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Update and Critical Reanalysis of IUPAC Benchmark Propagation Rate Coefficient Data

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Polymer Chemistry

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Response to Reviewers:

We thank the reviewers for their evaluation of our work and their insightful comments. Our point-by-point replies are given in red below. All changes to the text have been highlighted in red in the revised version of the manuscript.

Referee 1

The current work is of high importance. Propagation rate coefficients are key in understanding vinyl polymerization. The authors are all very well recognized and I support this work. Below some minor suggestions and comments:

Generally <2%: perhaps better <5%. Or have all number been checked compared to the reported previous contributions? Just to be sure this question.

We have replaced 2% with 5%

In this type of writing [M] should by [M]0 or at least a disclaimer should be added.

We have specified that initial [M] is precisely known, and that if the change in monomer concentration is assumed to be negligible, the major source of error is in the analysis of the molecular weight distribution. (Assuming negligible conversion is common practice as conversion is typically limited to around 1%. Some labs do, however, correct for conversion during the PLP experiment).

General comment: the introduction/abstract should clearly state these are vinyl monomers (or (PLP) conditions associated with it) that lead to one dominant macroradical type.

In fact, most of the benchmarked monomers are methacrylates, and hence not strictly vinyl monomers. We believe that the presence of a polymerizable C=C double bond is implied in the phrase 'common monomers in radical polymerization'. The phrase 'and their respective macroradicals' has been added in order to specify that benchmark values are obtained for the addition of the macroradical that is directly derived from the monomer, and not for macroradicals obtained through secondary reactions such as intramolecular chain transfer.

Table 1: a general person from kinetics directly jumping to Table 1 would probably say about the bold numbers that one always has correlation between A and EA. Hence, if only one number is in bold (as often the case in the table) this needs some extra context. Of course the A values are in power notation (of course one has the parametrization but note the typical procedure is a series of isothermal runs and then fitting).

It is clearly stated in the caption of Table 1 that values in bold are those for which a >1σ difference is observed between the revised and initial values. This is a fairly arbitrary cut-off, intended only to highlight the parameters for which relatively substantial revisions have taken place. For this reason, we have not made any further change to the text. To answer the reviewer's comment, as a result of the method used in this work, which explicitly takes into account systematic differences between results from different laboratories, the revised

estimates of uncertainty in E_A and k_p at 25°C are larger than the initial estimates. Due to the strong correlation between E_A and A, and the effect of extrapolating far from the experimental temperature range, the revised estimates of uncertainty in A are larger still. Thus it can occur that there is >1σ difference in E_A but the difference in estimates of A is <1σ, as is the case for styrene. In the case of butyl acrylate, the other monomer for which A or E_A (but not both) is bold, a substantial (>1σ) difference in k_p, combined with a small (<1σ) difference in E_A is responsible for the >1σ difference in A.

For a general reader (less in the PLP field) overtone should be explained.

We have added the phrase: " corresponding to chains that survived the first radical burst and were terminated by the second or subsequent radical bursts "

Later on the authors indeed confirm a well-chosen temperature, e.g. for acrylates sufficiently low T. Please add regarding the limit for high temperature acrylate interference the following ref: Polym. Chem. 2019 10, 4116.

This reference has been added to the text as reference 12

“In order to mitigate these problems, when one laboratory dominated the dataset, results from other laboratories were given extra weight”. I understand why this was done but a person from statistics would easily argue. I would rephrase a bit this sentence (later on the authors themselves start about this).

Indeed, this was carried out in the original data analysis (references 1, 3 and 4) but is not really defensible from a statistical standpoint. One of the aims of this work was to apply a more consistent method of weighting the data, so that results from different laboratories would have nearly equal weight regardless of the number of data points obtained by each laboratory.

In order to clear up any confusion, we have modified the sentence as follows:

In order to mitigate these problems, the following strategies were applied *in the original analysis*: When one laboratory dominated the dataset, results from other laboratories were given extra weight.[1,3,4]

“other words, we should not expect two laboratories to converge on the same parameter estimates, no matter how many times they repeat the experiments.” The focus is on the inflection point but the ideal world is a comparison of PLP-SEC traces. Of course practically this is far from easy (I don’t expect any change in the text).

Indeed, it would be better to compare the exact molecular weight distributions of the polymer, if these could be obtained free from error. Unfortunately, we are forced to use SEC or other analytical techniques to access the molecular weight distributions. Each technique brings its own errors and biases, and these are incorporated into the results. As each lab has somewhat different equipment and protocols, each has slightly different errors and biases, which must be taken into account in the data analysis. Thus, while it is reasonable to expect broad agreement from one laboratory to another, it is not uncommon for two laboratories to produce highly precise estimates of a rate coefficient which differ by more than the expected amount given the random variation within each laboratory's dataset. This would likely be the case even if the full

PLP-SEC traces were compared.

Perhaps Figure 5 can go to SI.

We believe that the inclusion of Figure 5 in the manuscript is justified as it shows (1) the differences (and similarities) between the 3 sets of parameter estimates for STY discussed in the manuscript (original benchmark values, revised analysis using only STY data, revised analysis using all benchmarked monomer data), (2) the effect on estimates of A, and (3) the estimated uncertainty in k_p of styrene as a function of temperature. These are key points of the analysis, and we feel it is important to include one example in the main text. Similar graphs for the remaining benchmarked monomers are included in the Supporting Information.

The conclusions are somewhat also with “new” elements, I mean not really mentioned before. I can understand the writing style here but one can still optimize.
We believe the reviewer is referring to the paragraph starting 'the existence of systematic differences between laboratories...' This has been moved from the Conclusions to the end of the Discussion section.

Referee: 2

This manuscript further enhances the accuracy in determining the kp values. The authors decided to come back to already existing information on benchmark kp values for 13 monomers, extended by the follow-up studies. A critical statistical analysis resulted in estimation of the interlaboratory errors in ln kp and EA that are recommended to be applied as estimates of uncertainty in kp values in the absence of the interlaboratory comparison.

This study is found as clever and useful. Even though the authors suggest the possible sources of errors in some originally determined benchmark values, it is pleasing to see that no critical differences between existing benchmark values and the revised estimates were found.

This points at the robustness of the PLP-SEC method and accuracy of already existing kp values (benchmarked as well as those not included in this work). I would like to make the point that these values do not suffer from the reproducibility in standard deviations up to 30 % stemming from the inaccuracy in the SEC method. Such message given in p.4, that may be incorrectly understood as a room for standard deviation in the SEC of the PLP-SEC method, is recommended to be softened a bit. This number comes from refs 28 and 29, which are round robin tests on determination Mw and Mn average molar masses, influenced by setting the baseline and integration limits in different laboratories (apart from other sources of errors). Such errors are not expected in determination of the inflection points and, therefore, ±8% in kp should not be directly correlated with 30 % potential error from SEC.

We have added the following note (p4, end of column 1):

It should be noted that this estimate of SEC reproducibility in the determination of average molar masses is influenced by selection of baselines and integration limits, which are not applicable to the identification of a single molar mass corresponding to the inflection point of the PLP-SEC trace. Hence, reproducibility in k_p determination by PLP-SEC is expected to be superior to that of determination of average molar masses.

Figure 4 is one of the core Figures of the manuscript. The captions should perhaps more directly contain the information that it comprises all the benchmarked monomers (following the title of this subchapter).

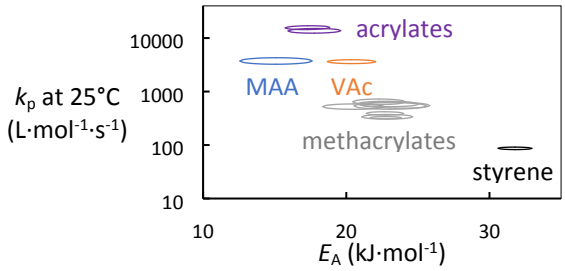
The phrase 'for all benchmarked monomers' has been added to the caption of Figure 4.

I recommend this manuscript as highly suitable for being published in Polymer Chemistry.

Additional changes:

- We have deleted the phrase 'and are reproduced in the Supporting Information' from the sentence 'These curated datasets were published in the original articles,[1-8] and are reproduced in the Supporting Information' (p3). This was included in error from an earlier draft of the manuscript – as the full datasets are readily accessible in the published literature it was thought to be redundant to reproduce them in the Supporting Information.
- References have been renumbered
- Some minor grammatical changes and corrections to citations (highlighted in red in the revised document)

Table of Contents Entry



The dataset used to generate IUPAC benchmark Arrhenius parameters for propagation rate coefficients in radical polymerization is extended and reanalyzed, taking into account systematic interlaboratory variation, to generate new parameter estimates and 95% joint confidence intervals.

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 and their respective macroradicals 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 <5%) 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 initial [M] precisely known (and assuming negligible consumption of monomer during the experiment), the accuracy of the technique primarily depends 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 corresponding to chains that survived the first radical burst and were terminated by the second or subsequent radical bursts, 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 81 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

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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

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.

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 ($L \cdot mol^{-1} \cdot s^{-1}$)	E_A ($kJ \cdot mol^{-1}$)	k_p at 25°C ($L \cdot mol^{-1} \cdot s^{-1}$)	T (°C)	N[c]	A ($L \cdot mol^{-1} \cdot s^{-1}$)	E_A ($kJ \cdot mol^{-1}$)	k_p at 25°C ($L \cdot mol^{-1} \cdot s^{-1}$)	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]	$\mathbf{10^{7.34(4)}}$	17.9(2)	$\mathbf{16.4(3) \times 10^3}$	-65–20	5	$\mathbf{10^{7.22(11)}}$	17.3(6)	$\mathbf{15.7(5) \times 10^3}$	-65–70	8
MAA[6]	$10^{6.19(8)}$	15.0(4)	$3.72(5) \times 10^3$	18–89	2	$10^{6.21(18)}$	15.1(1.0)	$3.73(21) \times 10^3$	18–89	2
MA[7]	$10^{7.15(5)}$	17.3(2)	$\mathbf{13.1(1) \times 10^3}$	-28–61	5	$10^{7.25(13)}$	17.8(7)	$\mathbf{13.7(5) \times 10^3}$	-26–61	4
VAc[8]	$10^{7.13(7)}$	20.4(4)	$3.60(4) \times 10^3$	5–70	6	$10^{7.13(12)}$	20.4(7)	$3.62(12) \times 10^3$	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 the 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

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.[5,7,11,12] These curated datasets were published in the original articles.[1-8]

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, the following strategies were applied *in the original analysis*: 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.[2,13]

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),[14-17] and 4 provided multiple k_p values across a range of temperatures.[13,18-20] 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.

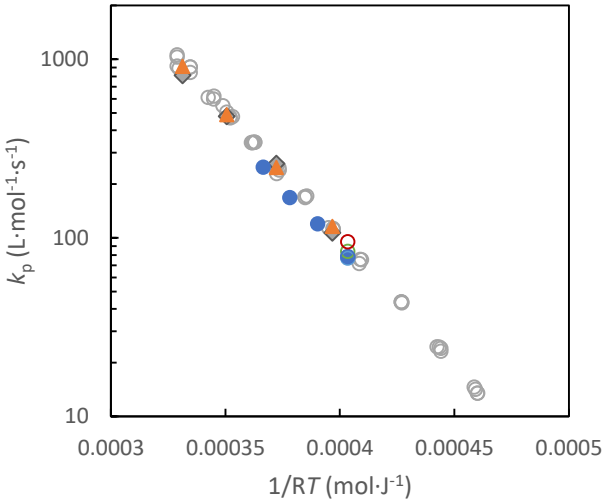

Figure 1. Dataset used to fit Arrhenius parameters for k_p of styrene radical polymerization in bulk. Open circles (grey): data from reference 13; filled diamonds (grey): data from reference 18; filled circles (blue): data from reference 19; filled triangles (orange) data from reference 20; remaining points from references 14-17.

In Figure 2, 95% JCRs are shown for the four studies[13,18-20] that provided sufficient data to estimate them, while the k_p values at 25°C from the 4 remaining studies[14-17] 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.

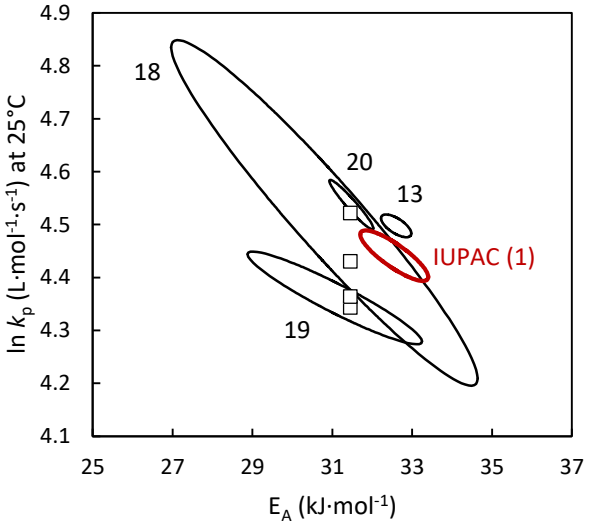

Figure 2. 95% Joint confidence regions (JCR) for Arrhenius parameters of k_p of styrene. In black, the JCRs corresponding to the individual studies of references 13 and 18-20. The open black squares represent 4 independent measures (references 14-17) of k_p at 25°C, shown at an arbitrary E_A. The red 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 13 and 20), 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 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):

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

In eq 5, $k_{p,ij}$ represents the j^{th} measurement of k_p from the i^{th} 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 i^{th} 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[13-20] of STY are grouped in Table 2, along with those of 8 additional studies[21-28] 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 average molar masses obtained by SEC.[29,30] It should be noted that this estimate of SEC reproducibility in the determination of average molar masses is influenced by selection of baselines and integration limits, which are not applicable to the identification of a single molar mass corresponding to the inflection point of the PLP-SEC trace. Hence, reproducibility in k_p determination by PLP-SEC is expected to be superior to that of determination of average molar masses.

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

reproducibility of SEC, the intralaboratory reproducibility (i.e. the same sample reanalysed using the same equipment) is generally good.[29,30] 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[31,32] 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.

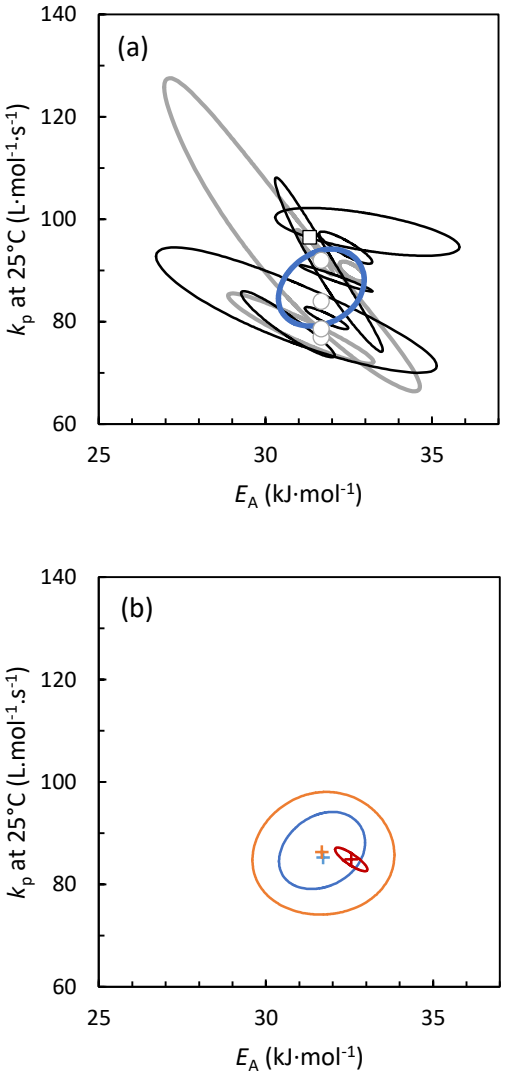

Figure 3. 95% Joint confidence regions (JCRs) for individual studies (a) and pooled data (b) for E_A and k_p at 25°C of styrene radical polymerization in bulk. (a) JCRs corresponding to references 17-20 shown in grey, additional data shown in black. Open circles represent k_p from single experiments (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

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:

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

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[33] 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[34] 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.

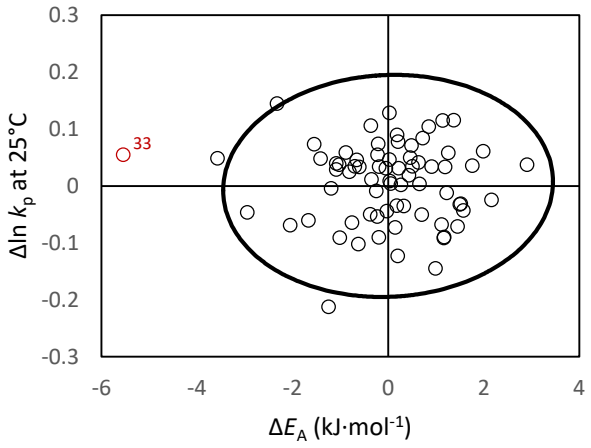

Figure 4. Interlaboratory variation in estimates of ln k_p at 25°C and E_A for all benchmarked monomers, and pooled 95% JCR. The point in red (reference 33) was considered an outlier and excluded from the study. Standard errors in ln k_p at 25°C and E_A are 0.08 and 1.4 kJ·mol^{-1}, respectively, with 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.

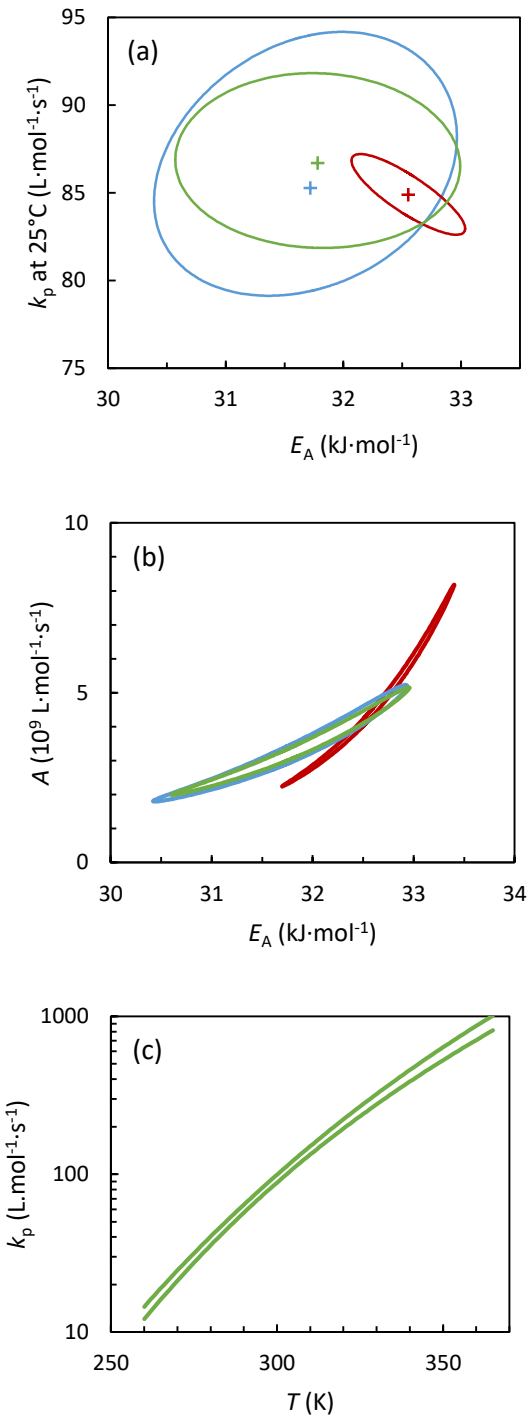

Figure 5. (a) Comparison of parameter estimates and 95% JCRs for E_A and ln k_p at 25°C of radical polymerization of styrene in bulk obtained using estimates of interlaboratory variation obtained from studies on styrene (blue) or from pooled studies of all benchmarked monomers (green). Original IUPAC 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

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.

