

# A Full Exploitation of the Pulsed Laser Polymerization Technique to Assess All Important Rate Coefficients in Acrylate Radical Polymerization

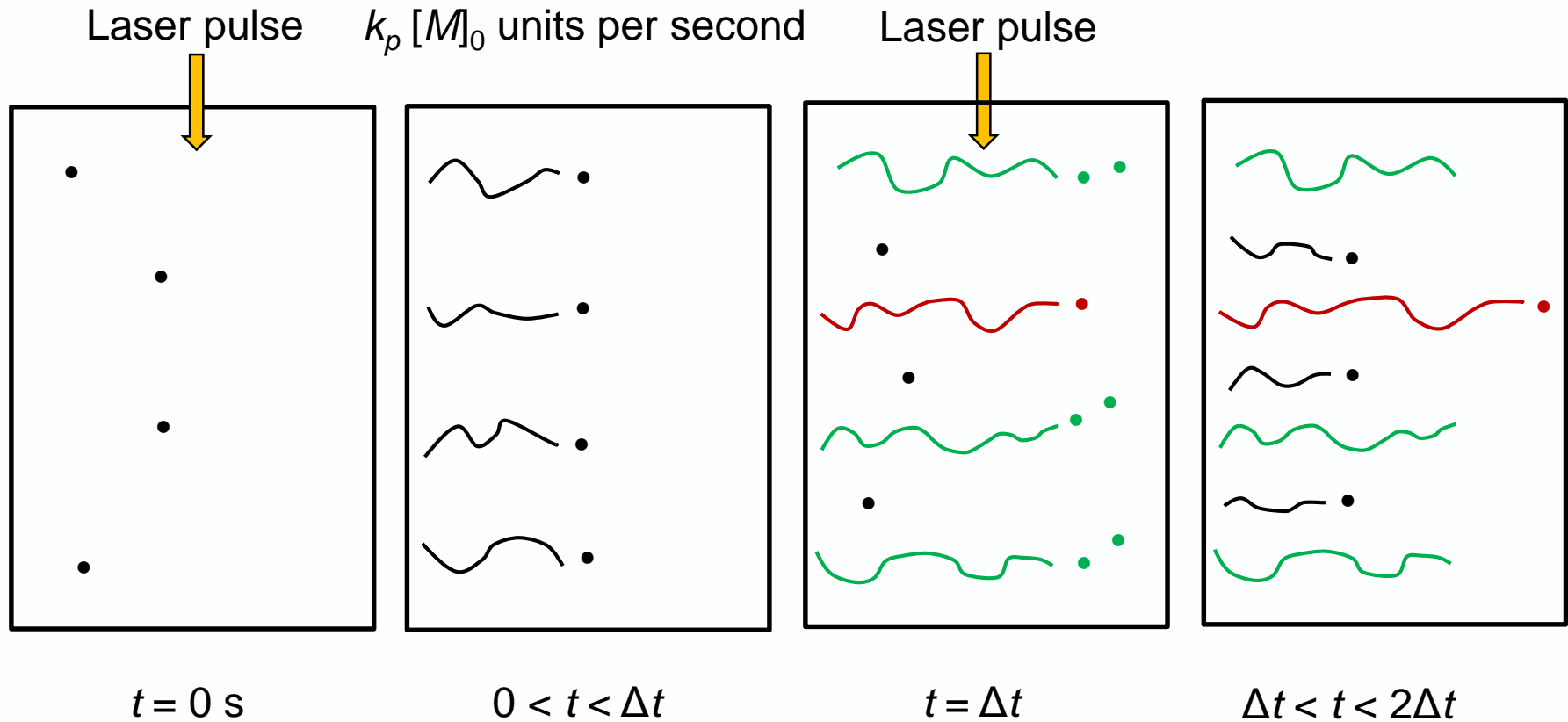
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Christopher Barner-Kowollik,<sup>2,3</sup> Marie-Françoise Reyniers,<sup>1</sup>  
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Technology (QUT)

