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ARTICLE

Update and Critical Reanalysis of IUPAC Benchmark Propagation Rate Coefficient Data

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We present an updated and expanded dataset of benchmark propagation rate coefficient (k_p) data obtained from pulsed laser polymerization (PLP) of 13 vinyl monomers (styrene, methyl methacrylate, ethyl methacrylate, butyl methacrylate, dodecyl methacrylate, cyclohexyl methacrylate, glycidyl methacrylate, benzyl methacrylate, isobornyl methacrylate, butyl acrylate, methacrylic acid (15% aq. solution), methyl acrylate and vinyl acetate. The data are reanalyzed using a statistical model that takes into account systematic interlaboratory variation, leading to significantly larger joint confidence regions and slightly adjusted figures relative to the original IUPAC benchmark publications. A full set of revised IUPAC benchmark values of pre-exponential factors, activation energies (EA) and k_p at 25°C are presented. 81 independent PLP studies were pooled to give estimates of the standard interlaboratory error in measurements of ln(k_p at 25°C) and E_A, which were obtained as 0.08 and 1.4 kJ·mol^{-1}, respectively, with a correlation coefficient of 0.04. We recommend that these values be used to estimate the uncertainty in PLP studies that have not been independently replicated.

Introduction

Between 1995 and 2017, the IUPAC Polymerization Kinetics Subcommittee published a series of papers[1-8] providing benchmark values for the activation energies (E_A) and pre-exponential factors (A) of propagation rate coefficients, k_p, of 13 common monomers in radical polymerization. These rate coefficients were measured using the pulsed laser polymerization (PLP) technique,[9] in which a laser is used to generate periodic bursts of radicals in a solution of monomer maintained at a controlled temperature for a sufficient time to convert a small fraction of the monomer (generally <2%) to polymer. A substantial fraction of the resulting polymer chains is initiated by one burst and terminated by the following burst, which are separated by a time, t_0, leading to a characteristically shaped polymer molar mass distribution (MMD) which depends on the propagation rate coefficient of the monomer under investigation. Specifically, a distinctive peak in the MMD corresponding to the chain length DP_0 is directly proportional to k_p, t_0, and monomer concentration [M] according to the relation $DP_0 = k_p[M]t_0$. With t_0 and [M] precisely known, the accuracy of the technique is directly dependent on the measurement of DP_0, typically determined from analysis of the polymer MMD measured by size exclusion chromatography (SEC). Even with careful SEC analysis utilizing the principal of universal calibration verified by multi-detector analysis, the principal source of uncertainty in the estimation of k_p arises from the polymer analysis, as detailed in the previous studies.[1-8]

The benchmark values were obtained by pooling the results of multiple laboratories (from 2 to 9 depending on the study) and verifying that certain experimental conditions (e.g. invariability with respect to pulse rate, presence of at least one overtone, etc.) were fulfilled. The resulting dataset has been highly useful to the polymerization community and underpin many further kinetic studies and simulations, which is demonstrated by their remarkable number of citations. These and other selected k_p data have recently been collected in a machine-readable database.[10]

Since the publication of the benchmark dataset for styrene more than 25 years ago, many further PLP studies have been carried out according to the IUPAC guidelines. These provide additional, independent data that can be used to refine the benchmark parameter estimates. Additionally, by pooling the results of 83 individual PLP studies on the 13 monomers, in this contribution we are able to provide an estimate of the interlaboratory variation resulting from systematic errors that are constant within a single study. Taking this variation into account, we arrive at larger but more realistic estimates of uncertainty than those originally published. It is important to note that while the original parameter estimates differ slightly from the revised values presented here, they remain within the margin of uncertainty for the updated estimates.

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Electronic Supplementary Information (ESI) available: Parameter estimates and 95% joint confidence regions for all individual studies; details of statistical calculations; 95% confidence bands for k_p of all monomers. See DOI: 10.1039/x0xx00000x

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Results and Discussion

IUPAC-benchmarked activation energies and pre-exponential factors are available for the monomers styrene (STY),[1] methyl methacrylate (MMA),[2] ethyl methacrylate (EMA),[3] *n*-butyl methacrylate (BMA),[3] *n*-dodecyl methacrylate (DMA),[3] cyclohexyl methacrylate (CHMA),[4] glycidyl methacrylate (GMA),[4] benzyl methacrylate (BnMA),[4] isobornyl methacrylate (iBoMA),[4] methacrylic acid (MAA),[5] *n*-butyl acrylate (BA),[6] methyl acrylate (MA),[7] and vinyl acetate (VAc).[8] These values are for the bulk monomer in all cases except for that of MAA, which is given for a 15% aqueous solution in water at natural pH. The parameters, as well as the calculated k_p at 25°C, are collated in Table 1, together with the estimated standard error in each parameter reported in the original studies.

Table 1. Comparison of originally published IUPAC benchmark values and re-analysed values (using expanded dataset) for Arrhenius parameters of propagation rate coefficients of vinyl monomers. Numbers in parentheses represent the standard error in the final digits: e.g. 32.5(3) represents 32.5 ± 0.3. Significant (>1σ) differences between original and revised values are highlighted in **bold**.

