Electronic Supplementary Material (ESI) for Polymer Chemistry.

# Supporting Information

# Propagation Rate Coefficient for Acrylic Acid Polymerization in Bulk and in Propionic Acid by PLP-SEC Method: Experiment and 3D Simulation

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**Content:**

## Tables

**Table S1.** The propagation rate coefficient, $k_p^{exp}$, for polymerization of acrylic acid, AA, of different concentration, [AA],in propionic acid as a function of initiator concentration, [I], laser pulse energy, $E_p$, number of pulses, $N_p$, laser pulse repetition rate, $f$, and degree of conversion, $\gamma$. The molar masses $M_1$ and $M_2$ correspond to the first and second maxima determined from the first derivative curve of MMDs.

| [AA], wt% | # of exp. | [I], mmol·L$^{-1}$ | $E_p$, mJ | $N_p$ | $f$, Hz | $\gamma$, % | $M_1$, g·mol$^{-1}$ | $M_2$, g·mol$^{-1}$ | $k_p^{exp}$, L·mol$^{-1}$·s$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| 10.1 | 1 | 5 | 3 | 300 | 250 | [a] | 10201 | 22544 | 19387 |
| | 2 | 5 | 3 | 300 | 250 | [a] | 10112 | 22377 | 19220 |
| | 3 | 5 | 3 | 500 | 250 | 3.20 | 10216 | 22177 | 19682 |
| | 4 | 5 | 3 | 500 | 250 | 3.20 | 10130 | 22123 | 19518 |
| | 5 | 5 | 3 | 100 | 500 | 0.50 | 4583 | 11552 | 17422 |
| | 6 | 5 | 3 | 100 | 500 | 0.50 | 3921 | 10314 | 14903 |
| | 7 | 5 | 3 | 300 | 500 | 0.85 | 4537 | 10847 | 17276 |
| | 8 | 5 | 3 | 300 | 500 | 0.85 | 4422 | 11105 | 16839 |
| | 9 | 5 | 3 | 500 | 500 | 2.76 | 4452 | 11046 | 17117 |
| | 10 | 5 | 3 | 500 | 500 | 2.76 | 4570 | 11065 | 17572 |
| 10.3 | 11 | 20 | 3 | 100 | 250 | 0.26 | 9478 | 23228 | 17763 |
| | 12 | 20 | 3 | 100 | 250 | 0.26 | 10598 | 25148 | 19861 |
| | 13 | 20 | 3 | 300 | 250 | 1.01 | 9136 | 22951 | 17187 |
| | 14 | 20 | 3 | 300 | 250 | 1.01 | 10231 | 25513 | 19247 |
| | 15 | 20 | 3 | 500 | 250 | 2.18 | 9448 | 22848 | 17878 |
| | 16 | 20 | 3 | 500 | 250 | 2.18 | 10296 | 24618 | 19483 |
| | 17 | 20 | 3 | 100 | 500 | 0.34 | 3991 | 11340 | 14967 |
| | 18 | 20 | 3 | 100 | 500 | 0.34 | 4472 | 11524 | 16770 |
| | 19 | 20 | 3 | 300 | 500 | 8.06 | 3933 | 10272 | 15342 |
| | 20 | 20 | 3 | 300 | 500 | 8.06 | 4420 | 11357 | 17238 |
| | 21 | 20 | 3 | 500 | 500 | 2.16 | 4026 | 10785 | 15237 |
| | 22 | 20 | 3 | 500 | 500 | 2.16 | 4476 | 11712 | 16937 |
| 19.9 | 23 | 5 | 3 | 100 | 250 | 0.27 | 23516 | 49786 | 22613 |
| | 24 | 5 | 3 | 100 | 250 | 0.27 | 23068 | 49526 | 22182 |