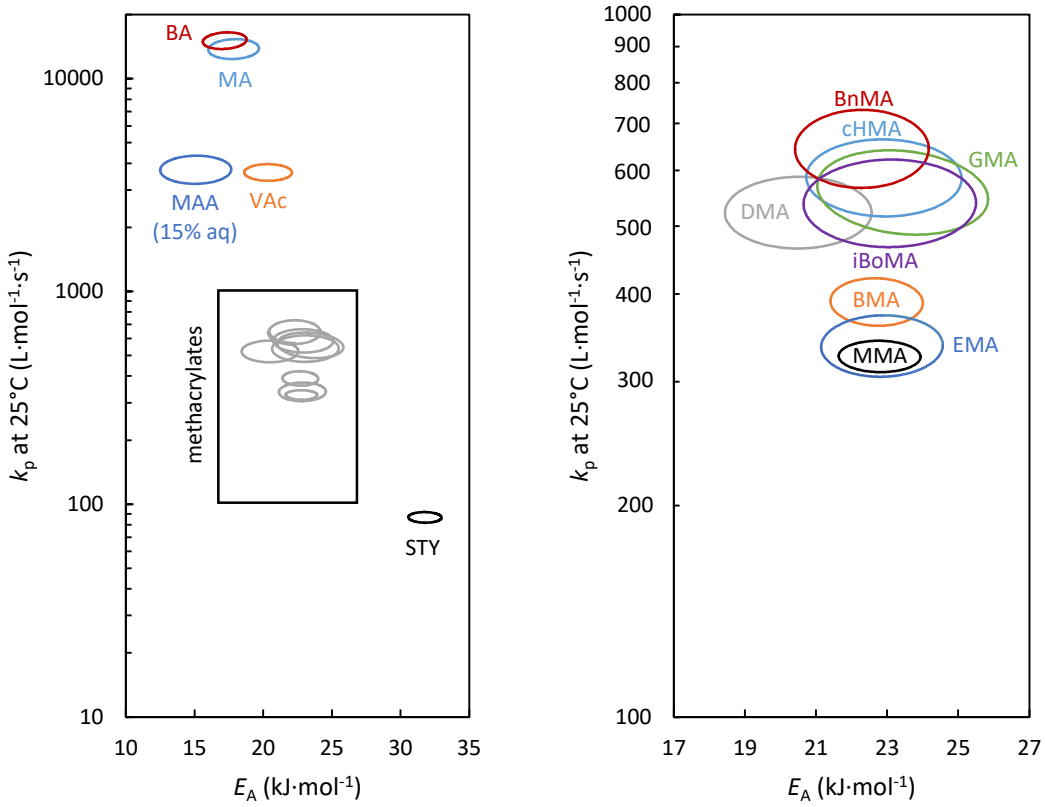

Figure 6. Revised 95% JCRs for monomers for which IUPAC benchmark values are available. MMA: methyl methacrylate; EMA: ethyl methacrylate; BMA: butyl methacrylate; iBoMA: isobornyl methacrylate; DMA: dodecyl methacrylate; GMA: glycidyl methacrylate; cHMA: cyclohexyl methacrylate; BnMA: benzyl methacrylate;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

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

Notes on data selection

Styrene. The data set from reference 1 (8 studies[13-20]) was augmented with 8 additional studies[21-28] 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.[28] in which MALDI-TOF MS was used to obtain the MMDs.

Methyl methacrylate. The data set from reference 2 (7 studies[14,17,21,35-38]) was augmented with 12 additional studies[28,39-49] published between 1997 and 2015, and covering a temperature range of –18-91.5°C. Analysis was by SEC using 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.,[48] 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[45,50,51]) 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[45,50-52]) was augmented with 4 additional studies[48,53-55] 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.,[48] 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[50-52]) 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[56-58]) 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[56,58]) was augmented with an additional study[59] 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[45,56,57]) was augmented with 1 additional study[60] published in 2011, and covering a temperature range of 14-72°C.

Isobornyl methacrylate. The data set from reference 4 (2 studies[56,57]) 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[33,61-65]) was augmented with 3 additional studies[66-68] 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,[68] in which MALDI-TOF MS was used to obtain the MMDs. One early study[33] 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[69,70]) 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[34,64,68,71,72]) was reanalysed. Analysis was by SEC using universal calibration, with the exception of Willemse et al.,[68] in which MALDI-TOF MS was used to obtain the MMDs. The results of reference 34, 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[36,64,73-76]) 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.

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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Supporting Information for Critical Reanalysis of IUPAC Benchmark Propagation Rate Coefficient Data

Sabine Beuermann, Simon Harrisson, Robin A. Hutchinson, Tanja Junkers and Gregory T. Russell

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Table S1. Estimates of k_p at 25°C, A and E_A for styrene from individual studies obtained by linear least squares fitting of ln k_p to $(1/T - 1/T_0)$, T_0 = 298.15 K. Units of E_A are kJ·mol^{-1}, while k_p and A are given in L·mol^{-1}·s^{-1}.

Ref.	T (°C)	k_p @ 25°C	Ln k_p @ 25°C	E_A	Log_{10} A[a]	N[b]	se[c]	V(ln k_p)[c] × 10^3	V(E_A)[c]	Cov(ln k_p, E_A)[c] × 10^3
S1	25	77.0	4.34			1	0.052	2.70		
S2	25	84.0	4.43			1	0.050[d]	2.50		
S3	25	78.6	4.36			1	0.050[d]	2.50		
S4	25	92.0	4.52			1	0.050[d]	2.50		
S5	30–90	92.0	4.52	30.8	7.36	4	0.075	5.27	2.33	-95.1
S6	25–55	78.4	4.36	31.1	7.34	4	0.023	0.411	0.756	-14.2
S7	30–90	93.5	4.54	31.5	7.49	4	0.011	0.108	0.0478	-1.95
S8	-12–93	89.8	4.50	32.6	7.66	45	0.042	0.0482	0.0228	-0. 431
S9[e]	25–60	96.5	4.57	31.3	7.47	2	0.050[d]	2.50	2.78	-59.0
S10[e]	18–57	81.4	4.40	30.9	7.33	10	0.092	1.53	2.82	-43.7
S11[e]	18–57	80.7	4.39	31.8	7.48	24	0.023	0.532	0.0665	-1.23
S12[e]	30–40	88.4	4.48	32.1	7.57	4	0.0055	0.0391	0.187	-2.43
S13[e]	18–47	97.4	4.58	33.1	7.78	6	0.037	0.259	1.21	-6.49
S14[e]	25–70	79.2	4.37	30.7	7.27	4	0.022	0.355	0.313	-8.54
S15[e]	50–120	89.5	4.49	31.9	7.54	10	0.052	1.61	0.415	-23.6
S16[e]	20–60	94.4	4.55	32.4	7.65	3	0.011	0.0741	0.101	-1.84
Average		86.8[f]	4.46	31.7	7.49	16(12)[g]		6.66	0.585	32.2

[a] calculated as $\text{Log}_{10} A = [\ln k_{p,298K} + E_A/(R \times 298K)]/\ln(10)$. [b] number of experimental points reported. [c] se: standard error in data points ($= \sqrt{\frac{SSR}{N-2}}$) where SSR is the sum of squared residuals to the linear fit; V(X): variance of X; Cov(X, Y): covariance of X and Y. [d] for studies with only one or two reported values, se was assumed to be 0.05, corresponding to a reproducibility of +/- 5% in the k_p measurement. [e] studies not included in Buback *et al.*, *Macromol. Chem. Phys.* 1995, **196**, 3267-3280 (S17). [f] Geometric mean of k_p values. [g] Here N represents the number of individual studies. The number in parentheses is the number of studies reporting an E_A value.

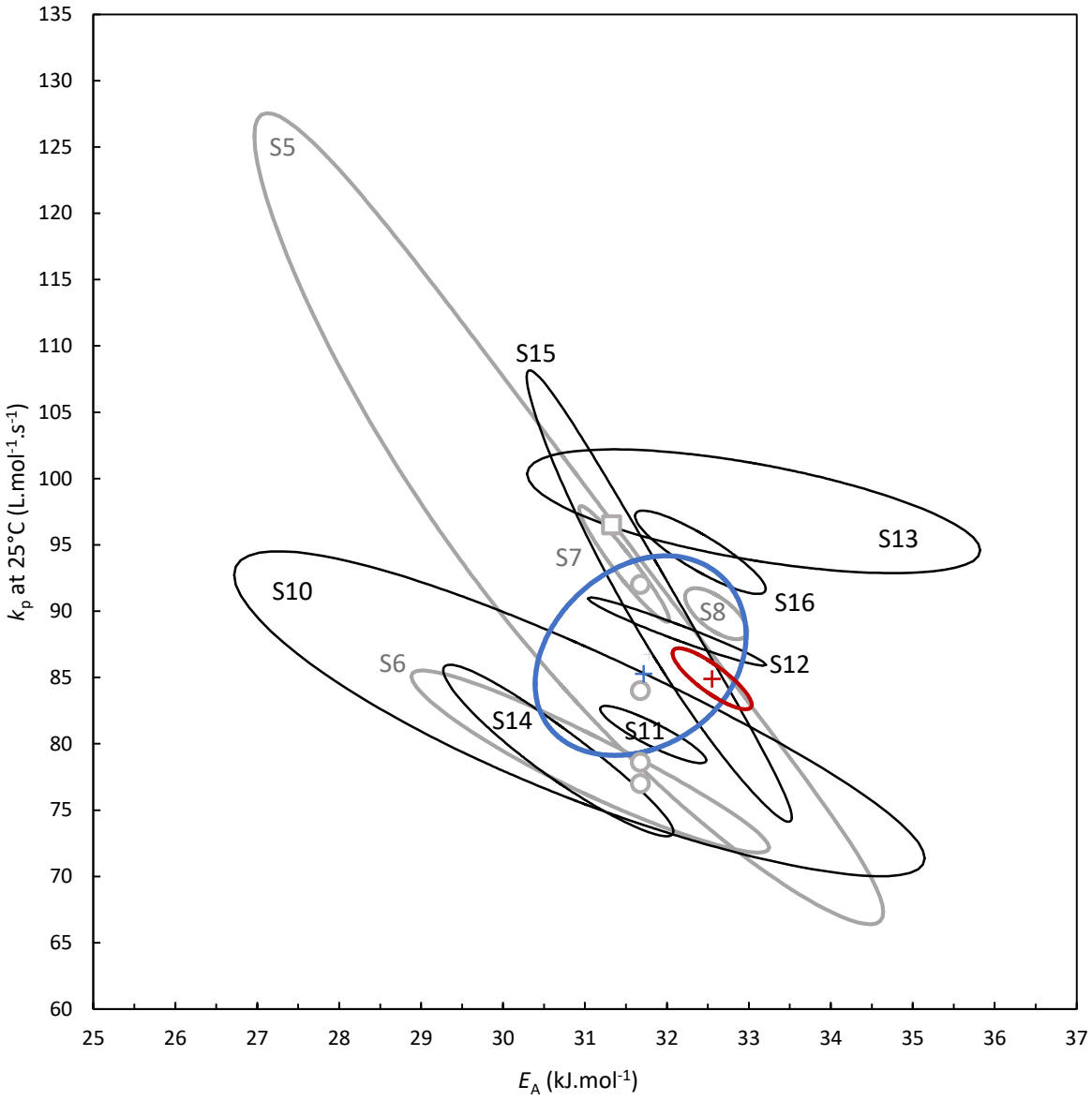


Figure S1. 95% JCRs for individual studies of k_p of styrene (grey: original data set;[S17] black: expanded data set), and for the weighted average of studies with estimated uncertainty from the pooled interlaboratory variance (blue). The originally calculated 95% joint confidence region,[S17] obtained by pooling the data points of the original IUPAC data set, is shown for comparison (red). Open circles represent the point estimates for k_p at 25°C of studies S1-S4, shown at the interlaboratory average E_A of 31.7 kJ.mol^{-1}. The open square represents the point estimate for k_p and E_A of study S9. Crosses represent the point estimates for the weighted average of studies (blue) and the original IUPAC benchmark value (red).

Table S2. Estimates of k_p at 25°C, A and E_A for methyl methacrylate from individual studies obtained by linear least squares fitting of ln k_p to $(1/T - 1/T_0)$, T_0 = 298.15 K. Units of E_A are kJ·mol^{-1}, while k_p and A are given in L·mol^{-1}·s^{-1}.

Ref.	T (°C)	k_p @ 25°C	Ln k_p @ 25°C	E_A	Log_{10} A[a]	N[b]	se[c]	V(ln k_p)[c] × 10^3	V(E_A)[c]	Cov(ln k_p, E_A)[c] × 10^3
S1	25	315	5.75				0.027	0.149		
S4	25	359	5.88				0.05[d]	2.50		
S9	25–60	372	5.92	22.4	6.50	2	0.05[d]	2.50	2.78	-59.0
S16	-18–25	348	5.85	24.4	6.81	3	0.013	0.151	0.0758	2.65
S18	25	294	5.69				0.012	0.0721		
S19	-1–70	317	5.76	23.9	6.69	12	0.035	0.110	0.0806	-0.727
S20	10–90	340	5.83	21.3	6.26	37	0.042	0.0871	0.0612	-1.57
S21	20–90	310	5.74	22.2	6.37	8	0.027	0.208	0.0937	-3.35
S22[d]	25	316	5.75			6	0.067	4.55		
S23[d]	20–25	319	5.77	24.6	6.81	11	0.030	0.185	7.17	26.9
S24[d]	25–60	331	5.80	22.0	6.38	12	0.044	0.519	0.661	-15.3
S25[d]	40–50	343	5.84	18.8	5.83	6	0.021	1.83	2.36	-64.4
S26[d]	30–70	317	5.76	23.9	6.69	11	0.076	2.52	2.85	-75.4
S27[d]	18–57	308	5.73	22.3	6.39	8	0.059	0.629	1.31	-16.2
S28[d]	6–47	299	5.70	23.6	6.60	24	0.041	0.0715	0.150	-0.278
S29[d]	40	338[f]	5.82[f]			2	0.05[d]	2.53[g]		
S30[d]	20–60	343	5.84	22.4	6.46	8	0.063	0.748	0.811	-14.4
S31[d]	11–92	344	5.84	22.9	6.54	18	0.018	0.0361	0.0202	-0.599
S32[d]	10–42	328	5.79	23.1	6.55	20	0.037	0.0705	0.238	-0.535
Average		336[e]	5.82	22.7	6.50	19(14)[f]		15.7	2.16	-25.6

[a] calculated as $\text{Log}_{10} A = [\ln k_{p,298K} + E_A/(R\times 298K)]/\ln(10)$. [b] number of experimental points reported. [c] se: standard error in data points ($= \sqrt{\frac{SSR}{N-2}}$) where SSR is the sum of squared residuals to the linear fit; V(X): variance of X; Cov(X, Y): covariance of X and Y. [d] studies not included in Beuermann *et al.*, *Macromol. Chem. Phys.,* 1997, **198**, 1545-1560 (S33). [e] Geometric mean of k_p values. [f] Measurements at 313K adjusted to 298 K using average E_A of all studies. [g] Variance at 298K (V_{298}) calculated as $V_{298} = V_{313} + V_{EA}*[1/R*(1/313-1/298)]^2 + \text{Cov}_{kp,EA}*[1/R*(1/313-1/298)]$, where V_{313} is the measured variance at 313K, and V_{EA} and $\text{Cov}_{kp,EA}$ are the estimated variance in E_A and covariance in E_A and ln k_p. [h] Here N represents the number of individual studies. The number in parentheses is the number of studies reporting an E_A value.

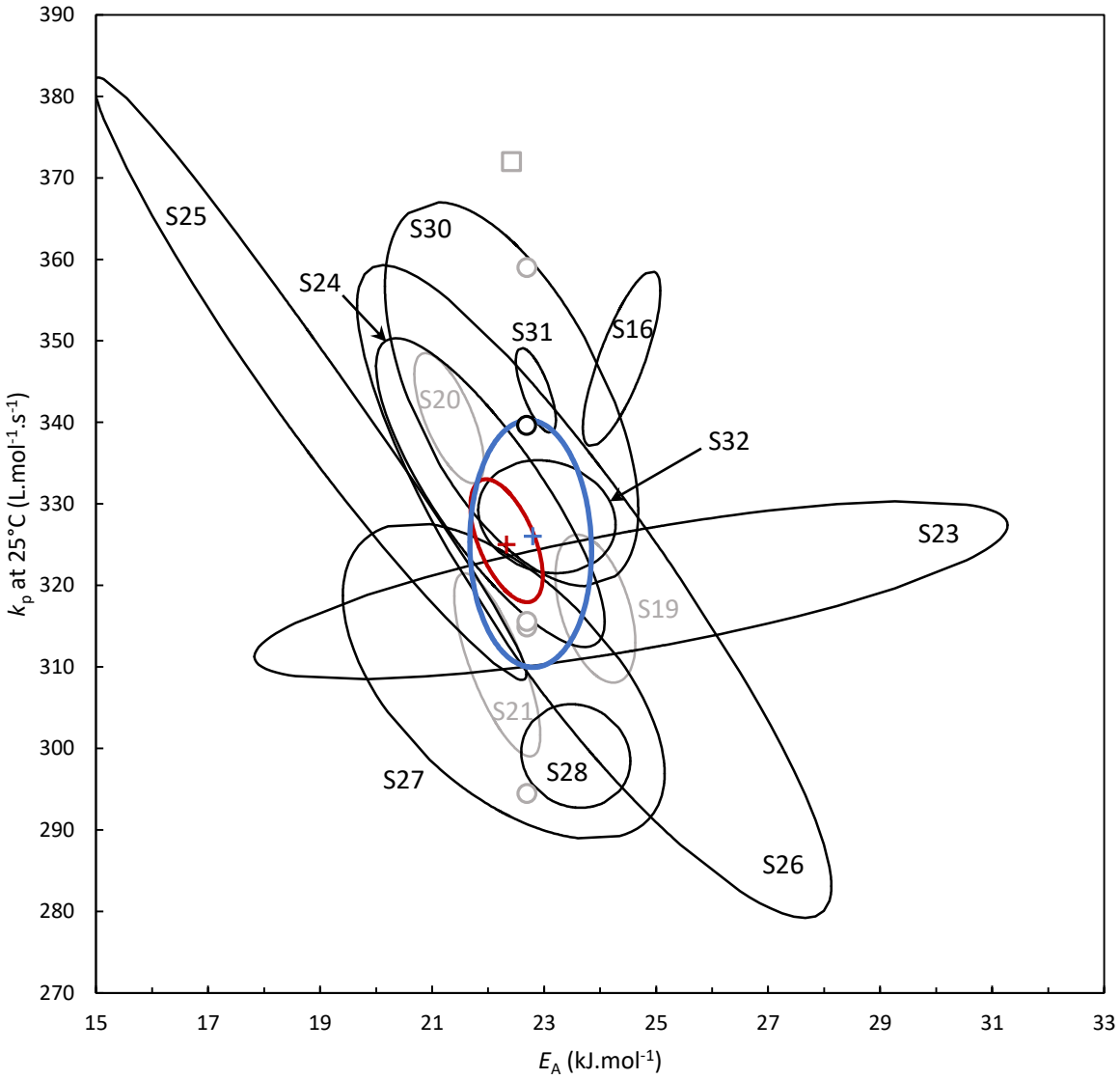


Figure S2. 95% JCRs for individual studies of k_p of methyl methacrylate (original data set:[S33] gray; expanded data set: black), and weighted average of studies with estimated uncertainty from the pooled interlaboratory variance (blue). The originally calculated 95% joint confidence region,[S33] obtained by pooling the data points of the original IUPAC data set, is shown for comparison (red). Open circles represent the point estimates for k_p at 25°C of studies S1, S4, S18 (in gray) and S22 (in black), shown at the interlaboratory average E_A of 22.4 kJ.mol^{-1}. The open square represents the point estimate for k_p and E_A of study S9.

Table S3. Estimates of k_p at 25°C, A and E_A for ethyl methacrylate from individual studies obtained by linear least squares fitting of ln k_p to $(1/T - 1/T_0)$, T_0 = 298.15 K. Units of E_A are kJ·mol^{-1}, while k_p and A are given in L·mol^{-1}·s^{-1}.

Ref.	T (°C)	k_p @ 25°C	Ln k_p @ 25°C	E_A	Log_{10} A[a]	N[b]	se[c]	V(ln k_p)[c] × 10^3	V(E_A)[c]	Cov(ln k_p, E_A)[c] × 10^3
S28	6–47	292	5.68	23.8	6.64	30	0.041	0.0559	0.146	-0.321
S34	10–90	354	5.87	21.4	6.31	9	0.024	0.0980	0.0442	-1.21
S35	10–90	356	5.88	22.6	6.52	30	0.055	0.292	0.136	-5.11
S31[d]	1–91	352	5.86	23.5	6.66	20	0.009	0.00700	0.00406	-0.0931
Average		337[e]	5.82	22.9	6.53	4[f]		9.34	1.15	-65.7

[a] calculated as $Log_{10} A = [\ln k_{p,298K} + E_A/(R \times 298K)]/\ln(10)$. [b] number of experimental points reported. [c] se: standard error in data points ($= \sqrt{\frac{SSR}{N-2}}$) where SSR is the sum of squared residuals to the linear fit; V(X): variance of X; Cov(X, Y): covariance of X and Y. [d] Study not included in Beuermann *et al.*, *Macromol. Chem. Phys.*, 2000, **201**, 1355–1364 (S36). [e] Geometric mean of k_p values. [f] Here N represents the number of individual studies.

