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Critically evaluated propagation rate coefficients for radical polymerizations: acrylates and vinyl acetate in bulk (IUPAC Technical Report)<https://doi.org/10.1515/pac-2018-1108>

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Abstract: Arrhenius parameters capturing the temperature dependence of radical polymerization propagation rate coefficients, k_p , for methyl acrylate, butyl acrylate, and vinyl acetate in bulk are reported, based on the fitting of benchmark data sets compiled from independent laboratories using the pulsed-laser polymerization/size exclusion chromatography method. The reported k_p values for acrylates hold for secondary-radical propagation and are needed to calculate effective propagation rate coefficients in situations where there is a significant population of mid-chain acrylate radicals resulting from backbiting, as will be the case at technically relevant temperatures. The results are compared to those previously reported for styrene and methacrylates to highlight the large differences in k_p values seen between the major monomer families.

Keywords: kinetics; polymer chemistry; polymerization; radical reactions.

Dedicated to: the memory of Prof. Dr. Oskar Friedrich Olaj for his contributions to the field of polymerization kinetics, including the introduction of the PLP-SEC method to experimentally determine radical propagation rate coefficients.

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1 Introduction

The development of the PLP-SEC method – pulsed-laser polymerization (PLP) combined with analysis of the chain-length distribution of the resulting polymer by size exclusion chromatography (SEC) – for determination of the propagation rate coefficient, k_p , has been of utmost importance in the investigation of the kinetics of radical polymerization. As summarized in previous technical reports [1–3], members of the Polymer Division Subcommittee on “Modeling of Polymerization Kinetics and Processes” have compiled

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critically-evaluated data from PLP-SEC experiments performed in several laboratories worldwide to report benchmark values of k_p for styrene [4] and methacrylate monomers [5–7] in bulk, as well as for methacrylic acid in aqueous solution [3]. The data, fit to provide Arrhenius parameters to allow estimation of k_p over a wide temperature range, have led to an improved understanding of propagation and have facilitated the reliable determination of associated rate coefficients for termination and transfer events in radical polymerizations.

The widespread adoption of the PLP-SEC technique to measure propagation rates stems from its ease of use and its reliability. Monomer containing a low concentration of photoinitiator (generally 1 to 10 mmol · L⁻¹) at a controlled temperature is exposed to periodic UV laser flashes for sufficient time (generally a few seconds to several minutes) to achieve fractional monomer conversion. The resulting polymer molar mass distribution (MMD) is analyzed off-line (typically by SEC) with k_p determined from a characteristic degree of polymerization L_i , using the simple relationship:

$$L_i = i \cdot k_p \cdot [M] \cdot t_d \quad (1)$$

where $[M]$ is the monomer concentration and t_d is the separation time between the periodic laser pulses [1–7]. Each pulse generates a new population of radicals, instantaneously (on the timescale of the kinetic events under investigation) increasing the probability for terminating the radicals generated by the i^{th} previous pulse, these having propagated up to the average (and near monodisperse) chain length L_i during the time interval $i \cdot t_d$. This enhanced termination results in features in the MMD – either peaks or distinct shoulders – that are identified by differentiation, with the maxima from the derivative plot providing the best estimate of k_p using eq. 1 [1, 4, 5]. Analysis of the MMD also provides an essential consistency check for the validity of the k_p estimate through the occurrence of a secondary inflection point located at twice the chain length of the first inflection point: $L_2 \approx 2 L_1$, with higher inflection points also seen for some systems. Further consistency criteria are the independence of the obtained value on initiator concentration, laser power, and pulse repetition rate. The uncertainty in the resultant estimates of k_p (generally regarded to be within 10 % based on analysis of the benchmark data sets [4–7]) is contingent on careful SEC analysis utilizing the principal of universal calibration verified by multi-detector analysis, as outlined in previous work [2, 3, 6, 7].