# Principle of PLP



1 macroradical type

$$L_j = (k_p [M]_0 \Delta t) j$$

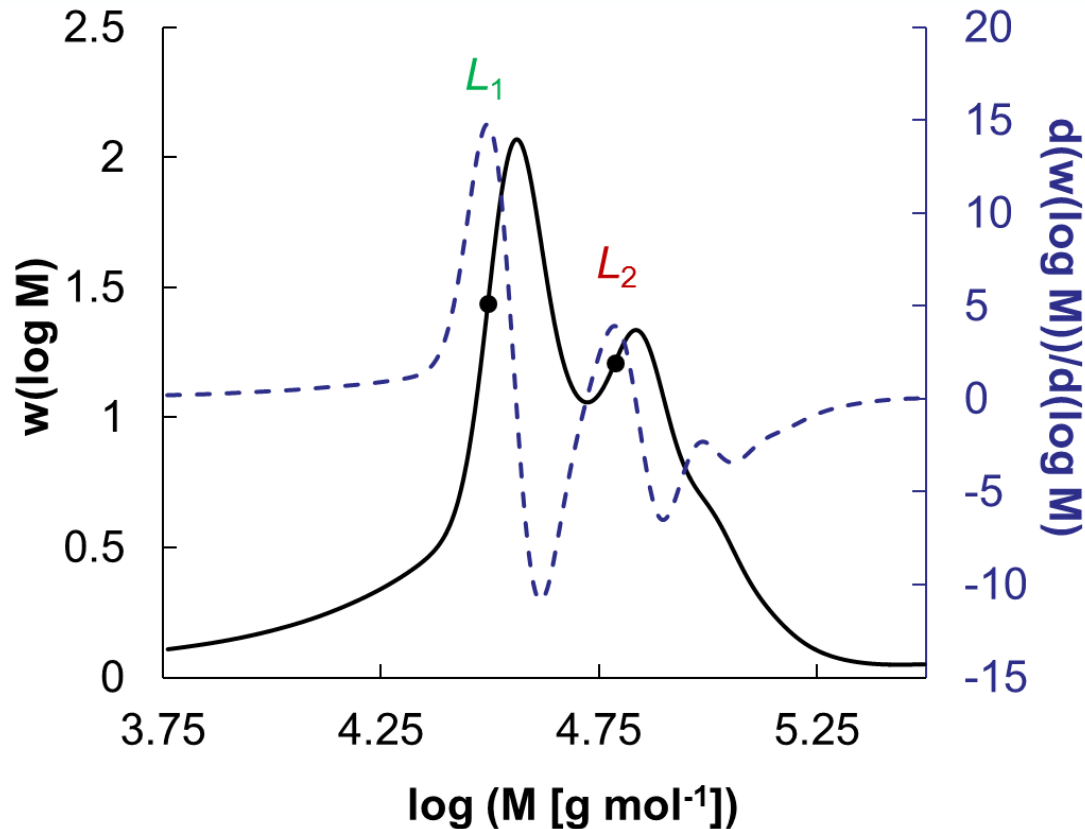
$$j = 1, 2, \dots$$

A. Aleksandrov, V. N. Genkin, M. Kitař, I. Smirnova and V. Sokolov, *Sov. J. Quantum Electron.*, 1977, **7**, 547-550.  
 O. F. Olaj, I. Bitai and F. Hinkelmann, *Macromol. Chem. Phys.*, 1987, **188**, 1689-1702.

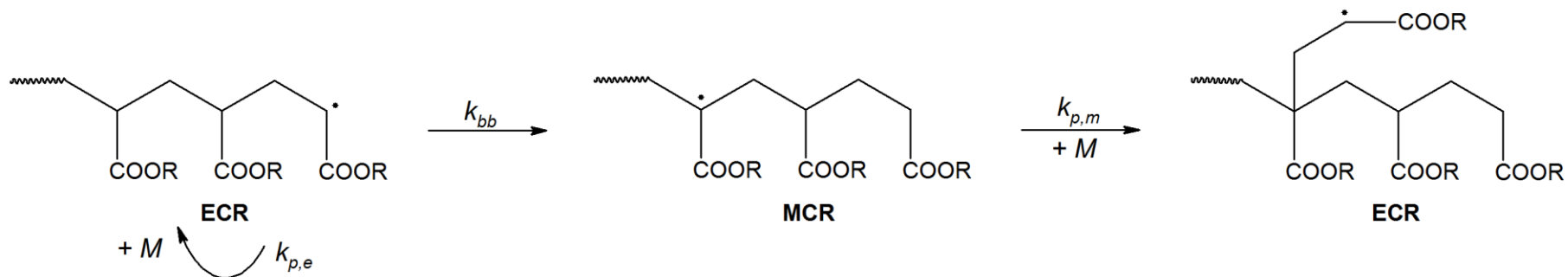
# Practical use of PLP

Size exclusion chromatography (SEC) analysis

$$k_p = L_j [M]_0^{-1} (j\Delta t)^{-1}; j = 1, 2, \dots$$

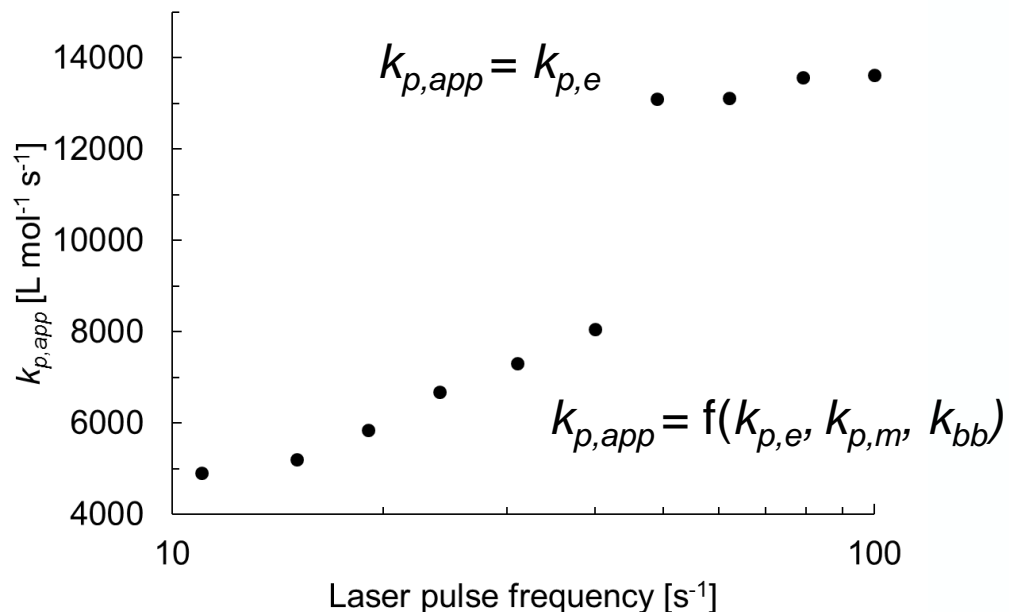


# Backbiting in acrylate PLP



$k_{bb}$  key parameter:

- rate retardation
- short-chain branches



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

B. Wenn and T. Junkers, *Macromol. Rapid Commun.*, 2016, **37**, 781-787.

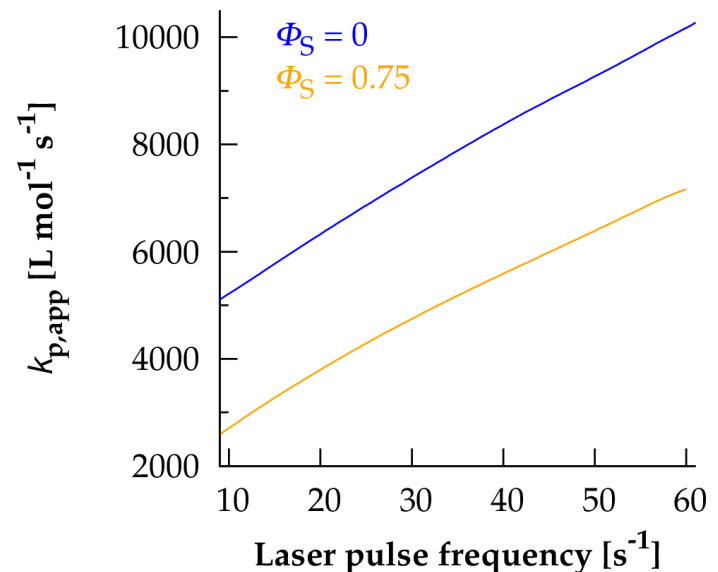
- **Method for the reliable estimation of  $k_{bb}$** 
  - Principle and advantages
  - *In silico* validation
  - Application to PLP of *n*-butyl acrylate
- Detailed analysis of the SEC trace
  - Model validation & visualization of the chain growth pattern
  - Importance of the photodissociation parameter
  - Importance of the chain initiation reactivity
  - Importance of the termination reactivity
- Conclusions

# Principle and advantages

	Equation	Bulk ( $\Phi_S = 0$ )	Solution ( $\Phi_S = 0.75$ )
$\tau_e$ [s]	$\frac{1}{k_{bb}}$	$10^{-3}$	$10^{-3}$
$\tau_m$ [s]	$\frac{1}{k_{p,m}(1 - \Phi_S)[M]_{0,bulk}}$	$1.4 \cdot 10^{-3}$	$5.7 \cdot 10^{-3}$

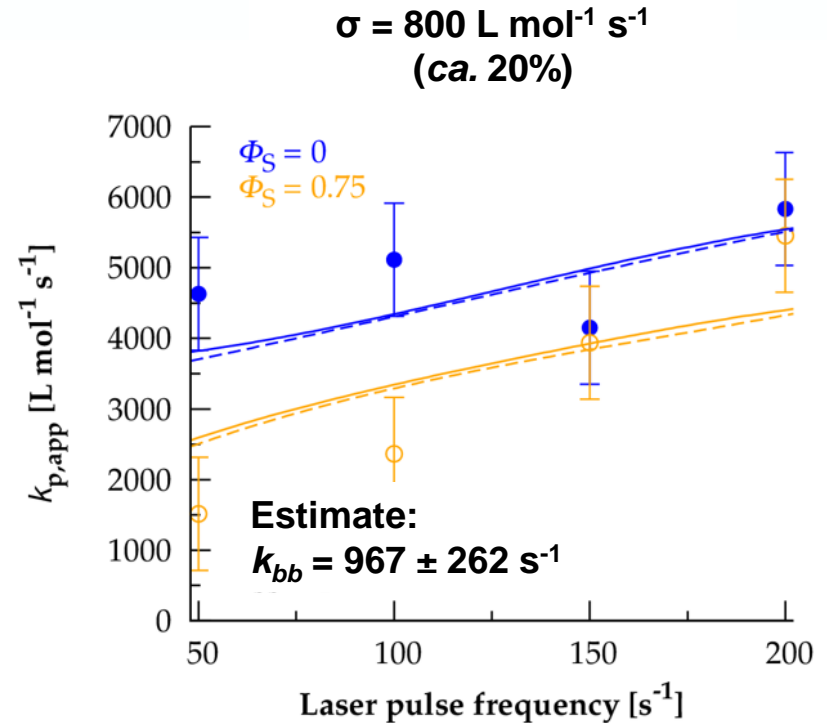
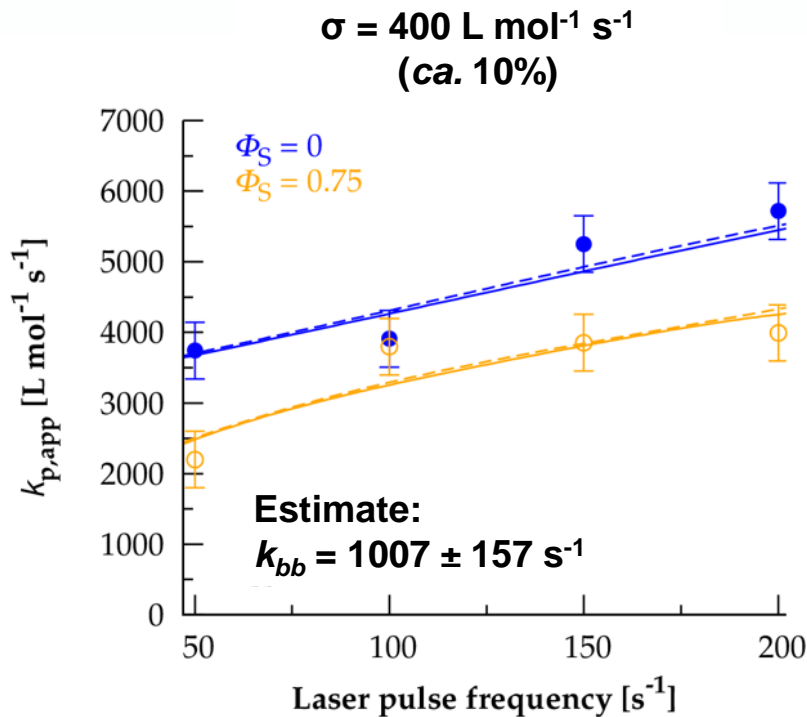
$\Phi_S = 0 \rightarrow \Phi_S = 0.75$ : factor 4 increase in the average MCR lifetime