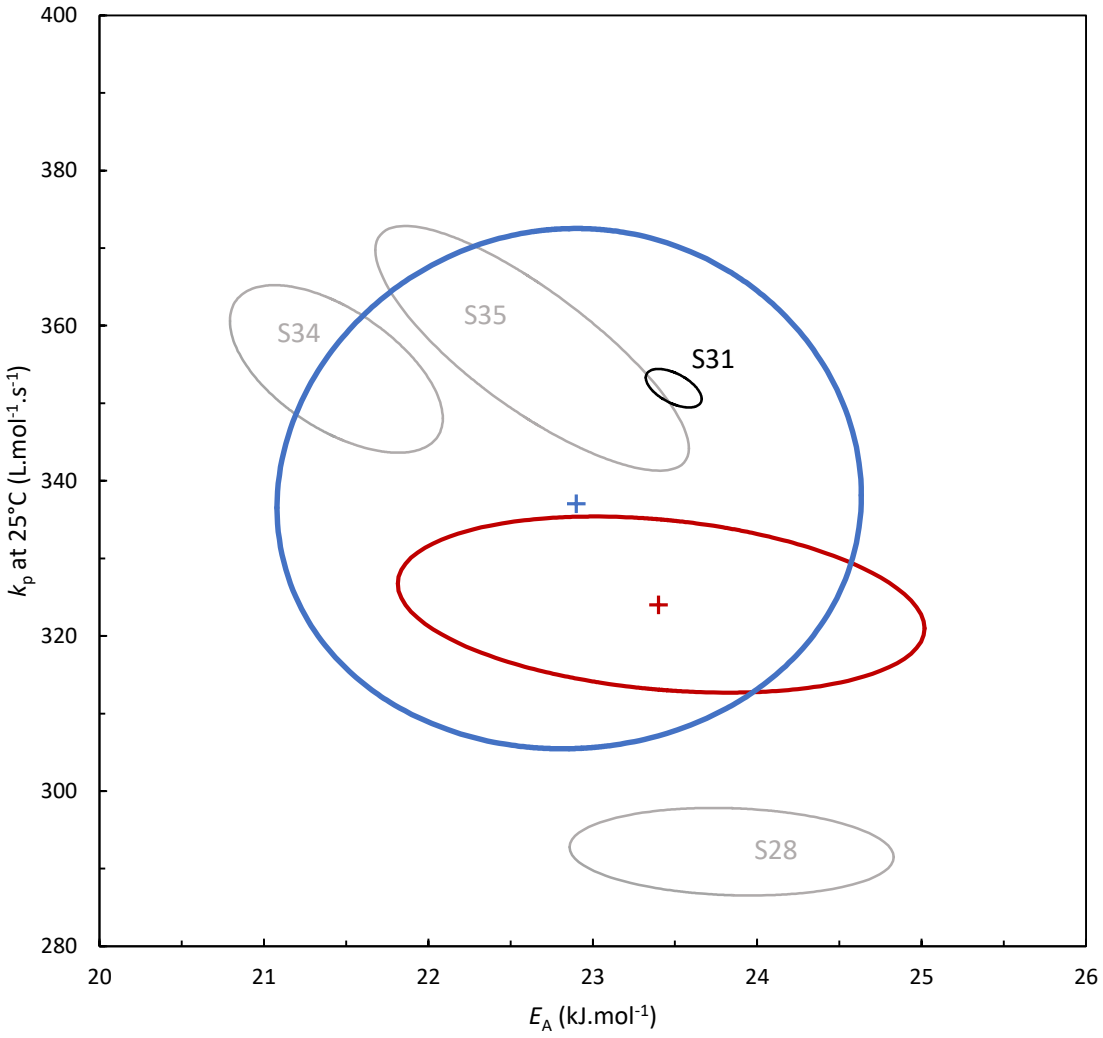


Figure S3. 95% JCRs for individual studies of k_p of ethyl methacrylate (original data set:[S36] gray; expanded data set: black), and weighted average of studies with estimated uncertainty from the pooled interlaboratory variance (blue). The originally calculated 95% joint confidence region,[S36] obtained by pooling the data points of the original IUPAC data set (restricted to the temperature range 0-50°C and counting points of S34 and S35 twice), is shown for comparison (red).

Table S4. Estimates of k_p at 25°C, A and E_A for butyl methacrylate from individual studies obtained by linear least squares fitting of ln k_p to $(1/T - 1/T_0)$, T_0 = 298.15 K Units of E_A are kJ·mol^{-1}, while k_p and A are given in L·mol^{-1}·s^{-1}.

Ref.	T (°C)	k_p @ 25°C	Ln k_p @ 25°C	E_A	Log_{10} A[a]	N[b]	se[c]	V(ln k_p)[c] × 10^3	V(E_A)[c]	Cov(ln k_p, E_A)[c] × 10^3
S37	-20–50	390	5.97	22.8	6.59	17	0.050	0.178	0.165	2.35
S35	10–90	403	6.00	21.8	6.42	42	0.072	0.543	0.165	-8.31
S34	10–90	399	5.99	21.7	6.41	10	0.026	0.117	0.0464	-1.47
S28	6–47	343	5.84	23.0	6.57	30	0.037	0.0465	0.118	-0.315
S38[d]	50–80	354	5.87	24.0	6.59	6	0.045	3.26	13.2	-62.3
S39[d]	50–80	400	5.99	22.8	6.75	6	0.056	5.12	2.08	-97.8
S32[d]	0–91	402	6.00	23.3	6.69	20	0.010	0.00758	0.00438	-0.101
S40[d]	1–70	420	6.04	23.0	6.66	7	0.044	0.301	0.233	-2.26
Average		383[e]	5.95	22.2	6.58	8[f]		1.41	0.118	-7.41

[a] calculated as $\text{Log}_{10} A = [\ln k_{p,298K} + E_A/(R \times 298K)]/\ln(10)$. [b] number of experimental points reported. [c] se: standard error in data points ($= \sqrt{\frac{SSR}{N-2}}$) where SSR is the sum of squared residuals to the linear fit; V(X): variance of X; Cov(X, Y): covariance of X and Y. [d] studies not included Beuermann *et al.*, *Macromol. Chem. Phys.* 2000, **201**, 1355–1364 (S36) [e] Geometric mean of k_p values. [f] Here N represents the number of individual studies.

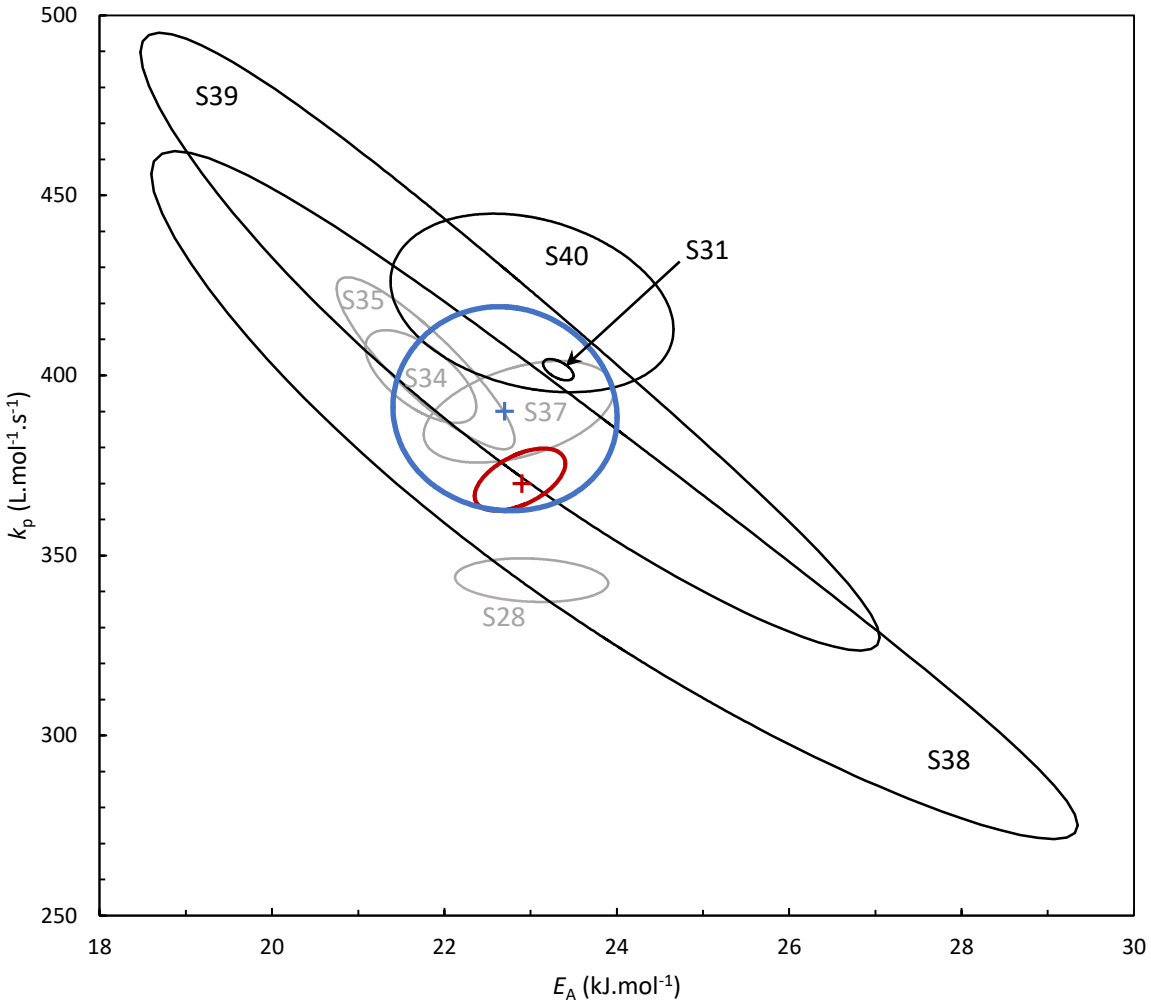


Figure S4. 95% JCRs for individual studies of k_p of butyl methacrylate (original data set:[S36] gray; expanded data set: black), and weighted average of studies with estimated uncertainty from the pooled interlaboratory variance (blue). The originally calculated 95% joint confidence region,[S36] obtained by pooling the data points of the original IUPAC data set, is shown for comparison (red).

Table S5. Estimates of k_p at 25°C, A and E_A for dodecyl methacrylate from individual studies obtained by linear least squares fitting of ln k_p to $(1/T - 1/T_0)$, T_0 = 298.15 K. Units of E_A are kJ·mol^{-1}, while k_p and A are given in L·mol^{-1}·s^{-1}.

Ref.	T (°C)	k_p @ 25°C	Ln k_p @ 25°C	E_A	Log_{10} A[a]	N[b]	se[c]	V(ln k_p)[c] × 10^3	V(E_A)[c]	Cov(ln k_p, E_A)[c] × 10^3
S40	9–60	503	6.22	20.9	6.36	27	0.092	0.484	0.709	-10.9
S38	10–90	523	6.26	20.8	6.37	33	0.056	0.233	0.112	-3.95
S37	10–60	539	6.29	20.0	6.23	9	0.019	0.0436	0.0585	-0.416
Average		522[d]	6.26	20.5	6.32	3[e]		1.18	0.268	-15.5

[a] calculated as $\text{Log}_{10} A = [\ln k_{p,298K} + E_A/(R \times 298K)]/\ln(10)$. [b] number of experimental points reported. [c] se: standard error in data points ($= \sqrt{\frac{SSR}{N-2}}$) where SSR is the sum of squared residuals to the linear fit; V(X): variance of X; Cov(X, Y): covariance of X and Y. [d] Geometric mean of k_p values. [e] Here N represents the number of individual studies.

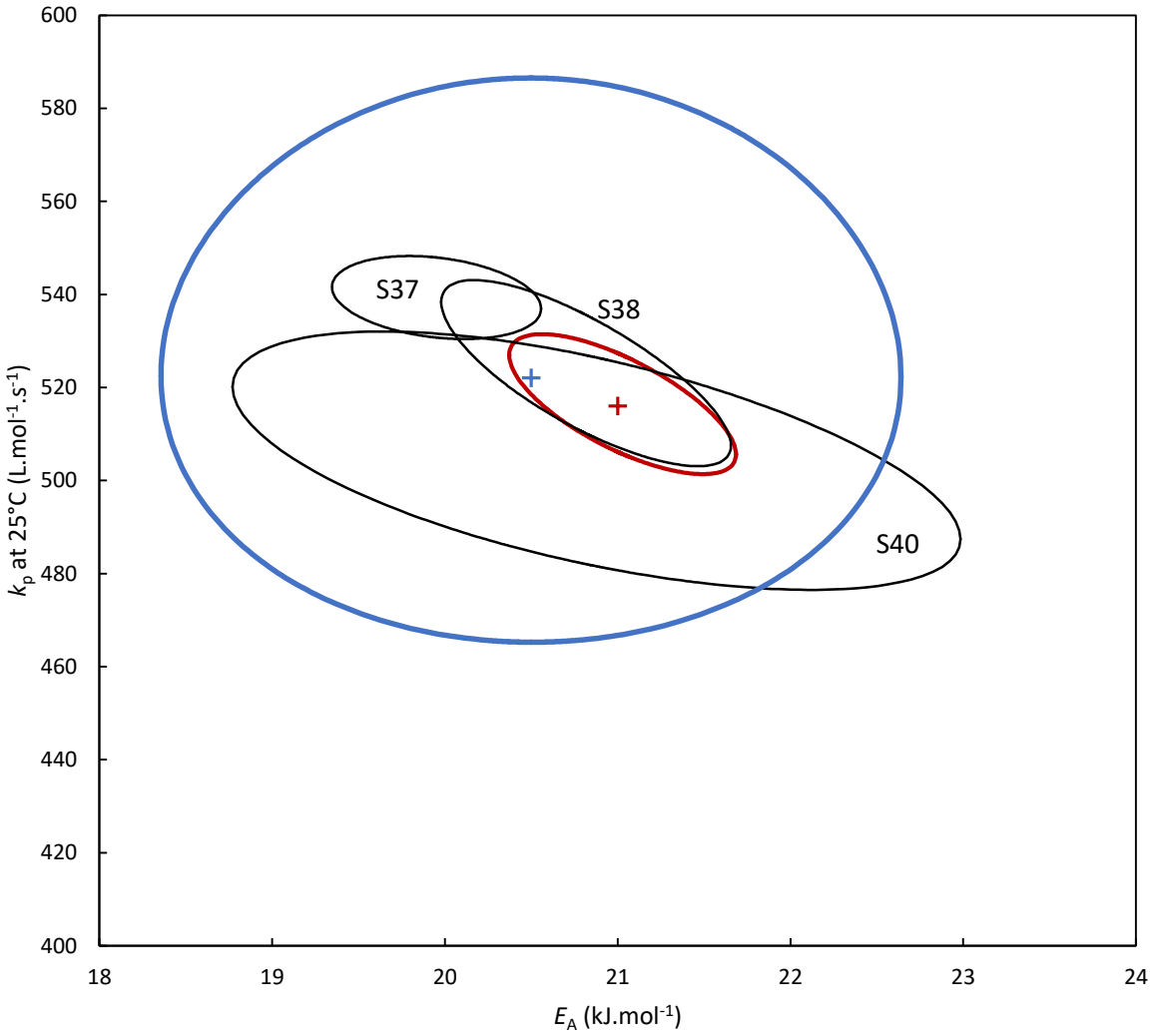


Figure S5. 95% JCRs for individual studies of k_p of dodecyl methacrylate (black), and weighted average of studies with estimated uncertainty from the pooled interlaboratory variance (blue). The originally calculated 95% joint confidence region,[S36] obtained by pooling the data points of the original IUPAC data set, is shown for comparison (red).

Table S6. Estimates of k_p at 25°C, A and E_A for cyclohexyl methacrylate from individual studies obtained by linear least squares fitting of ln k_p to $(1/T - 1/T_0)$, T_0 = 298.15 K. Units of E_A are kJ·mol^{-1}, while k_p and A are given in L·mol^{-1}·s^{-1}.

Ref.	T (°C)	k_p @ 25°C	Ln k_p @ 25°C	E_A	Log$_{10}$ A[a]	N[b]	se[c]	V(ln k_p)[c] × 10^3	V(E_A)[c]	Cov(ln k_p, E_A)[c] × 10^3
S41	10–90	615	6.42	22.2	6.67	34	0.059	0.372	0.135	-6.03
S42	21–91	602	6.40	22.0	6.64	10	0.037	0.618	0.516	-15.7
S43	30–70	547	6.30	24.3	6.99	18	0.036	0.162	0.0953	-2.93
Average		587[d]	6.38	22.8	6.77	3[e]		1.41	1.60	-76.7

[a] calculated as Log$_{10}$ A = [ln $k_{p,298K}$ + E_A/(R×298K)]/ln(10). [b] number of experimental points reported. [c] se: standard error in data points (= $\sqrt{\frac{SSR}{N-2}}$) where SSR is the sum of squared residuals to the linear fit; V(X): variance of X; Cov(X, Y): covariance of X and Y. [d] Geometric mean of k_p values. [e] Here N represents the number of individual studies.

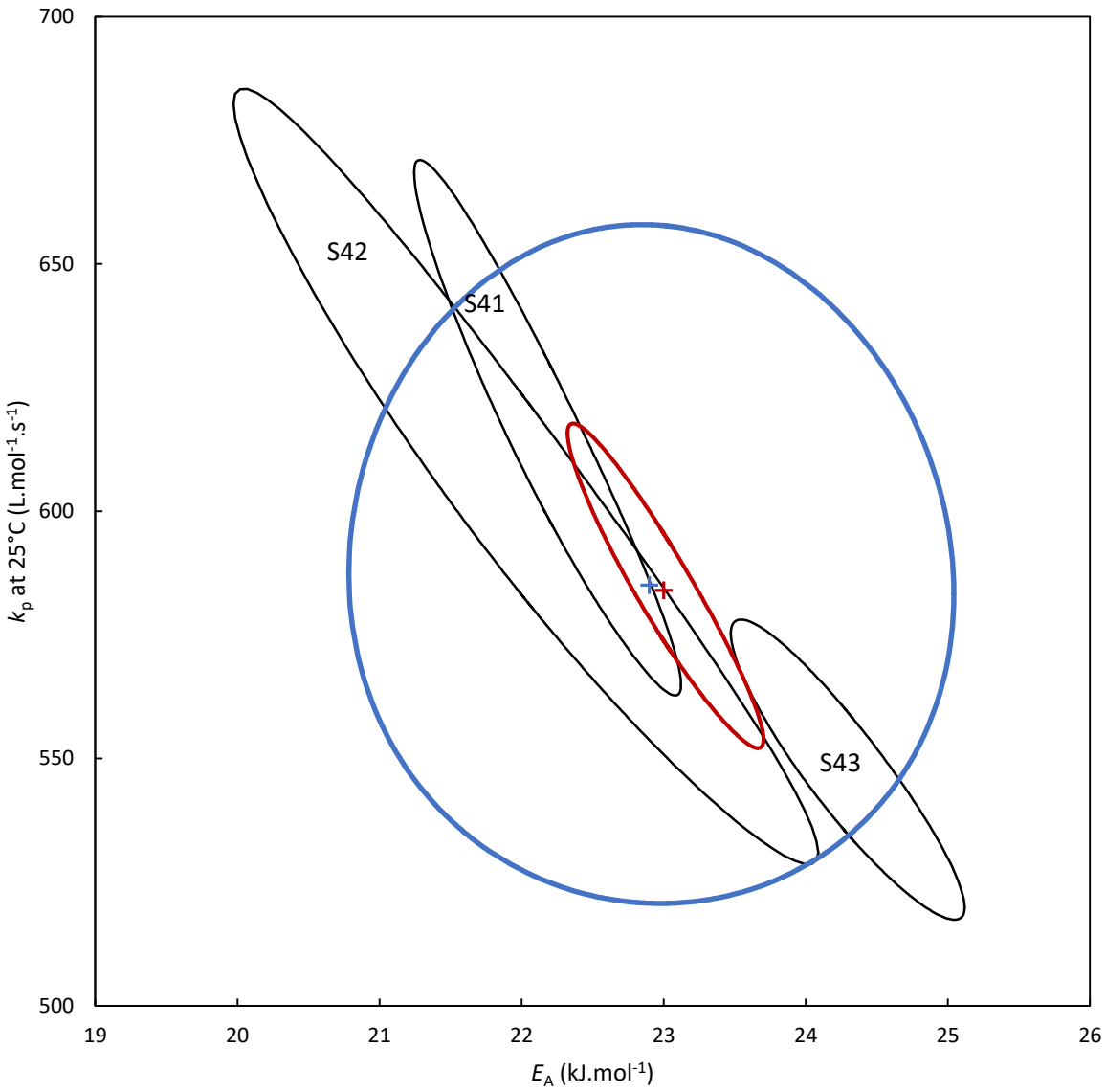


Figure S6. 95% JCRs for individual studies of k_p of cyclohexyl methacrylate (black), and weighted average of studies with estimated uncertainty from the pooled interlaboratory variance (blue). The originally calculated 95% joint confidence region,[S44] obtained by pooling the data points of the original IUPAC data set, is shown for comparison (red).

Table S7. Estimates of k_p at 25°C, A and E_A for glycidyl methacrylate from individual studies obtained by linear least squares fitting of ln k_p to $(1/T - 1/T_0)$, T_0 = 298.15 K. Units of E_A are kJ·mol^{-1}, while k_p and A are given in L·mol^{-1}·s^{-1}.

Ref.	T (°C)	k_p @ 25°C	Ln k_p @ 25°C	E_A	Log_{10} A[a]	N[b]	se[c]	V(ln k_p)[c] × 10^3	V(E_A)[c]	Cov(ln k_p, E_A)[c] × 10^3
S41	30–90	572	6.35	23.3	6.84	22	0.069	0.106	0.337	-16.8
S43	20–61	588	6.38	26.2	7.35	10	0.017	0.0514	0.0904	-1.46
S45[f]	60–90	541	6.29	20.3	6.29	6	0.036	4.68	1.43	-80.0
Average		566[d]	6.34	23.2	6.83	3[e]		1.81	8.59	123

[a] calculated as $Log_{10} A = [\ln k_{p,298K} + E_A/(R \times 298K)]/\ln(10)$. [b] number of experimental points reported. [b] se: standard error in data points ($= \sqrt{\frac{SSR}{N-2}}$) where SSR is the sum of squared residuals to the linear fit; V(X): variance of X; Cov(X, Y): covariance of X and Y. [c] for studies with only one or two reported values, se was assumed to be 0.05, corresponding to a reproducibility of +/- 5% in the k_p measurement. [d] Geometric mean of k_p values. [e] Here N represents the number of individual studies. [f] study not included in Beuermann et al., *Macromol. Chem. Phys.* 2003, **204**, 1338–1350 (S44). Data points at temperatures >90°C were excluded to reduce interference from depropagation.

