II/III/IV} + R_{i,e} \xrightarrow{k_{\mathrm{t,0e}}^{\mathrm{app}}(i)} P_i\left(+P_0\right)$ | $1.3\times10^{10}$ | 8.4 | *f* |
| **16** | | $R_{0,e}^{I/II/III/IV} + R_{i,m} \xrightarrow{k_{\mathrm{t,0m}}^{\mathrm{app}}(i)} P_i\left(+P_0\right)$ | $4.2\times10^{9}$ | 6.6 | *g* |

[a] $\Delta[R_0]$ is calculated via **Equation S2** for $\lambda = 351 \times 10^{-9}$ m, $E_{\mathrm{pulse}} = 1.5 \times 10^{-3}$ J, $V = 4\times10^{-7}$ m$^3$, $L = 1.04 \times 10^{-2}$ m, and $\Phi$ of 0.42[6]; $\Delta[R_0]$ at the first laser pulse is equal to $1.04 \times 10^{-5}$ mol L$^{-1}$ (initial DMPA concentration= 2.5 x $10^{-3}$ mol L$^{-1}$). [b] higher chain initiation rate because of reaction 8, as a higher number of initiator radicals prone to chain initiation.[8,11] [c] Chain length dependent propagation considered.[12,13] [d] Chain length dependent (apparent) termination rate coefficients considered with $k_{\mathrm{t}}^{\mathrm{app}}(1,1)$ reported here, taking into account correction factor 2[14] and literature based fraction of termination by recombination.[15,16] fraction of termination by recombination (0.9 (entry 11), 0.3 (entry 12), and 0.1 (entry 13)) in agreement with literature data.[10] [e] Assumed equal to $k_{\mathrm{t,ee}}^{\mathrm{app}}(1,1)$; [f] Assumed equal to $k_{\mathrm{t,ee}}^{\mathrm{app}}(i,1)$; $k_{\mathrm{t,ee}}^{\mathrm{app}}(1,1)$ is reported here. [g] Assumed equal to $k_{\mathrm{t,em}}^{\mathrm{app}}(i,1)$; $k_{\mathrm{t,em}}^{\mathrm{app}}(1,1)$ is reported here. [h] MeBez= methyl benzoate formed during *β*-scission of dimethoxybenzyl radical; [i] mid-chain radical

### S3.1 Photodissociation kinetics

The concentration of initiator radicals generated at each laser pulse ($\Delta[R_0]$) is calculated as:

$$\Delta[R_0] = 2\Phi_{diss}\frac{E_{pulse}\lambda}{hcN_A\Omega \mathrm{L}}[1-\exp(-2.303\varepsilon[\mathrm{DMPA}]L)] \tag{S2}$$

in which $\Phi_{\mathrm{diss}}$ is the quantum yield of photodissociation (0.42), $E_{\mathrm{pulse}}$ the laser pulse energy ($1.5\times10^{-3}\,\mathrm{J}$), $\lambda$ the laser wavelength ($351\times10^{-9}\,\mathrm{m}$), $h$ the Planck constant ($6.63\times10^{23}\,\mathrm{J\ s}$), $c$ the speed of light ($3\times10^{9}\,\mathrm{m\ s^{-1}}$), $N_{\mathrm{A}}$ the Avogadro constant ($6.02\times10^{23}\,\mathrm{mol^{-1}}$), $\Omega$ the optical cross-sectional area ($3.85\times10^{-5}\ \mathrm{m^2}$), $L$ the optical path length ($1.04\times10^{-2}\ \mathrm{m}$), $\varepsilon$ the molar absorptivity of the photoinitiator ($28\,\mathrm{m^2\ mol^{-1}}$), and [DMPA] is the concentration of photoinitiator, which is updated after each pulse.

### S3.2 Chain length dependencies

Chain length dependent propagation kinetics are accounted based on work of Heuts and Russell [12] and for details readers are referred to the work by Marien *et al.* [2]

$$k_p(i) = k_p\left[1 + C_1\exp(-\frac{\ln(2)}{i_{1/2}}i)\right] \tag{S3}$$

Here *i* refers to the chain length (0 for an initiator-derived radical), in contrast to the equation as originally reported in which *i* = 1 for an initiator-derived radical. In this work $C_1 = 10$ and $i_{1/2} = 1$ considered based on the work Haven *et al.*.[13]

Chain length dependent (apparent) termination kinetics are evaluated via the composite $k_t$ model, For the low monomer conversion ranges as encountered during PLP, it suffices to consider [10,17]:

$$k_t^{app}(i,i) = k_t^{app}(1,1)i^{-\alpha_S} \qquad i \le i_c \tag{S4}$$

$$k_t^{app}(i,i) = k_t^{app}(1,1)i_c^{-\alpha_S+\alpha_L}i^{-\alpha_L} \qquad i > i_c \tag{S5}$$

in which $\alpha_S$ and $\alpha_L$ express the chain length dependence for short and long radicals, and $i_c$ is the cross-over chain length. In this work $\alpha_S = 0.85$, $\alpha_L = 0.16$, and $i_c = 30$ are used based on the work of Barth *et al.* [10].