Variation of  $\Phi_S$  allows to improve the sensitivity toward  $k_{bb}$



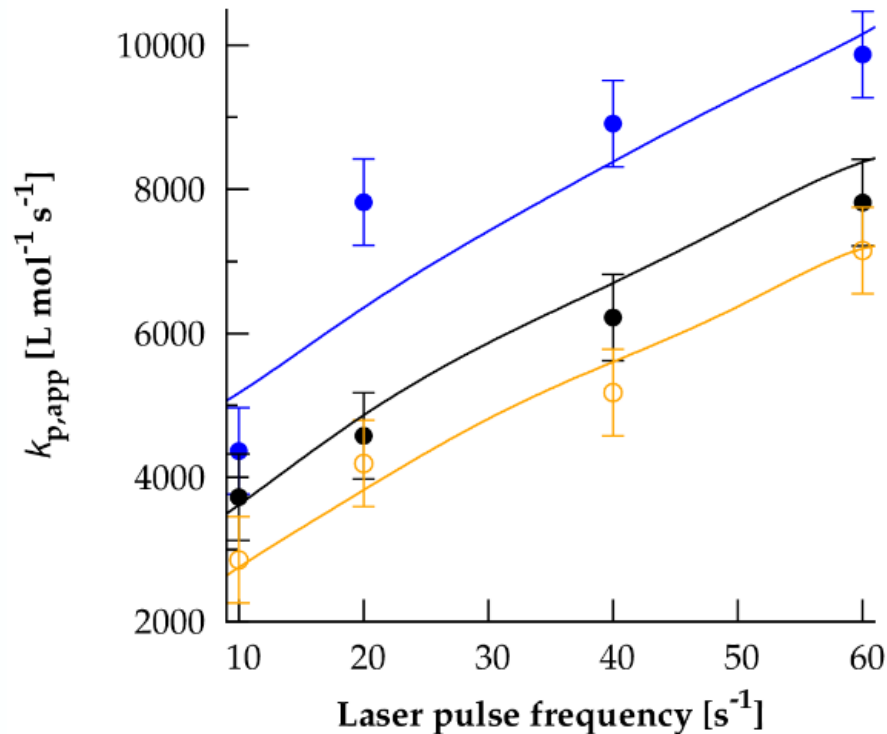
# In silico validation

Regression to simulated  $k_{p,app}$  data ( $k_{bb}$  input = 1000 s<sup>-1</sup>) superimposed with an artificial random error (Gaussian sampling with a standard deviation  $\sigma$ )



**Even for a very large experimental error the method is still very accurate**

Y. W. Marien, P. H. M. Van Steenberge, K. B. Kockler, C. Barner-Kowollik, M.-F. Reyniers, D. R. D'hooge and G. B. Marin, *Polym. Chem.*, 2016, DOI: 10.1039/c6py01468b.

Application to PLP of *n*BuA

$T = 303 \text{ K}$

Solvent: butyl propionate ( $\Phi_S = 0, 0.5, 0.75$ )

$[\text{DMPA}] = 2.5 \cdot 10^{-3} \text{ mol L}^{-1}$

$E_{\text{pulse}} = 1.5 \cdot 10^{-3} \text{ J}$

$k_{bb} = 171 \pm 21 \text{ s}^{-1}$  (95% confidence interval)

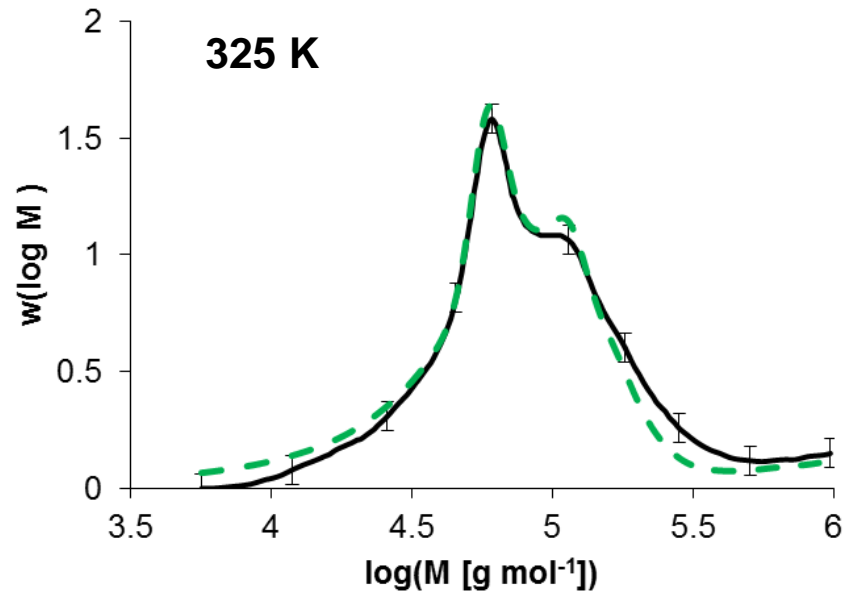
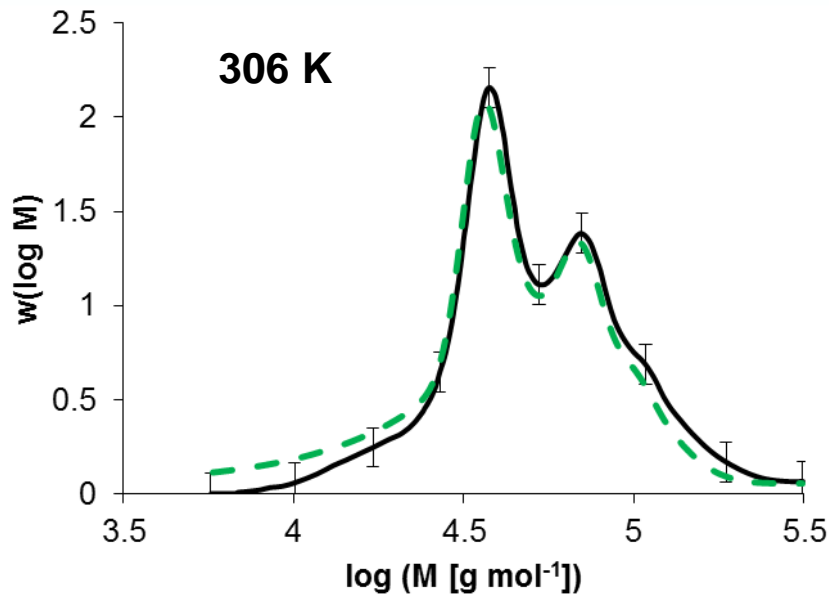
$F = 1084 \gg F_{\text{tab}} = 4.84$