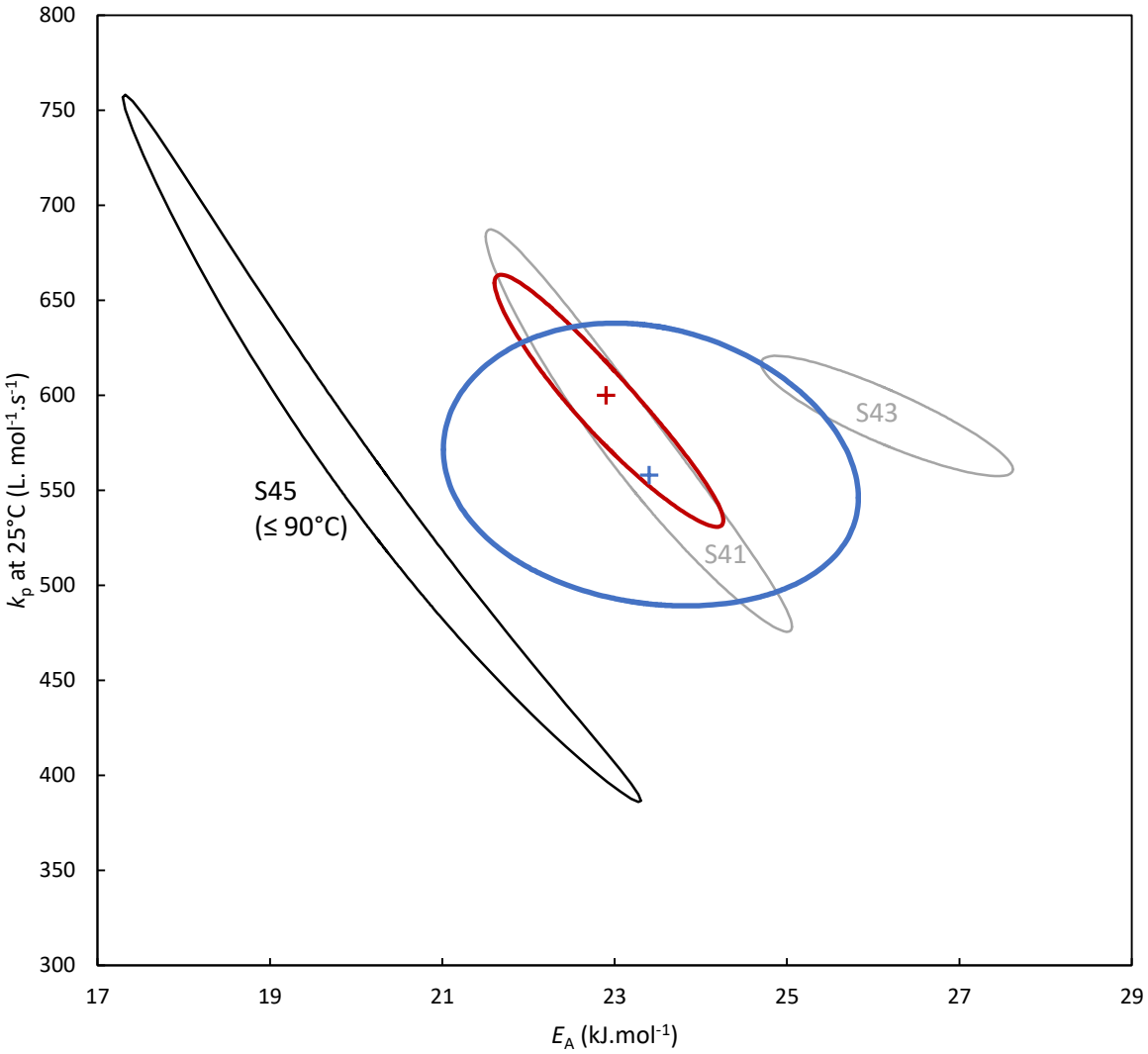


Figure S7. 95% JCRs for individual studies of k_p of glycidyl methacrylate (original data set[S44]: gray; expanded data set: black), and weighted average of studies with estimated uncertainty from the pooled interlaboratory variance (blue). The originally calculated 95% joint confidence region,[S44] obtained by pooling the data points of the original IUPAC data set, is shown for comparison (red).

Table S8. Estimates of k_p at 25°C, A and E_A for benzyl methacrylate from individual studies obtained by linear least squares fitting of ln k_p to $(1/T - 1/T_0)$, T_0 = 298.15 K. Units of E_A are kJ·mol^{-1}, while k_p and A are given in L·mol^{-1}·s^{-1}.

Ref.	T (°C)	k_p @ 25°C	Ln k_p @ 25°C	E_A	Log_{10} A[a]	N[b]	se[c]	V(ln k_p)[c] × 10^3	V(E_A)[c]	Cov(ln k_p, E_A)[c] × 10^3
S41	21–90	620	6.43	22.0	6.64	10	0.043	0.523	0.230	-8.81
S42	22–70	619	6.43	23.0	6.83	10	0.018	0.0959	0.0804	-2.28
S28	6–50	723	6.58	23.2	6.92	29	0.037	0.0475	0.128	-0.412
S46[d]	13–73	648	6.47	21.1	6.51	12	0.029	0.104	0.108	-1.93
Average		651[e]	6.489	22.3	6.72	4[f]		5.28	0.928	25.9

[a] calculated as $\text{Log}_{10} A = [\ln k_{p,298K} + E_A/(R \times 298K)]/\ln(10)$. [b] number of experimental points reported. [c] se: standard error in data points ($= \sqrt{\frac{SSR}{N-2}}$) where SSR is the sum of squared residuals to the linear fit; V(X): variance of X; Cov(X, Y): covariance of X and Y. [d] study not included in Beuermann et al., *Macromol. Chem. Phys.* 2003, **204**, 1338–1350 (S44). [e] Geometric mean of k_p values. [f] Here N represents the number of individual studies.

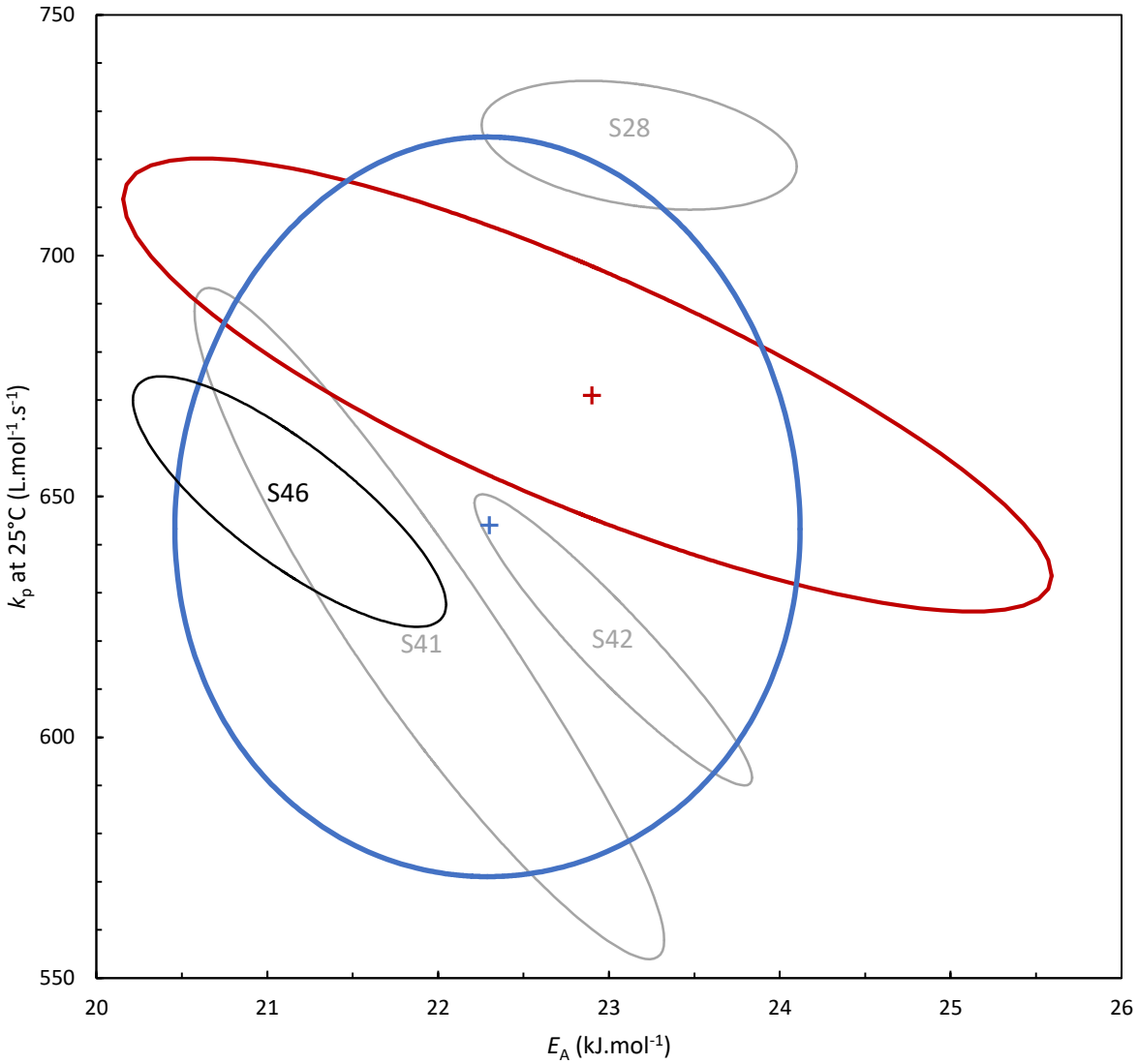


Figure S8. 95% JCRs for individual studies of k_p of benzyl methacrylate (original data set:[S44] gray; expanded data set: black), and weighted average of studies with estimated uncertainty from the pooled interlaboratory variance (blue). The originally calculated 95% joint confidence region,[S44] obtained by pooling the data points of the original IUPAC data set in the restricted temperature range 10–55°C, and counting data from S41 and S42 twice, is shown for comparison (red).

Table S9. Estimates of k_p at 25°C, A and E_A for isobornyl methacrylate from individual studies obtained by linear least squares fitting of ln k_p to $(1/T - 1/T_0)$, T_0 = 298.15 K. Units of E_A are kJ·mol^{-1}, while k_p and A are given in L·mol^{-1}·s^{-1}.

Ref.	***T* (°C)**	**k_p @ 25°C**	**Ln k_p @ 25°C**	**E_A**	**Log$_{10}$ *A*[a]**	**N[b]**	**se[c]**	**V(ln k_p)[c] × 10^3**	**V(E_A)[c]**	**Cov(ln k_p, E_A)[c] × 10^3**
S41	10–90	491.3	6.20	22.9	6.71	28	0.057	0.376	0.139	-6.00
S42	0–91	588.1	6.38	23.3	6.85	15	0.021	0.0468	0.0349	-0.793
Average		538[d]	6.29	23.1	6.78	2[e]		16.1	0.0732	34.4

[a] calculated as Log$_{10}$ A = [ln $k_{p,298K}$ + E_A/(R×298K)]/ln(10). [b] number of experimental points reported. [c] se: standard error in data points (= $\sqrt{\frac{SSR}{N-2}}$) where SSR is the sum of squared residuals to the linear fit; V(X): variance of X; Cov(X, Y): covariance of X and Y. [d] Geometric mean of k_p values. [e] Here N represents the number of individual studies.

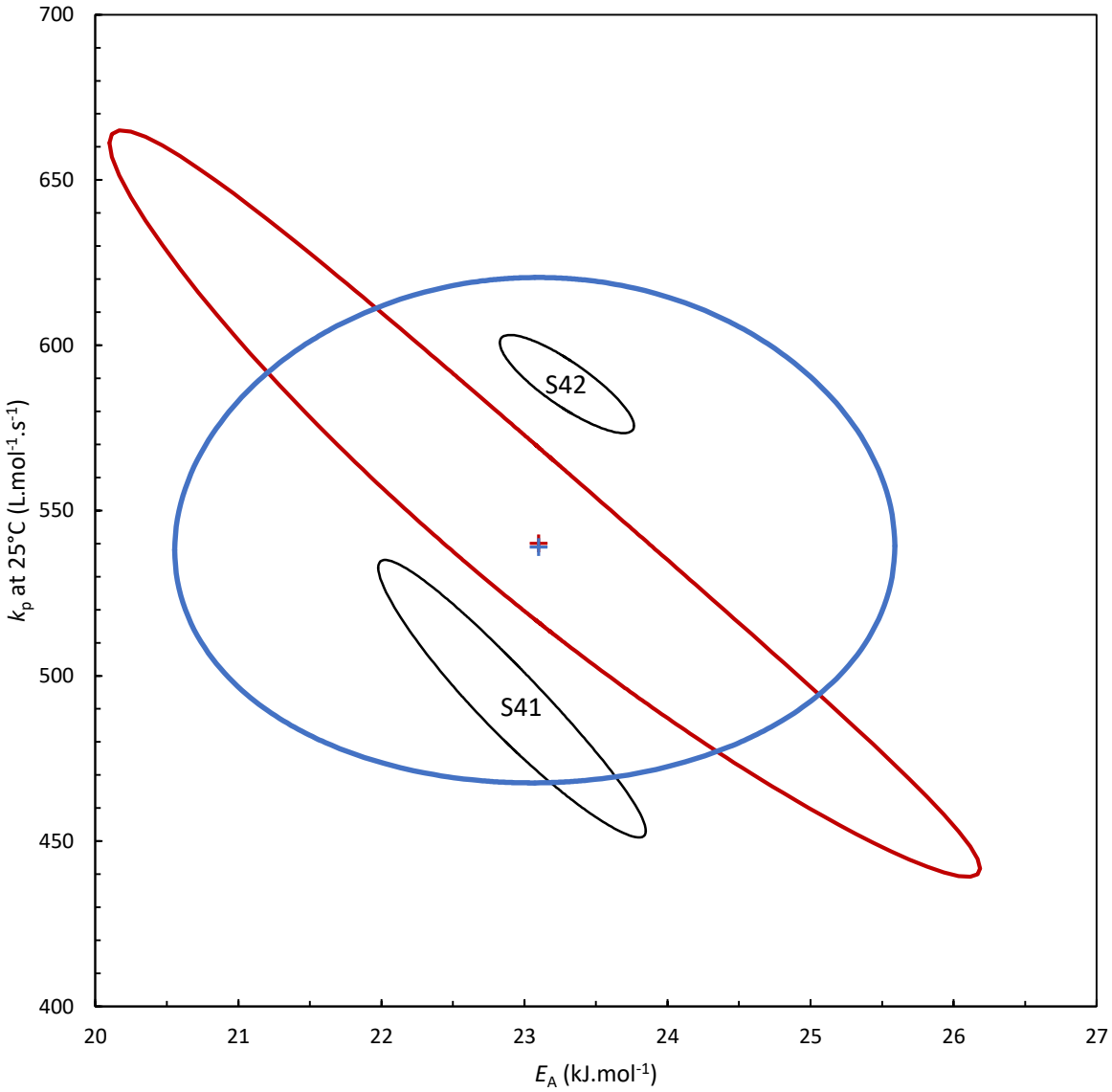


Figure S9. 95% JCRs for individual studies of k_p of isobornyl methacrylate (black), and weighted average of studies with estimated uncertainty from the pooled interlaboratory variance (blue). The originally calculated 95% joint confidence region,[S44] obtained by pooling the data points of the original IUPAC data set in the restricted temperature range of 30–80°C and counting the data points of S42 twice, is shown for comparison (red).

Table S10. Estimates of k_p at 25°C, A and E_A for butyl acrylate from individual studies obtained by linear least squares fitting of ln k_p to $(1/T - 1/T_0)$, T_0 = 298.15 K. Units of E_A are kJ·mol^{-1}, while k_p and A are given in L·mol^{-1}·s^{-1}.

Ref.	T (°C)	k_p @ 25°C	Ln k_p @ 25°C	E_A	Log$_{10}$ A[a]	N[b]	se[c]	V(ln k_p)[c] × 10^3	V(E_A)[c]	Cov(ln k_p, E_A)[c] × 10^3
S47	-65–-46	12.1	9.40	15.5	6.81	25	0.14	44.6	1.99	295
S48	-36–15	15.5	9.65	16.1	7.01	15	0.033	0.330	0.0865	4.73
S49	-41–15	14.8	9.60	18.0	7.33	30	0.030	0.152	0.0286	1.87
S50	-8–-7	13.5[d]	9.51[d]			4	0.15[e]	20.4[e]		
S51	11	15.7[d]	9.66[d]			2	0.083[e]	5.65[e]		
S52[f]	12–70	15.8	9.67	18.1	7.36	15	0.030	0.150	0.111	-3.16
S53[f]	30–50	17.3	9.76	14.5	6.77	4	0.050	4.10	5.53	-139
S54[f]	-25–38	15.5	9.65	18.6	7.44	17	0.013	0.0192	0.0106	0.320
S55[g]	*5–20*	*15.8*	*9.67*	*11.3*	*6.17*	*37*	*0.042*	*0.304*	*0.836*	*14.6*
Average		14.9[h]	9.61	16.9	7.12	7(5)[i]		12.1	2.73	4.92

[a] calculated as Log$_{10}$ A = [ln $k_{p,298K}$ + E_A/(R×298K)]/ln(10). [b] number of experimental points reported. [c] se: standard error in data points (= $\sqrt{\frac{SSR}{N-2}}$) where SSR is the sum of squared residuals to the linear fit; V(X): variance of X; Cov(X, Y): covariance of X and Y. [d] k_p @ 25°C adjusted from experimental temperature of -7.5°C (S50) or 10.8°C (S51) using the average activation energy of 16.9 kJ.mol^{-1}. [e] se and V(ln k_p) corrected by adding V(E_A)/[R(1/298.15-1/T)]^2+cov(E_A, ln k_p)/[R(1/298.15-1/T)] to the variance obtained at the experimental temperatures of -7.5°C and 10.8°C, where V(E_A) and cov(E_A, ln k_p) are the variance of the average activation energy and its covariance with ln k_p and T is -7.5°C or 10.8°C respectively. [f] study not included in Asua et al., *Macromol. Chem. Phys.* 2004, **205**, 2151–2160 (S56). [g] These results were excluded from the calculation of the interlaboratory mean and variance. [h] Geometric mean of k_p values. [i] Here N represents the number of individual studies. Number in parentheses is the number of studies reporting an E_A value.

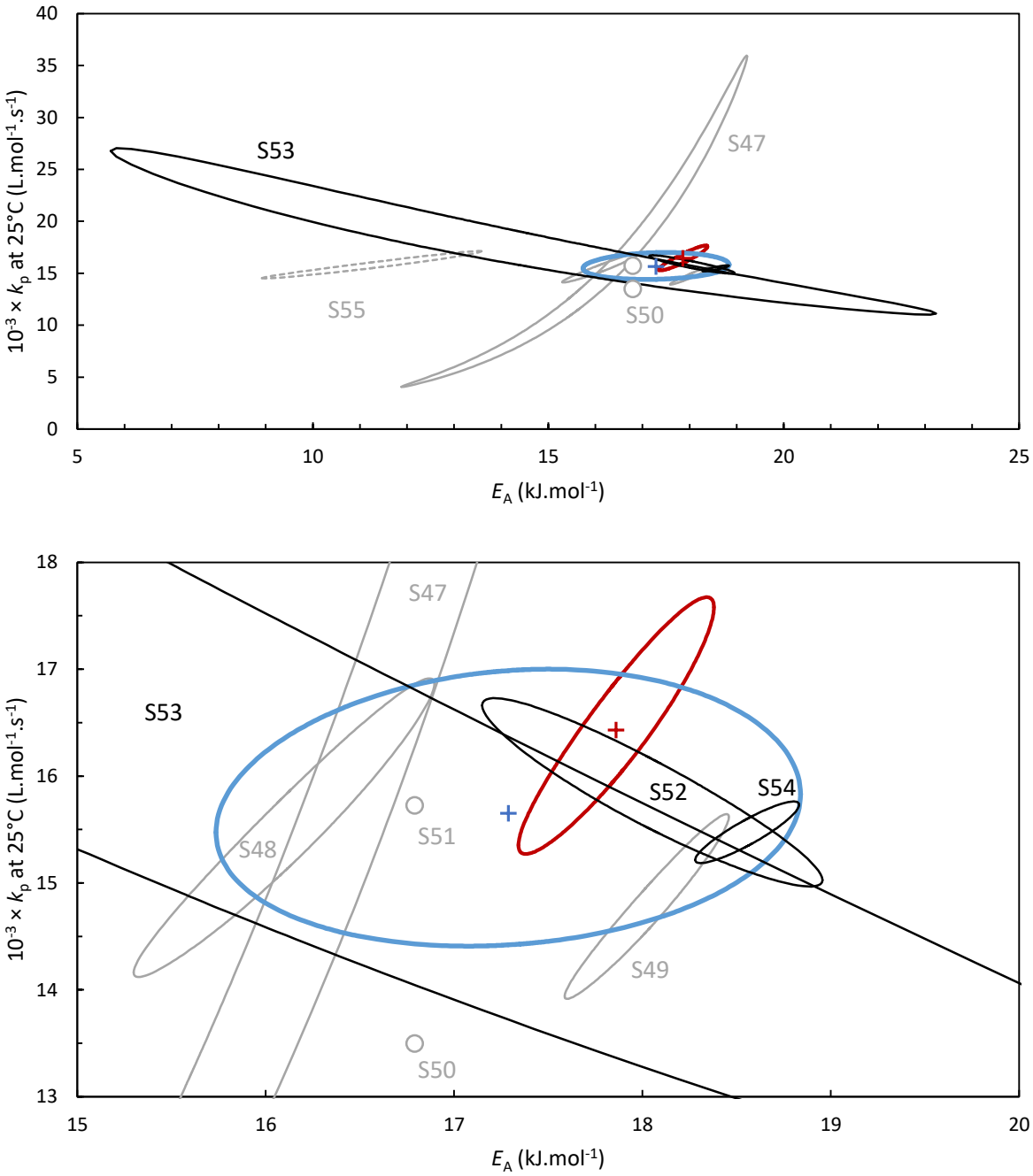


Figure S10. (a) 95% JCRs for individual studies of k_p of butyl acrylate (original data set:[S56] gray; expanded data set: black), and weighted average of studies with estimated uncertainty from the pooled interlaboratory variance (blue). The originally calculated 95% joint confidence region,[S56] obtained by pooling the data points of the original IUPAC data set, is shown for comparison (red). The data from reference S55 (dotted line) was excluded from the calculation of the pooled interlaboratory variance. Data from references S50 and S51 were adjusted to 25°C using the average activation energy of 16.9 kJ.mol^{-1}. (b) shows an expanded view of the region containing the 95% JCRs corresponding to references S48-S49, S52 and S54 and the point estimates of references S50 and S51.

