Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.

Electronic supplementary information for: "Access to the *β*-scission rate coefficient in acrylate radical polymerization by careful scanning of pulse laser frequencies at elevated temperature"

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Contents

S1 Experimental SEC details for application of the proposed method

This section describes the details of the bulk PLP experiments of *n*-butyl acrylate (*n*BuA) at 413 K. Typical SEC traces with the corresponding derivative at the outer pulse laser frequencies of the considered range are shown in **Figure S1**. These SEC traces used to determine the apparent propagation rate coefficient ($k_{\mathrm{p,app}}$; **Equation (1)** in the main text; i=1) by locating the (first) inflection point of the log MMD plot.

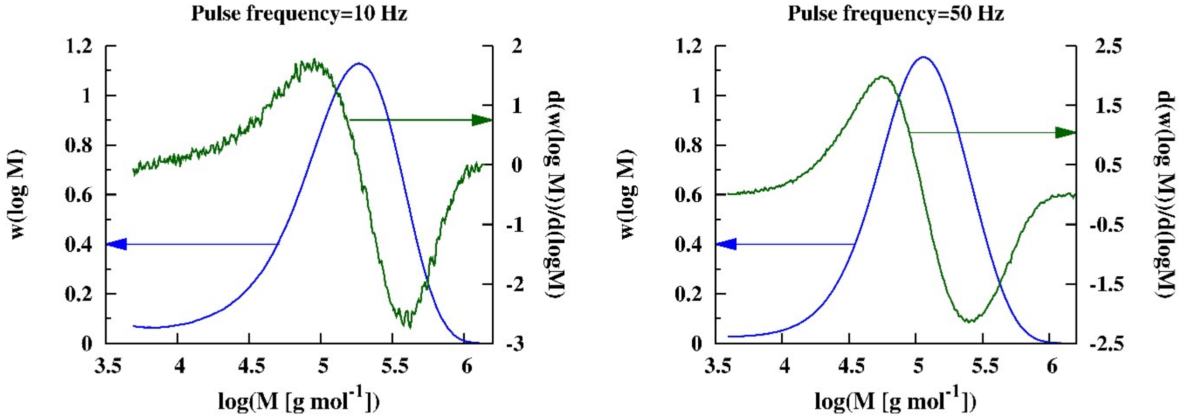

Figure S1 Experimental PLP-SEC trace (full blue line) and corresponding first derivative (full green line) for PLP of *n*BuA at 413 K under bulk conditions; Initial conditions: $[\mathrm{DMPA}]_0 = 2.5\times10^{-3}$ mol L^{-1} and $\mathrm{E_{pulse}} = 1.5\times10^{-3}$ J. Number of pulses: 20 at frequency of 10 Hz and 60 at frequency of 50 Hz.

S2 Correction for SEC broadening

The molar mass distribution (MMD) obtained from PLP experiments shows broadening.[1] In this work, SEC-broadening is accounted based on the method proposed by Buback *et al.*[2] For a more detailed description and derivation the reader is referred to previous work.[3,4] 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 $(\sigma_\upsilon b) = 0.04$ used based on the literature data.[1,5]

S3 Kinetic modeling details

The reaction scheme and corresponding literature based Arrhenius parameters of PLP of *n*-butyl acrylate (*n*BuA) at high temperature used in the kinetic Monte Carlo (*k*MC) simulations are summarized in **Table 1** in the main text. Thermal self-initiation and macropropagation reactions are neglected based on the results (***cf.*** **Figure 1** in main text and detailed discussion in this section)

