

Critically evaluated rate coefficients in radical polymerization – 8.

Propagation rate coefficients for vinyl acetate in bulk

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Summary

Propagation rate coefficients, k_p , reported by several groups for radical polymerization of bulk vinyl acetate (VAc) are critically evaluated. All data were obtained by the combination of pulsed-laser polymerization (PLP) and subsequent polymer analysis by size exclusion chromatography (SEC), as recommended by the IUPAC Working Party on *Modeling of Polymerization Kinetics and Processes*. Although a small ($\sim 15\%$) increase in k_p is observed as laser pulse repetition rate is increased from low (25-100 Hz) to high (300-500 Hz) values, all of the data fulfill the required consistency criteria and thus are combined into a benchmark set covering the temperature range of 5 to 70 °C. The data are fitted well by an Arrhenius relation resulting in a pre-exponential factor of $1.35 \times 10^7 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ and an activation energy of 20.4 kJ·mol⁻¹, with 95% confidence ellipsoids for the parameters also presented.

Keywords: radical polymerization, kinetics, vinyl acetate, pulsed laser polymerization

1. Introduction

The development of the PLP-SEC method^[1] – 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 (RP). As a result, the reliability and accuracy in estimation of not only this parameter but also other rate coefficients – e.g. the termination rate coefficient, k_t ^[2] – measured relative to it have been considerably improved. Therefore the IUPAC Subcommittee on *Modeling of Polymerization Kinetics and Processes* has recommended PLP-SEC as the method of choice for determining k_p .^[3]

The PLP-SEC method evaluates the propagation rate coefficient using the following equation:^[4]

$$L_i = ik_p[M]t_d \quad (1)$$

Here $[M]$ is the monomer concentration and t_d is the separation time between the periodic laser pulses. Each such pulse generates a fresh population of highly concentrated radicals, instantaneously (on the timescale of RP kinetic events) increasing the probability for terminating the radicals generated by the i^{th} previous pulse, these having propagated up to average (and nearly monodisperse) chain length L_i during the time interval $i \times t_d$. This enhanced termination results in features – either peaks or distinct shoulders – in the molar-mass distribution (MMD) of the resulting (dead) polymer. Differentiation of the MMD highlights the location of these features: a point of inflection on the low-MM side of an MMD peak is a maximum in the derivative trace, while a peak is where the derivative trace crosses the chain-length axis. It is found that the maxima from the derivative plot generally provide the best estimate of k_p using Equation (1).^[3] This is because although pulsing instantaneously generates radicals to enhance the rate of termination, the termination itself is not instantaneous but instead plays out over a

period of time that is small but non-negligible in comparison with t_d . Thus it is the low-MM inflection of each peak or shoulder that best corresponds to average growth length between pulses.^[1] Ordinarily the first peak in the MMD, generated by termination between radicals from successive pulses, is the most pronounced such that the first point of inflection (L_1) is most reliably located and should be used in Equation (1) for determination of k_p .^[3]

In addition to simplicity, the PLP-SEC method provides self-consistency criteria for reliable k_p estimation. The main criterion is 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.^{[1],[3]} Further consistency criteria are the independence of the obtained k_p on initiator concentration, laser power, and pulse repetition rate (prf).^[3]

By now the PLP-SEC method has been applied to a multitude of monomers, enabling a series of benchmark papers^{[3],[5]–[10]} reporting accurate Arrhenius parameters for k_p of a significant range of monomers. While the established consistency criteria have been fulfilled relatively easily for bulk styrene^[3] and methacrylate^{[5]–[7]} systems, difficulties have arisen for acrylates. Namely, poly(alkyl acrylate) MMDs generated at 100 Hz or lower and at temperatures above about 20 °C have shown at best a broadened PLP structure, and at worst no PLP structure at all. This has resulted in poor estimates of k_p , as evidenced by deviation from Arrhenius behavior (above about 20 °C) when measured at pulse repetition rates of 100 Hz or lower.^{[8],[10]}

After about a decade of investigation, consensus emerged that intramolecular chain transfer to polymer – commonly known as ‘backbiting’ – is the reason behind this behavior of acrylates.^{[8],[10],[11]} This reaction results in the formation of so-called mid-chain radicals (MCRs), which are more stable than chain-end radicals (CERs), and thus exhibit considerably lower propagation activity. In terms of PLP, this has two consequences. The first is that formation of MCRs destroys the linear relationship between reaction time and average (radical) chain length: when a subsequent pulse arrives, radicals that have undergone backbiting will be smaller than those that have not, thus creating a broadened MMD.^{[8],[10]} The second effect is that the average

chain length grown between pulses is an average over both the MCR and CER populations, and thus the ‘effective’ k_p is lower than that for CERs. The issue here is that any factor that influences the balance between MCRs and CERs will change the effective k_p . For example, because backbiting has a considerably higher activation energy than CER propagation, increasing the temperature increases the frequency of backbiting relative to chain-end growth, and thus the effective k_p is lowered relative to CER k_p , explaining non-Arrhenius behavior above 20 °C. Similarly, increasing the pulse repetition rate acts to decrease the time between pulses, meaning that fewer MCRs are created on the PLP timescale. Thus the effective k_p is closer in value to the CER k_p . In practical terms it has been found that pulse repetition rates above 100 Hz are generally sufficient to give negligible backbiting between pulses, resulting in successful PLP experiments that deliver k_p estimates that may be taken as CER values. Pulsing rates of 500 Hz are now routinely used to overcome the complication of backbiting in PLP of acrylates up to temperatures of 70 °C.^{[10],[12]}