Table S11. Estimates of k_p at 25°C, A and E_A for methacrylic acid (15% aq. solution) from individual studies obtained by linear least squares fitting of ln k_p to $(1/T - 1/T_0)$, T_0 = 298.15 K. Units of E_A are kJ·mol^{-1}, while k_p and A are given in L·mol^{-1}·s^{-1}.

Ref.	T (°C)	k_p @ 25°C	Ln k_p @ 25°C	E_A (kJ.mol$^{-1)}$	Log$_{10}$ A[a]	N[b]	se[c] × 10^3	V(ln k_p)[c] × 10^3	V(E_A)[c] × 10^3	Cov(ln k_p, E_A)[c] × 10^3
S57	18–89	3.60	6.24	15.3	6.71	17	43	0.212	162	-4.08
S58	20–60	3.86	6.20	14.9	6.85	12	8.7	0.0116	15.7	-0.286
Average		3.73[d]	6.22	15.1	6.22	2[e]		2.35	69	-12.8

[a] calculated as Log$_{10}$ A = [ln $k_{p,298K}$ + E_A/(R×298K)]/ln(10). [b] number of experimental points reported. [c] se: standard error in data points (= $\sqrt{\frac{SSR}{N-2}}$) where SSR is the sum of squared residuals to the linear fit; V(X): variance of X; Cov(X, Y): covariance of X and Y. [d] Geometric mean of k_p values. [e] Here N represents the number of individual studies.

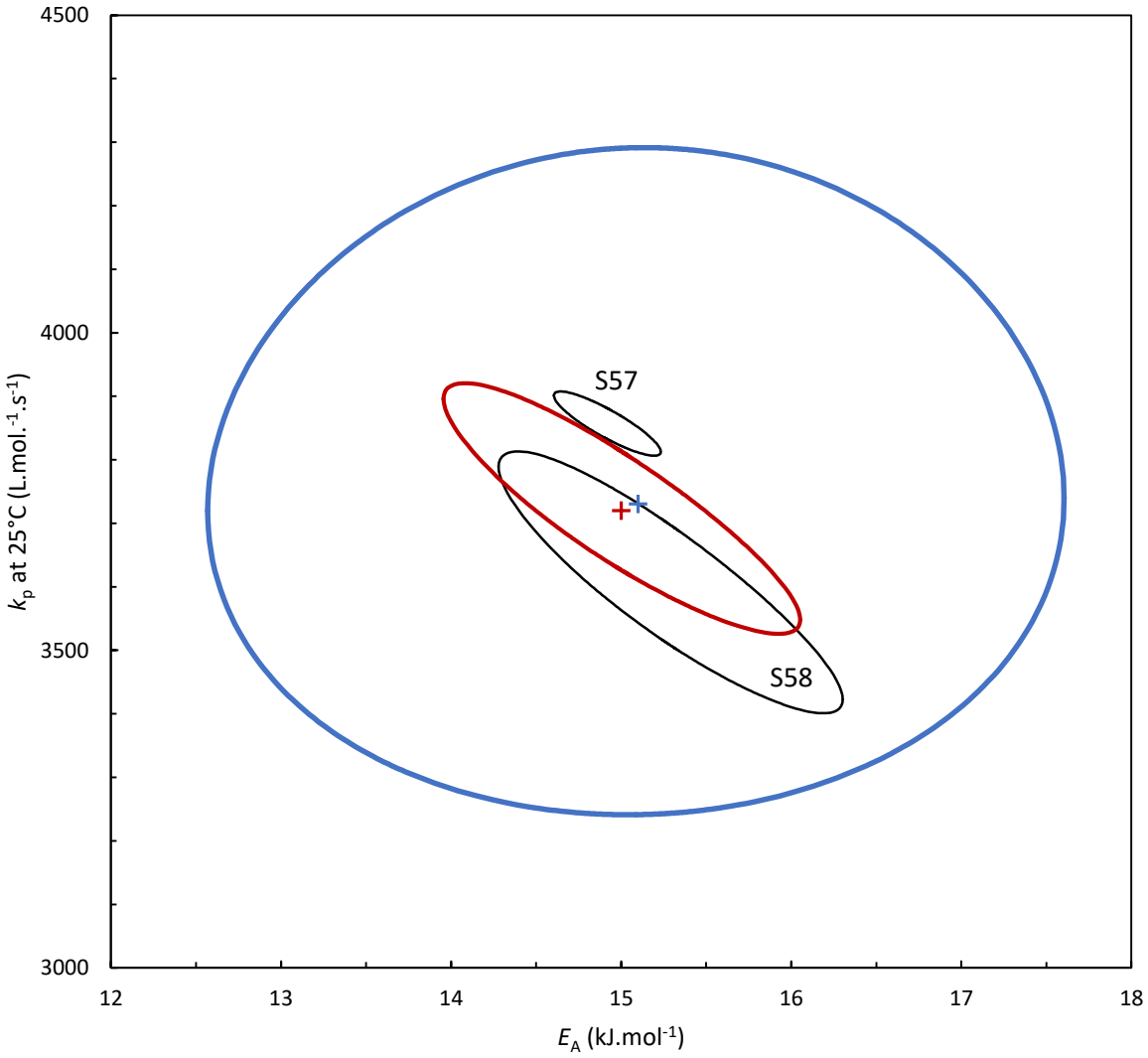


Figure S11. 95% JCRs for individual studies of k_p of methacrylic acid in 15% aqueous solution (black), and weighted average of studies with estimated uncertainty from the pooled interlaboratory variance (blue). The originally calculated 95% joint confidence region,[S59] obtained by pooling the data points of the original IUPAC data set, is shown for comparison (red).

Table S12. Estimates of k_p at 25°C, A and E_A for methyl acrylate from individual studies obtained by linear least squares fitting of ln k_p to $(1/T - 1/T_0)$, T_0 = 298.15 K. Units of E_A are kJ·mol^{-1}, while k_p and A are given in L·mol^{-1}·s^{-1}.

Ref.	***T* (°C)**	**k_p @ 25°C**	**Ln k_p @ 25°C**	**E_A**	**Log$_{10}$ *A*[a]**	**N[b]**	**se[c]**	**V(ln k_p)[c] × 10^3**	**V(E_A)[c]**	**Cov(ln k_p, E_A)[c] × 10^3**
S60	-26–61	12.9	9.46	16.2	6.94	39	0.047	0.0666	0.0388	0.640
S50	-19–32	13.1	9.48	17.8	7.23	41	0.087	0.569	0.276	10.3
S54	-25–37	14.7	9.59	18.3	7.38	18	0.0084	0.00714	0.00413	0.115
S61[d]	*-28–-15*	*17.6*	*9.77*	*19.2*	*7.60*	*2*	*0.05*[b]	*47.2*	*8.19*	*613*
S62	11-61	14.1	9.56	19.0	7.48	12	0.059	0.391	1.48	61.6
Average		13.7[d]	9.52	17.8	7.26	4[e]		3.71	2.11	61.6

[a] calculated as Log$_{10}$ A = [ln $k_{p,298K}$ + E_A/(R×298K)]/ln(10). [b] number of experimental points reported. [c] se: standard error in data points (= $\sqrt{\frac{SSR}{N-2}}$) where SSR is the sum of squared residuals to the linear fit; V(X): variance of X; Cov(X, Y): covariance of X and Y. [d] These results, which were extrapolated from high pressure experiments, were excluded from the calculation of the interlaboratory mean and variance. [e] Geometric mean of k_p values. [f] Here N represents the number of individual studies.

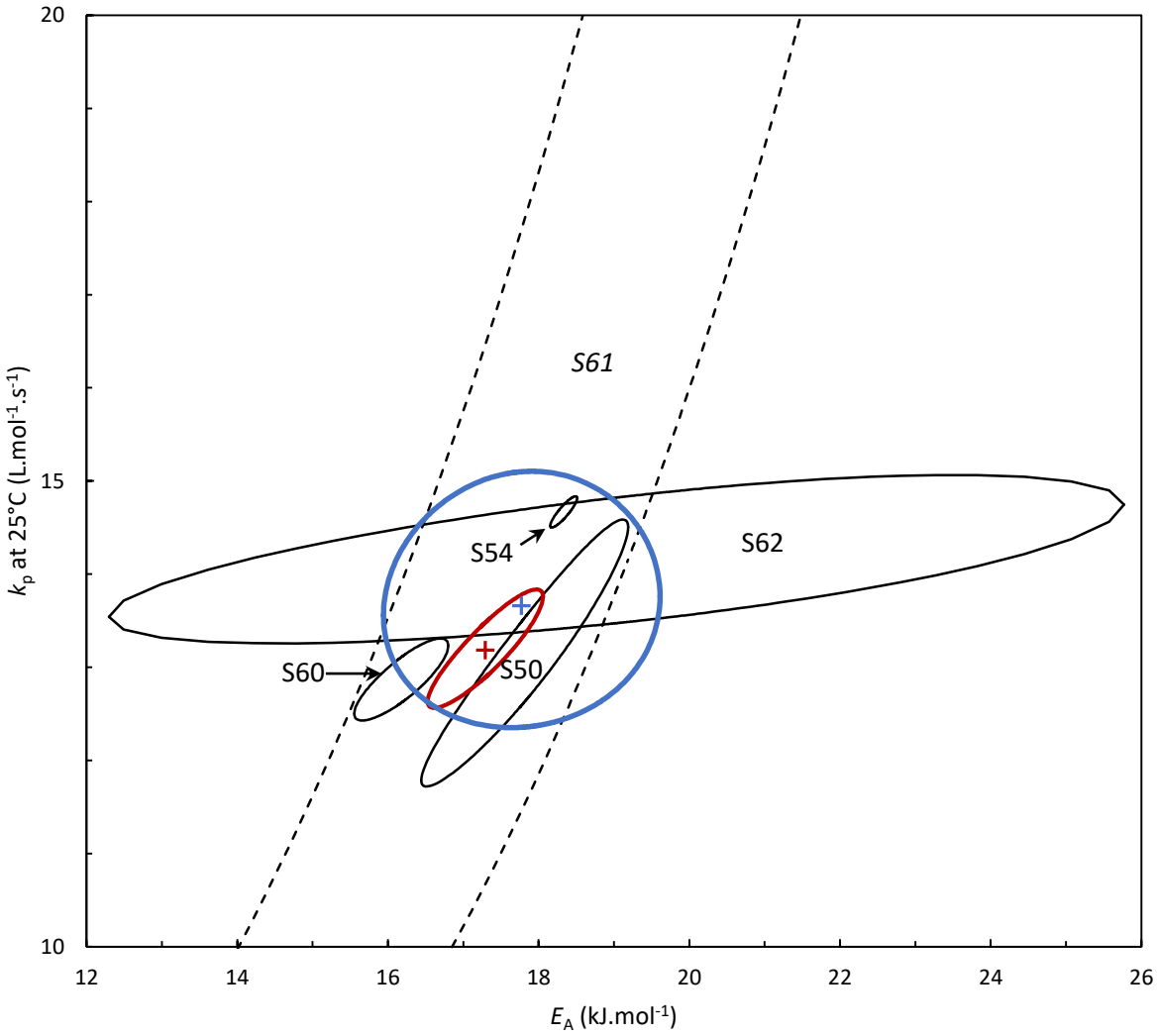


Figure S12. 95% JCRs for individual studies of k_p of methyl acrylate (black), and weighted average of studies with estimated uncertainty from the pooled interlaboratory variance (blue). The originally calculated 95% joint confidence region,[S60] obtained by pooling the data points of the original IUPAC data set, is shown for comparison (red). The results of S61 (dashed line) were excluded from the calculations, as these results were extrapolated from high pressure experiments.

Table S13. Estimates of k_p at 25°C, A and E_A for vinyl acetate from individual studies obtained by linear least squares fitting of ln k_p to $(1/T - 1/T_0)$, T_0 = 298.15 K. Units of E_A are kJ·mol^{-1}, while k_p and A are given in L·mol^{-1}·s^{-1}.

Ref.	T (°C)	k_p @ 25°C × 10^3	Ln k_p @ 25°C	E_A	Log_{10} A	N	se[a]	V(ln k_p) × 10^3	V(E_A)	Cov(ln k_p, E_A) × 10^3
S63	5–70	4.06	8.31	21.7	7.42	17	0.080	0.619	0.683	-12.8
S20	10–60	3.59	8.19	20.4	7.12	21	0.050	0.126	0.199	-1.21
S50	9–56	3.47	8.15	22.2	7.43	13	0.102	0.846	5.20	14.5
S64	10–60	3.89	8.26	19.1	6.93	40	0.073	0.281	0.572	-9.18
S65	25–65	3.38	8.13	21.7	7.34	53	0.093	0.585	0.717	-17.4
S66	14–61	3.38	8.13	18.6	6.78	33	0.063	0.176	0.276	-3.97
Average		3.62[d]	8.19	20.6	7.17	6[e]		5.94	2.34	6.81

[a] calculated as $\text{Log}_{10} A = [\ln k_{p,298K} + E_A/(R \times 298\ K)]/\ln(10)$. [b] number of experimental points reported. [c] se: standard error in data points ($= \sqrt{\frac{SSR}{N-2}}$) where SSR is the sum of squared residuals to the linear fit; V(X): variance of X; Cov(X, Y): covariance of X and Y. [d] Geometric mean of k_p values. [e] Here N represents the number of individual studies.

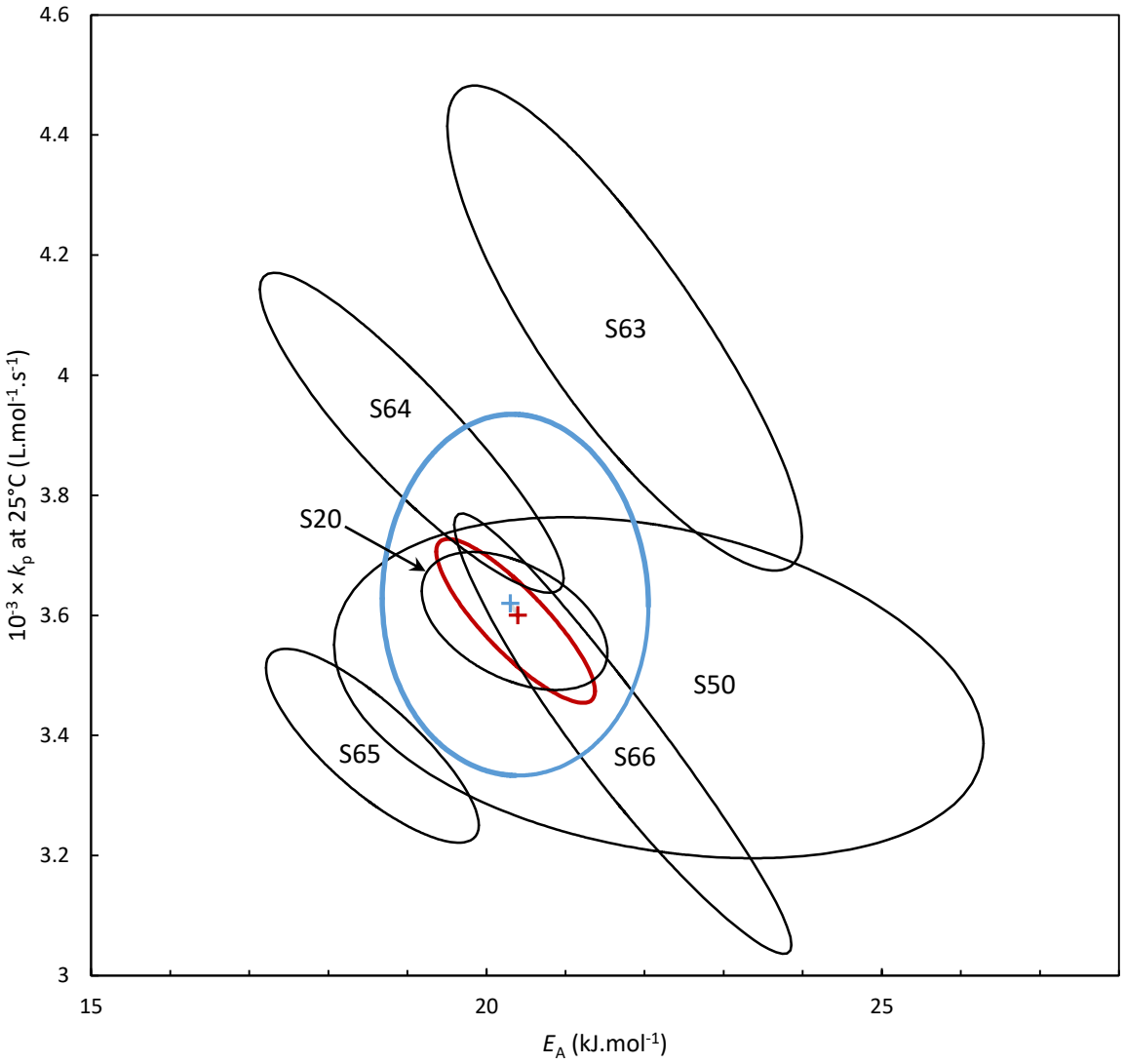


Figure S12. 95% JCRs for individual studies of k_p of vinyl acetate (black), and weighted average of studies with estimated uncertainty from the pooled interlaboratory variance (blue). The originally calculated 95% joint confidence region,[S67] obtained by pooling the data points of the original IUPAC data set, is shown for comparison (red).

2. Example calculation of 95% JCR from pooled interlaboratory variance.

The method is illustrated using the methyl acrylate data (Table S12). The pooled interlaboratory variances in ln k_p at 25°C (6.01×10^{-3}), E_A (1.88 $(kJ \cdot mol^{-1})^2$) and the covariance (4.17×10^{-3} $kJ \cdot mol^{-1}$) were added to the respective estimated variances and covariances from the linear fits (Table S14). The resulting covariance matrices, $\boldsymbol{C}_i$, were inverted to form weight matrices, $\boldsymbol{W}_i$ (eq. S1)

$$\boldsymbol{W} = \boldsymbol{C}^{-1} = \begin{bmatrix} V(\ln k_p) & Cov(\ln k_p, E_A) \\ Cov(\ln k_p, E_A) & V(E_A) \end{bmatrix}^{-1} = \frac{1}{\det(\boldsymbol{C})} \begin{bmatrix} V(E_A) & -Cov(\ln k_p, E_A) \\ -Cov(\ln k_p, E_A) & V(\ln k_p) \end{bmatrix} \quad \text{(S1)}$$

$$\det(\boldsymbol{C}) = V(E_A) \times V(\ln k_p) - [cov(\ln k_p, E_A)]^2$$

The weighted average was obtained from equation S2:

$$\overline{\begin{bmatrix} \ln k_p \\ E_A \end{bmatrix}} = \left(\sum_i \boldsymbol{W}_i \right)^{-1} \sum_i \boldsymbol{W}_i \begin{bmatrix} \ln k_p \\ E_A \end{bmatrix}_i \quad \text{(S2)}$$

The covariance matrix of the weighted average is given by $(\sum_i \boldsymbol{W}_i)^{-1}$. This leads to a weighted average ln *k*p of 9.52, with estimated variance 1.56×10^{-3}, E_A of 17.8 $kJ \cdot mol^{-1}$ with estimated variance 0.523 $(kJ \cdot mol^{-1})^2$, and estimated covariance of 2.10×10^{-3} $kJ \cdot mol^{-1}$.