S3.1 Photodissociation kinetics

The concentration of initiator radicals generated after each laser pulse ($\Delta[R]_0$) is calculated as:[6,7]

$$\Delta[R]_0 = 2\Phi_{\mathrm{diss}} \frac{E_{\mathrm{pulse}}\lambda}{h\, c\, N_{\mathrm{A}}\, \Omega\, l}\left[1-\exp\left(-2.303\ \varepsilon\ [\mathrm{DMPA}]\ l\right)\right] \tag{S2}$$

where Φ_{diss} is the quantum yield of photodissociation (0.42[6]), E_{pulse} the laser pulse energy ($1.5\times10^{-3}\,\mathrm{J}$), λ 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_{A} the Avogadro constant ($6.02\times10^{23}\,\mathrm{mol^{-1}}$), Ω the optical cross-sectional area ($3.85\times10^{-5}\ \mathrm{m}^2$), l the optical path length ($1.04\times10^{-2}\ \mathrm{m}$), ε the molar absorptivity of the photoinitiator ($28\ \mathrm{m}^2\ \mathrm{mol}^{-1}$), and [DMPA] is the concentration of photoinitiator.

S3.2 Negligible impact of macromonomer addition reaction under PLP conditions

The macromonomers formed in the beta-scission reaction can further propagate with end-chain and mid-chain radicals. The macromonomer propagation reaction adds more complexity to the kinetics of *n*-butyl acrylate free-radical polymerization. The simulations were carried out considering the macromonomer propagation reaction and its rate coefficient was varied from minimum to maximum values as reported in the literature.[8] For simplicity, MCRs were treated as ECRs to even enlarge a possible effect. The effect is although negligible as shown in **Figure S2-Figure S4**.

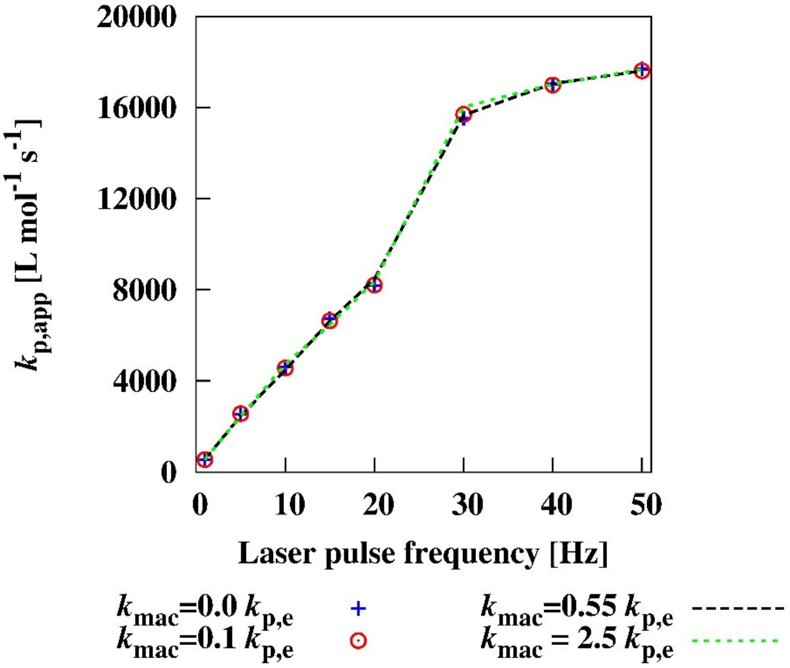

Figure S2 Effect of macromonomer propagation reactivity on the apparent propagation rate coefficient ($k_{p,app}$; **Equation (1)** in the main text; i=1) in bulk PLP of *n*-butyl acrylate. The simulations were carried out by changing the macromonomer propagation rate coefficient (k_{mac}). Other parameters as in **Table 1** in main text; 413 K. For simplicity the MCR rate coefficient is taken equal to the one of ECRs and to even enlarge a possible effect.