Much as with the acrylates, the first applications of the PLP-SEC method to (bulk) vinyl acetate (VAc) had only limited success.^{[13]–[15]} It was not possible to determine k_p at temperatures above 25 °C at a pulse repetition rate of 10 Hz, as the PLP-generated MMDs were broadened and featureless.^[14] Only a drastic decrease in radical concentration, e.g. decreasing benzoin concentration from 5.0 to 0.2 mmol·L⁻¹ at a given laser pulse energy, resulted in the emergence of PLP structure.^[14] The application of lasers that achieve higher repetition rates has led to further studies of VAc propagation by multiple research groups,^{[16]–[20]} expanding the available results over a broader temperature range such that it is now possible to compile a benchmark data set for this industrially-relevant system. The benchmark data set is presented in Section 2, followed by discussion in Section 3 of a relatively small (~15%) but systematic increase seen in the measured k_p values as prr is increased from 50 to 500 Hz.^{[17],[19]}

2. Results

The available experimental data from six different groups have been combined into a benchmark set for k_p of bulk VAc. As discussed in previous benchmark papers, the uncertainty associated with individual measurements is dependent on both PLP and SEC conditions, but can be considered to be on the order of 10%, provided proper procedures are followed.^{[3],[5]} The individual experimental values collected in Table 1 all meet the IUPAC consistency criteria, and were obtained over a range of conditions, as detailed below. The data are combined and ordered according to temperature, with other pertinent experimental details – pulse repetition rate (prf), average laser-pulse energy (E_p), and photoinitiator type and concentration ($[I]$). It is noted that the critically evaluated data set of Table 1 is the largest yet assembled for a single monomer, with the following groups providing these data:

a) *Hutchinson, Beuermann, and co-workers (DuPont laboratories).*^{[14],[15]} The k_p values obtained by using low photoinitiator concentrations with prf of 10 Hz^[14] have been carefully reconsidered in a subsequent publication;^[15] in addition, application of a new laser operable up to a prf of 100 Hz resulted in MMDs with improved PLP structure. A total of 21 data points collected at varying prf (25-100 Hz) and laser power (1.5-25 mJ/pulse) covered the temperature range of 10-60 °C using benzoin as initiator at a concentration of 1 mmol·L⁻¹. As part of the investigation, Mark–Houwink–Kuhn–Sakurada (MHKS) parameters were determined as $K = 15.6 \times 10^{-5}$ dL·g⁻¹ and $a = 0.708$ using triple-detector SEC analysis.^[15] These values, used by the other groups contributing benchmark values to the combined data set (Table 1), have subsequently been validated both by triple-detector SEC and by comparing to output from a light-scattering detector.^{[19],[21]}

b) *Manders and van Herk (Eindhoven laboratories).*^[16] Experiments have been performed in bulk over the temperature range of 9.4 to 55.5 °C with 1 mmol·L⁻¹ of 2,2-

dimethoxy-2-phenylacetophenone (DMPA) combined with a laser pulse energy of 40 mJ, or with 0.4 mmol·L⁻¹ of photoinitiator in combination with a pulse energy of 30 mJ. Pulse repetition rates have been chosen to be 50, 75 and 100 Hz.

c) *Barner-Kowollik, Junkers and co-workers (Karlsruhe laboratories).*^[17] Two series of experiments were carried out with 5 mmol·L⁻¹ of DMPA using a laser with energy of 1.5 mJ·pulse⁻¹. The experiments of the first series were conducted at prr of 100, 150, 250 and 500 Hz at a temperature of 40.5 °C. The second series of experiments were carried out at 500 Hz over the temperature range of 4.7 to 70.2 °C.

d) *Buback and Kattner (Göttingen laboratories).*^[18] A series of experiments were carried out at 40.5 °C and varying prr (100, 200, 300 and 400 Hz) with 90 mmol·L⁻¹ dicumyl peroxide (DCP) used as photoinitiator at a laser pulse energy density of 2.63 mJ·cm⁻². A second series of experiments were run at prr of 50, 100, and 400 Hz also at 40.5 °C, but with a lower pulse energy density of 0.86 mJ·cm⁻². A final series of experiments was carried out at 400 Hz over the temperature range of 10 to 60 °C at constant pulse energy density (0.86 mJ·cm⁻²).

e) *Hutchinson et al. (Kingston laboratories).*^[19] The group has used the PLP-SEC method to investigate VAc polymerization over a range of 25 to 65 °C, with experiments conducted at prr of 100, 200, 300, 400, and 500 Hz at each temperature and laser pulse energy in the range of 3.5 to 5.3 mJ. While most work was conducted using benzoin photoinitiator at 5 mmol·L⁻¹, DMPA (5 mmol·L⁻¹) and DCP (90 mmol·L⁻¹) were also used at 30 and 50 °C to confirm that the prr dependence of k_p is independent of initiator type. For some experiments at 50 and 65 °C, the MMD was analyzed using both light scattering and refractive index detectors; the resulting k_p estimates were in good agreement, with the average of the two values reported in Table 1.

f) *Beuermann et al. (Potsdam laboratories).*^[20] The PLP-SEC method has been applied by this group for estimation of k_p for VAc polymerization over a range of 14.1 to 61.2 °C, with 32 experiments conducted at prr of 50 and 100 Hz and with a laser pulse energy of 2 mJ. Benzoin (0.9–1.2 mmol·L⁻¹) and 2-methyl-4'-(methylthio)-2-morpholinopropiophenone (MMMP, 1.0 mmol·L⁻¹) were used as photoinitiators.

Table 1. Critically evaluated values of propagation rate coefficient, k_p , for bulk vinyl acetate polymerization at ambient pressure measured as a function of temperature, Θ , laser pulse repetition rate, prr, average laser-pulse energy, E_p , initiator type and concentration, $[I]$.^a

$\Theta/^\circ\text{C}$	prr/Hz	E_p/mJ	Initiator	$[I]/\text{mmol}\cdot\text{L}^{-1}$	$k_p/\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$	Ref.
4.7	500	1.5	DMPA	5	2180	[17]
4.7	500	1.5	DMPA	5	2080	[17]
9.4	50	40	DMPA	1	1990	[16]
9.4	50	40	DMPA	1	1930	[16]
10	25-100		Benzoin		2224	[15]
10	25-100		Benzoin		2242	[15]
10	25-100		Benzoin		2310	[15]
10	25-100		Benzoin		2345	[15]
10	25-100		Benzoin		2364	[15]
10	25-100		Benzoin		2502	[15]
10	25-100		Benzoin		2566	[15]
10	400	0.86	DCP	90	2794	[18]
10	400	0.86	DCP	90	2668	[18]
10	400	0.86	DCP	90	2730	[18]
10	400	0.86	DCP	90	2668	[18]
10.1	100	40	Benzoin	1	2500	[16]