These variances are subsequently used to generate a 95% joint confidence region, using equation S3:[S68]

$$(\boldsymbol{\beta} - \widehat{\boldsymbol{\beta}})^{\mathrm{T}} \left(\sum_i \boldsymbol{W}_i \right) (\boldsymbol{\beta} - \widehat{\boldsymbol{\beta}}) < c \quad \text{(S3)}$$

Where $\boldsymbol{\beta}$ is a column vector containing ln k_p and E_A, $\widehat{\boldsymbol{\beta}}$ is the estimated value of $\boldsymbol{\beta}$, and *c* is a critical value drawn from Hotelling's T^2 distribution with 2 and 58 degrees of freedom corresponding to the 95% significance level (*c* = 6.44). The 58 degrees of freedom correspond to the 71 studies for which estimates of both ln *k*p and E_A are available, minus the 13 monomers investigated. Use of a χ^2 distribution with 2 degrees of freedom in place of the T^2 distribution results in a slightly smaller JCR (*c* = 5.99).

A confidence band for k_p vs. temperature can be obtained from the same covariance matrix using equation S4:[S68]

$$\left| \ln\left(\frac{k_p}{\widehat{k_p}}\right) \right| < \sqrt{c} \left(V(\ln k_{p0}) + \frac{V(E_A)}{R^2} \left(\frac{1}{T} - \frac{1}{T_0}\right)^2 - 2\frac{Cov(\ln k_p, E_A)}{R} \left(\frac{1}{T} - \frac{1}{T_0}\right) \right)^{\frac{1}{2}} \quad \text{(S4)}$$

Table S13: Calculation of weighted average and covariance matrix for ln k_p at 25°C and E_A of methyl acrylate. Units of E_A are kJ·mol^{-1}, while k_p is given in L·mol^{-1}·s^{-1}.

Ref.	**ln k_p @ 25°C**	**E_A**	***C***			***W***			**weighted**	
			$V(\ln k_{p,0}) \times 10^3$	$V(E_A)$	*Cov.* $\times 10^3$	$w_{\ln kp}$	w_{EA}	w_{Cov}	A^a	B^a
S60	9.46	16.2	6.07	1.92	4.81	165	0.521	-0.412	1553	4.53
S50	9.48	17.8	6.58	2.16	14.5	154	0.470	-1.03	1444	-1.42
S54	9.59	18.3	6.02	1.898	4.28	166	0.531	-0.378	1590	6.10
S62	9.56	19.0	6.41	2.53	12.2	158	0.400	-0.764	1491	0.31
weighted average	**9.52**	**17.8**	**1.56**	**0.523**	**2.10**	**643**	**1.92**	**-2.59**	**6078**	**9.53**

[a] $A = w_{\ln kp} \times \ln k_p + w_{Cov} \times E_A$; $B = w_{EA} \times E_A + w_{Cov} \times \ln k_p$

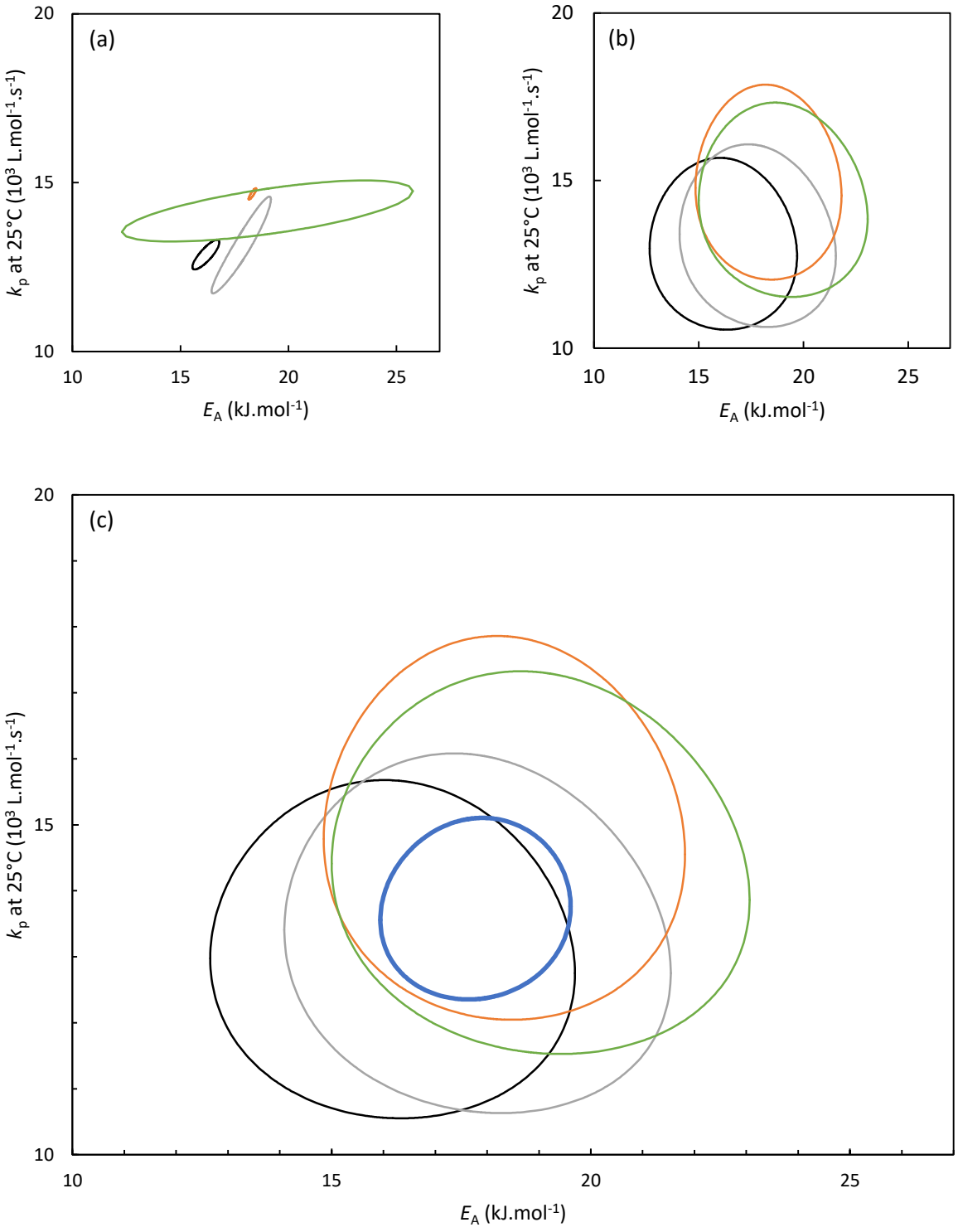


Figure S13. Process of obtaining a combined 95% joint confidence region: JCRs for the individual studies (a) are recalculated to include the interlaboratory variation (b). A combined JCR (c, shown in blue) is obtained from the weighted average of the individual estimates and the corresponding covariance matrix (Table S13)

3. Confidence bands for k_p:

The 95% confidence bands for k_p were obtained from equation S13, setting c = 6.44, T_0 = 298 K and using the values for $V(\ln k_{p,0})$, $V(E_A)$ and $Cov(\ln k_{p,0}, E_A)$ shown in Table S14

Table S14: Parameters for calculation of 95% confidence bands for k_p. Units of E_A are kJ·mol^{-1}, while $k_{p,0}$ is given in L·mol^{-1}·s^{-1}.

Monomer	$\ln k_{p,0}$	E_A	$V(\ln k_{p,0}) \times 10^3$	$V(E_A)$	$Cov(\ln k_{p,0}, E_A) \times 10^3$
STY	4.46	32.5	0.442	0.215	-0.432
MMA	5.78	22.3	0.338	0.183	-0.293
EMA	5.82	23.4	1.53	0.491	-0.643
BMA	5.97	22.9	0.834	0.274	0.819
DMA	6.26	21.0	2.08	0.713	0.0955
CHMA	6.37	23.0	2.13	0.704	-1.16
GMA	6.33	22.9	2.53	0.831	-7.81
BnMA	6.47	22.9	2.20	0.520	-0.0138
iBoMA	6.29	23.1	3.11	0.984	0.149
BA	9.66	17.9	1.05	0.374	2.74
MAA	8.22	15.0	3.06	0.985	1.05
MA	9.52	17.3	1.56	0.523	2.10
VAc	8.19	20.4	1.07	0.440	-0.460

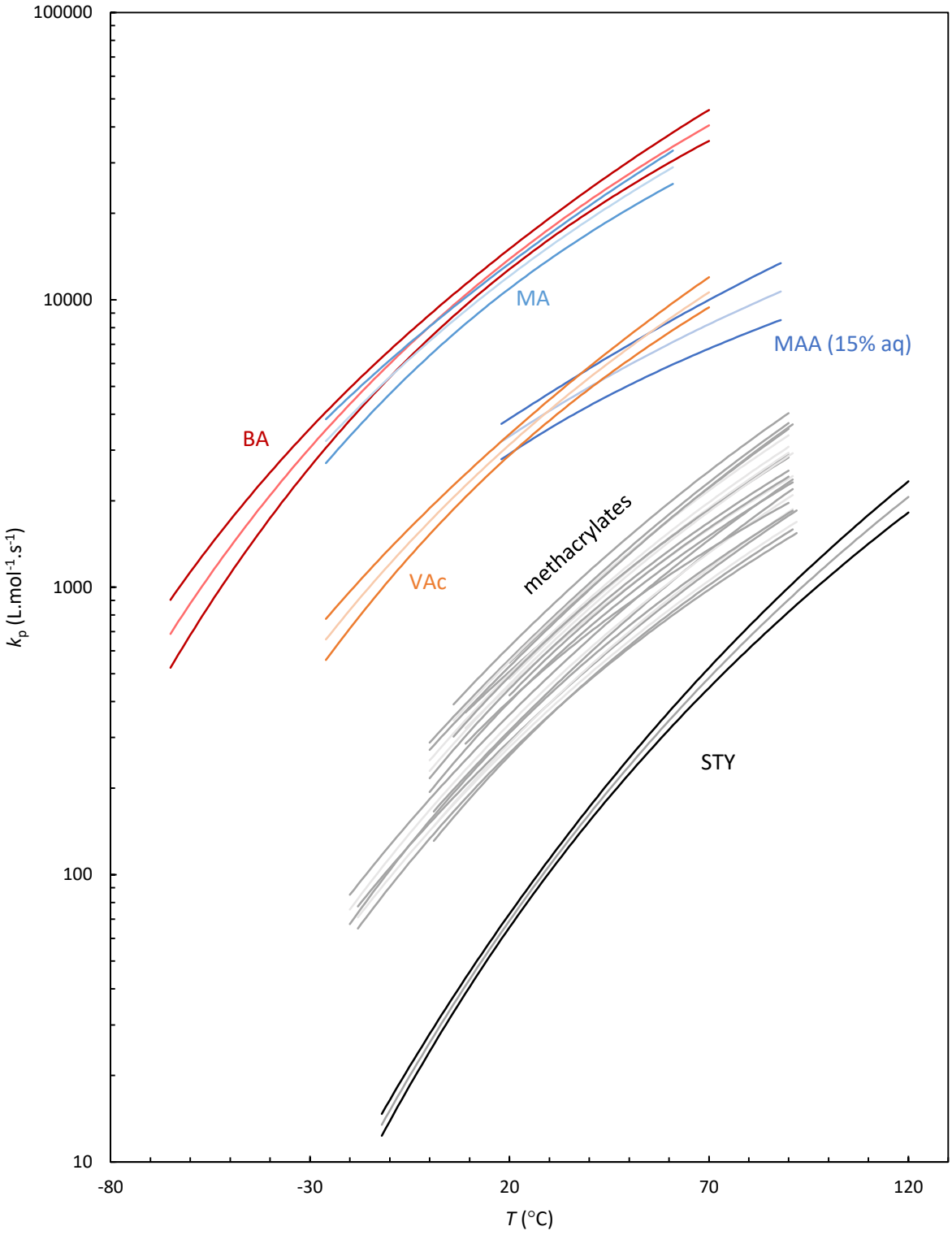


Figure S14. 95% confidence bands for k_p of styrene (STY), butyl acrylate (BA), methacrylic acid (MAA, 15% aqueous solution), methyl acrylate (MA) and vinyl acetate (VAc).

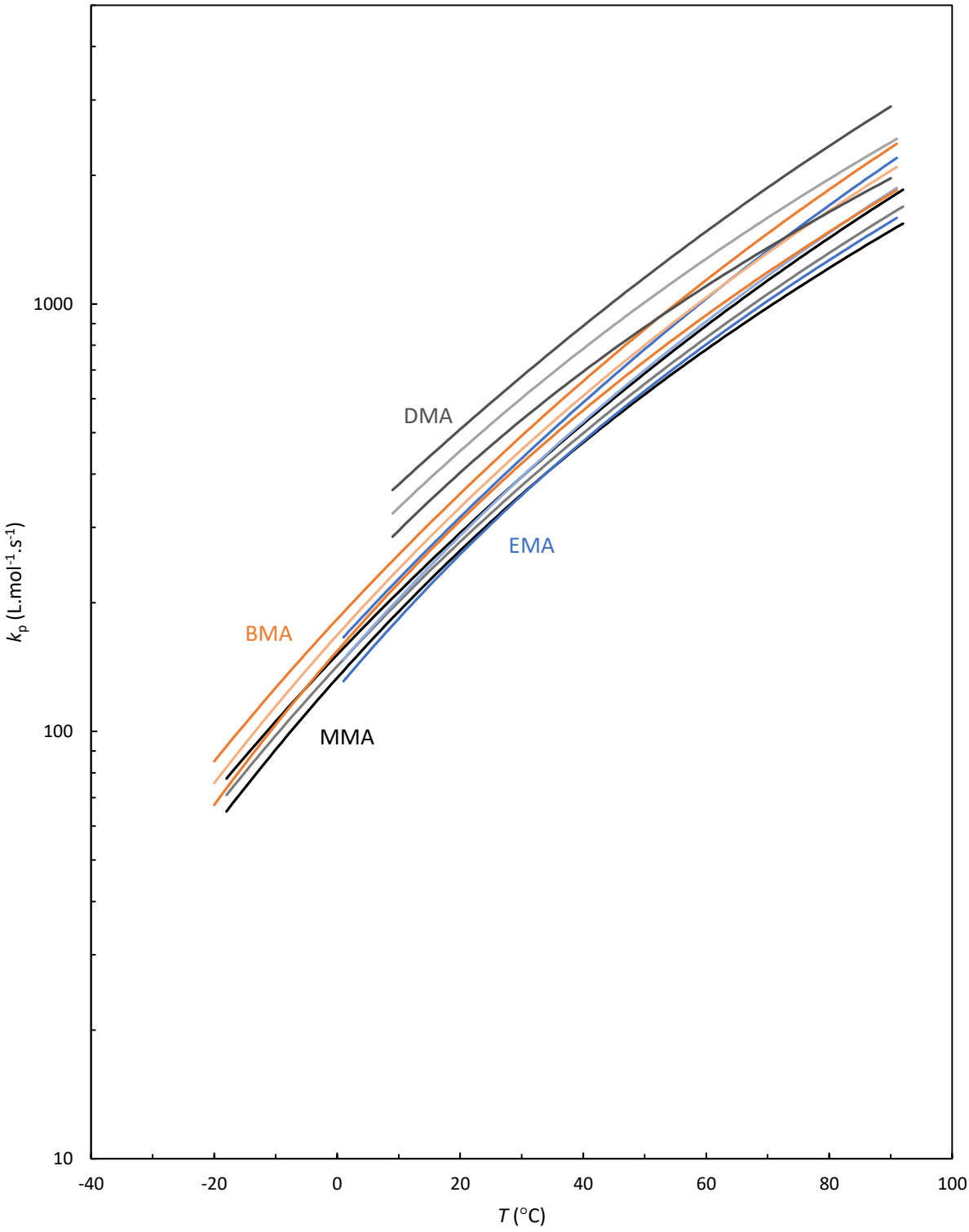


Figure S15. 95% confidence bands for k_p of linear methacrylates: methyl methacrylate (MMA), ethyl methacrylate (EMA), butyl methacrylate (BMA) and dodecyl methacrylate (DMA).

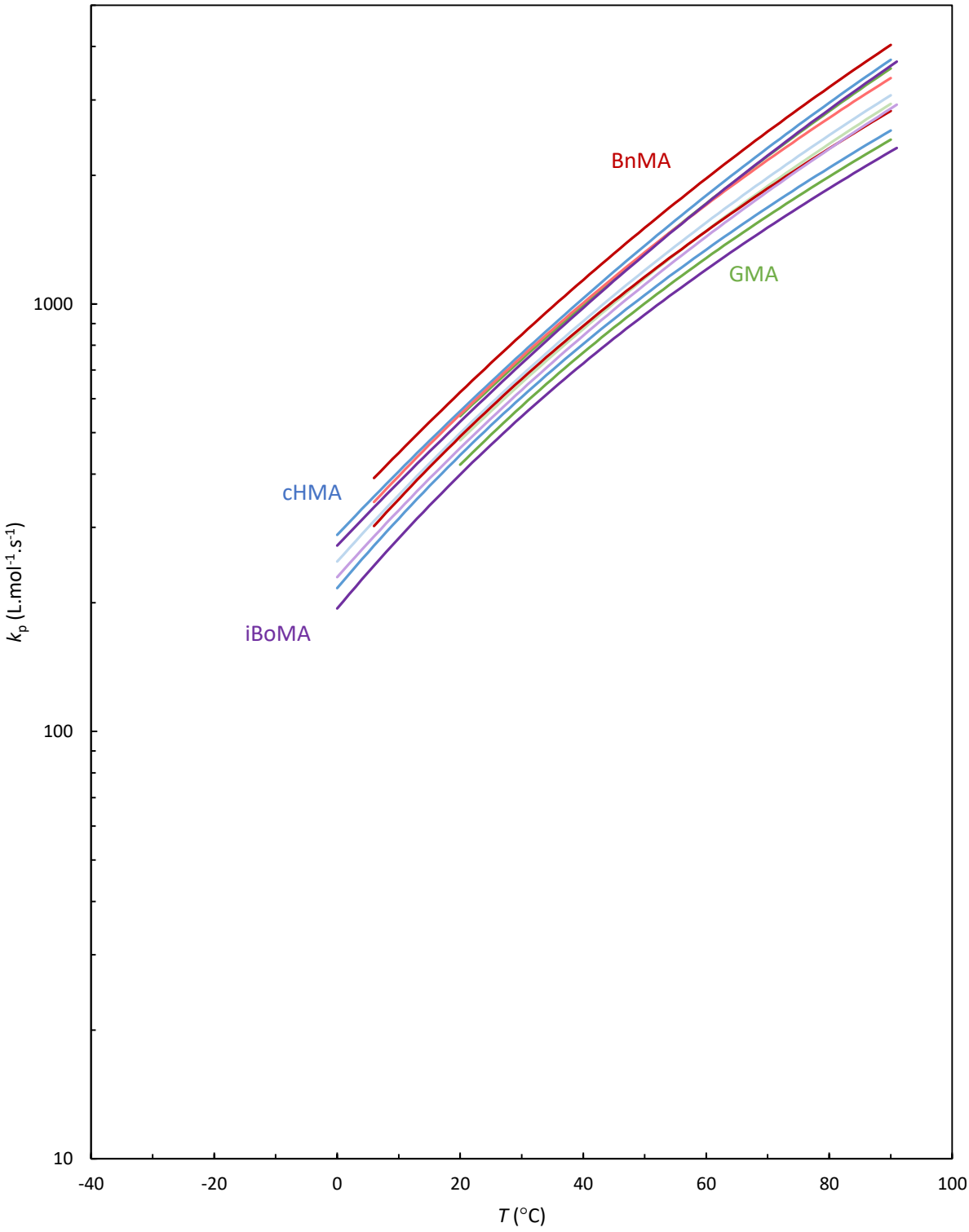
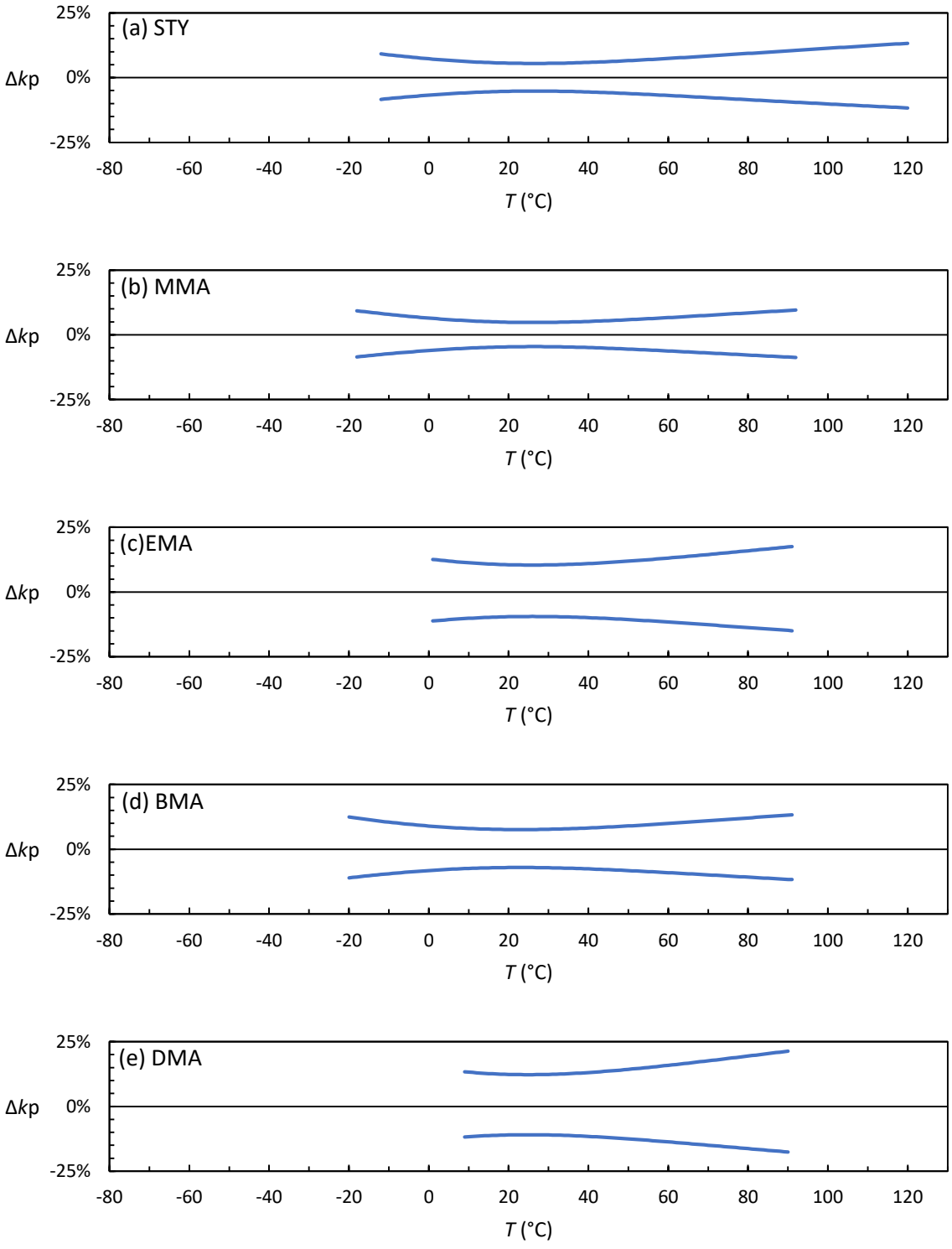
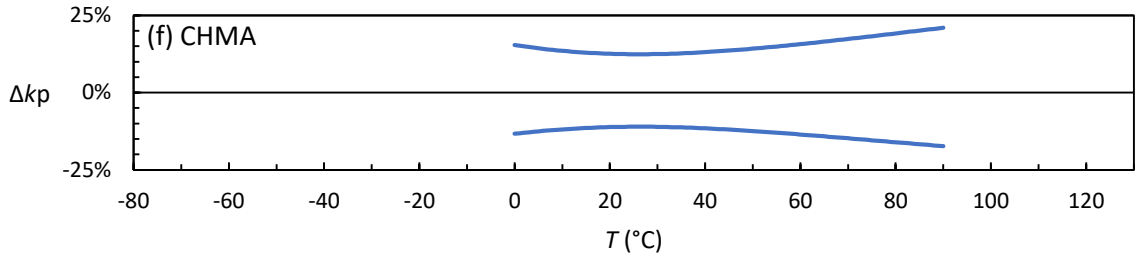
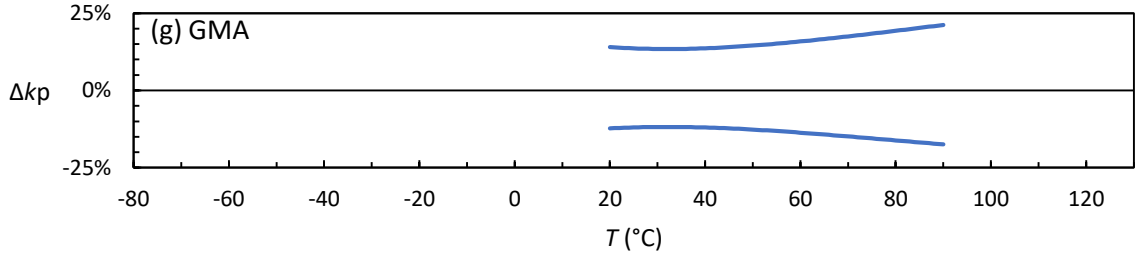
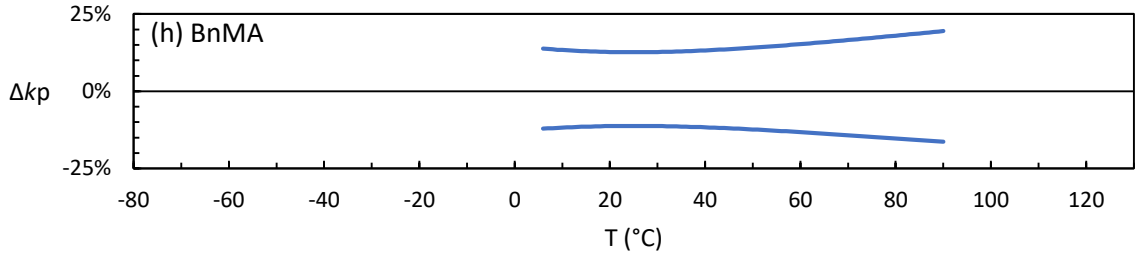