| [AA], wt% | # of exp. | [I], mmol·L$^{-1}$ | $E_\mathrm{p}$, mJ | $N_\mathrm{p}$ | $f$, Hz | $\gamma$, % | $M_1$, g·mol$^{-1}$ | $M_2$, g·mol$^{-1}$ | $k_\mathrm{p}^\mathrm{exp}$, L·mol$^{-1}$·s$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| 19.9 | 25 | 5 | 3 | 300 | 250 | 2.00 | 24025 | 50202 | 23305 |
| | 26 | 5 | 3 | 300 | 250 | 2.00 | 24238 | 50057 | 23511 |
| | 27 | 5 | 3 | 500 | 250 | 2.73 | 24616 | 50930 | 23967 |
| | 28 | 5 | 3 | 500 | 250 | 2.73 | 24798 | 51153 | 24144 |
| | 29 | 5 | 3 | 50 | 500 | 0.08 | 9917 | 23255 | 19053 |
| | 30 | 5 | 3 | 50 | 500 | 0.08 | 9971 | 23886 | 19158 |
| | 31 | 5 | 3 | 100 | 500 | a) | 9833 | 22462 | 18898 |
| | 32 | 5 | 3 | 100 | 500 | a) | 9977 | 24010 | 19177 |
| | 33 | 5 | 3 | 300 | 500 | 0.40 | 10430 | 25403 | 20072 |
| | 34 | 5 | 3 | 300 | 500 | 0.40 | 10429 | 25383 | 20069 |
| | 35 | 5 | 3 | 500 | 500 | 2.47 | 10303 | 24347 | 20036 |
| | 36 | 5 | 3 | 500 | 500 | 2.47 | 10444 | 24303 | 20310 |
| | 37 | 20 | 3 | 50 | 250 | 0.14 | 22323 | 50436 | 21464 |
| | 38 | 20 | 3 | 50 | 250 | 0.14 | 21920 | 49921 | 21076 |
| | 39 | 20 | 3 | 100 | 250 | 0.37 | 22891 | 49754 | 22035 |
| | 40 | 20 | 3 | 100 | 250 | 0.37 | 22800 | 49486 | 21947 |
| | 41 | 20 | 3 | 300 | 250 | 1.05 | 23456 | 49985 | 22656 |
| | 42 | 20 | 3 | 300 | 250 | 1.05 | 23373 | 51079 | 22575 |
| | 43 | 20 | 3 | 500 | 250 | 2.00 | 23284 | 51469 | 22597 |
| | 44 | 20 | 3 | 500 | 250 | 2.00 | 23222 | 51681 | 22537 |
| | 45 | 20 | 3 | 50 | 500 | a) | 9577 | 22893 | 18417 |
| | 46 | 20 | 3 | 50 | 500 | a) | 9392 | 23002 | 18062 |
| | 47 | 20 | 3 | 100 | 500 | 0.11 | 9586 | 23339 | 18432 |
| | 48 | 20 | 3 | 100 | 500 | 0.11 | 9642 | 23176 | 18538 |
| | 49 | 20 | 3 | 300 | 500 | 0.41 | 10112 | 24152 | 19472 |
| | 50 | 20 | 3 | 300 | 500 | 0.41 | 10066 | 24139 | 19383 |
| | 51 | 20 | 3 | 500 | 500 | 1.64 | 10149 | 24280 | 19662 |
| | 52 | 20 | 3 | 500 | 500 | 1.64 | 10174 | 24216 | 19711 |
| 39.0 | 53 | 5 | 3 | 50 | 250 | a) | 55952.7 | 112552 | 27153 |
| | 54 | 5 | 3 | 50 | 250 | a) | 55960.9 | 105425 | 27157 |
| | 55 | 5 | 3 | 100 | 250 | 0.20 | 56911 | 111065 | 27630 |
| | 56 | 5 | 3 | 100 | 250 | 0.20 | 55733 | 113177 | 27058 |

| [AA], wt% | # of exp. | [I], mmol·L$^{-1}$ | $E_p$, mJ | $N_p$ | $f$, Hz | $\gamma$, % | $M_1$, g·mol$^{-1}$ | $M_2$, g·mol$^{-1}$ | $k_p^{exp}$, L·mol$^{-1}$·s$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| | 57 | 5 | 3 | 300 | 250 | 0.78 | 64094 | 168008 | 31209 |
| | 58 | 5 | 3 | 300 | 250 | 0.78 | 63144 | 160528 | 30746 |
| | 59 | 5 | 3 | 500 | 250 | 1.36 | 73553 | 181949 | 35919 |
| | 60 | 5 | 3 | 500 | 250 | 1.36 | 65419 | 174812 | 31946 |
| | 61 | 5 | 3 | 50 | 500 | 0.11 | 25259 | 56311 | 24516 |
| | 62 | 5 | 3 | 50 | 500 | 0.11 | 24505 | 54987 | 23784 |
| | 63 | 5 | 3 | 100 | 500 | 0.09 | 25181 | 55739 | 24438 |
| | 64 | 5 | 3 | 100 | 500 | 0.09 | 25226 | 55556 | 24481 |
| | 65 | 5 | 3 | 300 | 500 | 1.05 | 26435 | 65064 | 25779 |
| | 66 | 5 | 3 | 300 | 500 | 1.05 | 26910 | 61343 | 26242 |
| | 67 | 5 | 3 | 500 | 500 | 0.90 | 28161 | 62781 | 27441 |
| | 68 | 5 | 3 | 500 | 500 | 0.90 | 28440 | 63980 | 27713 |
| 39.1 | 69 | 20 | 3 | 50 | 250 | 0.10 | 55693 | 110044 | 26975 |
| | 70 | 20 | 3 | 50 | 250 | 0.10 | 56180 | 109866 | 27211 |
| | 71 | 20 | 3 | 100 | 250 | 0.59 | 57575 | 115607 | 27956 |
| | 72 | 20 | 3 | 100 | 250 | 0.59 | 57623 | 116261 | 27980 |
| | 73 | 20 | 3 | 300 | 250 | 0.51 | 60432 | 134549 | 29331 |
| | 74 | 20 | 3 | 300 | 250 | 0.51 | 60619 | 135205 | 29422 |
| | 75 | 20 | 3 | 500 | 250 | 0.33 | 64105 | 169253 | 31086 |
| | 76 | 20 | 3 | 500 | 250 | 0.33 | 64011 | 168616 | 31041 |
| | 77 | 20 | 3 | 50 | 500 | 0.15 | 23425 | 54930 | 22698 |
| | 78 | 20 | 3 | 50 | 500 | 0.15 | 23081 | 59814 | 22365 |
| | 79 | 20 | 3 | 100 | 500 | 0.31 | 25677 | 56497 | 24901 |
| | 80 | 20 | 3 | 100 | 500 | 0.31 | 25999 | 57185 | 25213 |
| | 81 | 20 | 3 | 300 | 500 | 0.79 | 27250 | 62844 | 26490 |
| | 82 | 20 | 3 | 300 | 500 | 0.79 | 27804 | 61527 | 27029 |
| | 83 | 20 | 3 | 500 | 500 | 0.92 | 29190 | 64648 | 28394 |
| | 84 | 20 | 3 | 500 | 500 | 0.92 | 23081 | 59814 | 27802 |
| 54.5 | 85 | 5 | 3 | 50 | 500 | 0.17 | 40504 | 85728 | 27886 |
| | 86 | 5 | 3 | 50 | 500 | 0.17 | 40326 | 84844 | 27763 |
| | 87 | 5 | 3 | 100 | 500 | 0.24 | 40974 | 90152 | 28219 |
| | 88 | 5 | 3 | 100 | 500 | 0.24 | 41987 | 91638 | 28917 |