Monomer	Original IUPAC Benchmark Values[a]					Revised IUPAC Benchmark Values[b]				
	A (L·mol^{-1}·s^{-1})	E_A (kJ·mol^{-1})	k_p at 25°C (L·mol^{-1}·s^{-1})	T (°C)	N[c]	A (L·mol^{-1}·s^{-1})	E_A (kJ·mol^{-1})	k_p at 25°C (L·mol^{-1}·s^{-1})	T (°C)	N[c]
STY[1]	$10^{7.63(6)}$	**32.5(3)**	86(1)	-12–93	8	$10^{7.51(19)}$	**31.8(5)**	87(2)	-12–120	16
MMA[2]	$10^{6.42(4)}$	22.3(3)	325(3)	-18–90	7	$10^{6.50(08)}$	22.8(4)	325(6)	-18–92	19
EMA[3]	$10^{6.61(11)}$	23.4(6)	324(5)	6–50	3	$10^{6.53(20)}$	22.9(7)	337(13)	1–91	4
BMA[3]	$10^{6.58(4)}$	22.9(2)	**370(4)**	-20–90	4	$10^{6.57(09)}$	22.7(5)	**390(11)**	-20–91	8
DMA[3]	$10^{6.40(4)}$	21.0(3)	516(6)	9–90	3	$10^{6.31(15)}$	20.5(8)	522(24)	9–90	3
CHMA[4]	$10^{6.80(4)}$	23.0(3)	584(8)	10–90	3	$10^{6.78(15)}$	22.9(8)	585(27)	10–90	3
GMA[4]	$10^{6.79(8)}$	22.9(5)	**600(15)**	20–90	2	$10^{6.85(16)}$	23.4(9)	**558(29)**	20–90	3
BnMA[4]	$10^{6.83(18)}$	22.9(1.1)	671(13)	10–55	3	$10^{6.71(13)}$	22.3(7)	643(30)	6–90	4
iBoMA[4]	$10^{6.79(19)}$	23.1(1.2)	540(23)	30–70	2	$10^{6.77(18)}$	23.1(9)	539(30)	0–91	2
BA[5]	**$10^{7.34(4)}$**	17.9(2)	**16.4(3) x 10^3**	-65–20	5	**$10^{7.22(11)}$**	17.3(6)	**15.7(5) x 10^3**	-65–70	8
MAA[6]	$10^{6.19(8)}$	15.0(4)	3.72(5) x 10^3	18–89	2	$10^{6.21(18)}$	15.1(1.0)	3.73(21) x 10^3	18–89	2
MA[7]	$10^{7.15(5)}$	17.3(2)	**13.1(1) x 10^3**	-28–61	5	$10^{7.25(13)}$	17.8(7)	**13.7(5) x 10^3**	-26–61	4
VAc[8]	$10^{7.13(7)}$	20.4(4)	3.60(4) x 10^3	5–70	6	$10^{7.13(12)}$	20.4(7)	3.62(12) x 10^3	5–70	6

[a] Values reported in references 1-8. [b] This work. [c] Number of studies used to determine Arrhenius parameters

A notable aspect of the IUPAC benchmarking studies was the care that was taken to provide estimates not only of E_A and A, but also of their uncertainties. These were presented as 95% joint confidence regions (JCRs): an identically constructed study would be expected to produce parameter estimates within these regions 95% of the time, assuming that the experimental errors are independent and identically distributed. In all cases, the JCRs were highly correlated – the error in A depended greatly on the error in E_A, leading to elongated, banana-shaped JCRs.

The correlation between the errors in A and E_A is due to nature of the Arrhenius relationship (eq. 1)

$$k_p = A\, e^{-\frac{E_A}{RT}} \qquad (1)$$

Experimentally, A is determined by extrapolating experimental k_p vs T data to infinite temperature. Thus, a small variation in E_A will result in a large variation in the extrapolated value of A. The resulting JCRs can be difficult to compare, as the uncertainty in A is dominated by the uncertainty in E_A.

This correlation can be reduced by modifying the Arrhenius relationship as follows (eq. 2):

$$k_p = k_{p0}\, e^{-\frac{E_A}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)} \qquad (2)$$

In eq. 2, k_{p0} is the k_p at a reference temperature T_0, chosen to be within the range of experimentally accessible temperatures. This corresponds to a simple change of variables, and the pre-exponential factor A can be obtained by setting $1/T = 0$. By appropriate choice of T_0, the correlation between k_{p0} and E_A can be greatly reduced, or even eliminated. As a result, uncertainties in the parameters of the Arrhenius relationship can be presented concisely as follows (eq. 3):

$$k_p = \left(k_{p0} \pm \sigma_{k_{p0}}\right) e^{-\frac{\left(E_A \pm \sigma_{E_A}\right)}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)} \qquad (3)$$

where σ_{kp0} and σ_{EA} represent the uncertainties in k_{p0} and E_A, respectively, and T_0 is the temperature at which these uncertainties are uncorrelated.[‡] The uncertainty in the pre-exponential factor is then obtained from the propagation of errors as (eq. 4)

$$\frac{\sigma_A}{A} = \sqrt{\left(\frac{\sigma_{k_{p0}}}{k_{p0}}\right)^2 + \left(\frac{\sigma_{E_A}}{RT_0}\right)^2} \qquad (4)$$

In the remainder of this paper, this representation of the Arrhenius relationship is used. The reference temperature is set at 25°C (298.15 K), a temperature which falls within the experimental datasets of all monomers under consideration. In this way, the activation energies and rate coefficients at 25°C can readily be compared.

Data treatment

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In establishing a set of benchmark values, the IUPAC group first needed to establish a reliable set of data points. This was done by including only data that met a set of experimental conditions including duplicate experimental runs, the presence of at least one overtone peak in the molar mass distribution, and invariance of the results with respect to changes in the radical concentration, pulse repetition rate and duration of irradiation. The temperature range was limited to less than 90°C in the case of methacrylates[2-4] to avoid interference from depropagation reactions, and less than 20°C[6] or 60°C[7] in the case of acrylates to avoid interference from backbiting.[5,7,11] These curated datasets were published in the original articles,[1-8] and are reproduced in the Supporting Information.