The PLP-SEC technique was successfully applied to styrene and methacrylates using pulse repetition rates from 1 to 50 Hz over temperatures ranging from 0 to 90 °C. While a significant difference in propagation rate coefficients was found between styrene (activation energy E_A of 32.5 kJ · mol⁻¹, with a k_p value of 69 dm³ · mol⁻¹ · s⁻¹ at 20 °C) [4] and methyl methacrylate (MMA, with an E_A of 22.4 kJ · mol⁻¹ and a k_p value of 273 dm³ · mol⁻¹ · s⁻¹ at 20 °C) [5], family-type behavior was found for the methacrylates having different ester groups, with E_A values within a narrow band of 21 to 23 kJ · mol⁻¹ [2, 6, 7]. Within the methacrylate family, values of bulk k_p increase by 50 % with the size of the linear ester group from MMA to dodecyl methacrylate (DMA) [6]. Values of k_p for cyclic methacrylate esters, such as benzyl, cyclohexyl, and oxiranylmethyl (commonly known as glycidyl), and for 4,7,7-trimethylbicyclo[2.2.1]heptan-3-yl (commonly known as isobornyl) are double that of MMA, and are represented with less than 15 % variation by a single Arrhenius relation [7].

While this approach was successfully applied to styrene and methacrylates by several research groups in the 1990s, as summarized in the IUPAC benchmark papers [4, 7], it proved difficult to achieve similar results for vinyl acetate and acrylates, important components of polymeric coatings and adhesives. Significant difficulties were encountered in the determination of k_p by PLP-SEC for these monomers due to their more rapid chain-growth kinetics, as well as the occurrence of side reactions. Dating back to the 1991 study by Davis *et al.* [8], it was found that, rather than producing well-structured distributions, the PLP-generated polyacrylate MMDs were broad and indistinct, as was also found in a 1994 study of vinyl acetate (VAc) [9]. Extensive investigation of these phenomena over the past two decades has led to consensus and the publication of benchmark PLP-SEC data sets for two alkyl acrylates (methyl and butyl) and for vinyl acetate in bulk. The resulting Arrhenius parameters are summarized and compared to those for styrene and alkyl methacrylates in this report in order to contrast the differences in k_p for various monomer families.

2 Results

2.1 Acrylates

Early PLP-SEC investigations showed that poly(alkyl acrylate) MMDs generated at 100 Hz or lower and at temperatures above 20 °C showed, at best, a broadened PLP structure and, at worst, no PLP structure at all [8, 10, 11]. Various hypotheses were put forward to interpret these results, including high rates of transfer to monomer, significant exotherms during laser illumination, and intermolecular chain transfer to polymer confounding accurate MMD analysis by SEC. A combination of experimental and theoretical investigations, however, determined that these hypotheses were insufficient to explain the loss of PLP structure [12, 14]. After about a decade of investigation, consensus emerged that intramolecular chain transfer to polymer, commonly known as ‘backbiting’, is the reason behind the behavior; the interested reader is directed to ref. [12, 14] for an overview of the extensive evidence supporting this conclusion.

Backbiting results in the formation of tertiary or so-called mid-chain radicals (MCRs) that are significantly more stable than secondary chain-end radicals (CERs) and thus exhibit considerably lower propagation activity. At any moment, an effective propagation rate coefficient k_p^{eff} can be defined from the propagation rate r_{prop} ,

$$r_{\text{prop}} = (k_p [\text{CER}] + k_p^{\text{MCR}} [\text{MCR}]) [\text{M}] \quad (2)$$

where [CER] and [MCR] are the concentrations of chain-end and mid-chain radicals, respectively. With $k_p^{\text{MCR}} \ll k_p$, under conditions of radical stationarity (not true for PLP in general, but valid for polymerization with continuous initiation or PLP with very little periodic change in radical concentration at the low termination limit), an expression for k_p^{eff} can be derived in terms of the chain-end propagation rate coefficient k_p , the backbiting rate coefficient k_{bb} , the rate coefficient for addition to the tertiary MCR k_p^{MCR} , and the monomer concentration.

$$k_p^{\text{eff}} = \frac{k_p}{\left(1 + \frac{k_{\text{bb}}}{k_p^{\text{MCR}} [\text{M}]}\right)} \quad (3)$$

Equation 3 illustrates how the backbiting reaction significantly reduces the polymerization rate, a result that must properly be accounted for when formulating mechanistic models to represent radical acrylate polymerization [15].