| [AA], wt% | # of exp. | [I], $\mathrm{mmol \cdot L^{-1}}$ | $E_p$, mJ | $N_p$ | $f$, Hz | $\gamma$, % | $M_1$, $\mathrm{g \cdot mol^{-1}}$ | $M_2$, $\mathrm{g \cdot mol^{-1}}$ | $k_p^{exp}$, $\mathrm{L \cdot mol^{-1} \cdot s^{-1}}$ |
|---|---|---|---|---|---|---|---|---|---|
| | 89 | 5 | 3 | 200 | 500 | 1.10 | 45706 | 97517 | 31614 |
| | 90 | 5 | 3 | 200 | 500 | 1.10 | 43754 | 95395 | 30264 |
| | 91 | 5 | 3 | 300 | 500 | 1.72 | 45937 | 96914 | 31874 |
| | 92 | 5 | 3 | 300 | 500 | 1.72 | 47075 | 96211 | 32663 |
| 77.6 | 93 | 5 | 3 | 15 | 500 | 0.07 | 68549 | 130317 | 32755 |
| | 94 | 5 | 3 | 15 | 500 | 0.07 | 70146 | 128825 | 33518 |
| | 95 | | | 15 | 500 | 0.07 | 68391 | 122744 | 32680 |
| | 96 | 5 | 3 | 25 | 500 | 0.21 | 69663 | 123027 | 33312 |
| | 97 | 5 | 3 | 25 | 500 | 0.21 | 70795 | 127644 | 33853 |
| | 98 | 5 | 3 | 50 | 500 | 0.48 | 71945 | 127938 | 34449 |
| | 99 | 5 | 3 | 50 | 500 | 0.48 | 69984 | 120781 | 33510 |
| | 100 | 5 | 3 | 100 | 500 | 1.23 | 76033 | 130017 | 36544 |
| | 101 | 5 | 3 | 100 | 500 | 1.23 | 75336 | 128825 | 36209 |
| 100 | 102 | 5 | 3 | 15 | 500 | 0.05 | 86298 | 164816 | 31618 |
| | 103 | 5 | 3 | 15 | 500 | 0.05 | 87498 | 161436 | 32058 |
| | 104 | 5 | 3 | 35 | 500 | 0.31 | 89331 | 168267 | 32771 |
| | 105 | 5 | 3 | 35 | 500 | 0.31 | 90365 | 169434 | 33151 |
| | 106 | 5 | 3 | 50 | 500 | 0.88 | 97949 | 175792 | 36035 |
| | 107 | 5 | 3 | 50 | 500 | 0.88 | 97949 | 177828 | 36035 |
| | 108 | 5 | 4 | 15 | 500 | 0.08 | 84333 | 157036 | 30903 |
| | 109 | 5 | 4 | 15 | 500 | 0.08 | 85310 | 158855 | 31261 |
| | 110 | 5 | 4 | 25 | 500 | 0.36 | 89331 | 167109 | 32779 |
| | 111 | 5 | 4 | 25 | 500 | 0.36 | 89331 | 165196 | 32779 |
| | 112 | 5 | 4 | 50 | 500 | 0.17 | 88512 | 156315 | 32448 |
| | 113 | 5 | 4 | 50 | 500 | 0.17 | 88512 | 154170 | 32448 |