10.9	100	40	Benzoin	1	2250	[16]
14.1	50	2	Benzoin	1	2367	[20]
14.6	50	2	Benzoin	1	2473	[20]
14.6	50	2	MMMP	1	2483	[20]
15.0	100	2	Benzoin	1.1	2496	[20]
15.7	100	2	MMMP	1.0	2697	[20]
15.8	100	2	Benzoin	1.1	2695	[20]
15.8	100	2	MMMP	1.0	2619	[20]
16.2	50	2	MMMP	1.0	2551	[20]
19.8	500	1.5	DMPA	5	3680	[17]
20	25-100		Benzoin		2830	[15]
20	25-100		Benzoin		3005	[15]
25	25-100		Benzoin		3412	[15]
25	25-100		Benzoin		3605	[15]
25	25-100		Benzoin		3630	[15]
25	400	0.86	DCP	90	3940	[18]
25	400	0.86	DCP	90	3851	[18]
25	400	0.86	DCP	90	3940	[18]
25	400	0.86	DCP	90	3940	[18]
25.2	100	4	Benzoin	5	3166	[19]
25.2	200	4	Benzoin	5	3439	[19]
25.2	300	4	Benzoin	5	3597	[19]
25.2	400	4	Benzoin	5	3711	[19]
25.2	500	4	Benzoin	5	3682	[19]
26.7	50	2	Benzoin	1.1	3539	[20]
26.9	50	2	Benzoin	1.1	3467	[20]
26.9	50	2	MMMP	1.0	3800	[20]

27.8	50	2	MMMP	1.0	3853	[20]
28.0	100	2	Benzoin	1.2	3868	[20]
28.2	100	2	Benzoin	1.2	3695	[20]
28.2	100	2	MMMP	1.0	3910	[20]
28.7	100	2	MMMP	1.0	3916	[20]
28.9	50	30	DMPA	0.4	3720	[16]
28.9	75	30	DMPA	0.4	4040	[16]
28.9	75	30	DMPA	0.4	4040	[16]
28.9	100	30	DMPA	0.4	4280	[16]
28.9	100	30	DMPA	0.4	4210	[16]
29.4	100	40	DMPA	1	4160	[16]
29.4	100	40	DMPA	1	4160	[16]
29.4	50	40	DMPA	1	3630	[16]
29.4	50	40	DMPA	1	3160	[16]
29.7	500	1.5	DMPA	5	5000	[17]
30	100	5.7	Benzoin	5	3684	[19]
30	100	5.7	Benzoin	5	3600	[19]
30	100	5.7	DMPA	5	3437	[19]
30	100	5.7	DCP	90	3490	[19]
30	200	5.7	Benzoin	5	3996	[19]
30	200	5.7	DMPA	5	3886	[19]
30	300	5.7	Benzoin	5	3597	[19]
30	400	5.7	Benzoin	5	3711	[19]
30	400	5.7	DMPA	5	4021	[19]
30	500	5.7	Benzoin	5	4108	[19]
30	500	5.7	DMPA	5	4007	[19]
30	500	5.7	DCP	90	4238	[19]

30.1	500	1.5	DMPA	5	5130	[17]
39.8	500	1.5	DMPA	5	6320	[17]
40	25-100		Benzoin		5432	[15]
40	25-100		Benzoin		5514	[15]
40	100	3.5	Benzoin	5	4660	[19]
40	200	3.5	Benzoin	5	4669	[19]
40	300	3.5	Benzoin	5	5365	[19]
40	400	3.5	Benzoin	5	5641	[19]
40	500	3.5	Benzoin	5	5773	[19]
40.2	500	1.5	DMPA	5	5980	[17]
40.5	100	1.5	DMPA	5	4850	[17]
40.5	150	1.5	DMPA	5	5820	[17]
40.5	250	1.5	DMPA	5	6250	[17]
40.5	500	1.5	DMPA	5	6450	[17]
40.5	100	2.63	DCP	90	4768	[18]
40.5	100	2.63	DCP	90	4823	[18]
40.5	200	2.63	DCP	90	5255	[18]
40.5	200	2.63	DCP	90	5285	[18]
40.5	200	2.63	DCP	90	5142	[18]
40.5	200	2.63	DCP	90	4992	[18]
40.5	300	2.63	DCP	90	5603	[18]
40.5	300	2.63	DCP	90	5603	[18]
40.5	300	2.63	DCP	90	5638	[18]
40.5	300	2.63	DCP	90	5603	[18]
40.5	400	2.63	DCP	90	5868	[18]
40.5	400	2.63	DCP	90	5829	[18]
40.5	400	2.63	DCP	90	5599	[18]

40.5	400	2.63	DCP	90	5475	[18]
40.5	50	0.86	DCP	90	5399	[18]
40.5	50	0.86	DCP	90	5525	[18]
40.5	50	0.86	DCP	90	5461	[18]
40.5	50	0.86	DCP	90	6199	[18]
40.5	100	0.86	DCP	90	5412	[18]
40.5	100	0.86	DCP	90	5412	[18]
40.5	100	0.86	DCP	90	5538	[18]
40.5	100	0.86	DCP	90	5667	[18]
40.5	400	0.86	DCP	90	6388	[18]
40.5	400	0.86	DCP	90	6243	[18]
40.5	400	0.86	DCP	90	5694	[18]
40.5	400	0.86	DCP	90	5826	[18]
42.2	50	2	Benzoin	1.0	5074	[20]
42.3	50	2	Benzoin	1.0	5015	[20]
43.3	50	2	MMMP	0.9	5196	[20]
44.2	100	2	Benzoin	1.0	5596	[20]
44.8	100	2	Benzoin	1.0	5550	[20]
44.9	50	2	MMMP	0.9	5510	[20]
45.0	100	2	MMMP	0.9	5691	[20]
45.3	100	2	MMMP	0.9	5845	[20]
49.9	500	1.5	DMPA	5	7950	[17]
50	25-100		Benzoin		6634	[15]
50	25-100		Benzoin		6688	[15]
50	25-100		Benzoin		6974	[15]
50	400	0.86	DCP	90	7613	[18]
50	400	0.86	DCP	90	7613	[18]