## S4 Relevance of regression analysis

Regression analyses were carried using both bulk and solution $k_{p,app}$ data at each temperature (main text results). The correlation coefficient between the two parameters $k_{bb}$ and $k_{p,m}$ for the low temperature regression analyses considering only bulk data and by combining bulk and solution data are shown in **Table S6** (left vs. right column). The correlation coefficients between the two parameters are below the threshold value of 0.95[18,19] upon considering both bulk and solution data (right column). With only bulk data (left column) higher values results, highlighting the relevance of the consideration of both bulk and solution data.

**Table S6: Correlation coefficient for $k_{bb}$ and $k_{p,m}$**

| **Temperature (K)** | **Correlation coefficient for $k_{bb}$ and $k_{p,m}$** | |
|---|---|---|
| | **Only bulk $k_{p,app}$ data** | **Bulk and solution $k_{p,app}$ data** |
| 303 | 0.98 | 0.91 |
| 313 | 0.94 | 0.94 |
| 323 | 0.95 | 0.93 |

The details of the estimated $k_{bb}$ and $k_{p,m}$ values at all temperatures are shown in **Table S7**. With the consideration of both bulk and solution data the confidence intervals become more narrow and the estimated value as such is globally in the range of the confidence interval based on bulk data only.

**Table S7: $k_{bb}$ and $k_{p,m}$ obtained by regression to bulk data only and bulk and solution data combined**

| **Temp. (K)** | **303 K** | | **313 K** | | **323 K** | |
|---|---|---|---|---|---|---|
| | $k_{bb}$ | $k_{p,m}$ | $k_{bb}$ | $k_{p,m}$ | $k_{bb}$ | $k_{p,m}$ |
| **Bulk** | 268.5±99.3 | 8.7±7.2 | 436.1±191.7 | 15.1±11.8 | 786.9±541.1 | 32.6±32.1 |
| **Bulk and sol.** | 285.3±50.5 | 12.7±5.6 | 416.8±95.5 | 18.3±7.8 | 605.3±140.2 | 26.6±11.8 |

Similar results for $k_{\beta}$ are highlighted in **Table S8** (high temperature PLP).

**Table S8: $k_{\beta}$ obtained by regression to bulk data only and bulk and solution data combined**

| Temp. (K) | **383 K** | **393 K** | **403 K** | **413 K** |
|---|---|---|---|---|
| | $k_{\beta}$ | $k_{\beta}$ | $k_{\beta}$ | $k_{\beta}$ |
| **Bulk** | 75.2±28.9 | 151.1±13.0 | 340.0±60.5 | 397.3±250.0 |
| **Bulk and solution** | 71.5±9.7 | 125.4±20.7 | 265.9±91.2 | 434.1±41.2 |

**Table S9: Comparison of backbiting rate coefficient ($k_{bb}$) with literature data**

| Parameters | This work | Plessis *et al.*[20] | Nikitin *et al.*[3] | Nikitin *et.al.*[16] | Barth *et al.*[10] | Hamzehlou *et al.*[15] |
|---|---|---|---|---|---|---|
| Temperature (K) | | | | | | |
| A ($s^{-1}$) | 5.38 ×$10^7$ | 3.5 × $10^7$ | 4.84 ×$10^7$ | 7.41 ×$10^7$ | 1.60 ×$10^8$ | 3.20 ×$10^{10}$ |
| $E_a$ (kJ $mol^{-1}$) | 30.6±5.4 | 29.3 | 31.7 | 32.7 | 34.7 | 52.3 |
| 303 | 285.3±50.5 | 311 | 166 | 171 | 167 | 31 |
| 313 | 416.8±95.5 | 451 | 248 | 259 | 259 | 60 |
| 323 | 605.3±140.2 | 639 | 362 | 381 | 391 | 111 |

**Table S10: Comparison of tertiary propagation rate coefficient ($k_{p,m}$) with literature data**

| Parameters | This work | Nikitin *et al.*[3] | Nikitin *et al.*[16] | Barth *et al.*[10] |
|---|---|---|---|---|
| Temperature (K) | | | | |
| A (L $mol^{-1}$ $s^{-1}$) | 1.94×$10^6$ | 1.52×$10^6$ | 1.2×$10^6$ | 9.2×$10^5$ |
| $E_a$ (kJ $mol^{-1}$) | 30.1±9.7 | 28.9 | 28.6 | 28.3 |
| 303 | 12.7±5.6 | 16 | 14 | 12 |
| 313 | 18.3±7.8 | 23 | 20 | 17 |
| 323 | 26.6±11.8 | 32 | 28 | 24 |

**Table S11: Comparison of beta-scission rate coefficient ($k_\beta$) with the literature data**

| Parameters | This work | Nikitin *et al.*[16] | Hamzehlou *et al.*[15] |
|---|---|---|---|
| Temperature (K) | | | |
| A ($s^{-1}$) | 8.03×$10^{12}$ | 1.49×$10^9$ | 1.47×$10^9$ |
| $E_a$ (kJ $mol^{-1}$) | 81.1±18.2 | 63.9 | 55.4 |
| 383 | 71.5±9.7 | 2.9 | 40.9 |
| 393 | 125.4±20.7 | 4.8 | 63.6 |
| 403 | 265.9±91.2 | 7.8 | 96.9 |
| 413 | 434.1±41.2 | 12.3 | 144.6 |

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