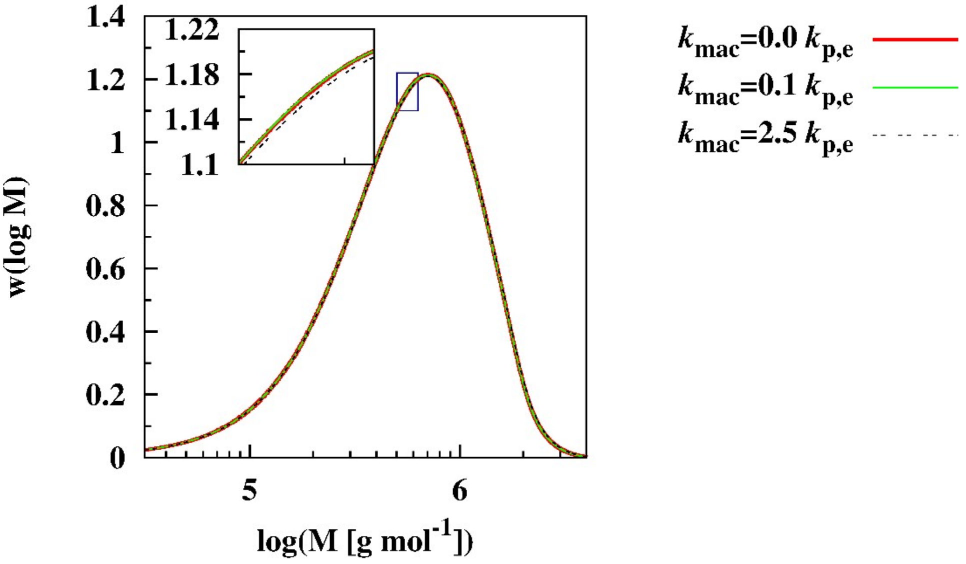

Figure S3 Corresponding log-MMD for **Figure S2** at frequency =10 Hz (also **Figure 1 (right)** in the main text).

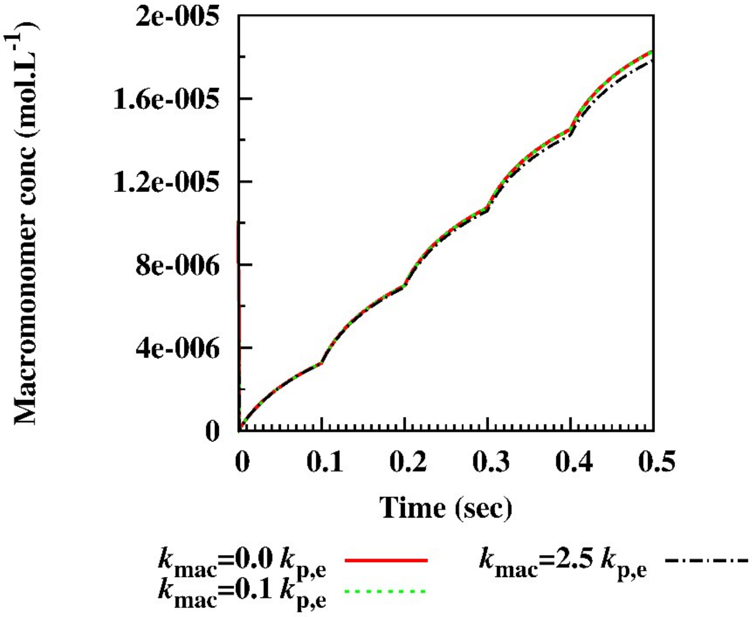

Figure S4 Corresponding macromonomer concentrations for **Figure S3**.

S3.3 Chain length dependencies

Chain length dependent propagation kinetics are accounted based on (details in reference 6; based on work of Heuts and Russell [9]).

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

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.

Chain length dependent termination kinetics are evaluated via the composite k_t model, For the low monomer conversion ranges as encountered during PLP, it suffices to consider:

$$k_t^{app}(i,i) = k_t^{app}(1,1)\, i^{-\alpha_S} \qquad i \le i_c \tag{S1}$$

$$k_t^{app}(i,i) = k_t^{app}(1,1)\, i_c^{-\alpha_S+\alpha_L} i^{-\alpha_L} \qquad i > i_c \tag{S2}$$

in which α_S and α_L express the chain length dependence for short and long radicals, and i_c is the cross-over chain length (details in reference 5).