50	400	0.86	DCP	90	7790	[18]
50	400	0.86	DCP	90	7790	[18]
50	100	3.7	Benzoin	5	5855	[19]
50	100	3.7	Benzoin	5	5860	[19]
50	100	3.7	Benzoin	5	5738	[19]
50	100	3.7	Benzoin	5	6081	[19]
50	200	3.7	Benzoin	5	6328	[19]
50	200	3.7	DMPA	5	5845	[19]
50	200	3.7	DMPA	5	6171	[19]
50	200	3.7	DCP	90	7291	[19]
50	200	3.7	DCP	90	6159	[19]
50	300	3.7	Benzoin	5	6982	[19]
50	300	3.7	DMPA	5	6673	[19]
50	300	3.7	DCP	90	6866	[19]
50	400	3.7	Benzoin	5	6750	[19]
50	400	3.7	DMPA	5	6992	[19]
50	400	3.7	DCP	90	7562	[19]
50	500	3.7	Benzoin	5	7412	[19]
50	500	3.7	Benzoin	5	7427	[19]
50	500	3.7	Benzoin	5	7850	[19]
50	500	3.7	Benzoin	5	7683	[19]
50	500	3.7	DMPA	5	7097	[19]
50	500	3.7	DCP	90	7573	[19]
50.5	500	1.5	DMPA	5	7990	[17]
54.4	50	40	DMPA	1	6110	[16]
55	25-100		Benzoin		7187	[15]
55	25-100		Benzoin		7259	[15]

55.5	100	40	DMPA	1	7430	[16]
57.3	50	2	Benzoin	0.9	6618	[20]
57.3	50	2	Benzoin	0.9	6411	[20]
58.8	50	2	MMMP	0.9	6262	[20]
58.9	50	2	MMMP	0.9	6157	[20]
59.1	100	2	Benzoin	1.0	7962	[20]
59.6	100	2	Benzoin	1.0	8013	[20]
60	25-100		Benzoin		8778	[15]
60	25-100		Benzoin		9136	[15]
60	400	0.86	DCP	90	9509	[18]
60	400	0.86	DCP	90	9662	[18]
60	100	3.5	Benzoin	5	7305	[19]
60	200	3.5	Benzoin	5	8257	[19]
60	300	3.5	Benzoin	5	8730	[19]
60	400	3.5	Benzoin	5	9300	[19]
60	500	3.5	Benzoin	5	9823	[19]
60.2	500	1.5	DMPA	5	10580	[17]
60.4	500	1.5	DMPA	5	10430	[17]
60.8	100	2	MMMP	0.9	7916	[20]
61.2	100	2	MMMP	0.9	7878	[20]
65	100	4.3	Benzoin	5	8376	[19]
65	200	4.3	Benzoin	5	8269	[19]
65	300	4.3	Benzoin	5	9380	[19]
65	400	4.3	Benzoin	5	9425	[19]
65	500	4.3	Benzoin	5	10587	[19]
69.5	500	1.5	DMPA	5	12880	[17]
70.2	500	1.5	DMPA	5	13700	[17]

^aSpecific information on prr and photoinitiator concentration for individual experiments reported in reference [15] is not available.

The k_p estimates from the individual PLP-SEC experiments at 10, 30, and 50 °C are plotted as a function of prr in Figure 1. The scatter seen at each temperature/prr condition is typical when compared with other k_p benchmark data sets.^{[3],[5]–[10]} To determine whether the variation with prr is systematic, the global fit of the Arrhenius equation to the complete data set is compared with the fits of the data measured at lower prr (≤ 100 Hz) and higher prr (≥ 300 Hz).

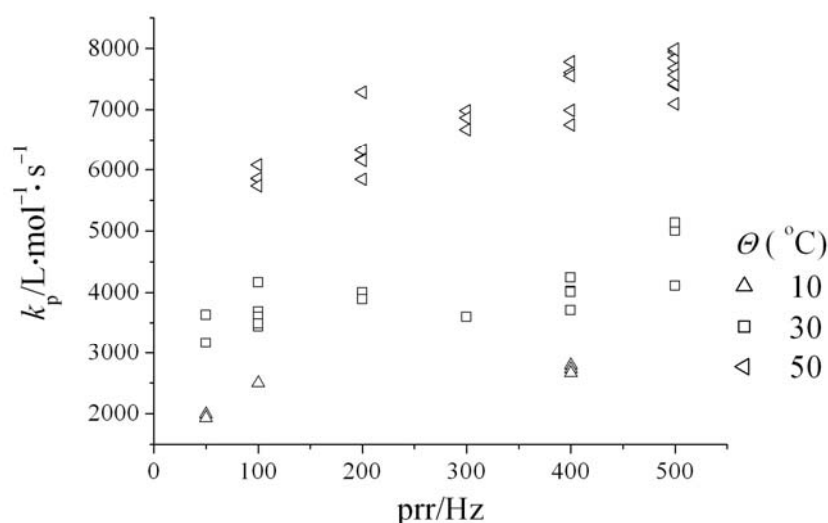


Figure 1. Propagation rate coefficient, k_p , vs. pulse repetition rate, prr, for bulk vinyl acetate as determined by PLP-SEC experiments at 10, 30, and 50 °C, as indicated.