[a] data are not available

**Table S2.** Chemical and physical parameters used for 3D simulation of the PLP of acrylic acid (AA) in propionic acid (PA).

| Parameters | AA | Ref. | PA | Ref. |
|---|---|---|---|---|
| Molar mass, $M_M$ $g \cdot mol^{-1}$ | 72.06 | | 74.08 | |
| Heat of polymerization, $(-H_p)$ $kJ \cdot mol^{-1}$ | 77.5 | [1] | | |
| Specific heat, $C_p$ $J \cdot kg^{-1} \cdot °C^{-1}$ | $C_{p0}+C_{p1}T$ ($T$ in °C) | [2] | $C_{p0}+C_{p1}T$ ($T$ in °C) | [3] |
| $C_{p0}$ $J \cdot kg^{-1} \cdot °C^{-1}$ | 1891.8 | | 2280.1 | |
| $C_{p1}$ $J \cdot kg^{-1} \cdot °C^{-2}$ | 4.38 | | 2.8555 | |
| Conductivity, $\lambda_M$ $W \cdot m^{-1} \cdot K^{-1}$ | $\lambda_{M0}-\lambda_{M1}T$ ($T$ in K) | [4] | $\lambda_{M0}-\lambda_{M1}T$ ($T$ in K) | [5] |
| $\lambda_{M0}$ $W \cdot m^{-1} \cdot K^{-1}$ | 0.2434 | | 0.1827 | |
| $\lambda_{M1}$ $W \cdot m^{-1} K^{-2}$ | $2.875 \times 10^{-4}$ | | $1.205 \times 10^{-4}$ | |
| Density, $\mu_T$ $g \cdot cm^{-3}$ | $\mu_0-\mu_1 T$ ($T$ in °C) | [1] | $\mu_0-\mu_1 T$ ($T$ in °C) | [3] |
| $\mu_0$ $g \cdot cm^{-3}$ | 1.07088 | | 1.0199 | |
| $\mu_1$ $g \cdot cm^{-3} \cdot °C^{-1}$ | $1.0989 \times 10^{-3}$ | | $1.1 \times 10^{-3}$ | |
| Activation energy for $k_p$, $E_a(k_p)$ $kJ \cdot mol^{-1}$ | 16.7 | a) | | |
| Pre-exponential factor for $k_p$, $A(k_p)$ $L \cdot mol^{-1} \cdot s^{-1}$ | $2.54 \times 10^7$<br>(100 wt% of AA)<br>$2.27 \times 10^7$<br>(54.5 wt% of AA) | this work | | |
| Activation energy for $k_t$, $E_a(k_t)$ $kJ \cdot mol^{-1}$ | 15.5 | [6] | | |
| Pre-exponential factor for $k_t$, $A(k_t)$ $L \cdot mol^{-1} \cdot s^{-1}$ | $6.1 \times 10^{10}$ | this work | | |
| Mode of termination (fraction of disproportionation) | 0.05 | [6] | | |

a)unpublished experimental data

**Table S3.** Physical parameters used for 3D simulation of the PLP of acrylic acid in the quartz cell surrounded by water and air.

| | Heat conductivity, $W \cdot m^{-1} \cdot K^{-1}$ | Specific heat, $C_p$ $J \cdot kg^{-1} \cdot {}^\circ C^{-1}$ | Ref. |
|---|---|---|---|
| Air | 0.024 (25 °C) | | [7] |
| Water | 0.58 (25 °C) | | [7] |
| Quartz | 3.0 (25 °C) | 728 (25 °C) | [8],[9] |

**Table S4.** Chemical parameters used for PREDICI simulation of PLP of acrylic acid

| Parameters | Values | Ref. |
|---|---|---|
| Activation energy for $k_{bb}$,$E_a(k_{bb})$ $kJ \cdot mol^{-1}$ | 41.74 | [6] |
| Pre-exponential factor for $k_{bb}$, $A(k_{bb})$ $s^{-1}$ | $4.25 \times 10^9$ | [6] |
| Activation energy for $k_p^b$,$E_a(k_p^b)$ $kJ \cdot mol^{-1}$ | 35.940 | [6] |
| Pre-exponential factor for $k_p^b$, $A(k_p^b)$ $L \cdot mol^{-1} \cdot s^{-1}$ | $6.12 \times 10^7$ | [6] |
| Activation energy for $k_t^{bb}$, $E_a(k_t^{bb})$ $kJ \cdot mol^{-1}$ | 15.5 | [6] |
| Pre-exponential factor for $k_t^{bb}$,$A(k_t^{bb})$ $L \cdot mol^{-1} \cdot s^{-1}$ | $6.1 \times 10^9$ | this work |
| Activation energy for $k_t^{sb}$,$E_a(k_t^{sb})$ $kJ \cdot mol^{-1}$ | 15.5 | [6] |
| Pre-exponential factor for $k_t^{sb}$, $A(k_t^{sb})$ $L \cdot mol^{-1} \cdot s^{-1}$ | $3.36 \times 10^{10}$ | this work |
| Mode of termination, $\delta^{sb}$ (fraction of disproportionation) | 0.4 | [6] |
| Mode of termination, $\delta^{bb}$ (fraction of disproportionation) | 0.8 | [6] |
| Activation energy for $k_{trM}$,$E_a(k_{trM})$ $kJ \cdot mol^{-1}$ | 16.7 | [6] |
| Pre-exponential factor for $k_{trM}$, $A(k_{trM})$ $L \cdot mol^{-1} \cdot s^{-1}$ | $1.91 \times 10^3$ | [6] |
| Activation energy for $k_{trM}^t$ ,$E_a(k_{trM}^t)$ $kJ \cdot mol^{-1}$ | 35.94 | [6] |
| Pre-exponential factor for $k_{trM}^t$ , $A(k_{trM}^t)$ $L \cdot mol^{-1} \cdot s^{-1}$ | $4.53 \times 10^3$ | [6] |