S4 Extra information related to effect of the beta-scission rate coefficient on the inflection point for different laser pulse frequencies (related to Figure 2 and 3 in the main text)

S4.1 Effect of temperature

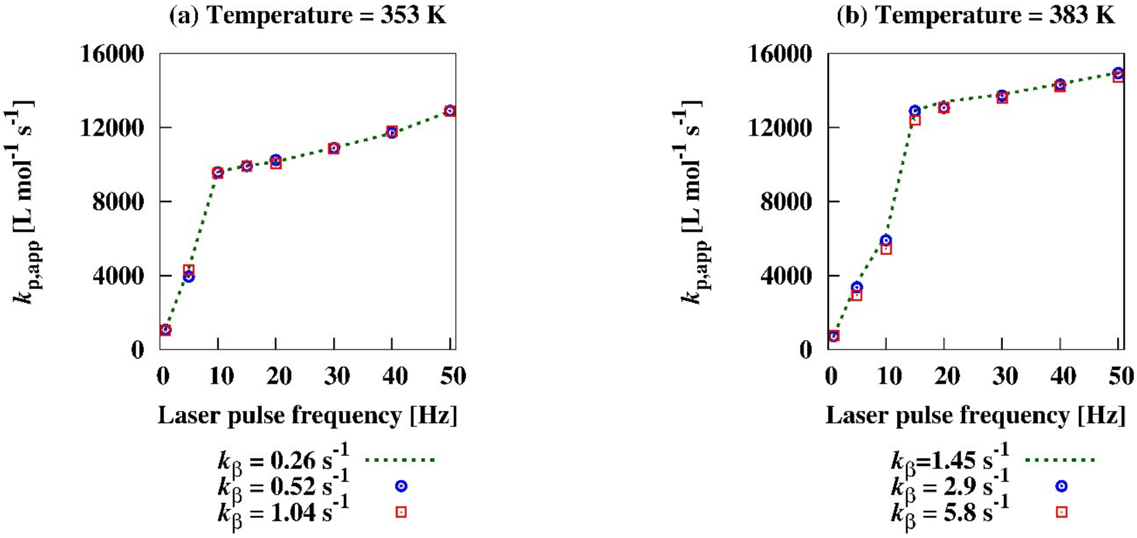

Figure S5 Sensitivity of β-scission rate coefficient (k_β) on $k_{p,app}$ in PLP of *n*-butyl acrylate by kinetic Monte Carlo (*k*MC) simulations at temperatures (a) 353 K (left) and (b) 383 K (right). Reference k_β = 0.52 s^{-1} at 353 K and reference k_β = 2.9 s^{-1} at 383 K. Simulation conditions: ϕ_s=0; other parameters: **Table 1** in main text.