The results of the linear least-squares fitting of the Arrhenius relation $\ln(k_p) = \ln(A) - E_A/RT$ are summarized in Table 2 and plotted in Figures 2 and 3. The fit to the overall data set of 178 experiments from Table 1 for the temperature range of 4.7 to 70.2 °C is given by Equation (2).

$$\ln[k_p / (\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1})] = 16.42 - 2455 \cdot T^{-1} / K^{-1} \quad (2)$$

The associated pre-exponential factor A and activation energy E_A are $1.35 \times 10^7 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ and $20.4 \text{ kJ} \cdot \text{mol}^{-1}$, respectively.

The principal source of the data scatter in Figure 2 is the influence of prr on k_p , as can be seen from the Figure 3 comparison of the overall fit with the fits to the low prr and high prr data sets. As summarized in Table 2, the k_p value calculated at 50 °C using the “low prr” fit is 15% lower than the value calculated from the “high prr” fit. Both estimates, however, are within 10% of the k_p value calculated using the entire data set. Moreover, the 95% joint confidence intervals for the A and E_A estimates overlap, as shown in Figure 4; these ellipsoids were determined by non-linear least-squares^[22] fitting with weighting on the basis of a constant relative error in individual k_p measurements. For VAc, the activation energy is in the range of 19.2 to 21.1 kJ·mol⁻¹ and the preexponential factor is 0.83×10^7 to 1.76×10^7 L·mol⁻¹·s⁻¹. In this context, note that the Arrhenius parameters deduced from both linear and nonlinear fitting are identical within experimental accuracy. The confidence interval for the complete VAc data set is of similar size to that determined from the benchmark set of methyl acrylate.^[10]

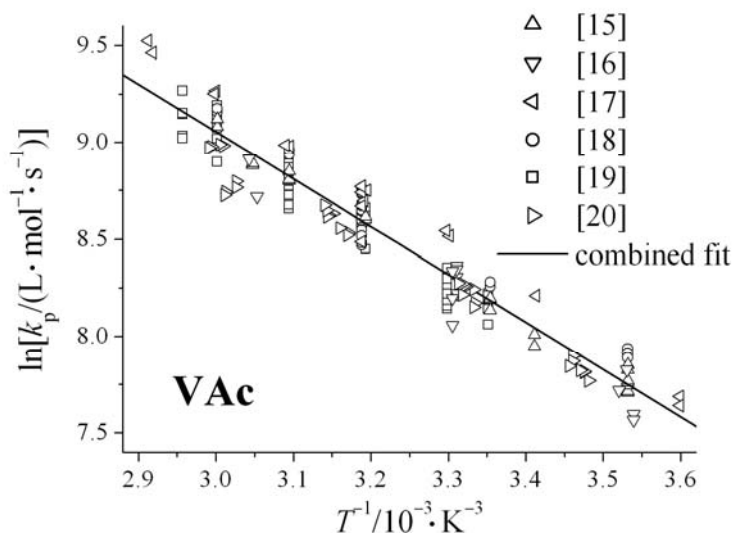


Figure 2. Arrhenius plot of all Table 1 values of the propagation rate coefficient, k_p , for bulk vinyl acetate polymerization. Equation (2), the best-fit line to all the points, is also shown.

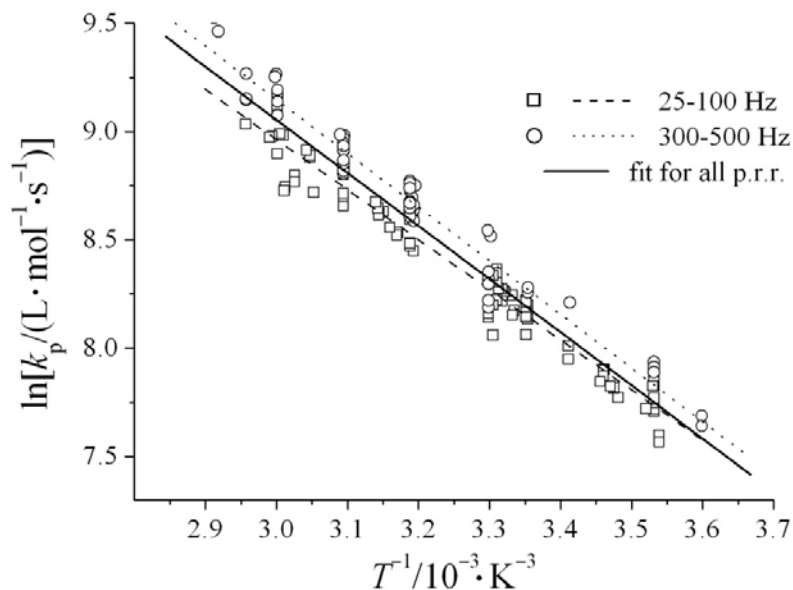


Figure 3. A comparison of the Arrhenius fits to k_p values for bulk vinyl acetate obtained from PLP-SEC experiments conducted at lower prr (25-100 Hz) and higher prr (300-500 Hz) with the fit of the entire Table 1 data set, viz. Equation (2). The associated Arrhenius parameters are given in Table 2.

Table 2. Arrhenius parameters for bulk vinyl acetate obtained by fitting of Table 1 data measured by PLP-SEC in the specified intervals of pulse repetition rates (prr).

prr range / Hz	N number of points	A / $\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$	E_A / $\text{kJ}\cdot\text{mol}^{-1}$	k_p at 50 °C / $\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$
25-500	178	1.35×10^7	20.4	6 800
25-100	95	8.09×10^6	19.2	6 370
300-500	67	1.59×10^7	20.6	7 440