**Table S5.** The parameters influencing the increase of temperature during the PLP of acrylic acid (AA), methyl acrylate (MA) and butyl acrylate (BA) at 25 °C.

| Parameter | Monomer | | | |
|---|---|---|---|---|
| | AA | MA | BA | VAc |
| Molar mass, $M_M$ $g{\cdot}mol^{-1}$ | 72.06 | 86.09 | 128.17 | 86.09 |
| Heat of polymerization, $(-\Delta H_p)$ $kJ{\cdot}mol^{-1}$ | 77500[1] | 81790[10] | 77290[13] | 87900[17] |
| Specific heat, $C_p^M$ $J{\cdot}kg^{-1}{\cdot}°C^{-1}$ | 2000[2] | 2000[10] | 1960[14] | 1770[17] |
| $\beta$, °C | 538 | 475 | 308 | 577 |
| $k_p$, $L{\cdot}mol^{-1}{\cdot}s^{-1}$ | 30140[this work] | 13130[11] | 16160[15] | 3600[18] |
| $k_t$, $L{\cdot}mol^{-1}{\cdot}s^{-1}$ | $1.2\times10^8$[this work] | $2.3\times10^8$[12] | $1.4\times10^8$[16] | $5.2\times10^8$[19],[20] |
| $k_p/k_t$ $(\times 10^{-4})$ | 2.51 | 0.57 | 1.15 | 0.069 |

**Figures**

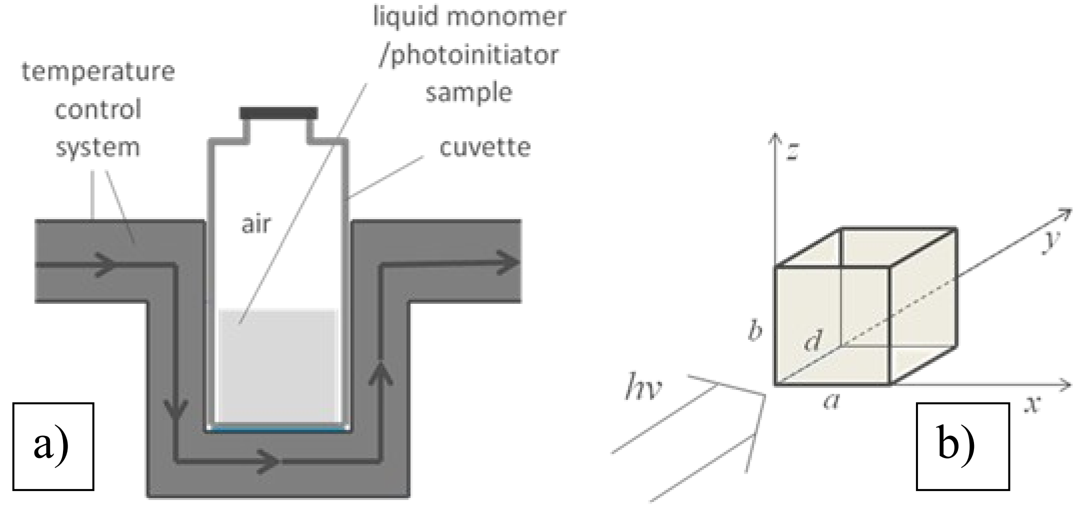

**Figure S1.**Configuration of a cuvette containing sample solution in a thermostatted temperature controlled system(a) and dimensions of monomer/photoinitiator sample of rectangular parallelepiped shape showing the assigned coordinate system (b).

