

A NOVEL INTERPRETATION OF MEASURED AND SIMULATED PLP DATA

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Key Words: kinetic modeling, polymerization kinetics, rate coefficients, *n*-butyl acrylate, vinyl acetate

Pulsed laser polymerization (PLP) is an interesting technique to study individual reactions.¹⁻⁴ In PLP, photoinitiator radical fragments are generated at laser pulses with a frequency ν (or dark time $\Delta t = \nu^{-1}$). Depending on the PLP conditions and the monomer type, the molar mass distribution (MMD) can possess specific characteristics, allowing the determination of intrinsic rate coefficients. Most known is that under well-chosen conditions a multimodal MMD with inflection points L_j ($j = 1, 2, \dots$) is obtained, allowing the determination of the propagation rate coefficient k_p ($[M]_0$: initial monomer concentration):

$$k_p = \frac{L_j}{[M]_0(j\Delta t)} \quad (1)$$

In this contribution, kinetic Monte Carlo (*kMC*) modeling is applied to allow a further understanding and exploitation of PLP. For PLP of acrylates, regression analysis to low frequency inflection point data at various solvent volume fractions is proposed as an additional new method to estimate the backbiting rate coefficient k_{bb} .⁵ Moreover, it is demonstrated that photodissociation, chain initiation and termination reactivities can be extracted from the complete PLP MMD.⁶ For the first time, the ratio of MMD peak heights has been used for the fast and reliable estimation of the photodissociation quantum yield Φ .⁷ For PLP of vinyl acetate a unique combination of *ab initio* calculated rate coefficients and *kMC* simulations is considered to explain the experimental⁸ ν dependency of the observed k_p (cf. Case 4 in Figure 1; Eq. (1) with k_p^{obs}). Via a stepwise extension of the *kMC* model (cf. 4 cases in Figure 1), the ν dependency is attributed to backbiting of tail radicals formed via head-to-head propagation.⁹ In contrast to acrylates, backbiting of head radicals is shown to be kinetically insignificant in VAc PLP, further highlighting the chemical difference between both vinyl monomer types.

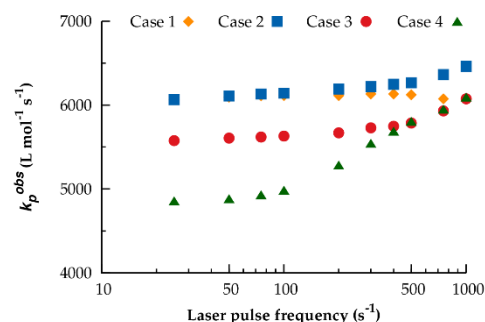


Figure 8 - Simulated ν dependency of the observed k_p in vinyl acetate PLP at 323 K. Case 1 (\blacklozenge): chain length independent head-to-tail prop., Case 2 (\blacksquare): chain length dependent head-to-tail prop., Case 3 (\bullet): chain length dependent head-to-tail, head-to-head, tail-to-tail, and tail-to-head prop., and Case 4 (\blacktriangle): Case 3 with backbiting by head and tail radicals, and mid-chain prop.

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