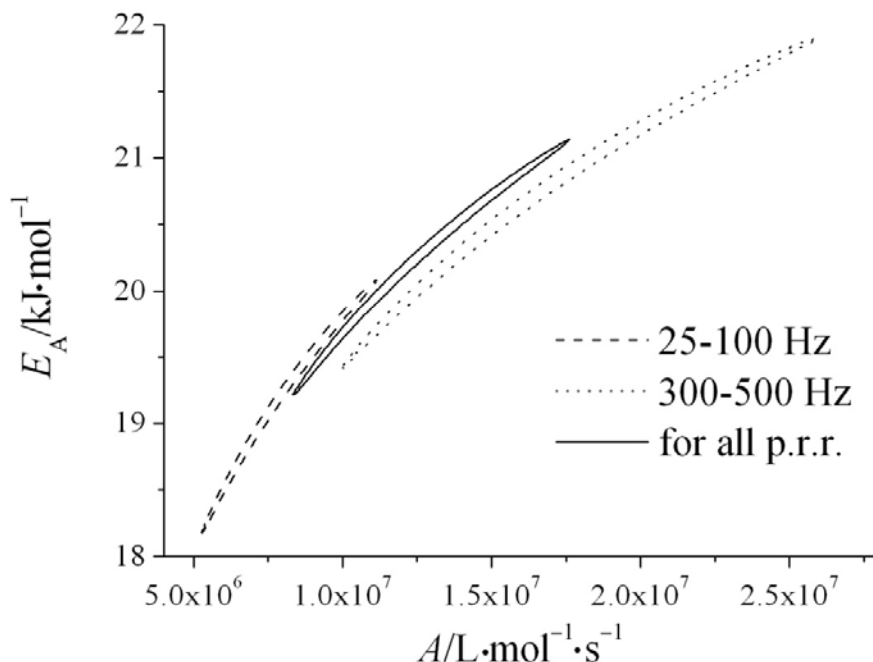


Figure 4. 95% joint-confidence intervals for the Arrhenius parameters for k_p of bulk vinyl acetate polymerization, as estimated from fitting of the data in Table 1 (see text and Figure 3).

The Arrhenius parameters estimated by electron paramagnetic resonance (EPR) spectroscopy for vinyl pivalate in heptane solution ($E_A = 20.5 \text{ kJ}\cdot\text{mol}^{-1}$, $A = 1.39 \times 10^7 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$)^[23] are surprisingly close to the VAc values of Equation (2), although a recent study using the PLP-SEC method results in significantly different values for bulk vinyl pivalate ($E_A = 17.4 \text{ kJ}\cdot\text{mol}^{-1}$, $A = 6.78 \times 10^6 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$).^[21] This makes clear that additional investigations are necessary to further explore the propagation behavior of the vinyl ester family.

3. Discussion

From the analysis of the combined data set, a small but systematic increase in the PLP-determined k_p values with increasing laser prr was found, as also observed in individual studies of VAc propagation kinetics.^{[17],[19]} While a definitive cause for this behavior has not been identified, various hypotheses are considered below.

a) *Chain-length dependent propagation (CLDP)*. Very small radicals propagate faster than long radicals.^[24] It is known that a dependence of the propagation rate coefficient on radical chain length can lead to some variation in the k_p values estimated by the PLP technique.^[25] Specifically, if prr is increased, then growth time between pulses is reduced such that radicals achieve a shorter chain length between pulses and thus have a slightly higher apparent k_p value due to CLDP. While this explanation is qualitatively consistent with VAc results, the chain lengths reached under PLP conditions are greater than 100 for the vast majority of the Table 1 data (except for 10 °C pulsed at 500 Hz) and there is no reason to expect VAc to exhibit a stronger CLDP than methyl methacrylate (MMA) or styrene, both of which show a somewhat smaller k_p dependence on prr than is observed here.^[24] In fact it took many years before this small effect (under standard conditions) was recognized as a genuine effect in MMA and styrene data rather than just being noise.^[26] Furthermore, reported chain-length-dependent k_p values at high chain lengths have been attributed to SEC column band broadening effects.^[27] (Note that more discussion of the influence of SEC broadening on PLP analysis is found in previous IUPAC benchmark publications.^{[5],[10]}) In addition, chain-length dependence of propagation is not associated with a loss of structure in the polymer MMDs, as is observed with VAc at low prr.^{[14],[19]}

A related factor to consider is the first addition step in the chain-growth process, in which the primary radical generated by photoinitiator decomposition adds to VAc monomer. It is known that addition of radicals to VAc monomer is reduced relative to addition to other monomers, as seen by copolymerization study of VAc with acrylates, methacrylates, and styrene.^{[28],[29]} It is also known that the rate of VAc (co)polymerization is retarded in aromatic solvents such as toluene, due to slow addition of monomer to the toluene radical formed after transfer to solvent.^{[30]–[32]} For effective PLP experimentation, both radicals formed by decomposition of the photoinitiator must be sufficiently active to attack the VAc double bond; if

not, the efficiency of initiation suffers as half of the primary radicals formed are only able to terminate existing growing chains rather than initiate new ones.^[33] A related factor is the concentration of radicals generated by the laser pulse which, along with prr, influences the overall shape of the distribution and thus the determination of k_p (see point *c* below). Nonetheless, the dependence of k_p on pulse repetition rate has been found to be independent of choice of the photoinitiator,^{[19],[20]} suggesting that the lowered propensity of VAc monomer to radical attack is not the reason for the observed behavior.

Before proceeding it is noted that if CLDP is the cause of the prr dependence in Figures 1 and 3, then the ‘true’ value of k_p , that for long chains, is the value at low prr.

b) *Intramolecular chain transfer to polymer.* In the PLP experiments carried out at 40.5 °C by Junkers et al.,^[17] the k_p value increased by 30% as prr was increased from 100 to 500 Hz. This effect is qualitatively the same as with acrylates (see above). As VAc is a constitutional isomer of methyl acrylate, Junkers et al.^[17] suggested that backbiting occurs in VAc systems, and is the main reason for the observed increase in k_p with prr. However, this hypothesis is contradicted by branching studies that show intramolecular transfer to polymer during VAc homopolymerization and copolymerization with ethylene is negligible or very low relative to corresponding acrylate systems.^{[34]–[36]} Furthermore, Kattner and Buback^[33] did not detect mid-chain VAc radicals via EPR probing of the radical population, despite using conditions under which MCRs are prevalent for acrylates. Thus, it can be concluded that intramolecular chain transfer to polymer is not likely to be the reason for the prr dependence of VAc k_p .