Once the dataset had been established, further issues were encountered in analysing the data:

- Only a limited number of laboratories were suitably equipped to carry out the experiment, so relatively few laboratories participated in each study.
- The number of data points provided by each laboratory was not constant, so that there was a risk that a single laboratory that provided a large number of data points would dominate the dataset.
- Different laboratories carried out experiments over different temperature ranges.

In order to mitigate these problems, when one laboratory dominated the dataset, results from other laboratories were given extra weight.[1,3,4] Likewise, when results at high or low temperature were dominated by a single laboratory, the temperature range was restricted to exclude those results.[3,4] The remaining weighted results were pooled, and either fitted directly to eq. 1 (using nonlinear least squares fitting), or transformed by taking the natural logarithm of k_p and fitting a straight line as a function of $1/T$. As the k_p is determined by analysis of a MMD, usually obtained by SEC in which the elution volume of a polymer is approximately proportional to the logarithm of its molecular weight, errors in ln k_p are constant, and this transformation of the data does not bias the parameter estimates.[2,12]

While these strategies were quite effective at reducing the impact of a single laboratory on the combined datasets, they have some disadvantages. The weighting procedure is somewhat arbitrary, while restricting the temperature range can involve discarding a significant quantity of data. The most important issue, however, is the assumption, implicit in the procedure of fitting a single line to the combined dataset, that the experimental errors in each point are uncorrelated. In practice, this is not the case.

To take styrene as an example, the IUPAC paper[1] contained data from 8 studies, of which 4 provided values at a single temperature (25°C),[13-16] and 4 provided multiple k_p values across a range of temperatures.[12,17-19] As shown in Figure 1, the resulting data set is dominated by the results of one study,[12] shown in grey. In an attempt to compensate for this, in the original analysis[1] the results of the other studies were given three times as much weight in the fitting.

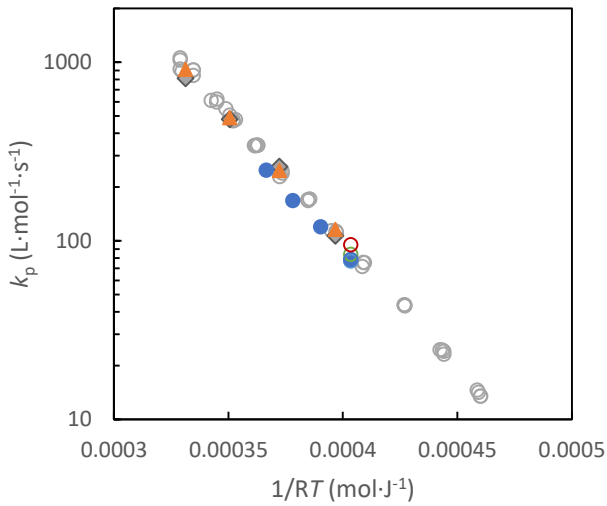

Figure 1. Dataset used to fit Arrhenius parameters for k_p of styrene radical polymerization in bulk. Open circles (grey): data from reference 12; filled diamonds (grey): data from reference 17; filled circles (blue): data from reference 18; filled triangles (orange) data from reference 19; remaining points from references 13-16.

In Figure 2, 95% JCRs are shown for the four studies[12,17-19] that provided sufficient data to estimate them, while the k_p values at 25°C from the 4 remaining studies[13-16] are represented as open squares, shown at an arbitrary E_A. Additionally, the 95% JCR[1] for the fit to the combined, weighted data is shown in red.

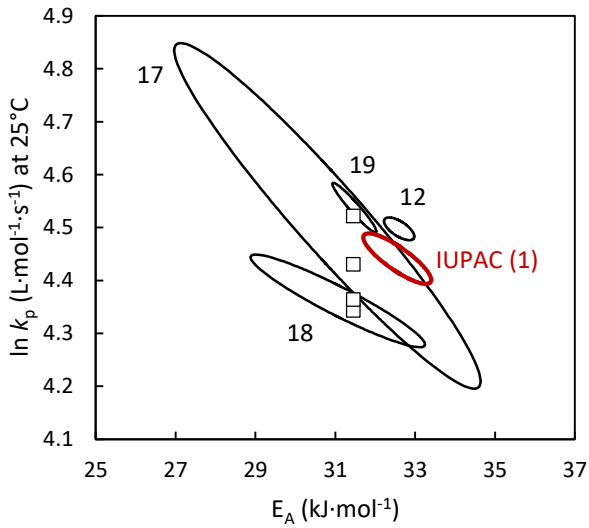

Figure 2. 95% Joint confidence regions (JCR) for Arrhenius parameters of k_p of styrene. In black, the JCRs corresponding to the individual studies of references 12 and 17-19. The open black squares represent 4 independent measures (references 13-16) of k_p at 25°C, shown at an arbitrary E_A. The red JCR corresponds to the original IUPAC benchmark fit (reference 1) to the combined, weighted data.

It is apparent from Figure 2 that while the studies individually give quite precise estimates of the Arrhenius parameters (particularly so for references 12 and 19), these estimates are incompatible with each other. Furthermore, the JCR for the fit to the combined data overlaps only the least precise of the 4

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individual JCRs, and is consistent with only one of the point estimates of k_p at 25°C. This is a strong indication that there is significant interlaboratory variation in the data. In other words, we should not expect two laboratories to converge on the same parameter estimates, no matter how many times they repeat the experiments. Small systematic differences between laboratories in equipment, operator technique and raw materials result in observable differences in the parameter estimates. As such, the statistical model for the k_p data should include a term for interlaboratory variation (eq. 5):

$$\ln k_{\mathrm{p},ij} = \left(\ln k_{\mathrm{p0}} + \varepsilon_i\right) - \frac{(E_\mathrm{A}+\eta_i)}{\mathrm{R}}\left(\frac{1}{T} - \frac{1}{T_0}\right) + \delta_{ij} \qquad (5)$$

In eq 5, $k_{\mathrm{p},ij}$ represents the jth measurement of k_p from the ith study. The random experimental error is represented by δ_{ij}, while ε_i and η_i represent the error in the parameters k_{p0} and E_A, respectively, associated with all measurements from the ith study. These errors are all assumed to be drawn from normal distributions with means of 0 and variances of $V(\delta_i)$, $V(\varepsilon)$, and $V(\eta)$. Note that $V(\delta_i)$ may vary from one study to another.