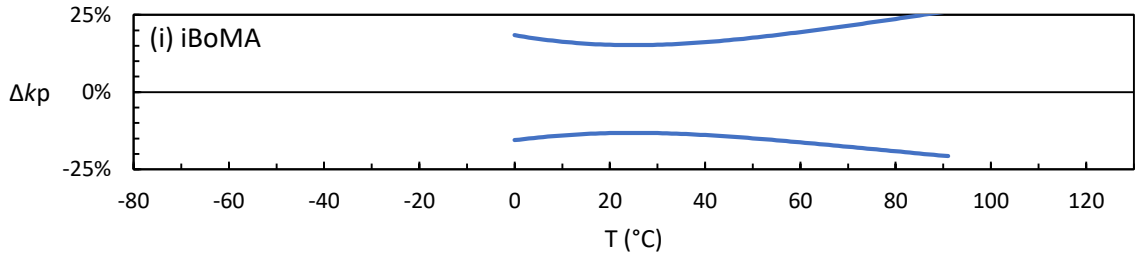
Figure S16. 95% confidence bands for k_p of cyclic methacrylates: cyclohexyl methacrylate (cHMA), glycidyl methacrylate (GMA), benzyl methacrylate (BnMA) and isobornyl methacrylate (iBoMA).

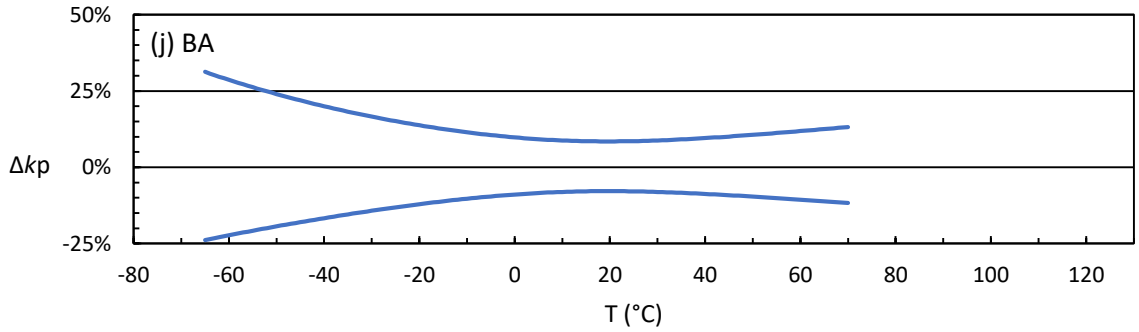

(a) STY
(b) MMA
(c)EMA
(d) BMA
(e) DMA
Δkp
25%
0%
-25%
-80
-60
-40
-20
0
20
40
60
80
100
120
T (°C)


(f) CHMA
Δkp
25%
0%
-25%
-80 -60 -40 -20 0 20 40 60 80 100 120
T (°C)


(g) GMA
Δkp
25%
0%
-25%
-80 -60 -40 -20 0 20 40 60 80 100 120
T (°C)


(h) BnMA
Δkp
25%
0%
-25%
-80 -60 -40 -20 0 20 40 60 80 100 120
T (°C)


(i) iBoMA
Δkp
25%
0%
-25%
-80 -60 -40 -20 0 20 40 60 80 100 120
T (°C)


(j) BA
Δkp
50%
25%
0%
-25%
-80 -60 -40 -20 0 20 40 60 80 100 120
T (°C)

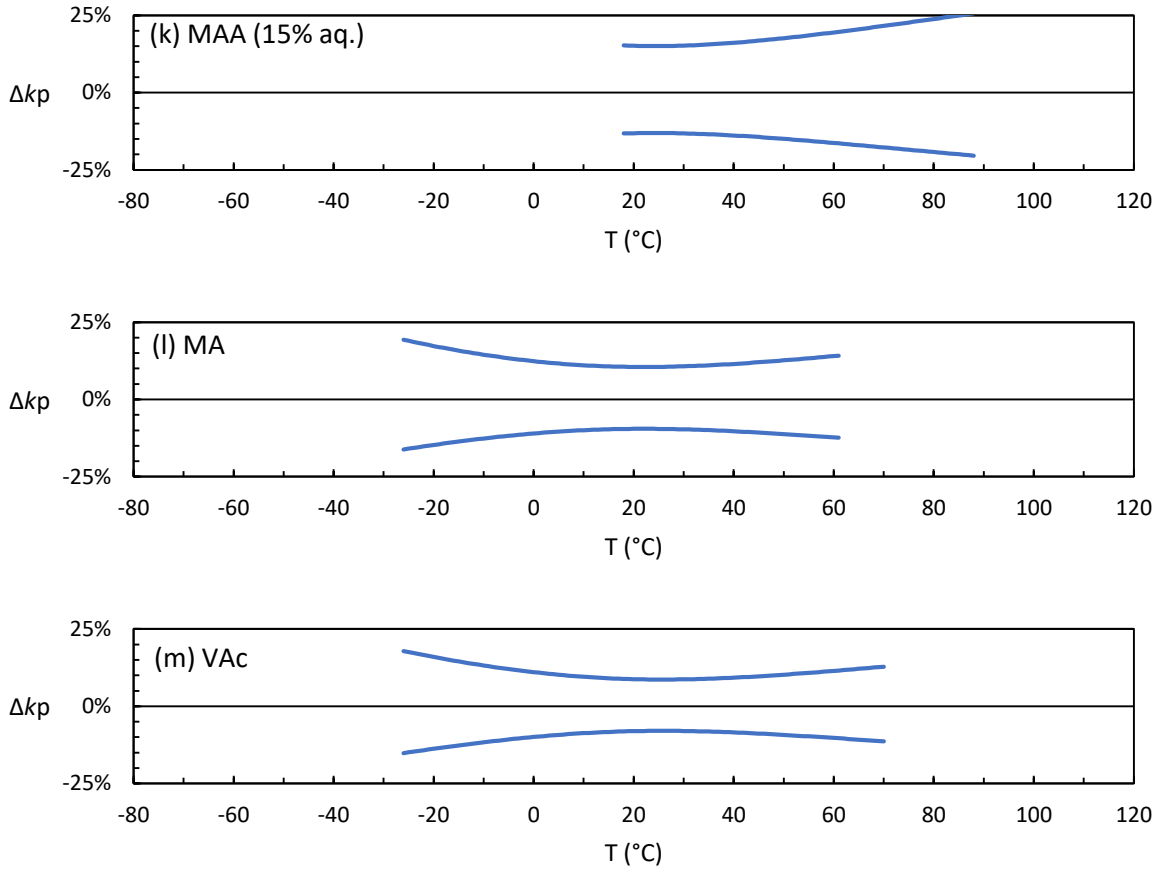


Figure S17. 95% confidence bands for k_p of vinyl monomers, expressed as relative deviation from the best fit to the experimental data ($\Delta k_p = \frac{k_p - \hat{k}_p}{\hat{k}_p}$). (a) styrene (STY); (b) methyl methacrylate (MMA); (c) ethyl methacrylate (EMA); (d) butyl methacrylate (BMA); (e) dodecyl methacrylate (DMA); (f) cyclohexyl methacrylate (cHMA); (g) glycidyl methacrylate (GMA); (h) benzyl methacrylate (BnMA); (i) isobornyl methacrylate (iBoMA); (j) butyl acrylate (BA); (k) methacrylic acid (MAA, 15% aqueous solution); (l) methyl acrylate (MA); (m) vinyl acetate (VAc).

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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 and their respective macroradicals 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 <5%) 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 initial [M] precisely known (and assuming negligible consumption of monomer during the experiment), the accuracy of the technique primarily depends 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 corresponding to chains that survived the first radical burst and were terminated by the second or subsequent radical bursts, 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 81 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

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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

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.

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 ($L \cdot mol^{-1} \cdot s^{-1}$)	E_A ($kJ \cdot mol^{-1}$)	k_p at 25°C ($L \cdot mol^{-1} \cdot s^{-1}$)	T (°C)	N[c]	A ($L \cdot mol^{-1} \cdot s^{-1}$)	E_A ($kJ \cdot mol^{-1}$)	k_p at 25°C ($L \cdot mol^{-1} \cdot s^{-1}$)	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]	$\mathbf{10^{7.34(4)}}$	17.9(2)	**16.4(3) x 10^3**	-65–20	5	$\mathbf{10^{7.22(11)}}$	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 the 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

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.[5,7,11,12] These curated datasets were published in the original articles.[1-8]

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, the following strategies were applied *in the original analysis*: 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.[2,13]

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),[14-17] and 4 provided multiple k_p values across a range of temperatures.[13,18-20] 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.

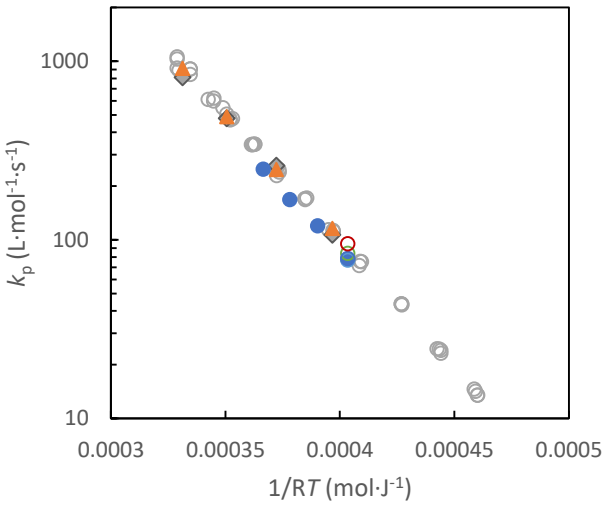

Figure 1. Dataset used to fit Arrhenius parameters for k_p of styrene radical polymerization in bulk. Open circles (grey): data from reference 13; filled diamonds (grey): data from reference 18; filled circles (blue): data from reference 19; filled triangles (orange) data from reference 20; remaining points from references 14-17.

In Figure 2, 95% JCRs are shown for the four studies[13,18-20] that provided sufficient data to estimate them, while the k_p values at 25°C from the 4 remaining studies[14-17] 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.

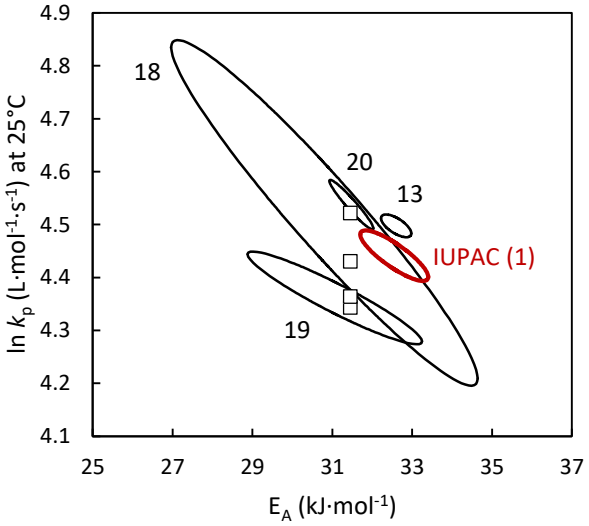

Figure 2. 95% Joint confidence regions (JCR) for Arrhenius parameters of k_p of styrene. In black, the JCRs corresponding to the individual studies of references 13 and 18-20. The open black squares represent 4 independent measures (references 14-17) of k_p at 25°C, shown at an arbitrary E_A. The red 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 13 and 20), 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 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):

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

In eq 5, $k_{p,ij}$ represents the j^{th} measurement of k_p from the i^{th} 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 i^{th} 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[13-20] of STY are grouped in Table 2, along with those of 8 additional studies[21-28] 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 average molar masses obtained by SEC.[29,30] It should be noted that this estimate of SEC reproducibility in the determination of average molar masses is influenced by selection of baselines and integration limits, which are not applicable to the identification of a single molar mass corresponding to the inflection point of the PLP-SEC trace. Hence, reproducibility in k_p determination by PLP-SEC is expected to be superior to that of determination of average molar masses.

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

reproducibility of SEC, the intralaboratory reproducibility (i.e. the same sample reanalysed using the same equipment) is generally good.[29,30] 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[31,32] 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.

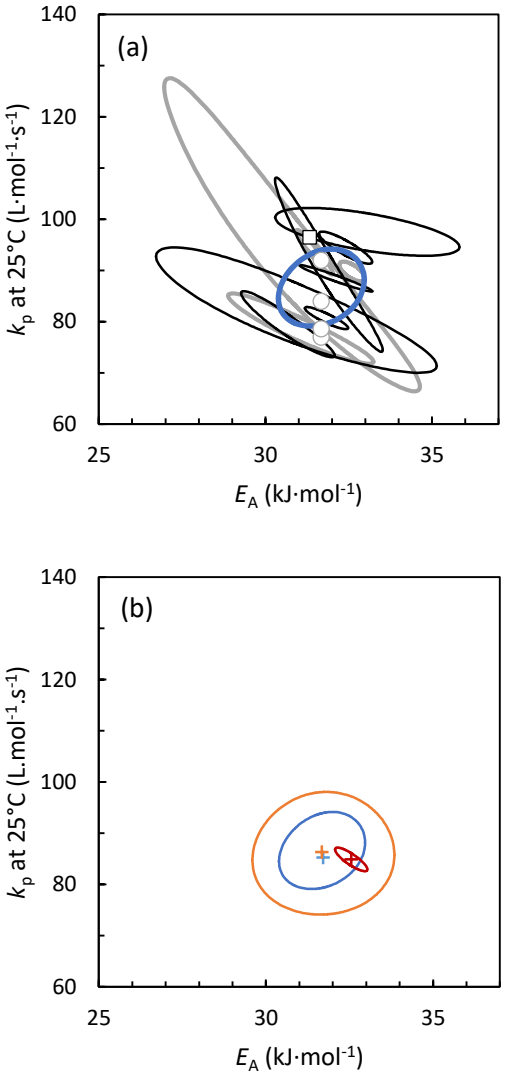

Figure 3. 95% Joint confidence regions (JCRs) for individual studies (a) and pooled data (b) for E_A and k_p at 25°C of styrene radical polymerization in bulk. (a) JCRs corresponding to references 17-20 shown in grey, additional data shown in black. Open circles represent k_p from single experiments (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

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[33] 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[34] 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.

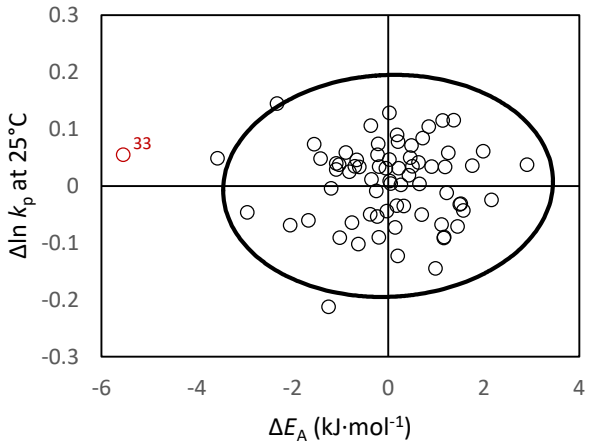

Figure 4. Interlaboratory variation in estimates of ln k_p at 25°C and E_A for all benchmarked monomers, and pooled 95% JCR. The point in red (reference 33) was considered an outlier and excluded from the study. Standard errors in ln k_p at 25°C and E_A are 0.08 and 1.4 kJ·mol^{-1}, respectively, with 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.