Y. W. Marien, P. H. M. Van Steenberge, K. B. Kockler, C. Barner-Kowollik, M.-F. Reyniers, D. R. D'hooge and G. B. Marin, *Polym. Chem.*, 2016, DOI: 10.1039/c6py01468b.



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# Model validation

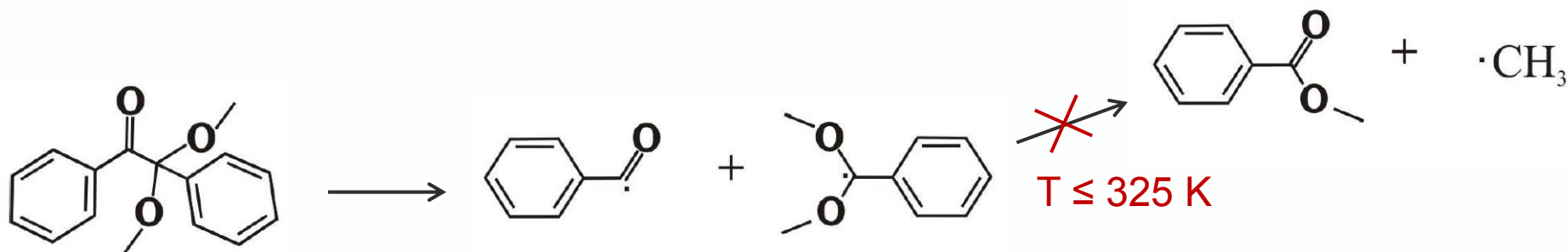


- ✓  $\Delta[R_0] = 2\Phi \frac{E_{pulse}\lambda}{hcN_A V} [1 - \exp(-2.303\varepsilon[I_2]L)]$
- ✓ Different chain initiation reactivity DMPA radical fragments
- ✓ Chain length dependent termination kinetics (composite  $k_t$  model)

Y. W. Marien, P. H. M. Van Steenberge, C. Barner-Kowollik, M. F. Reyniers, D. R. D'hooge and G. B. Marin, *Macromolecules*, 2016 (submitted).