S4.2 Effect of solvent fraction

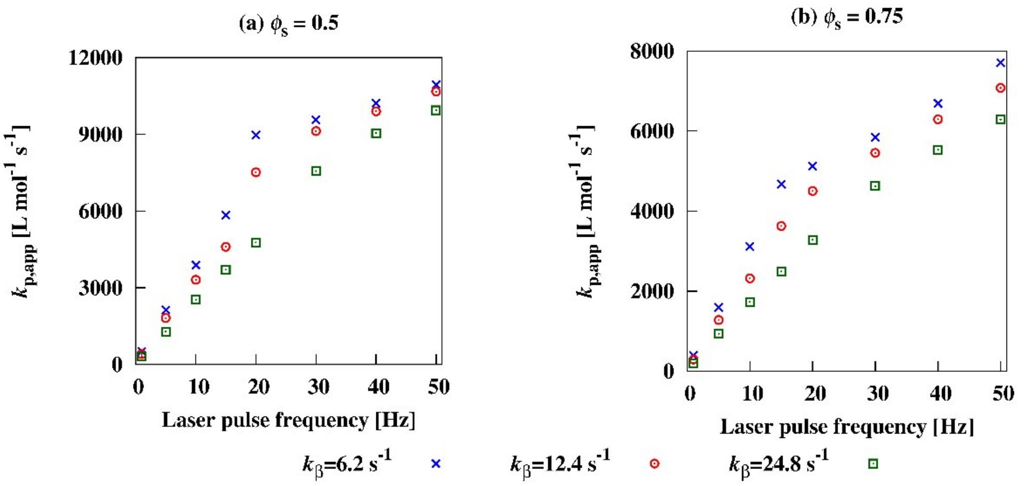

Figure S6 Influence of solvent amount on sensitivity of beta-scission rate coefficient *(*k_β) on $k_{p,app}$ in PLP of *n*-butyl acrylate by kinetic Monte Carlo (*k*MC) simulations. (a) ϕ_s=0.5 (left) and (b) ϕ_s=0.75 (right). Simulation conditions: 413 K, k_β= 12.41 s^{-1}; other parameters: **Table 1** in main text.