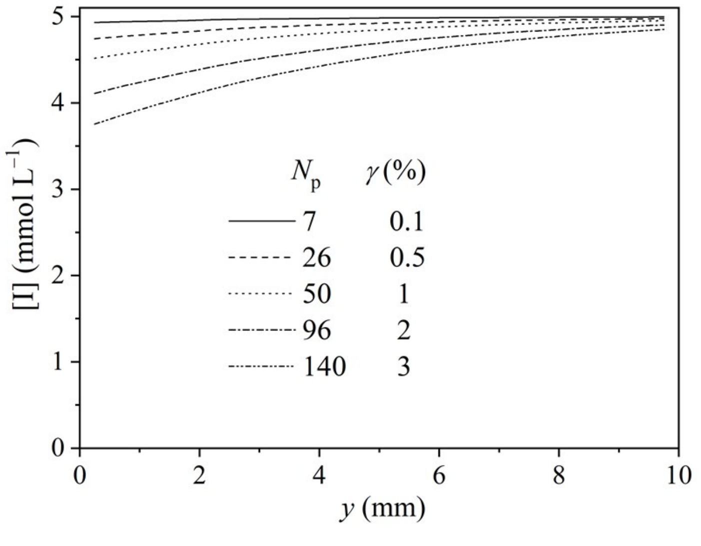

**Figure S2.** The evolution of initiator (DMPA) concentration distributions along the centerline in the *y* direction during PLP of bulk AA at 25 °C at different monomer conversions ($\gamma$) and number of laser pulses ($N_p$). Simulation conditions are [I] = 5 mmol·L$^{-1}$, $E_p$ = 3 mJ and $f$ = 500 Hz. The physical and chemical parameters are taken from Tables S2 and S3.

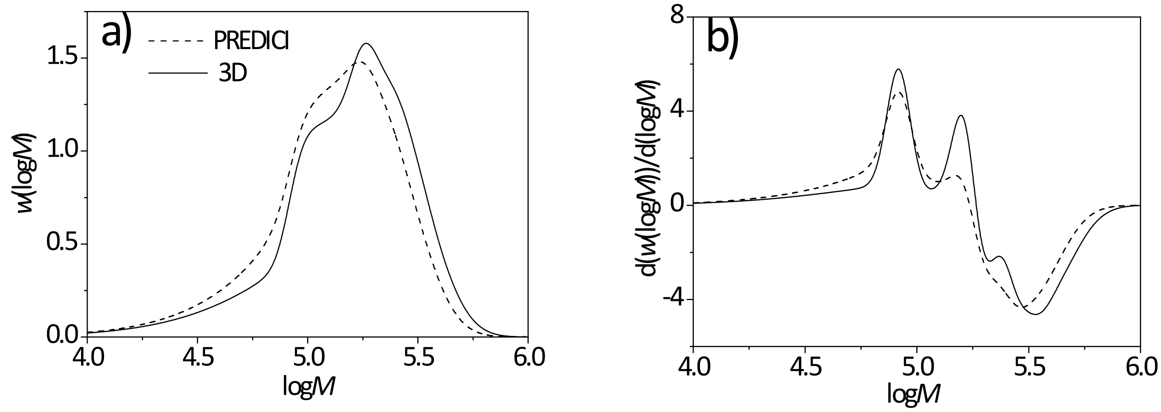

**Figure S3.** MMDs (a) and their first derivative curves (b) obtained by the 3D and PREDICI simulations for AA bulk polymerization at 25 °C. Parameters for the simulations are taken from Tables S2, S3 and S4 of SI with $f$ = 500 Hz, $N_p$ = 15 and $[O_2] = 4.9 \times 10^{-5}$ mol·L$^{-1}$. For the 3D simulation, [I] = 5 mmol·L$^{-1}$, $E_p$ = 3 mJ were used while for the PREDICI simulation $[R_0]$ (the initial concentration of primary radicals) was set to $4 \times 10^{-6}$ mol·L$^{-1}$.

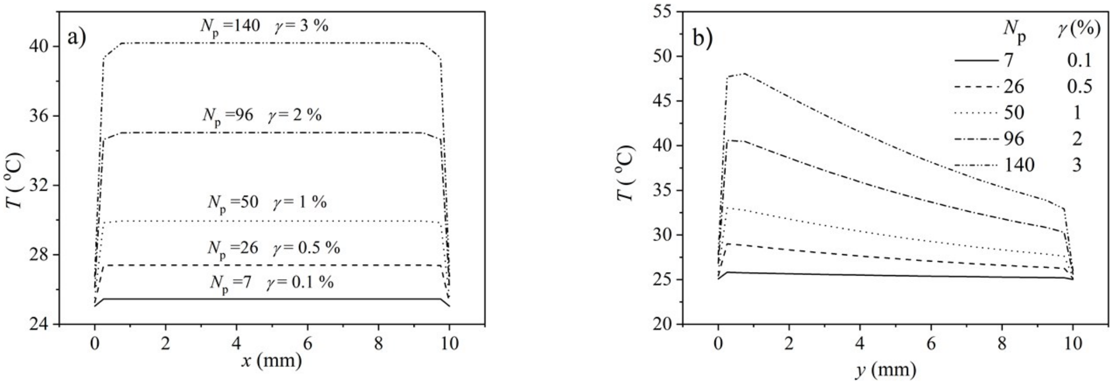

**Figure S4.** The evolution of spatial temperature distributions along the centerline in the $x$(a) and $y$(b) directions during PLP of bulk AA after different $N_p$ and $\gamma$. Initial temperature (that is supported by the temperature control system) for AA polymerization is 25°C. Simulation conditions are [I] = 5 mmol·L$^{-1}$, $E_p$ = 3 mJ and $f$ = 500 Hz. The physical and chemical parameters are taken from Tables S2 and S3.