The question then becomes: how can we estimate the Arrhenius parameters while taking into account the systematic interlaboratory variation? Equation 5 suggests that the best estimates of $V(\varepsilon)$ and $V(\eta)$ will be obtained from the sum of squared differences between the parameter estimates of individual studies and the average of all studies.

The parameter estimates of individual studies[12-19] of STY are grouped in Table 2, along with those of 8 additional studies[20-27] that were published after the original IUPAC paper, but which meet the conditions for inclusion. This gives a total of 16 independent estimates of ln k_p at 25°C and 12 independent estimates of E_A, with standard deviations of 0.082 and 0.77 kJ·mol^{-1}, respectively. The standard deviation in ln k_p corresponds to a relative standard deviation (RSD) in k_p of ±8%, which compares well with typical reproducibility standard deviations of up to 30% for molar masses obtained by SEC.[28,29]

Table 2. Estimates of k_p and E_A from individual PLP studies of styrene radical polymerization in bulk, and statistics for the population of parameter estimates. Numbers in parentheses represent the standard error in the final digits: e.g. 4.344(50) represents 4.344 ± 0.050

Reference	Ln k_p at 25°C	E_A (kJ·mol^{-1})	n^c
13	4.344(50[b])		1
14	4.431(50[b])		1
15	4.364(50[b])		1
16	4.522(50[b])		1
12	4.497(07)	32.6(0.2)	45
18	4.361(20)	31.1(0.9)	4
19	4.538(11)	31.5(0.2)	4
20[a]	4.570(50[b])	31.3(1.7[b])	2
21[a]	4.399(39)	30.9(1.7)	10
22[a]	4.390(07)	31.8(0.3)	24
23[a]	4.482(06)	32.1(0.4)	4
24[a]	4.579(16)	33.1(1.1)	6
25[a]	4.372(19)	30.7(0.6)	4
26[a]	4.495(40)	31.9(0.6)	10
27[a]	4.547(09)	32.4(0.3)	3
Variance	0.00666	0.585	
Covariance	0.00322		
Standard deviation	0.082	0.76	
Correlation coefficient (ρ)[d]	0.052		
Mean	4.46(2)	31.7(2)	

[a] study published subsequent to original IUPAC STY paper. [b] assuming a standard error in k_p of ± 5% [c] number of data points reported in each study [d] correlation coefficient, $\rho = \frac{Cov(\ln k_p, E_A)}{\sigma_{\ln k_p}\sigma_{E_A}}$

The mean of the individual studies provides an estimate of the Arrhenius parameters, which are found to be 4.46 ± 0.02 (ln k_p) and (31.7 ± 0.2) kJ·mol^{-1} (E_A), with a correlation coefficient, ρ, of 0.052 indicating that the uncertainties in the two values are essentially uncorrelated. The estimate for ln k_p at 25°C is in good agreement with the original fit to the combined weighted data, but the estimate for E_A is significantly (~3σ) lower. This is because less weight is given to the study with the most datapoints,[12] whose E_A of 32.6 kJ·mol^{-1} dominated the combined fit presented in the original analysis.[1] As a result, the estimate for A is also significantly (~2σ) lower than the originally reported benchmark value, with a revised value of $10^{7.49 \pm 0.08}$ L·mol^{-1}·s^{-1}, compared to the originally published[1] value of $10^{7.63 \pm 0.06}$ L·mol^{-1}·s^{-1}.

In order to take the varying precision of the individual estimates into account, we then calculated the weighted average of the k_p and E_A estimates, weighting each pair of parameter estimates according to the sum of the estimated interlaboratory variance and the variance estimated from the individual study. For the studies reporting only one or two k_p values, the reproducibility of the k_p measurement was assumed to be ± 5%. We believe this to be a conservative estimate of precision in a single laboratory; in contrast to the larger variance in interlaboratory

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reproducibility of SEC, the intralaboratory reproducibility (i.e. the same sample reanalysed using the same equipment) is generally good.[28,29] Full details of the statistical treatment are given in the Supporting Information.

This gave estimated values of 4.46 ± 0.03 for ln k_p at 25°C (k_p = (86 ± 3) L·mol^{-1}·s^{-1}), and (31.7 ± 0.4) kJ·mol^{-1} for E_A, values scarcely different to the unweighted average. The uncertainties in ln k_p at 25°C and E_A are only slightly correlated (ρ = 0.24). While the weighted average leads to a higher uncertainty in the estimate of E_A, it remains significantly (~2σ) lower than the originally published value of 32.5 kJ·mol^{-1}.