# Hidden information in the SEC trace on chain initiation

DMPA typical photoinitiator



DMPA

Benzoyl radical

Dimethoxy benzyl radical

$k_{ini} \neq 0 \text{ L mol}^{-1} \text{ s}^{-1}$

$k_{ini} = 0 \text{ L mol}^{-1} \text{ s}^{-1}$

→ inhibiting effect

M. Buback, M. Busch and C. Kowollik, *Macromol. Theory Simul.*, 2000, **9**, 442-452.

H. Fischer, R. Baer, R. Hany, I. Verhoolen and M. Walbiner, *J. Chem. Soc.-Perkin Trans. 2*, 1990, 787-798.

C. Barner-Kowollik, P. Vana and T. P. Davis, *J. Polym. Sci. Pol. Chem.*, 2002, **40**, 675-681.

Z. Szablan, T. M. Lovestead, T. P. Davis, M. H. Stenzel and C. Barner-Kowollik, *Macromolecules*, 2007, **40**, 26-39

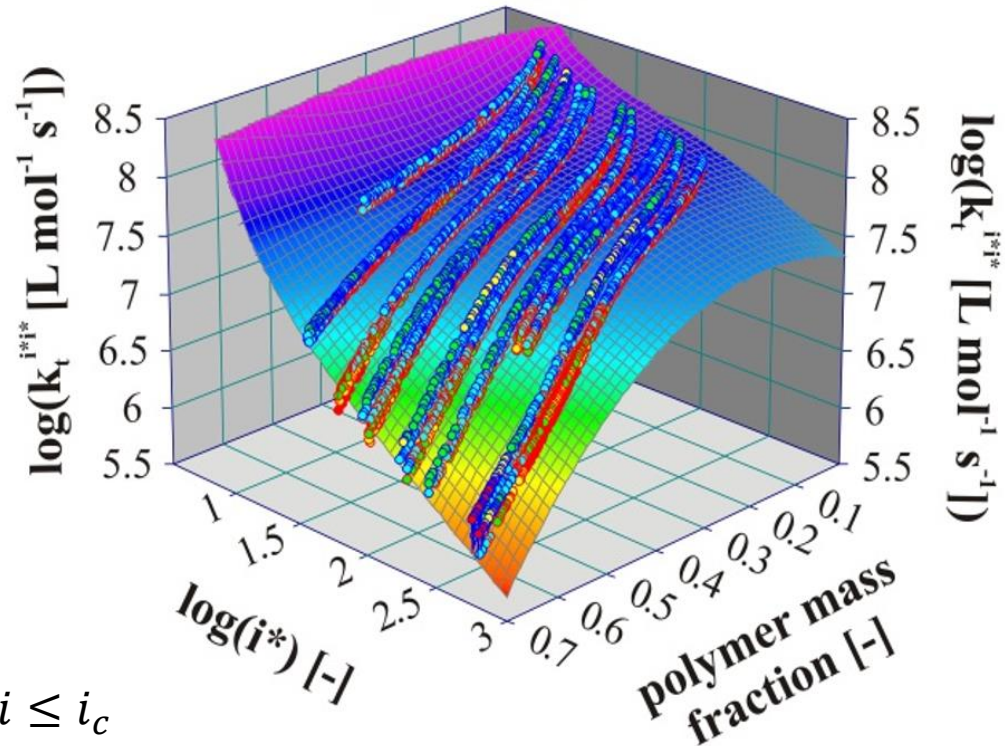
# Hidden information in the SEC trace on termination

- Diffusional limitations
- RAFT-CLD-T technique
- PLP: low conversions

Composite  $k_t$  model:

$$k_t^{app}(i, i) = k_t^{app}(1, 1) i^{-\alpha_S} \quad i \leq i_c$$

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



P. Derboven, D. R. D'hooge, M.-F. Reyniers, G. B. Marin and C. Barner-Kowollik, *Macromolecules*, 2015, **48**, 492-501.

# Visualization of the chain growth pattern

- Method for the reliable estimation of  $k_{bb}$ 
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# Importance of $\Delta[R_0]$

Negligible effect on position  
inflection point

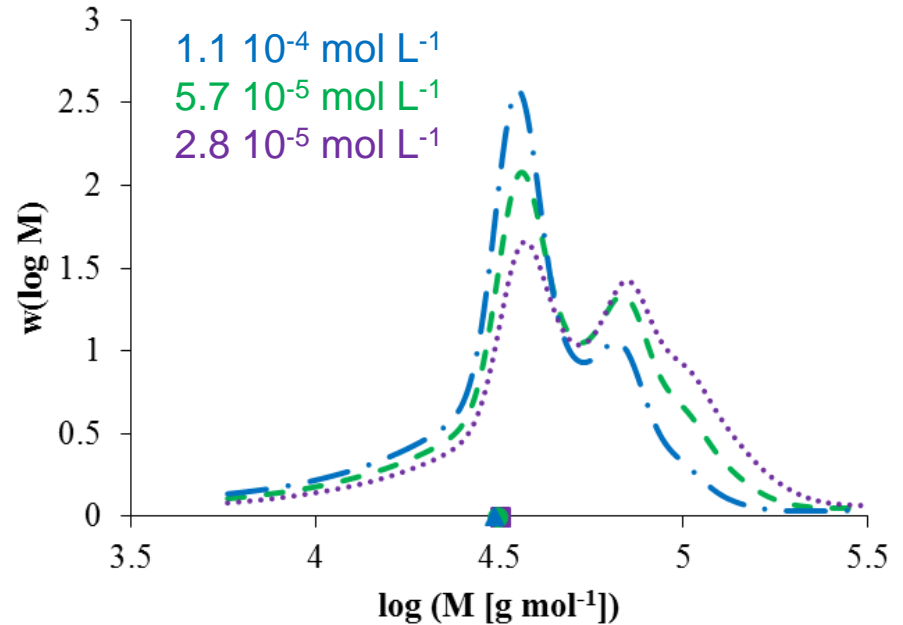
Strong effect on peak intensities

$\Delta[R_0] \gg$ : consistency check not  
possible

## Design of PLP experiments:

1. Identification correct order of  
magnitude  $\Delta[R_0]$
2. Selection adequate values for  $E_{\text{pulse}}$  and  $[I_2]$  via:

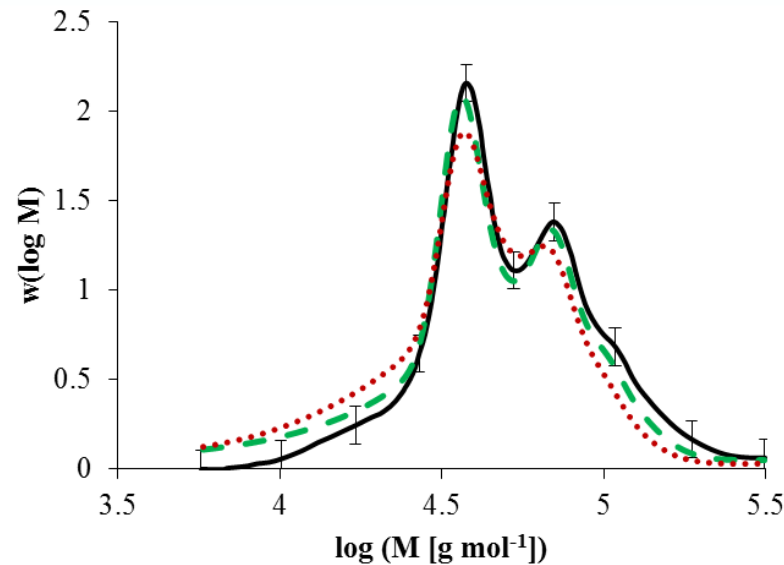
$$\Delta[R_0] = 2\Phi \frac{E_{\text{pulse}}\lambda}{hcN_A V} [1 - \exp(-2.303\varepsilon[I_2]L)]$$