## Schemes

### Scheme S1. Reactions of ideal model of radical polymerization used in 3D simulation

***Initiation*** $\mathrm{I} \xrightarrow{k_\mathrm{d}} 2\mathrm{R}_0$

$\mathrm{R}_0 + \mathrm{M} \xrightarrow{k_\mathrm{i}} \mathrm{R}_1$

***Propagation*** $\mathrm{R}_\mathrm{i} + \mathrm{M} \xrightarrow{k_\mathrm{p}} \mathrm{R}_{\mathrm{i}+1}$

***Termination by disproportionation***

$\mathrm{R}_\mathrm{i} + \mathrm{R}_\mathrm{m} \xrightarrow{\delta k_\mathrm{t}} \mathrm{P}_\mathrm{i} + \mathrm{P}_\mathrm{m}$

***Termination by combination***

$\mathrm{R}_\mathrm{i} + \mathrm{R}_\mathrm{m} \xrightarrow{(1-\delta) k_\mathrm{t}} \mathrm{P}_{\mathrm{i}+\mathrm{m}}$

### Scheme S2.Additional reactions included in PREDICI simulation

***Backbiting*** $\mathrm{R}_\mathrm{i} \xrightarrow{k_\mathrm{bb}} \mathrm{R}_\mathrm{i}^\mathrm{b}$

***Reinitiation*** $\mathrm{R}_\mathrm{i}^\mathrm{b} + \mathrm{M} \xrightarrow{k_\mathrm{p}^\mathrm{b}} \mathrm{R}_{\mathrm{i}+1}$ (+SCB)

***Chain transfer to monomer***

$\mathrm{R}_\mathrm{i} + \mathrm{M} \xrightarrow{k_\mathrm{trM}} \mathrm{P}_\mathrm{i} + \mathrm{R}_1$

$\mathrm{R}_\mathrm{i}^\mathrm{b} + \mathrm{M} \xrightarrow{k_\mathrm{trM}^\mathrm{t}} \mathrm{P}_\mathrm{i} + \mathrm{R}_1$

***Termination by disproportionation***

$\mathrm{R}_\mathrm{i}^\mathrm{b} + \mathrm{R}_\mathrm{j}^\mathrm{b} \xrightarrow{k_\mathrm{td}^\mathrm{bb}} \mathrm{P}_\mathrm{i} + \mathrm{P}_\mathrm{j}$

$\mathrm{R}_\mathrm{i} + \mathrm{R}_\mathrm{j}^\mathrm{b} \xrightarrow{k_\mathrm{td}^\mathrm{sb}} \mathrm{P}_\mathrm{i} + \mathrm{P}_\mathrm{j}$

***Termination by combination***

$\mathrm{R}_\mathrm{i}^\mathrm{b} + \mathrm{R}_\mathrm{j}^\mathrm{b} \xrightarrow{k_\mathrm{tc}^\mathrm{bb}} \mathrm{P}_{\mathrm{i}+\mathrm{j}}$

$\mathrm{R}_\mathrm{i} + \mathrm{R}_\mathrm{j}^\mathrm{b} \xrightarrow{k_\mathrm{tc}^\mathrm{sb}} \mathrm{P}_{\mathrm{i}+\mathrm{j}}$

## S1 Derivation of equation for the upper level of conversion

In the following derivation it is assumed that the solution of acrylic and propionic acid is ideal. Moreover, the contribution of low concentration of initiator on processes associated with heat transfer in the sample has been ignored.

The sample of volume $V$ contains monomer M and solvent S with masses $m_{\mathrm{M}}$ and $m_{\mathrm{S}}$, respectively. During polymerization, part of monomer $\Delta m_{\mathrm{M}}$ ($\Delta m_{\mathrm{M}} << m_{\mathrm{M}}$) is converted into the polymer resulting in the release of heat $Q$. Considering the polymerization at adiabatic condition, the following expression could be written for the increase of temperature, $\Delta T$, in $V$ from the heat balance

$$\Delta T\left(m_{\mathrm{M}}C_{\mathrm{p}}^{\mathrm{M}}+m_{\mathrm{S}}C_{\mathrm{p}}^{\mathrm{S}}\right)=Q=\frac{\Delta m_{\mathrm{M}}}{M_{\mathrm{M}}}(-\Delta H_{\mathrm{p}}) \tag{S1}$$