With this knowledge, it is possible to interpret the broadened structure seen for polyacrylate MMDs formed by PLP experiments conducted at lowered repetition rates and elevated temperatures. These operating conditions lead to an increased probability of backbiting, such that the chain length grown between pulses is averaged over both the MCR and CER populations. The solution to this problem, thus, is to increase the pulse repetition rate (decrease t_d in eq. 1) so that fewer MCRs are created on the PLP timescale. In practical terms it has been found that pulse repetition rates above 100 Hz are required to give negligible backbiting between pulses for temperatures greater than 20 °C, resulting in successful PLP experiments that deliver k_p estimates that may be taken as CER values; *i.e.* a true value of k_p , rather than k_p^{eff} [12–15].

While lasers with pulsing rates of 500 Hz are now routinely used to overcome the complication of backbiting in PLP of acrylates, only data acquired at 100 Hz and lower were available when the benchmark set for butyl acrylate (BA) was published in 2004 [12]. Consisting of 113 critically-evaluated data points measured between –65 and 20 °C, the E_A for propagation of BA chain-end radicals was determined to be 17.9 kJ · mol^{–1}, about 5 kJ · mol^{–1} lower than the corresponding value for methacrylates. This difference is much larger than the ±0.5 kJ · mol^{–1} uncertainty in E_A estimates determined by non-linear least-squares fitting and the generation of 95 % joint confidence intervals of the Arrhenius parameters; a detailed description of the experimental

uncertainties and data evaluation [12] will not be repeated here. The extrapolation of the best-fit Arrhenius relationship for BA has since been verified with PLP-SEC data obtained at 500 Hz up to temperatures of 60 °C [16], with the k_p value of $14\,300\text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ at 20 °C [12] more than 40 times higher than that of butyl methacrylate (BMA) [6]. More recently, a benchmark data set for methyl acrylate (MA) has been compiled, covering a temperature range of –28 to 60 °C and pulse repetition rates between 60 and 500 Hz; an E_A of $17.3\text{ kJ} \cdot \text{mol}^{-1}$ and 20 °C k_p value of $11\,700\text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$, with similar uncertainties as for BA, were determined [14].

2.2 Vinyl acetate

A benchmark PLP-SEC data set for k_p of VAc is the most recent addition to the ongoing series of IUPAC publications [17]. Much as with acrylates, the first applications of the PLP-SEC method to (bulk) vinyl acetate had only limited success [9], but for different reasons. In the case of VAc, the generally accepted explanation for the difficulties observed at pulse repetition rates below 100 Hz is the high value of the termination rate coefficient [9, 17]. The application of lasers that achieve higher repetition rates led to further studies of vinyl acetate propagation by multiple research groups, expanding the available results over a broader temperature range: the fit to the 178 critically-evaluated experiments covering the temperature range of 5 to 70 °C yielded an activation energy E_A of $20.4\text{ kJ} \cdot \text{mol}^{-1}$ and a k_p value of $3100\text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ at 20 °C [17]. However, a systematic increase of 15 % was found in the measured k_p values as laser pulse repetition rate increased from 50 to 500 Hz. A number of factors, including SEC band broadening, the changing shape of the MMD as it moves from high-termination (*i.e.* almost all radicals generated by a pulse are terminated before arrival of the next pulse) toward low-termination conditions with increasing pulse repetition rate [18], and the influence of head-to-head addition on k_p , were explored. Since all of the data met the established PLP consistency criteria, it was concluded that, despite the small systematic variation in bulk k_p estimates with pulse repetition rate, none should be excluded from the benchmark data set. The extra variation, however, is reflected in greater uncertainty in the reported best-fit Arrhenius parameters: the 95 % confidence interval in E_A extends from 19.2 to $21.1\text{ kJ} \cdot \text{mol}^{-1}$ [17].