A 95% JCR[30,31] can be calculated for these parameters, but is significantly larger than the originally published JCR due to the severe reduction in degrees of freedom. The original dataset contains only 4 independent estimates of E_A, compared to the 61 data points used to calculate the original JCR, while 12 estimates of E_A are available using the expanded dataset. As a result, the critical value of the F-distribution used to obtain the JCR is taken from the $F_{2,3}$ distribution (original dataset) or $F_{2,11}$ distribution (expanded dataset) as 19.1 or 8.0, respectively, as opposed to the $F_{2,59}$ distribution, which gives a critical value of 6.4.[§] Figure 3a shows the JCR for the expanded dataset (in blue), overlaid on the JCRs of the individual studies. This JCR encompasses significant portions of most of the individual JCRs and point estimates of k_p. Figure 3b shows the comparison between the originally published JCR (red), the JCR recalculated from the original data of reference 1 taking into account the interlaboratory variation (orange), and the JCR obtained from the expanded dataset (blue). Gratifyingly, when interlaboratory variation is taken into account, the inclusion of additional studies results in a negligible change in the parameter estimates, while significantly improving their precision. While the revised parameter estimates fall outside the originally determined JCR; the original parameter estimates remain within the revised JCR, indicating that these original estimates remain consistent with the experimental data.

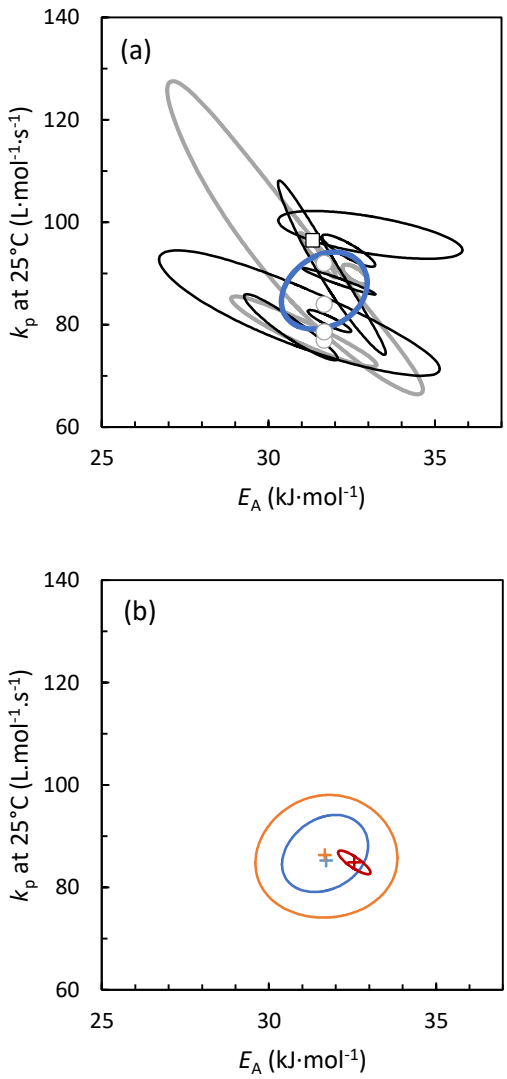

Figure 3. 95% Joint confidence regions (JCRs) for individual studies (a) and pooled data (b) for E_A and k_p at 25°C of styrene radical polymerization in bulk. (a) JCRs corresponding to references 17-20 shown in grey, additional data shown in black. Open circles represent k_p from single experiments (refs 13-16), shown at an arbitrary E_A. Open square shows estimate of k_p and E_A from reference 20. As only two experiments were carried out, a JCR could not be determined. Blue JCR represents the JCR that corresponds to the average of all individual estimates. (b) Original IUPAC benchmark JCR and parameter estimates (red); revised JCR and parameter estimates based on original IUPAC dataset (orange); revised JCR and parameter estimates using extended dataset (blue).

Extension to all benchmarked monomers

This approach to determining the JCR while taking into account interlaboratory variation works well when there are at least 5 independent studies. However, the majority of the IUPAC benchmark studies comprised 2 to 4 laboratories. With so few independent data points, the 95% JCRs become unfeasibly large. Thus, we sought an alternative method to estimate the typical interlaboratory variation in estimation of Arrhenius parameters for propagation rate coefficients by PLP.

Assuming that the error was roughly constant regardless of the monomer being studied, we calculated the pooled interlaboratory covariance matrix of all 13 monomers for which

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benchmark Arrhenius parameters are available as the weighted average of the variances and covariances of the individual parameter estimates for each monomer, according to equation 7:

$$s^2_{pooled} = \frac{\sum_i (N_i - 1) s_i^2}{\sum_i (N_i - 1)} \quad (7)$$

The pooled variance included 81 independent estimates of ln k_p and 71 independent estimates of E_A. This gave a standard deviation for the interlaboratory error in ln k_p at 25°C of 0.08, and in E_A of 1.4 kJ·mol^{-1}, with a correlation coefficient of 0.04. This can be used to calculate a 95% JCR for the interlaboratory error, which is shown in Figure 4. One study[32] on butyl acrylate was excluded from this calculation as its estimate of E_A deviated substantially from the mean of the remaining studies of the same monomer. It should be noted that this study was carried out over a very small temperature range (5-25°C), which may explain the imprecision in the estimate of E_A in this case. A second study[33] on methyl acrylate was also excluded as the results were obtained at high pressure and extrapolated back to ambient pressure. The deviations of the parameter estimates of each individual study from the mean E_A and ln k_p at 25°C for the appropriate monomer are also shown in Figure 4. Of the 71 points included, all but 3 fall within the estimated 95% JCR, in line with expectation (5% of 71 ≈ 4). Thus, we recommend that this estimate of uncertainty be applied to PLP studies from individual laboratories that have not yet been independently replicated.