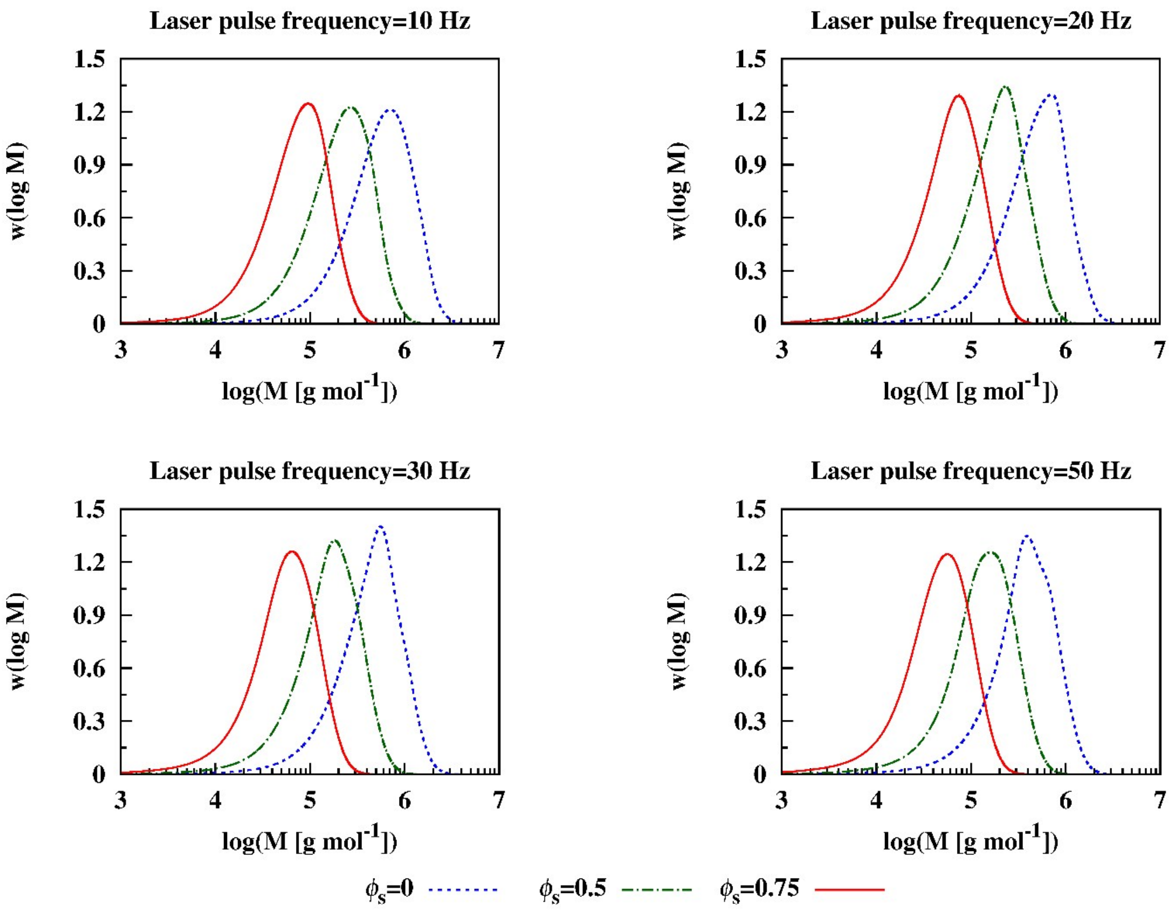

Figure S7 Solvent fraction effect on log-MMD in PLP of *n*-butyl acrylate at selected laser pulse frequencies by *k*MC simulations. Simulation conditions: 413 K, k_β= 12.4 s^{-1}; other parameters: **Table 1** in main text.

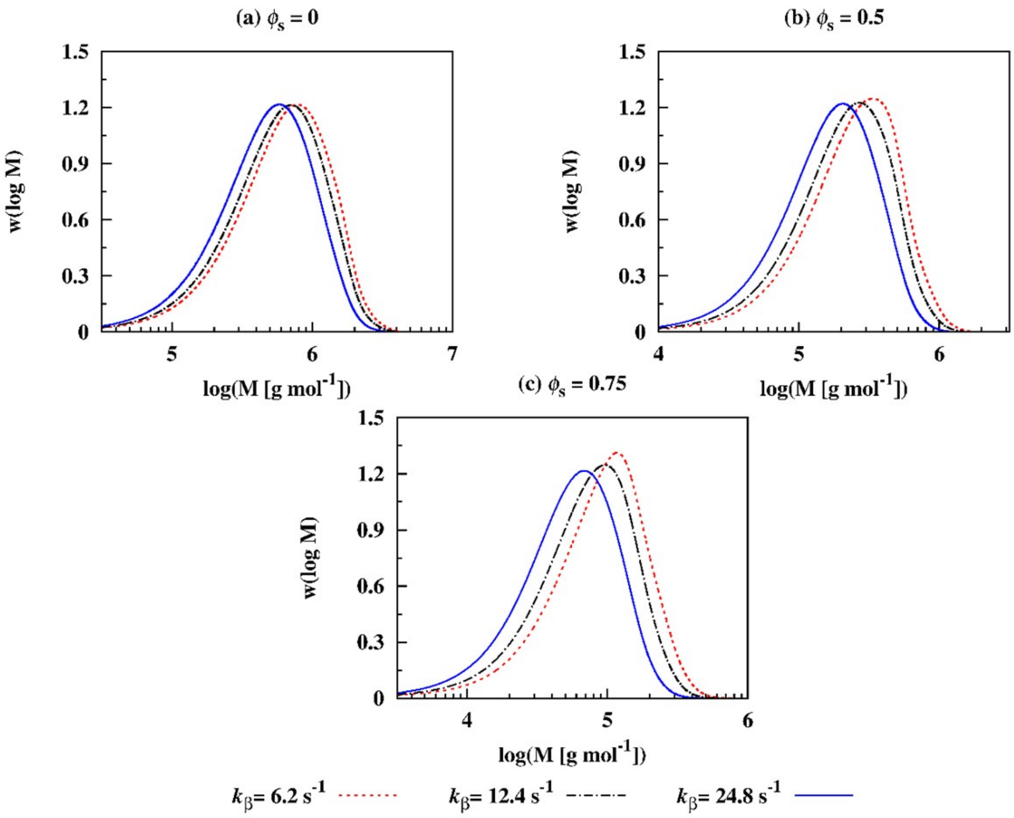

Figure S8 log-MMD for solvent fraction influence on sensitivity of beta-scission rate coefficient (k_β) on $k_{p,app}$ in PLP of n-butyl acrylate by kMC simulations. (a) ϕ_s=0 (top-left), (b) ϕ_s=0.5 (top-right) and (c) ϕ_s=0.75 (bottom-center). Simulation conditions: Temperature=413 K; frequency=10 Hz*;* other parameters: **Table 1** in main text.

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