# Importance of the chain initiation reactivity

## Assuming equal chain initiation reactivity:

- Conversion is overestimated
- A less distinct second peak is obtained, unfavorable for  $k_p$  determination

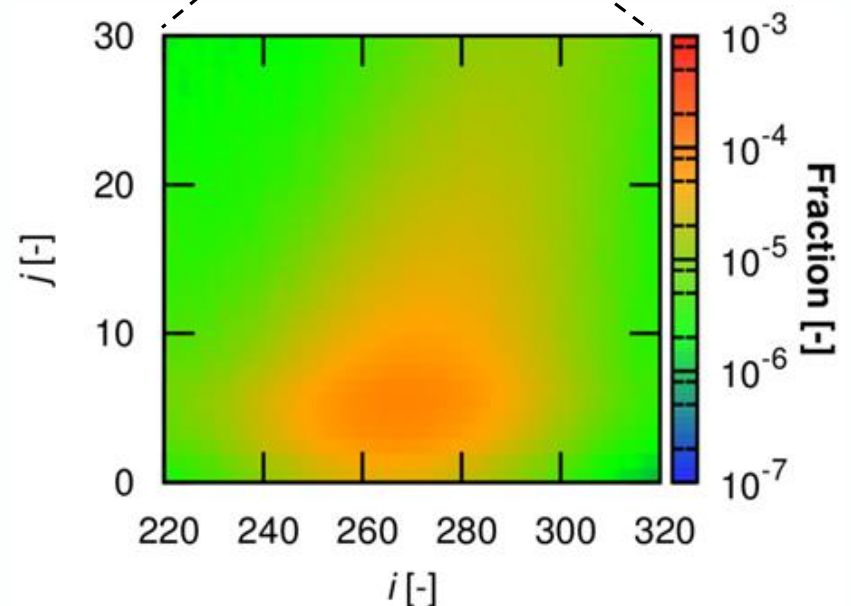
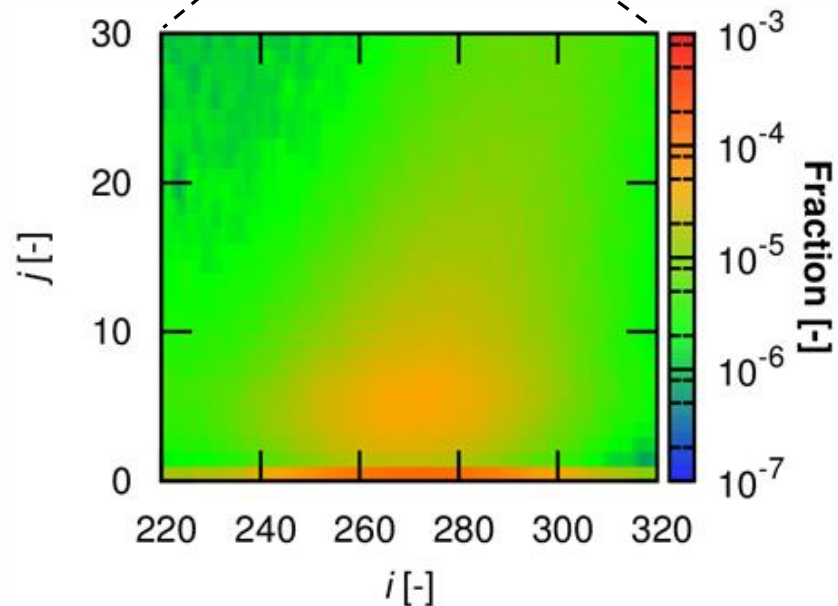
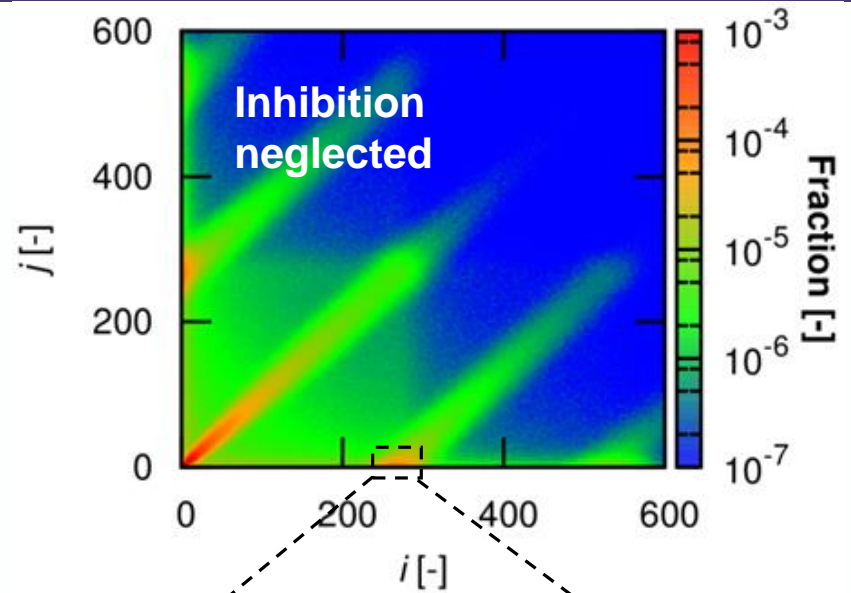
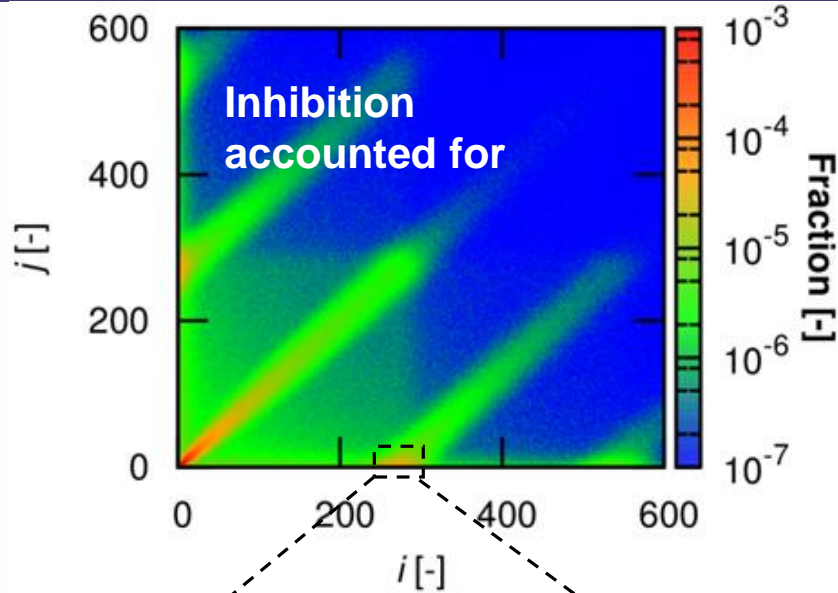