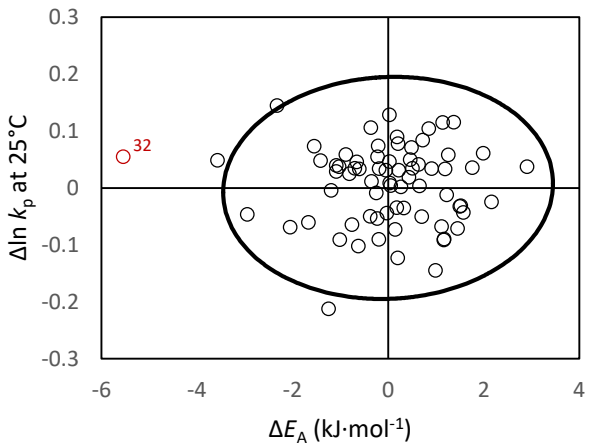

Figure 4. Interlaboratory variation in estimates of ln k_p at 25°C and E_A, and pooled 95% JCR. The point in red (reference 32) was considered an outlier and excluded from the study. Standard errors in ln k_p at 25°C and E_A are 0.08 and 1.4 kJ·mol^{-1}, respectively, with a correlation coefficient of 0.05

Applying this estimate of the interlaboratory variation to the case of STY, we arrive at essentially the same parameter estimates as before: ln k_p at 25°C of 4.46 ± 0.02, E_A of (31.8 ± 0.5) kJ·mol^{-1}, and a covariance of -0.37 kJ·mol^{-1}, corresponding to a correlation coefficient of -0.04. The standard error in ln k_p is slightly reduced relative to the previous estimate, while that of E_A is slightly greater. Full details of these calculations are given in the Supporting Information.

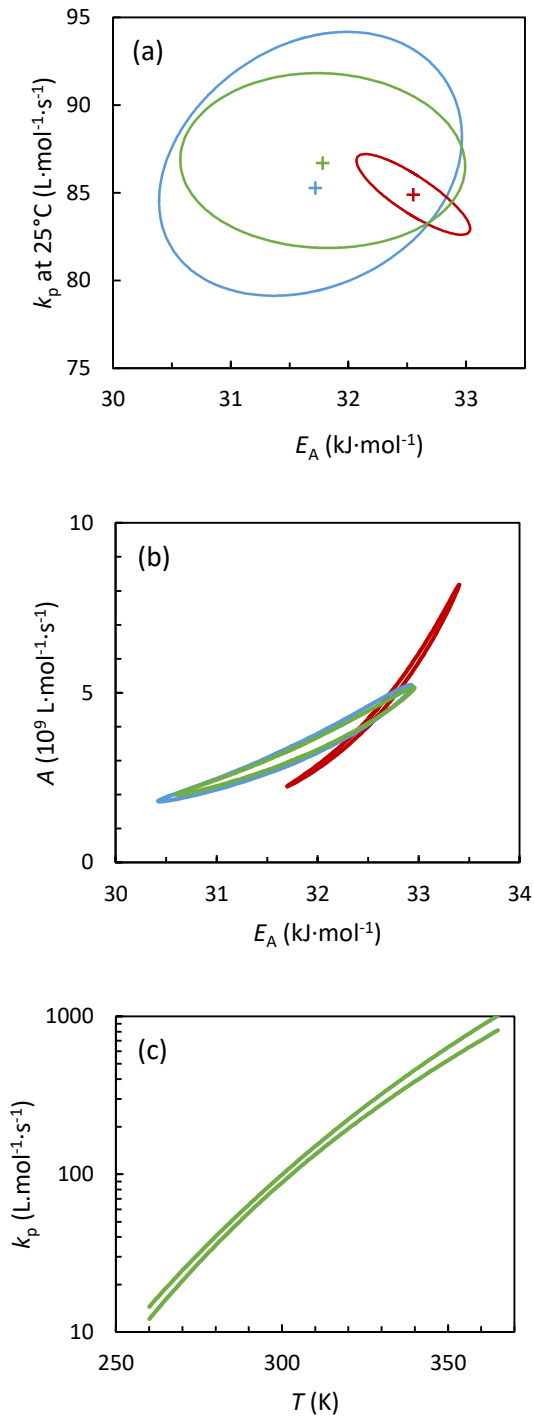

Figure 5. (a) Comparison of parameter estimates and 95% JCRs for E_A and ln k_p at 25°C of radical polymerization of styrene in bulk obtained using estimates of interlaboratory variation obtained from studies on styrene (blue) or from pooled studies of all benchmarked monomers (green). Original IUPAC benchmark JCR and parameter estimates (red) are shown for comparison. (b) The same JCRs shown for the pre-exponential factor, A, and E_A. (c) 95% confidence bands for k_p of radical polymerization of styrene in bulk from 262 K to 364 K.

The 95% JCR for the parameter estimates is somewhat smaller, however, due to the greater number of studies used to estimate the interlaboratory error. The JCRs and corresponding

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parameter estimates are shown for comparison in Figure 5 for k_p at 25°C and E_A (Figure 5a) as well as A and E_A (Figure 5b).

For practical purposes there is little difference between the JCRs obtained for the Arrhenius parameters of STY from the pooled variance data for all monomers or from the styrene studies only. Both cover the same range of E_A (30-33 kJ·mol^{-1}) and a similar range of ln k_p at 25°C (4.34-4.58 vs 4.37-4.54, equivalent to k_p ranges of 77-98 and 79-94 L·mol^{-1}·s^{-1}, respectively). Both include the original parameter estimates of 4.44 and 32.5 kJ·mol^{-1}, although both new parameter estimates fall outside the originally published 95% JCR. Finally, the estimated uncertainty in k_p tallies well with the intuition of experienced researchers in the field, who typically estimate an uncertainty of ± 10% in k_p values obtained by PLP.

The 95% confidence bands for k_p as a function of temperature in the range of 260-365 K are shown in Figure 5c. If the pooled interlaboratory variance is used to calculate the confidence band, the uncertainty in k_p is roughly ± 6% near 298 K, rising to approximately ± 10% at the extremities of the investigated temperature range. A slightly broader confidence band is obtained if only the styrene studies are used, with uncertainties of 8-15% depending on the temperature. Confidence bands for k_p of all benchmarked monomers can be found in the Supporting Information.

