

Supporting Information to

Critically Evaluated Rate Coefficients in Radical Polymerization - 7. Secondary-Radical Propagation Rate Coefficients for Methyl Acrylate in Bulk

*Christopher Barner-Kowollik, Sabine Beuermann, Michael Buback, Patrice Castignolles,
Bernadette Charleux, Michelle L. Coote, Robin A. Hutchinson, Thomas Junkers, Igor Lacík,
Gregory T. Russell, Marek Stach, Alex M. van Herk*

**for individual addresses and affiliations see main manuscript*

EXPERIMENTAL

Chemicals. Methyl acrylate (MA, Aldrich 99 %) stabilized with ≤ 100 ppm monomethyl ether hydroquinone was used after removing of inhibitor by inhibitor remover column (Aldrich). 2,2-dimethoxy-2-phenyl acetophenone (DMPA, Aldrich, 99%) was used as photoinitiator.

Pulsed-laser polymerization. Bulk PLPs were carried out in the temperature range -26.4 to 80 °C using three DMPA concentrations: $0.5 \cdot 10^{-3}$, $5 \cdot 10^{-3}$ and $20 \cdot 10^{-3}$ mol·L⁻¹. The density of MA was obtained from the relation $\rho_{\text{MA}} / \text{g} \cdot \text{cm}^{-3} = 0.9774 \cdot \exp(-1.26 \cdot 10^{-3} \cdot T / ^\circ\text{C})$.¹ The excimer pulsed-laser (ExciStar XS 500, Coherent) operated on the 351 nm XeF line was employed. Pulse repetition rates of 250 and 500 Hz were used at an incident laser energy of about 3 mJ per pulse. Polymerizations were carried out in a QS110 cell (Hellma-Worldwide) with 10 mm path length. The monomer solution was purged with nitrogen for 2 min in the cell and sealed with a PTFE stopper. The polymerization cell was thermostated in the thermostat for about 20 min just prior polymerization, then placed into a thermostated holder and subjected to laser pulsing. Depending on polymerization conditions, between 40 and 200 pulses in a single burst were used to keep conversion below 5%. For sequential PLP experiments, the total number of pulses was divided into 10 sequences of laser pulses with 10 s delay between subsequent sequences of pulses. Post-polymerization was suppressed by pouring the polymerization mixture into a sample vial containing a few crystals of hydroquinone monomethyl ether. High-vacuum drying at ambient temperature to constant weight was used for removing residual MA. The degree of monomer conversion was determined gravimetrically.

Size-exclusion chromatography. Molecular mass distributions of poly(methyl acrylate), poly(MA), samples were obtained by size-exclusion chromatography in THF using a PSS (Mainz, Germany) column setup consisting of an 8 x 50 mm PSS SDV 5 μm guard column and three 8 x 300 mm PSS SDV 5 μm columns with pore sizes 10^2 , 10^3 and 10^5 Å placed in a column heater set to 40 °C. The flow rate of 1 mL·min⁻¹ was controlled by toluene as an internal standard. Loop 100 μL and polymer concentration ~ 3 mg·mL⁻¹ were used. Calibration between 374 and 2 570 000 g·mol⁻¹ was performed by the PSS polystyrene calibration kit. PSS WinGPC^{®8} was used for data acquisition and evaluation. A Waters system (degasser, 515 pump, column heater, DRI 2414) and a Rheodyne injector 7725i were applied as hardware. For evaluation of the MMDs, the MHKS parameters $a = 0.741$ and $K = 10.2 \cdot 10^{-5}$ dL·g⁻¹ and $a = 0.700$ and $K = 14.1 \cdot 10^{-5}$ dL·g⁻¹ for poly(MA)¹ and polystyrene,² respectively, were employed.

Collated PLP–SEC data for methyl acrylate obtained at temperatures above 60 °C

$T / ^\circ\text{C}$	f / Hz	E_p / mJ	$c_1 / \text{mmol}\cdot\text{L}^{-1}$	$k_p / \text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$	Ref
70	500	3.0	5	28094	this work
70	500	3.0	5	27918	this work
70	500	3.0	5	28819	this work
70	500	3.0	5	29321	this work
70.9	500	1.5	5.00	35328	[1]
71.0	500	1.5	5.00	35332	[1]
80	500	3.0	5	29237	this work
80	500	3.0	5	27092	this work
80	500	3.0	5	28301	this work
80	500	3.0	5	27705	this work
81.2	500	1.5	5.00	33123	[1]
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- [1] T. Junkers, M. Schneider-Baumann, S.S.P. Koo, P. Castignolles and C. Barner-Kowollik *Macromolecules*, 2010, **43**, 10427–10434
[2] C. Strazielle, H. Benoit and O. Vogl *Eur. Polym. J.*, 1978, **14**, 331–334