Furthermore, what drives backbiting in acrylates is that the backbone C-H bonds are activated by adjacent carbonyl bonds.^[37] However, with VAc there is no chemical driving force for radical attack of the polymer backbone due to the presence of the oxygen atom adjacent to the backbone C-H. On the other hand, the pendant methyl group of VAc is rendered labile by the adjacent carbonyl group. This may lead to enhanced chain transfer to monomer (e.g., relative to

methyl acrylate) under PLP conditions, a reaction that can result in broadened, featureless MMDs at lower prr. Indeed, chain transfer to monomer was proposed as a possible explanation for the difficulties in obtaining good PLP structure at low prr (< 25 Hz).^{[14],[15]} However, well-structured MMDs are produced at the higher repetition rates used to generate the benchmark data compiled within this paper, and simulations have shown that transfer is not likely to interfere with k_p determination under these conditions.^[19]

Before proceeding it is noted that if intramolecular chain transfer is the cause of prr variation of VAc k_p , then the values measured at high prr more closely corresponds to CER propagation.

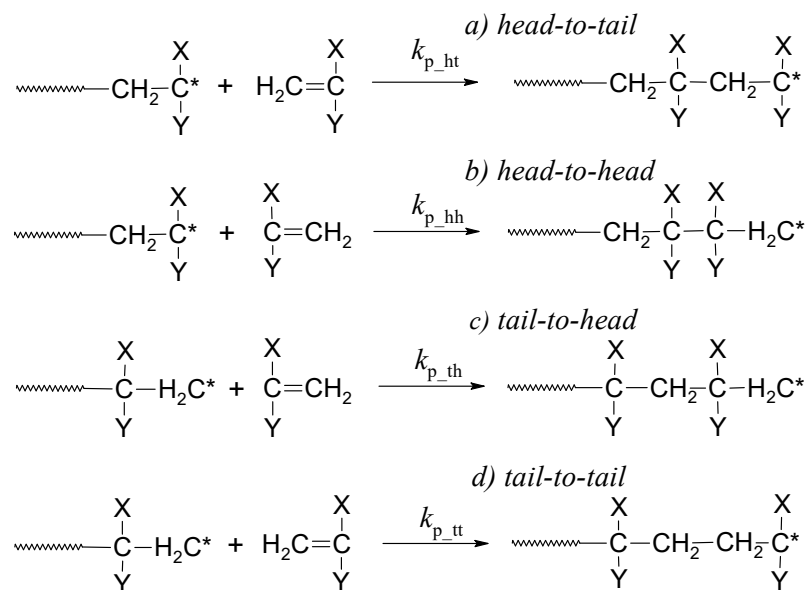
c) *Polymerization at the high-termination limit.* To explain their difficulties in the estimation of k_p from MMDs generated by 10 Hz PLP experiments for VAc, Hutchinson et al. hypothesized that the distributions were measured at the so-called high-termination-rate limit (HTRL).^[14] In this regime of PLP operation, the radical concentration remaining in the system is so low when the next pulse arrives that the new pulse eliminates practically all those radicals that remain. Thus, the population of radicals reaching a chain length $2k_p[M]t_d$ is not sufficient to produce an observable second peak in the first-derivative of the MMD, and the principal consistency criterion for the PLP-SEC method is not satisfied. By decreasing the concentration of initiator, Hutchinson et al. postulated that they were shifting the system away from the HTRL, and that this was the reason for successfully applying the PLP-SEC method up to 25 °C at 10 Hz.^[14]

This explanation has been revisited by Kattner,^[18] who considers that the VAc system moves towards the HTRL as pulse repetition rate is decreased from 500 to 100 Hz. At conditions at or close to this limit, the value of k_p estimated from the inflection point of the MMD will be slightly lower than the true value,^{[34],[39]} consistent with the observed effect of prr on VAc k_p seen in Figure 1. Furthermore, such a trend will be accentuated by SEC column broadening.^{[5],[27]}

Kattner showed that a decrease of pulse energy (an effect similar to a decrease in photoinitiator concentration) shifts the system away from the HTRL and allows the determination of k_p at lower pulse repetition rates.^[18] However, experiments by Monyatsi et al.^[19] found that k_p varies with prr in the same way for three different photoinitiators, despite differences in the resulting MMD shapes being an indication of differences in the radical concentration generated per pulse. The accompanying simulation study^[19] concluded that the influence of termination rate on the shape of the MMD results in less than a 10% decrease in k_p as prr is decreased from 500 to 100 Hz, a variation that is lower than that observed experimentally.

In summary, if termination-rate limit is the reason for the prr variation of VAc k_p , then the values in Table 1 are systematically low at low prr (because under such conditions the point of inflection underestimates the true k_p) while measurements at high prr will be closer to the true k_p value.

d) *Head-to-head addition.* A complicating factor in the propagation kinetics in VAc polymerization is the occurrence of 1 to 2% head-to-head addition, as first reported by Flory and Leutner.^[40] The head-to-head addition is a result of the low reactivity of VAc towards attack, such that radicals occasionally add across the monomer COC(O)CH_3 “head” rather than the less sterically-hindered CH_2 “tail” of the monomer. Considering head-to-head additions, the possible modes of radical propagation associated with monomer structure are shown in Scheme 1. For most monomers, the microstructure of the polymer chains produced indicates that head-to-tail propagation occurs exclusively, as this addition is favored on both steric and resonance grounds. For this usual situation, the head-to-tail rate coefficient ($k_{p,ht}$ in Scheme 1) can be considered as the sole homopropagation addition, and the other three addition mechanisms can be neglected. However, for monomers (such as VAc) for which the presence of head-to-head propagation is revealed, the kinetics of polymerization are more complicated, as four instead of one propagation reactions need to be considered.



Scheme 1. The propagation reactions in radical homopolymerization, accounting for the possibility of inverted monomer addition. In the case of vinyl acetate X is O-CO-CH₃ and Y is H.