where $(-\Delta H_{\mathrm{p}})$ and $M_{\mathrm{M}}$ are the heat of polymerization and the monomer molar mass, $C_{\mathrm{p}}^{\mathrm{M}}$ and $C_{\mathrm{p}}^{\mathrm{S}}$ are the specific heat capacity of monomer and solvent, respectively. When the mass fraction of monomer in solution is expressed as $\varphi=m_{\mathrm{M}}/(m_{\mathrm{M}}+m_{\mathrm{S}})$ and the degree of conversion is $\gamma=\Delta m_{\mathrm{M}}/m_{\mathrm{M}}$ ,following Equation (S2) for the $\Delta T$ could be written from Equation (S1):

$$\Delta T=\frac{\gamma(-\Delta H_{\mathrm{p}})}{M_{\mathrm{M}}C_{\mathrm{p}}^{\mathrm{M}}\left(1+\frac{(1-\varphi)C_{\mathrm{p}}^{\mathrm{S}}}{\varphi C_{\mathrm{p}}^{\mathrm{M}}}\right)} \tag{S2}$$

Assuming that the upper level of conversion results in the same increase of temperature $\Delta T_{\mathrm{u}}$ independently of $\varphi$, following relation can be written for the bulk polymerization ($\varphi$ = 1) of monomer:

$$\Delta T_{\mathrm{u}}=\frac{\gamma_{\mathrm{u}}\left(-\Delta H_{\mathrm{p}}\right)}{M_{\mathrm{M}}C_{\mathrm{p}}^{\mathrm{M}}} \tag{S3}$$

Using Equation (S3) and considering the upper level of conversion by Equation (S2) for the solution polymerization connecting $\Delta T_{\mathrm{u}}$ and $\gamma_{\mathrm{u}}^{\mathrm{S}}$, one derives Equation (2).

## Literature

1. ACRYLIC ACID, https://cameochemicals.noaa.gov/chris/ACR.pdf.
2. 2-Propenoic acid, https://webbook.nist.gov/cgi/cbook.cgi?ID=C79107&Units=SI&Mask=7.
3. PROPIONIC ACID, https://cameochemicals.noaa.gov/chris/PNA.pdf.
4. Acrylic Acid, A Summary of Safety and Handling, 4th Edition 2013, http://msdssearch.dow.com/PublishedLiteratureDOWCOM//dh_0933/0901b80380933166.pdf?filepath=a.
5. E. R. Peterson, PhD, Oklahoma State University, 1985.
6. N. F. G. Wittenberg, PhD, Georg August Universität Göttingen, 2013.
7. TYDEX, Quartz Glass for Optics, http://www.tydexoptics.com/ru/materials/for_transmission_optics/fused_silica/.
8. Quartz glass material Q - fused silica SiO2, http://www.elektrosteklo.ru/FS_visible_rus.htm.
9. J. Lalevée, X. Allonas and J. P. Fouassier, *Macromolecules*, 2006, **39**, 8216-8218.
10. Methyl Acrylate, http://www2.basf.us/acrylicmonomers/pdfs/methacry.pdf
11. C. Barner-Kowollik, S. Beuermann, M. Buback, P. Castignolles, B. Charleux, M. L. Coote, R. A. Hutchinson, T. Junkers, I. Lacík, G. T. Russell, M. Stach and A. M. van Herk, *Polymer Chemistry*, 2014, **5**, 204-212.
12. M. Buback, A. Kuelpmann and C. Kurz, *Macromolecular Chemistry and Physics*, 2002, **203**, 1065-1070.
13. N-butyl acrylate, https://cameochemicals.noaa.gov/chris/BTC.pdf.

14. Butyl acrylate, https://www.arkema.com/export/shared/.content/media/downloads/products-documentations/acrylicmonomers/Butyl-Acrylate-Asia.pdf.

15. J. M. Asua, S. Beuermann, M. Buback, P. Castignolles, B. Charleux, R. G. Gilbert, R. A. Hutchinson, J. R. Leiza, A. N. Nikitin, J.-P. Vairon and A. M. van Herk, *Macromolecular Chemistry and Physics*, 2004, **205**, 2151-2160.

16. A. N. Nikitin, R. A. Hutchinson, M. Buback and P. Hesse, *Macromolecules*, 2007, **40**, 8631-8641.

17. Methyl methacrylate, http://cameochemicals.noaa.gov/chris/MMM.pdf.

18. S. Beuermann, M. Buback, T. P. Davis, R. G. Gilbert, R. A. Hutchinson, O. F. Olaj, G. T. Russell, J. Schweer and A. M. van Herk, *Macromolecular Chemistry and Physics*, 1997, **198**, 1545-1560.

19. M. Buback and C. Kowollik, *Macromolecules*, 1998, **31**, 3211-3215.

20. A. N. Nikitin, I. Lacík and R. A. Hutchinson, *Macromolecules*, 2016, **49**, 9320-9335.