Similar calculations were carried out for all the monomers for which IUPAC benchmark data has been published, leading to the 95% JCRs and parameter estimates shown in Table 1 and Figure 6. For most monomers, the change in parameter estimates is minimal, however changes > 1σ in E_A were obtained for styrene (a difference of 0.7 kJ·mol^{-1}), and in k_p at 25°C for butyl methacrylate, glycidyl methacrylate, butyl acrylate and methyl acrylate. The maximum difference between original and revised values was 7% (k_p of GMA at 25°C) Comparing the JCRs shown in Figure 6, the trend towards higher k_p for methacrylates with longer side chains is evident, while the E_A seems independent of the side chain for all methacrylates except dodecyl methacrylate. Likewise the family-like behavior of the acrylates is clear, with butyl acrylate showing a higher k_p than methyl acrylate but a similar activation energy.

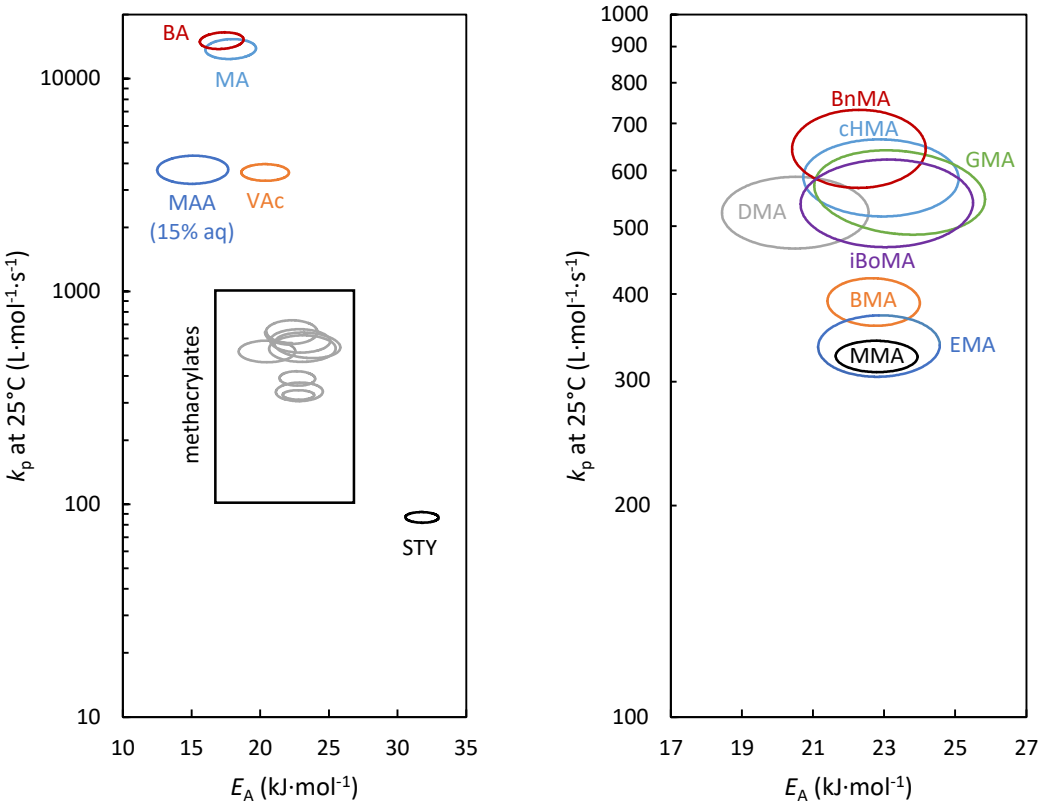

Figure 6. Revised 95% JCRs for monomers for which IUPAC benchmark values are available. MMA: methyl methacrylate; EMA: ethyl methacrylate; BMA: butyl methacrylate; iBoMA: isobornyl methacrylate; DMA: dodecyl methacrylate; GMA: glycidyl methacrylate; cHMA: cyclohexyl methacrylate; BnMA: benzyl methacrylate; VAc: vinyl acetate; MAA: methacrylic acid; MA: methyl acrylate; BA: butyl acrylate.

Notes on data selection

Styrene. The data set from reference 1 (8 studies[12-19]) was augmented with 8 additional studies[20-27] published between 1996 and 2006, and covering a temperature range of 18-120°C. Analysis was by SEC using polystyrene standards, with the exception of Willemse et al.[27] in which MALDI-TOF MS was used to obtain the MMDs.

Methyl methacrylate. The data set from reference 2 (7 studies[13,16,20,34-37]) was augmented with 12 additional studies[27,38-48] published between 1997 and 2015, and covering a temperature range of –18-91.5°C. Analysis was by SEC using

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poly(MMA) standards, with the exception of Willemse et al.,[27] in which MALDI-TOF MS was used to obtain the MMDs, and Gruendling et al.,[47] in which coupled SEC/ESI-MS was used to determine accurate MMDs. Differences between k_p values obtained by these methods and those obtained by SEC with MMA calibration were small compared to the typical interlaboratory variation.

Ethyl methacrylate. The data set from reference 3 (3 studies[44,49,50]) was augmented with 1 additional study[47] published in 2010, and covering a temperature range of 0-91.5°C. In this study, coupled SEC/ESI-MS was used to obtain the MMDs.

Butyl methacrylate. The data set from reference 3 (4 studies[44,49-51]) was augmented with 4 additional studies[47,52-54] published between 2004 and 2016, and covering a temperature range of 0-91.5 C. Analysis was by SEC using universal calibration, with the exception of Gruendling et al.,[47] for which coupled SEC/ESI-MS was used to determine accurate MMDs. Differences between k_p values obtained by this method and those obtained by SEC with universal calibration were small compared to the typical interlaboratory variation.

