Supporting Information for:

On the explanations of the recovery of PLP-molar mass distribution at high laser frequencies: a simulation study

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Initiation:

$$R_0 + M \rightarrow R_1,\ k_i$$

Propagation:

$$R_i + M \rightarrow R_{i+1},\ k_p$$

$$R_i^{MCR} + M \rightarrow R_{i+1},\ k_p^{MCR}$$

Backbiting:

$$R_i \rightarrow R_i^{MCR},\ k_{bb}$$

Chain transfer to monomer:

$$R_i + M \rightarrow P_i + R_1,\ k_{trm}$$

$$R_i^{MCR} + M \rightarrow P_i + R_1,\ k_{trm}^{MCR}$$

Termination:

$$R_i + R_j \rightarrow P_i + P_j,\ k_{td}$$

$$R_i^{MCR} + R_j \rightarrow P_i + P_j,\ k_{td}^{st}$$

$$R_i^{MCR} + R_j^{MCR} \rightarrow P_i + P_j,\ k_{td}^{MCR}$$

$$R_i + R_j \rightarrow P_{i+j},\ k_{tc}$$

$$R_i^{MCR} + R_j \rightarrow P_{i+j},\ k_{tc}^{st}$$

$$R_i^{MCR} + R_j^{MCR} \rightarrow P_{i+j},\ k_{tc}^{MCR}$$

$$R_i + R_0 \rightarrow P_i,\ k_t$$

$$R_i^{MCR} + R_0 \rightarrow P_i,\ k_t^{MCR}$$

Intermolecular transfer to polymer

$$R_i + P_j \rightarrow P_i + R_j^{MCR},\ k_{trp} * j$$

Scheme SI.1. Kinetic mechanism of the BA polymerization. The rate coefficients are shown in left-hand side of the reaction. M: BA monomer; R_i: chain-end radical with length *i*; R_i^{MCR}: MCR with length *i*; P_i: dead polymer with length *i*. R_0: radical generated in the laser pulse. k_{ti}^{st} is the geometrical average of the termination rates of the involved spices (e.g. $k_{tc}^{st} = \sqrt{k_{tc} * k_{tc}^{MCR}}$).

Table SI.1. Arrhenius parameters for the rate coefficients used for PLP simulation of BA.

Parameter	Frequency factor L mol^{-1} s^{-1} or s^{-1}	Activation energy kJ mol^{-1}	Reference
$k_i = k_p$	2.21×10^7	17.9	1
k_t	1.3×10^{10}	8.4	2
k_{bb}	7.40×10^7	32.7	3
k_p^{MCR}	1.58×10^6	28.9	4
k_{trm}	2.88×10^5	32.6	5
k_{trm}^{MCR}	2.2×10^5	46.1	5
k_t^{MCR}	1.29×10^7	4.0	5
[1]cd_s	0.1	---	6
[2]cd_t	0.9	---	6
k_{trp}	2.48×10^3	27.7	7

[1] cd_s termination by disproportionation ratio of chain-end radicals.
[2] cd_t termination by disproportionation ratio of MCRs.

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