Pulsed Laser Polymerization Revisited: From the Photodissociation Quantum Yield to the Chain Initiation, Propagation, Backbiting and Termination Reactivity

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Pulsed laser polymerization (PLP) is a well-established technique for the measurement of the propagation rate coefficient k_p.[1, 2] In PLP, photoinitiator radical fragments are generated at laser pulses with a frequency ν (or dark time $\Delta t = \nu^{-1}$), which under well-defined conditions leads to a multimodal molar mass distribution (MMD). Its inflection points L_j (j = 1, 2, …) can be directly linked to k_p via ($[M]_0$ = initial monomer concentration):

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

Recently, also the backbiting rate coefficient k_{bb} has been determined by performing PLP experiments at varying ν.[3-5] In this work,[5] it is demonstrated that by additionally varying the solvent volume fraction, it suffices to scan the low ν-range (Figure 1; middle), for which less expensive PLP equipment can be used, thus facilitating the determination of k_{bb} for a wide monomer range, an important task both from an academic and industrial point of view.

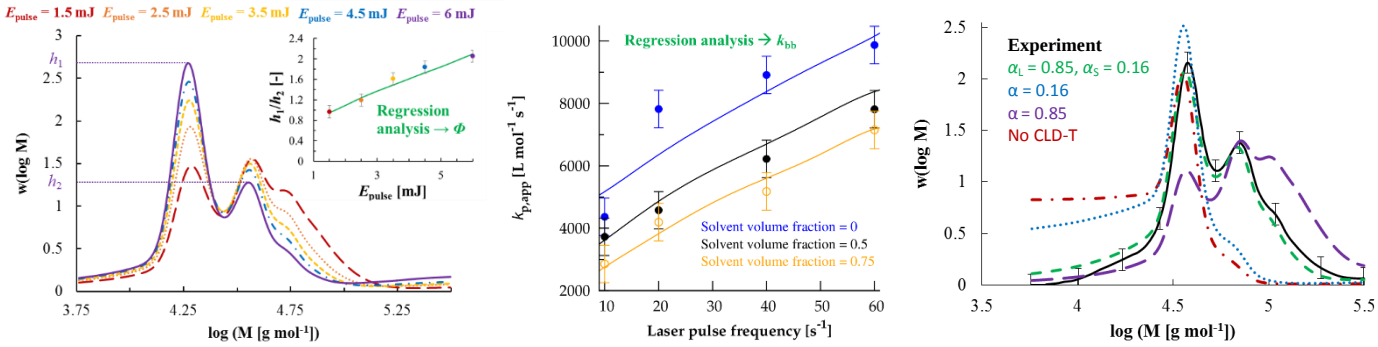

Figure 1. PLP applied for the estimation of Φ (left) and k_{bb} (middle), and benchmarking of $k_{t,app}$ models (right).

Moreover, via detailed kinetic Monte Carlo (*k*MC) simulations of acrylate PLP it is demonstrated that information on the photodissociation, chain initiation and termination reactivity can be extracted from the complete PLP MMD.[6] In particular, the peak heights can be used for the reliable estimation of the photodissociation quantum yield Φ (Figure 1; left).[7] In addition, for 2,2-dimethoxy-2-phenylacetophenone (DMPA), the typical photoinitiator for PLP, the disparate reactivities of the radical fragments are shown to be crucial for obtaining a well-defined multimodal MMD. Finally, typically used models for the apparent termination reactivity $k_{t,app}$ can be benchmarked at low monomer conversions, *i.e.* conditions not easily accessible with other techniques such as the RAFT-CLD-T technique[8] (Figure 1; right).

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