Dodecyl methacrylate. The data set from reference 3 (3 studies[49-51]) was reanalysed. No additional data were found that complied with the IUPAC guidelines for determination of k_p using PLP.

Cyclohexyl methacrylate. The data set from reference 4 (3 studies[55-57]) was reanalysed. No additional data were found that complied with the IUPAC guidelines for determination of k_p using PLP.

Glycidyl methacrylate. The data set from reference 4 (2 studies[55,57]) was augmented with an additional study[58] published in 2008. This study covered a temperature range of 60-195°C, but only results from 60-90°C were added to the dataset in order to avoid contamination of the k_p data from depropagation. In this study, SEC with both light scattering detection and universal calibration were used to obtain MMDs. The light scattering results were used in the current reanalysis. While the 3 studies gave consistent estimates of k_p at 25°C, they differed quite significantly in their estimate of E_A, ranging from 20.3 to 26.2 kJ·mol^{-1}. As a result, the 95% JCR shown in Figure 6 may underestimate the true uncertainty in E_A for this monomer, and further studies would be helpful.

Benzyl methacrylate. The data set from reference 4 (3 studies[44,55,56]) was augmented with 1 additional study[59] published in 2011, and covering a temperature range of 14-72°C.

Isobornyl methacrylate. The data set from reference 4 (2 studies[55,56]) was reanalysed. No additional data were found that complied with the IUPAC guidelines for determination of k_p using PLP. It should be noted that these estimates were not considered a benchmark as the Mark-Houwink constants for iBoMA were not independently determined for each data set.

Butyl acrylate. The data set from reference 6 (6 studies[32,60-64]) was augmented with 3 additional studies[65-67] published between 2008 and 2017, and covering a temperature range of -25-70°C. Analysis was by SEC using universal calibration, with the exception of Willemse et al,[67] in which MALDI-TOF MS was used to obtain the MMDs. One early study[32] was excluded from the analysis due to the unusually low reported activation energy.

Methacrylic acid (15% in water). The data set from reference 5 (2 studies[68,69]) was reanalysed. No additional data were found that complied with the IUPAC guidelines for determination of k_p using PLP.

Methyl acrylate. The data set from reference 7 (5 studies[33,63,67,70-71]) was reanalysed. Analysis was by SEC using universal calibration, with the exception of Willemse et al,[67] in which MALDI-TOF MS was used to obtain the MMDs. The results of reference 33, extrapolated to ambient pressure from experiments at high pressure, were excluded. No additional data was found that complied with the IUPAC guidelines for determination of k_p using PLP.

Vinyl acetate. The data set from reference 8 (6 studies[35,63,72-75]) was reanalysed. No additional data were found that complied with the IUPAC guidelines for determination of k_p using PLP.

Conclusions

Systematic differences between laboratories have a significant effect on the results obtained from PLP studies of the temperature dependence of the propagation rate coefficient of monomers in radical polymerization. These differences occurred despite significant efforts to standardize experimental protocols and must be taken into account when analyzing the results of interlaboratory studies. Failure to do so leads to significant underestimation of the uncertainty associated with the Arrhenius parameters, and may produce erroneous estimates when the experimental dataset is dominated by the results of a single study.

We have presented revised estimates of activation energies and pre-exponential factors (and their 95% JCRs) which explicitly account for the interlaboratory variation and also incorporate additional data sets published subsequently to the benchmark studies. In doing so, we have estimated the typical interlaboratory error as ± 0.08 for ln k_p (equivalent to ± 8% in k_p) and ± 1.4 kJ·mol^{-1} for E_A, with a correlation coefficient of 0.04. This may be used as an estimate of the uncertainty of a single study of k_p that has not been independently replicated.

The existence of systematic differences between laboratories underlines that in an interlaboratory study, it is better to have a relatively small number of results from many laboratories, rather than many results from a small number of laboratories. Repetition of experiments can reduce the uncertainty in a single laboratory's result, but once this becomes small relative to the interlaboratory uncertainty, no further increase in precision is obtained from additional experiments. This applies equally to experiments where many data points are obtained from a single experiment (for example in the determination of reactivity ratios by tracking the change in monomer feed composition with conversion, or the determination of Mark-Houwink-Sakurada constants from online viscosimetry). In these cases, data points from a single experimental run should be assumed to be correlated, and multiple independent experiments should

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be run in order to determine the uncertainty associated with the parameter estimates.

In summary, we make the following recommendations:

1. The revised estimates of k_p at 25°C, A, and E_A and their associated uncertainties given in Table 1 replace the previously reported values[1-8] as IUPAC benchmarks.
2. The estimated interlaboratory error of ± 8% in k_p and ± 1.4 kJ·mol^{-1} in E_A should be assumed to apply to all PLP studies, and can provide a first estimate of the uncertainty in reported values when no independent replication is available.

In addition, we note that the reported values for GMA show relatively poor agreement between replications, while the activation energy for dodecyl methacrylate is unusually low relative to the other methacrylates investigated. Further studies on these monomers would help to improve the accuracy of their parameter estimates.

Author Contributions

SH: Conceptualization, data curation, formal analysis, writing – original draft, writing – review and editing

SB, RAH, TJ, GTR: conceptualization, writing – review and editing

Conflicts of interest

There are no conflicts to declare.

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Notes and references

‡ T_0 is given by the harmonic mean of the experimental temperatures: $T_0 = \left(\frac{\sum T_i^{-1}}{N}\right)^{-1}$

§ $F_{\mu,\nu}$ refers to the F distribution with μ and ν degrees of freedom.

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