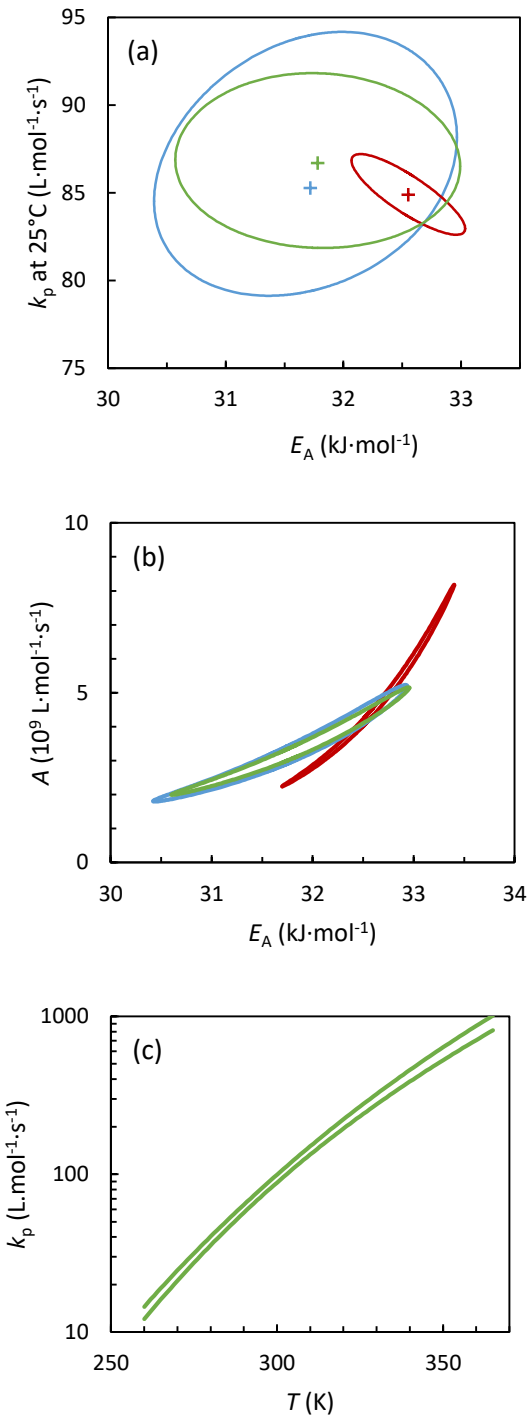

Figure 5. (a) Comparison of parameter estimates and 95% JCRs for E_A and ln k_p at 25°C of radical polymerization of styrene in bulk obtained using estimates of interlaboratory variation obtained from studies on styrene (blue) or from pooled studies of all benchmarked monomers (green). Original IUPAC 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

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.

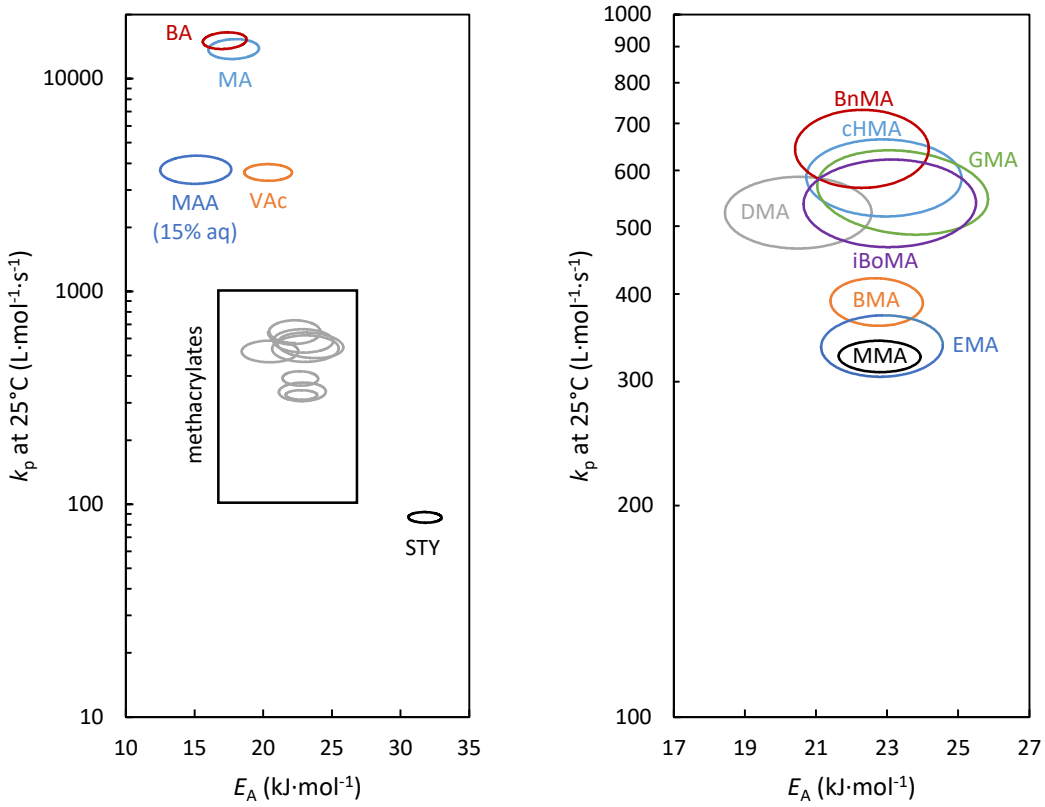

Figure 6. Revised 95% JCRs for monomers for which IUPAC benchmark values are available. MMA: methyl methacrylate; EMA: ethyl methacrylate; BMA: butyl methacrylate; iBoMA: isobornyl methacrylate; DMA: dodecyl methacrylate; GMA: glycidyl methacrylate; cHMA: cyclohexyl methacrylate; BnMA: benzyl methacrylate;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

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

Notes on data selection

Styrene. The data set from reference 1 (8 studies[13-20]) was augmented with 8 additional studies[21-28] 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.[28] in which MALDI-TOF MS was used to obtain the MMDs.

Methyl methacrylate. The data set from reference 2 (7 studies[14,17,21,35-38]) was augmented with 12 additional studies[28,39-49] published between 1997 and 2015, and covering a temperature range of –18-91.5°C. Analysis was by SEC using 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.,[48] 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[45,50,51]) 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[45,50-52]) was augmented with 4 additional studies[48,53-55] 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.,[48] 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[50-52]) 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[56-58]) 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[56,58]) was augmented with an additional study[59] 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[45,56,57]) was augmented with 1 additional study[60] published in 2011, and covering a temperature range of 14-72°C.

Isobornyl methacrylate. The data set from reference 4 (2 studies[56,57]) 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[33,61-65]) was augmented with 3 additional studies[66-68] 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,[68] in which MALDI-TOF MS was used to obtain the MMDs. One early study[33] 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[69,70]) 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[34,64,68,71,72]) was reanalysed. Analysis was by SEC using universal calibration, with the exception of Willemse et al.,[68] in which MALDI-TOF MS was used to obtain the MMDs. The results of reference 34, 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[36,64,73-76]) 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.

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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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 and their respective macroradicals 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 <5%) 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 initial [M] precisely known (and assuming negligible consumption of monomer during the experiment), the accuracy of the technique primarily depends 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 corresponding to chains that survived the first radical burst and were terminated by the second or subsequent radical bursts, 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 81 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

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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

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.

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 ($L \cdot mol^{-1} \cdot s^{-1}$)	E_A ($kJ \cdot mol^{-1}$)	k_p at 25°C ($L \cdot mol^{-1} \cdot s^{-1}$)	T (°C)	N[c]	A ($L \cdot mol^{-1} \cdot s^{-1}$)	E_A ($kJ \cdot mol^{-1}$)	k_p at 25°C ($L \cdot mol^{-1} \cdot s^{-1}$)	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]	$\mathbf{10^{7.34(4)}}$	17.9(2)	$\mathbf{16.4(3) \times 10^3}$	-65–20	5	$\mathbf{10^{7.22(11)}}$	17.3(6)	$\mathbf{15.7(5) \times 10^3}$	-65–70	8
MAA[6]	$10^{6.19(8)}$	15.0(4)	$3.72(5) \times 10^3$	18–89	2	$10^{6.21(18)}$	15.1(1.0)	$3.73(21) \times 10^3$	18–89	2
MA[7]	$10^{7.15(5)}$	17.3(2)	$\mathbf{13.1(1) \times 10^3}$	-28–61	5	$10^{7.25(13)}$	17.8(7)	$\mathbf{13.7(5) \times 10^3}$	-26–61	4
VAc[8]	$10^{7.13(7)}$	20.4(4)	$3.60(4) \times 10^3$	5–70	6	$10^{7.13(12)}$	20.4(7)	$3.62(12) \times 10^3$	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 the 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

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.[5,7,11,12] These curated datasets were published in the original articles.[1-8]

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, the following strategies were applied *in the original analysis*: 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.[2,13]

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),[14-17] and 4 provided multiple k_p values across a range of temperatures.[13,18-20] 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.

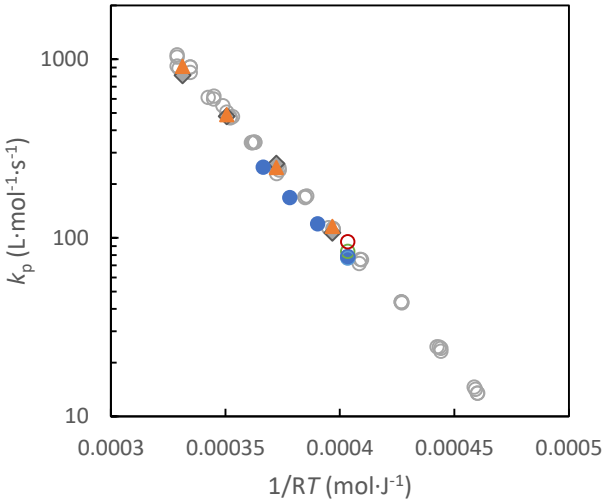

Figure 1. Dataset used to fit Arrhenius parameters for k_p of styrene radical polymerization in bulk. Open circles (grey): data from reference 13; filled diamonds (grey): data from reference 18; filled circles (blue): data from reference 19; filled triangles (orange) data from reference 20; remaining points from references 14-17.

In Figure 2, 95% JCRs are shown for the four studies[13,18-20] that provided sufficient data to estimate them, while the k_p values at 25°C from the 4 remaining studies[14-17] 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.

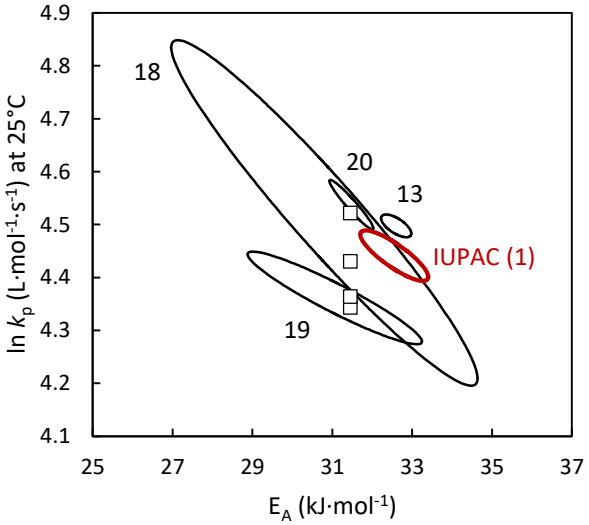

Figure 2. 95% Joint confidence regions (JCR) for Arrhenius parameters of k_p of styrene. In black, the JCRs corresponding to the individual studies of references 13 and 18-20. The open black squares represent 4 independent measures (references 14-17) of k_p at 25°C, shown at an arbitrary E_A. The red 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 13 and 20), 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 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):

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

In eq 5, $k_{p,ij}$ represents the j^{th} measurement of k_p from the i^{th} 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 i^{th} 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[13-20] of STY are grouped in Table 2, along with those of 8 additional studies[21-28] 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 average molar masses obtained by SEC.[29,30] It should be noted that this estimate of SEC reproducibility in the determination of average molar masses is influenced by selection of baselines and integration limits, which are not applicable to the identification of a single molar mass corresponding to the inflection point of the PLP-SEC trace. Hence, reproducibility in k_p determination by PLP-SEC is expected to be superior to that of determination of average molar masses.

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

reproducibility of SEC, the intralaboratory reproducibility (i.e. the same sample reanalysed using the same equipment) is generally good.[29,30] 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[31,32] 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.

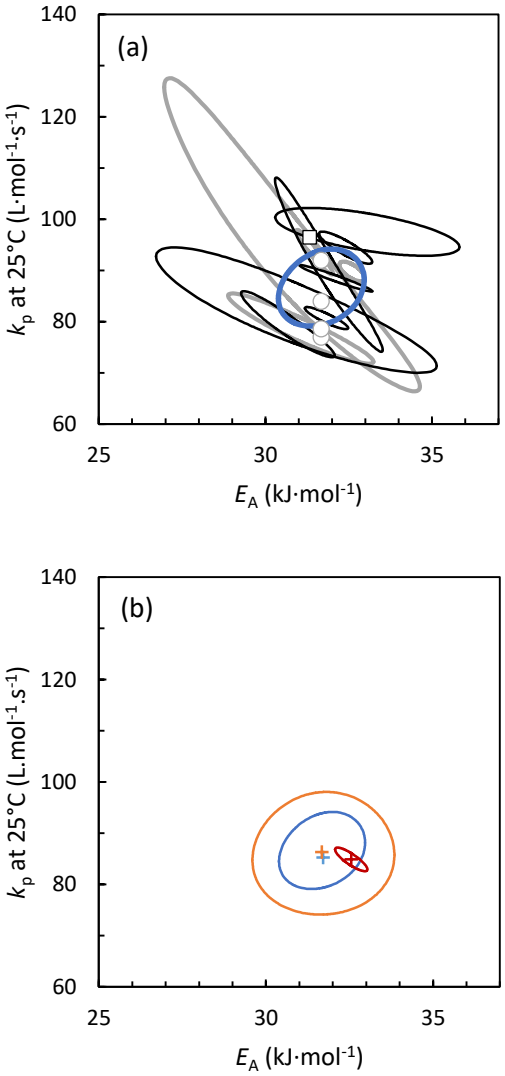

Figure 3. 95% Joint confidence regions (JCRs) for individual studies (a) and pooled data (b) for E_A and k_p at 25°C of styrene radical polymerization in bulk. (a) JCRs corresponding to references 17-20 shown in grey, additional data shown in black. Open circles represent k_p from single experiments (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

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[33] 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[34] 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.

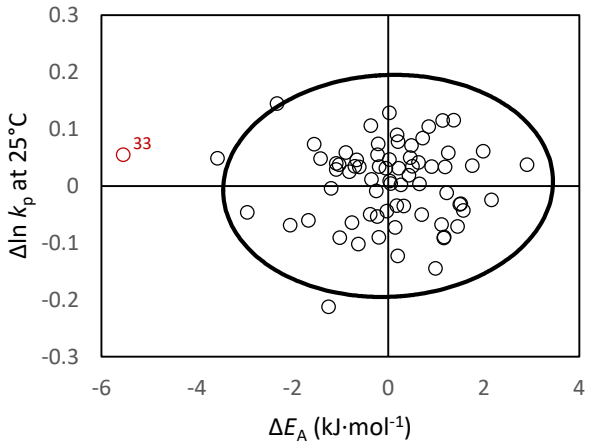

Figure 4. Interlaboratory variation in estimates of ln k_p at 25°C and E_A for all benchmarked monomers, and pooled 95% JCR. The point in red (reference 33) was considered an outlier and excluded from the study. Standard errors in ln k_p at 25°C and E_A are 0.08 and 1.4 kJ·mol^{-1}, respectively, with 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.

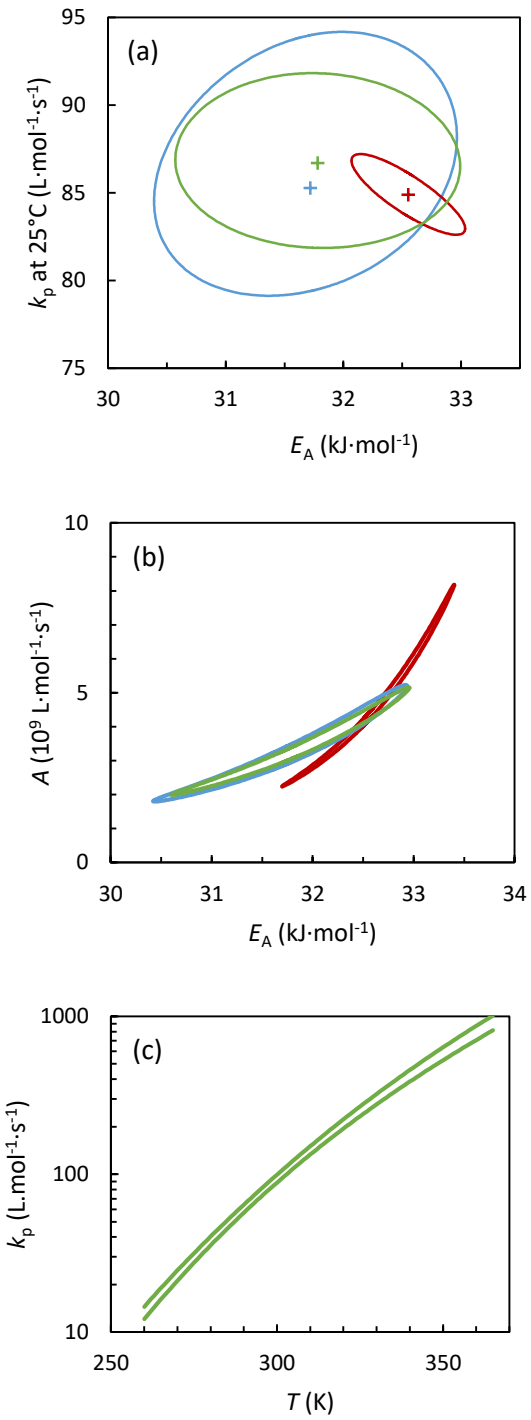

Figure 5. (a) Comparison of parameter estimates and 95% JCRs for E_A and ln k_p at 25°C of radical polymerization of styrene in bulk obtained using estimates of interlaboratory variation obtained from studies on styrene (blue) or from pooled studies of all benchmarked monomers (green). Original IUPAC 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

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.

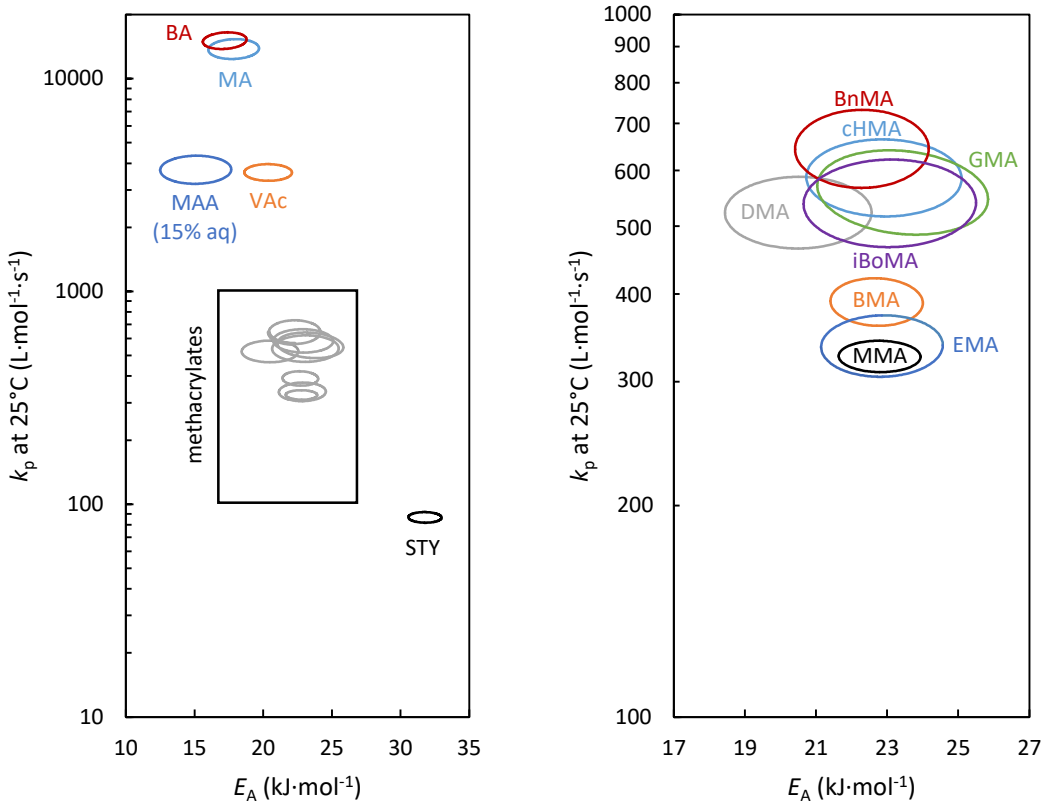

Figure 6. Revised 95% JCRs for monomers for which IUPAC benchmark values are available. MMA: methyl methacrylate; EMA: ethyl methacrylate; BMA: butyl methacrylate; iBoMA: isobornyl methacrylate; DMA: dodecyl methacrylate; GMA: glycidyl methacrylate; cHMA: cyclohexyl methacrylate; BnMA: benzyl methacrylate;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

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

Notes on data selection

Styrene. The data set from reference 1 (8 studies[13-20]) was augmented with 8 additional studies[21-28] 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.[28] in which MALDI-TOF MS was used to obtain the MMDs.

Methyl methacrylate. The data set from reference 2 (7 studies[14,17,21,35-38]) was augmented with 12 additional studies[28,39-49] published between 1997 and 2015, and covering a temperature range of –18-91.5°C. Analysis was by SEC using 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.,[48] 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[45,50,51]) 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[45,50-52]) was augmented with 4 additional studies[48,53-55] 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.,[48] 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[50-52]) 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[56-58]) 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[56,58]) was augmented with an additional study[59] 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[45,56,57]) was augmented with 1 additional study[60] published in 2011, and covering a temperature range of 14-72°C.

Isobornyl methacrylate. The data set from reference 4 (2 studies[56,57]) 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[33,61-65]) was augmented with 3 additional studies[66-68] 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,[68] in which MALDI-TOF MS was used to obtain the MMDs. One early study[33] 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[69,70]) 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[34,64,68,71,72]) was reanalysed. Analysis was by SEC using universal calibration, with the exception of Willemse et al.,[68] in which MALDI-TOF MS was used to obtain the MMDs. The results of reference 34, 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[36,64,73-76]) 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.

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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