Equation (3) has been derived^[19] to describe the dependence of an averaged propagation rate coefficient, k_p^{av} , on the four addition steps in Scheme 1.

$$k_p^{\text{av}} = k_{p_ht} - \frac{k_{p_ht} - k_{p_th} - 2k_{p_tt}}{1 + \frac{k_{p_tt}}{k_{p_hh}}} \quad (3)$$

Note that the k_p^{av} value does not change with varying monomer concentration in the system, and thus a single value can be used to describe VAc radical polymerization rate over the complete range of monomer conversion. However, the averaging is strictly valid only if the growing radicals are subjected to several cycles of transformation from normal radical to inverted (head-to-head reaction in Scheme 1) and back from inverted radical to normal (tail-to-tail reaction in Scheme 1). At the higher pulse repetition rates used in pulsed-laser polymerization, it is hypothesized that the radicals do not have sufficient time to achieve this averaged growth rate,

with the difference in values of k_{p_ht} (higher) and k_p^{av} (lower) causing the observed pulse repetition rate dependence.^[19] Under this scenario, the majority of radicals are not subjected to a head-to-head propagation defect when pulsed at high prr, meaning that analysis of the resulting MMD yields a k_p estimate close to k_{p_ht} , while at low prr all radicals are subjected to multiple head-to-head propagation events, and thus yield a lower value that is closer to k_p^{av} ; at intermediate prr, the PLP-determined k_p value is expected to increase from k_p^{av} at low prr towards k_{p_ht} at prr of 500 Hz.

Monyatsi et al.^[19] have shown that it is possible to select four microscopic propagation rate coefficients for VAc polymerization that explain the prr dependence of k_p . As an addition coefficient that is favored on both steric and resonance grounds, k_{p_ht} is higher than the others, with the relative value of k_{p_hh} set to satisfy the experimentally measured level of head-to-head addition (1 to 2%). It was found that the apparent dependence of k_p on pulse repetition rate could only be matched if the rates of addition of monomer to the “tail” radical (k_{p_th} and k_{p_tt}) was reduced by a factor of 50 to 100 compared with the rate of head-to-tail addition. While no independent measurements of the individual microscopic rate coefficients are available, the simulations provide an idea of the order of magnitude decrease in “tail” radical activity required to explain the experimentally observed variation in k_p with prr. However, with these parameter values a significant fraction of the radicals (~30%) were predicted to be in the inverted “tail” state, in conflict with the study of VAc by Kattner and Buback using EPR spectroscopy, in which only the “head” radical structure was observed.^[33] It is important to note that the simulation study by Monyatsi et al.^[19] also indicated that all experimental data may be fit with a single Arrhenius fit to yield a reasonable estimate of k_p^{av} .

Summing up this subsection, if there are head-to-head effects on overall k_p , then it is the measured values at high prr that corresponds more closely to a microscopic k_p , namely that of head-to-tail addition.

Summary and perspectives. The four explanations that have been presented are all consistent with the observed dependence of k_p on prr. It is quite likely that two or more of these effects are contributing to the observed trend. In the case of CLDP it will be the low-prr value that corresponds to a microscopic k_p , namely that for long chains, while at intermediate and high prr the k_p that is observed will be an averaged one, in this case over chain lengths. On the other hand, for the other three effects it is the high-prr value of k_p that has microscopic meaning; in case (c) the lower-prr values are simply underestimates, while in the other two cases they are averages over radical type (CERs and MCRs in the case of (b), head and tail in the case of (d)). This discussion suggests that it is possible that there is some sort of cancellation of effects, and thus the k_p at intermediate prr – as encapsulated in Equation (2) – is recommended for general use.

Lastly, it is interesting to consider the generality of effects (a)-(d). Of the monomers thus far studied by PLP-SEC, backbiting is only expected to operate for acrylate-like systems, while head-to-head addition is specific to vinyl esters. However, CLDP should be operative for all monomers, as should be the HTRL (although the specific conditions in which it is realized will vary from monomer to monomer). So it is well to be aware that there should always be some minor variation of k_p with prr using the PLP-SEC technique, as evidenced in this work. For VAc this effect is larger than for methacrylate and styrenic monomers, perhaps due to the larger range of prr encompassed by the benchmark data set.

4. Conclusion

From the simulation and experimental studies summarized above, it is evident that systematic variations in the k_p values determined for bulk VAc from MMDs generated over such a broad range of pulse repetition rates (25-500 Hz) can arise from multiple factors, including SEC band broadening, the changing shape of the MMD as it moves from high-termination toward low-

termination conditions with increasing pulse repetition rate, and the influence of head-to-head addition. Since all of the data included in Table 1 meet the established PLP consistency criteria, we conclude that, despite the small systematic variation in k_p estimates with prr, no values should be excluded from the benchmark data set. Thus, we recommend that the best-fit Arrhenius parameters of Equation 2 be used to represent the propagation kinetics of bulk VAc.

The benchmark data derived from application of the PLP-SEC technique were collected from six research groups covering the temperature range of 4.7 to 70.2 °C. The benchmark activation energy for vinyl acetate ($E_A = 20.4 \text{ kJ}\cdot\text{mol}^{-1}$) is intermediate between the benchmark values for methyl acrylate ($E_A = 17.3 \text{ kJ}\cdot\text{mol}^{-1}$)^[10] and methyl methacrylate ($E_A = 22.36 \text{ kJ}\cdot\text{mol}^{-1}$)^[5] with the pre-exponential factor ($A = 1.35 \times 10^7 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$) similar to that for methyl acrylate ($1.41 \times 10^7 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$)^[10] and almost an order of magnitude higher than that of methyl methacrylate ($2.67 \times 10^6 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$)^[5]. With these Arrhenius parameters k_p values of 323, 3 660 and 13 100 $\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ are calculated at 25 °C for homopolymerization of methyl methacrylate, vinyl acetate and methyl acrylate, respectively. Thus, the propagation rate coefficient for vinyl acetate is more than 10 times greater than that for methyl methacrylate and almost 4 times less than that for methyl acrylate chain-end propagation.

Acknowledgements

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Critically evaluated rate coefficients in radical polymerization – 8.

Propagation rate coefficients for vinyl acetate in bulk

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