A NOVEL INTERPRETATION OF MEASURED AND SIMULATED PLP DATA

Yoshi W. Marien, Laboratory for Chemical Technology, Ghent University
Paul H.M. Van Steenberge, Laboratory for Chemical Technology, Ghent University
Gilles B. Desmet, Laboratory for Chemical Technology, Ghent University
Christopher Barner-Kowollik, School of Chemistry, Physics and Mechanical Engineering, Queensland University of Technology; Macromolecular Architectures, Institut für Technische Chemie und Polymerchemie and Institut für Biologische Grenzflächen, Karlsruhe Institute of Technology
Marie-Françoise Reyniers, Laboratory for Chemical Technology, Ghent University
Guy B. Marin, Laboratory for Chemical Technology, Ghent University
Dagmar R. D’hooge, Laboratory for Chemical Technology and Centre for Textile Science and Engineering, Ghent University

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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 \(v\) (or dark time \(\Delta t = \frac{1}{v}\)). 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 \(L_i (i = 1, 2, \ldots)\) is obtained, allowing the determination of the propagation rate coefficient \(k_p\) ([\(M_0\]: initial monomer concentration]):

\[
k_p = \frac{l_i}{[M_0] \Delta t} \quad (1)
\]

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 \(\Phi\).\(^7\) For PLP of vinyl acetate a unique combination of \textit{ab initio} calculated rate coefficients and kMC simulations is considered to explain the experimental\(^8\) \(v\) dependency of the observed \(k_p\) (cf. Case 4 in Figure 1; Eq. (1) with \(k_p^{absc}\)). Via a stepwise extension of the kMC model (cf. 4 cases in Figure 1), the \(v\) 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.