3 Comparison of benchmark data

It is instructive to extend the comparison of the propagation rate coefficients from the previous PLP-SEC benchmark studies to include these most recent results. Table 1 compares the best-fit Arrhenius parameters

Table 1: Best-fit Arrhenius parameters and corresponding k_p values^a calculated at 20 °C estimated from critically evaluated PLP-SEC data sets describing the radical polymerization propagation rate coefficients of styrene, methacrylates, vinyl acetate, and acrylates.

Monomer	Ref.	Temp range (°C)	$A/(\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1})$	$E_A/(\text{kJ} \cdot \text{mol}^{-1})$	$k_p(20\text{ °C})/(\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1})$
Styrene	[4]	–12 to 90	4.27×10^7	32.5	69
Methacrylates					
Methyl	[5]	–1 to 90	2.67×10^6	22.4	270
Butyl	[6]	–20 to 90	3.80×10^6	22.9	320
Dodecyl	[6]	9 to 90	2.50×10^6	21.0	450
Vinyl Acetate	[17]	5 to 70	1.35×10^7	20.4	3100
Acrylates					
Methyl	[14]	–28 to 61	1.41×10^7	17.3	11 700
Butyl	[12]	–65 to 20	2.21×10^7	17.9	14 300

^aRelative uncertainty of k_p values calculated using these Arrhenius parameters is regarded to be $\pm 10\%$ with greater uncertainty of $\pm 15\%$ in the VAc results; see further discussion in the references listed.

Fig. 1: Best-fit Arrhenius representations (lines, covering temperature range 0 to 100 °C) of propagation rate coefficients (k_p) evaluated from PLP-SEC benchmark data sets (points, covering temperature range specified in Table 1) for styrene (Sty, O, solid line), methyl methacrylate (MMA, ■, dotted), vinyl acetate (VAc, Δ, short dash), and methyl acrylate (MA, ×, long dash). See Table 1 for further details and data references.

for the radical propagation of bulk styrene and alkyl (methyl, butyl, dodecyl) methacrylates taken from previous benchmark studies to the more recent values determined for VAc and alkyl (methyl, butyl) acrylates. A systematic effect of ester chain length on k_p is seen within a monomer family, with values for butyl (meth)acrylate being higher than the corresponding methyl ester in bulk by about 20 %. The value of k_p increases as the size of the linear ester methacrylate is further increased to dodecyl, although the increase cannot be unambiguously attributed to a change in the pre-exponential factor or the activation energy [6]. These differences within a family, although statistically significant, are quite small compared to the order-of-magnitude variation observed between monomer families illustrated in Fig. 1. The value of E_A decreases from 32.5 kJ · mol⁻¹ for styrene to about 17.5 kJ · mol⁻¹ for acrylates, with the corresponding 20 °C k_p values increasing by more than two orders of magnitude.

The critically-evaluated data summarized here continue to be useful to check computational techniques for the estimation of and experimental methodologies for the measurement of propagation rate coefficients, as well as to support efforts at modeling radical polymerizations involving these monomers. Efforts are underway to generalize the relative monomer reactivities necessary to represent copolymer composition and copolymerization rates, as well as to recommend methodologies and compile benchmark data sets to describe the formation and reaction of the mid-chain radicals formed during acrylate polymerization.

4 Membership of sponsoring body

The membership of the IUPAC Polymer Division was as follows:

Division President: Gregory T. Russell; Division Secretary: Michael G. Walter; Division Vice President: Christine Luscombe; Titular Members: Chris Fellows, Roger Hiorns, Robin Hutchinson, Igor Lacík, Natalie Stingelin, Paul D. Topham, Yusuf Yagci; Associate Members: Sabine Beuermann, Melissa Chin-Han Chan, Cláudio G dos Santos, Doo Sung Lee, Graeme Moad, Patrick Théato; National Representatives: Rameshwar Adhikari, Jiasong He, Michael Hess, Voravee P. Hoven, Chain-Shu Hsu, Peter Mallon, Olga E. Philippova, Mitsuo Sawamoto, Adriana Sturcova, Jan van Hest.

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