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

Yoshi Marien,¹ Paul Van Steenberge,¹ Katrin Kockler,² Christopher Barner-Kowollik,²,³ Marie-Françoise Reyniers,¹ Dagmar D'hooge,¹ and Guy B. Marin¹

¹Laboratory for Chemical Technology (LCT), Ghent University
²Preparative Macromolecular Chemistry, Karlsruhe Institute of Technology (KIT)
³School of Chemistry, Physics and Mechanical Engineering, Queensland University of Technology (QUT)
Principle of PLP

Laser pulse \( k_p [M]_0 \) units per second

\[ \begin{align*}
  &\text{Laser pulse} & \text{\( k_p [M]_0 \) units per second} & \text{Laser pulse} \\
  &\text{\( t = 0 \) s} & \text{\( 0 < t < \Delta t \)} & \text{\( t = \Delta t \)} & \text{\( \Delta t < t < 2\Delta t \)} \\
  &1 \text{ macroradical type} & \text{\( L_j = (k_p [M]_0 \Delta t) \) } & j = 1, 2, \ldots
\end{align*} \]

Size exclusion chromatography (SEC) analysis

\[ k_p = L_j [M]_0^{-1} (j \Delta t)^{-1}; \ j = 1, 2, \ldots \]
$k_{bb}$ key parameter:

- rate retardation
- short-chain branches


• **Method for the reliable estimation of** $k_{bb}$
  
  o Principle and advantages
  
  o *In silico* validation
  
  o Application to PLP of $n$-butyl acrylate

• Detailed analysis of the SEC trace
  
  o Model validation & visualization of the chain growth pattern
  
  o Importance of the photodissociation parameter
  
  o Importance of the chain initiation reactivity
  
  o Importance of the termination reactivity

• Conclusions
### Principle and advantages

<table>
<thead>
<tr>
<th>Equation</th>
<th>Bulk ($\Phi_S = 0$)</th>
<th>Solution ($\Phi_S = 0.75$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau_e [s]$</td>
<td>$\frac{1}{k_{bb}}$</td>
<td>$10^{-3}$</td>
</tr>
<tr>
<td>$\tau_m [s]$</td>
<td>$\frac{1}{k_{p,m}(1 - \Phi_S)[M]_0,bulk}$</td>
<td>$1.4 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

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

Variation of $\Phi_S$ allows to improve the sensitivity toward $k_{bb}$
Regression to simulated $k_{p,\text{app}}$ data ($k_{bb}$ input = 1000 s$^{-1}$) 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

Application to PLP of $n$BuA

$T = 303$ K

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

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

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

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

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

• Method for the reliable estimation of $k_{bb}$
  o Principle and advantages
  o \textit{In silico} validation
  o Application to PLP of \textit{n}-butyl acrylate

• \textbf{Detailed analysis of the SEC trace}
  o Model validation & visualization of the chain growth pattern
  o Importance of the photodissociation parameter
  o Importance of the chain initiation reactivity
  o Importance of the termination reactivity

• Conclusions
Model validation

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

- Different chain initiation reactivity DMPA radical fragments
- Chain length dependent termination kinetics (composite \(k_t\) model)

Hidden information in the SEC trace on chain initiation

DMPA typical photoinitiator

DMPA $\xrightarrow{\text{Benzoyl radical}}$ $\text{Dimethoxy benzyl radical}$

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

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

$\rightarrow$ inhibiting effect

Hidden information in the SEC trace on termination

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

Composite $k_t$ model:

$$k_{t}^{\text{app}}(i, i) = k_{t}^{\text{app}}(1,1)i^{-\alpha_s} \quad i \leq i_c$$

$$k_{t}^{\text{app}}(i, i) = k_{t}^{\text{app}}(1,1)i_c^{-\alpha_s+\alpha_L}i^{-\alpha_L} \quad i > i_c$$

Visualization of the chain growth pattern
Outline

• Method for the reliable estimation of $k_{bb}$
  o Principle and advantages
  o *In silico* validation
  o Application to PLP of $n$-butyl acrylate

• **Detailed analysis of the SEC trace**
  o Model validation & visualization of the chain growth pattern
  o **Importance of the photodissociation parameter**
    o Importance of the chain initiation reactivity
    o Importance of the termination reactivity

• Conclusions
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:

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

Importance of the chain initiation reactivity (2)
Importance of CLD-T kinetics

\[ k_{t}^{\text{app}}(i, i) = k_{t}^{\text{app}}(1,1)i^{-\alpha_S} \quad i \leq i_c \]
\[ k_{t}^{\text{app}}(i, i) = k_{t}^{\text{app}}(1,1)i_{c}^{-\alpha_S+\alpha_L}i^{-\alpha_L} \quad i > i_c \]

\[ k_{t}^{\text{app}}(i, i) = k_{t}^{\text{app}}(1,1)i^{-\alpha_L} \]
\[ k_{t}^{\text{app}}(i, i) = k_{t}^{\text{app}}(1,1)i^{-\alpha_S} \]
\[ k_{t}^{\text{app}}(i, i) = k_{t}^{\text{app}}(1,1) \]

(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

Conclusions

• Method for the reliable estimation of $k_{bb}$
  o Low frequency $k_{p,app}$ data $\rightarrow$ less expensive PLP equipment
  o Variation of $\Phi_S$ $\rightarrow$ high sensitivity toward $k_{bb}$
  o *In silico* validation + successful application to PLP of $n$BuA

• Detailed analysis of the SEC trace
  o Measured SEC traces accurately simulated
  o Disparate reactivities DMPA radical fragments confirmed and shown to be beneficial
  o Validity of models for apparent termination rate coefficients tested at low monomer conversions
Acknowledgements

- Long Term Structural Methusalems Funding by the Flemish Government
- Interuniversity Attraction Poles Program – Belgian State – Belgian Science Policy
- Fund for Scientific Research Flanders (FWO; G.0065.13N)
- STN program of the Helmholtz association (Karlsruhe Institute of Technology)