DMPA is an ideal photoinitiator due to its **non-ideal character**

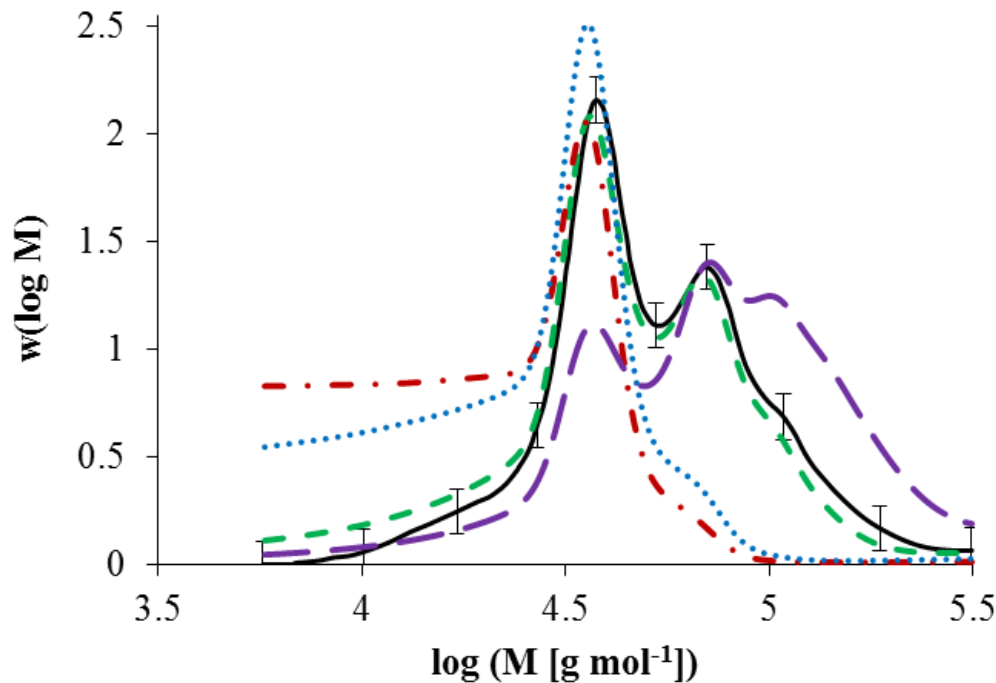
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# Importance of the chain initiation reactivity (2)



# Importance of CLD-T kinetics



Experiment†

$$k_t^{app}(i, i) = k_t^{app}(1, 1) i^{-\alpha_S} \quad i \leq i_c$$

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

$$k_t^{app}(i, i) = k_t^{app}(1, 1) i^{-\alpha_L}$$

$$k_t^{app}(i, i) = k_t^{app}(1, 1) i^{-\alpha_S}$$

$$k_t^{app}(i, i) = k_t^{app}(1, 1)$$

(Parameters‡:  $\alpha_S = 0.85$ ,  $\alpha_L = 0.16$ ,  $i_c = 30$ )

No CLD-T and single  $\alpha$  ( $\alpha_L$ ) leads to an overestimation the lower chain lengths

Single  $\alpha$  ( $\alpha_S$ ) leads to an overestimation of the higher chain lengths

Only the composite model yields a good fit with the experimentally recorded MMD

† C. Barner-Kowollik, F. Gunzler and T. Junkers, *Macromolecules*, 2008, **41**, 8971-8973.

‡ J. Barth, M. Buback, P. Hesse and T. Sergeeva, *Macromolecules*, 2010, **43**, 4023-4031.

# Conclusions

- Method for the reliable estimation of  $k_{bb}$ 
  - Low frequency  $k_{p,app}$  data  $\rightarrow$  less expensive PLP equipment
  - Variation of  $\Phi_S \rightarrow$  high sensitivity toward  $k_{bb}$
  - *In silico* validation + successful application to PLP of *n*BuA
- Detailed analysis of the SEC trace
  - Measured SEC traces accurately simulated
  - Disparate reactivities DMPA radical fragments confirmed and shown to be beneficial
  - Validity of models for apparent termination rate coefficients tested at low monomer conversions

# Acknowledgements

- Long Term Structural Methusalem Funding by the Flemish Government
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