Critically evaluated rate coefficients for free-radical polymerization. 1. propagation rate coefficient for styrene

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Critically evaluated rate coefficients for free-radical polymerization, 1

Propagation rate coefficient for styrene

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SUMMARY:
   Pulsed-laser polymerization (PLP) in conjugation with molecular weight distribution
(MWD) measurement has emerged as the method of choice for determining the propagation
rate coefficient k_p in free-radical polymerizations. Detailed guidelines for using this
technique (including essential internal consistency checks) and reporting the results
therefrom are given by the authors, members of the IUPAC Working Party on *Modeling of
kinetics and processes of polymerization*. The results for PLP-MWD k_p measurements
from many laboratories for bulk free-radical polymerization of styrene at low conversions
and ambient pressure are collated, and are in excellent agreement. They are therefore
recommended as constituting a benchmark data set, one that is best fitted by

$$k_p = 10^{7.630} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1} \exp \left(\frac{-32.51 \text{ kJ} \cdot \text{mol}^{-1}}{R \cdot T} \right)$$

(the confidence ellipsoid for the Arrhenius parameters is also given). These benchmark data
are also used to evaluate the merits of several other methods for determining k_p; it is found
that appropriately calibrated electron paramagnetic resonance spectroscopy appears to yield
reliable values of k_p for styrene.

1. Introduction

   This is the third publication of an IUPAC Working Party on *'Modeling of kinetics
and processes of polymerization'*. Previously[1,2] the emphasis was on the manifesta-

tions and causes of the difficulties of accurate and unambiguous measurements of free-radical polymerization rate parameters. This paper is the first in a series whose aim is to establish benchmark values of important rate coefficients in free-radical polymerization, and to set out means by which these can be reliably measured. Here we bring together the results of recent determinations of the propagation rate coefficient, k_p, for styrene at low conversions. Equally useful is the establishment of *reliable* techniques for measuring k_p. Earlier work[2-6)] suggests that the optimal method is that involving analysis of the molecular weight distribution (MWD) of polymer produced in pulsed-laser-initiated polymerization (PLP). This "PLP-MWD" technique is the *method of choice* for determining k_p: in the short time since its proposal and first implementation[7)], it has shown itself to be straightforward to use and remarkably free (by the standards of free-radical polymerization) of model-based assumptions; moreover, this technique as specified in the present paper, provides internal consistency checks of the reliablity of its results. The rapidity with which the use of this technique has spread is such that in the case of styrene, we are able to collate PLP-MWD results from a large number of studies and to recommend benchmark values of k_p.

2. Experimental considerations

The PLP-MWD tecchnique for determining k_p consists of two major experimental phases: (i) a pulsed-laser-initiated polymerization, and (ii) obtaining a molecular weight distribution. Experience has shown that many seemingly routine aspects of these procedures may in fact be of significance. We therefore draw attention to the following details to which consideration should be given in designing experiments and reporting the results therefrom.

2a. Pulsed-laser-initiated polymerization

Concerning the *laser* itself, the following aspects may be relevant: pulse duration; radiation wavelength; laser intensity (i. e., pulse energy); beam treatment (beam intensity reduction, optical path); and the absorbance of the polymerization medium (it is important to establish that a relatively homogeneous radical-production profile prevails along the optical path, i. e., that absorbance is not too high).

Factors relating to the *sample cell* include: its dimensions; its geometry, preferably such that the entire volume is irradiated by the laser beam; how the polymerization temperature is controlled and measured, including the extent to which intra-cell temperature fluctuations can be detected (the heat evolved by polymerization may cause significant temperature rises); and whether any stirring is effected.

Concerning the *polymerization,* the following should be stated: the source and purity (including any purification procedures) of all reagents; monomer, initiator and solvent concentrations, and the extent to which these are varied; temperature, including at least an estimate of its deviation during experiments (see above); time between laser pulses and variations thereof (note that this time may not be constant during a pulse sequence, something which should also be examined); total irradiation time (i. e., number of

pulses); the final conversion of monomer into polymer; whether any degassing was performed; and all post-polymerization procedures, e.g., addition of inhibitor, polymer isolation and purification.

2b. Determination of molecular weight distribution

An average molecular weight of PLP-MWD-produced polymer is not sufficient for evaluation of k_p: the molecular weight distribution needs to be determined. Although other methods such as matrix-assisted laser desorption/ionization (MALDI) mass spectroscopy[8] might come into their own for this purpose in the future, for the moment size exclusion chromatography (SEC, gel permeation chromatography) is the routine method that is used. Aspects of SEC setup that might be reported are: sample treatment prior to injection (freeze drying, direct injection, filtration); type of eluent and flow rate; column set and temperature, method of detection; and calibration (type and molecular weight range of polymer standards, and perhaps the Rayleigh ratio and solvent used to find the molecular weight of the standards, if this was performed using light scattering, as is normally the case). Calibration is particularly important, because k_p determination rests on the accurate conversion of elution volumes into absolute values of molecular weight. It is therefore recommended that calibration be effected using narrow molecular weight standards of the same polymer as that produced by the PLP. Even for homopolymerization this will not always be possible, and for copolymerization this will rarely be possible. In such cases one solution is to rely on universal calibration: the Mark-Houwink parameters employed, and their source(s), should definitely be reported, for both standard and unknown. As an alternative to universal calibration or use of standards (or as a check on both), SEC in conjunction with either on-line viscometry[9] or on-line light-scattering[10], or both[11-14], may be used. Another point is that it is essential to be aware that the Mark-Houwink parameters may not be constant for small chains, for such chains may not adopt the same coil conformation as long chains (an alternative to the Mark-Houwink relation suitable for short chains has recently been presented[15] which can be of assistance here). It is therefore preferable to choose PLP conditions so that the range of the molecular weight distribution used for determining k_p does not include very low molecular weights.

3. Evaluation of k_p

The propagation rate coefficient k_p is evaluated using the following equation:

$$L_i = i \cdot k_p \cdot [M] \cdot t_d \tag{1}$$

Here t_d is the 'dark time', the time between laser pulses; [M] is the monomer concentration; and i is a positive integer ($i = 1, 2 \ldots$) corresponding to a *degree of polymerization* L_i. (1) In specifying t_d, one should check that the laser is actually firing with the intended pulse repetition rate. (2) Monomer conversion should be kept as small as possible, preferably below, say, 2%. Further, calculations[16] suggest that a

reasonable [M] to use in Eq. (1) is the arithmetic mean of its initial and final values. It is for these reasons that measurement of final PLP conversions is recommended. (3) With regard to the chain lengths L_i, two issues arise: (a) Which features of an MWD should be taken for L_i specification?; and (b) What type of MWD should be used for this specification? These matters will now be discussed in turn.

(3 a) In their original work[7], Olaj et al. assumed a kinetic model and calculated the molecular weight distributions that would results from PLP. They calculated the degree of polymerization L_1 from Eq. (1), and found that this *corresponded most closely* to a point of inflection of their calculated MWD, specifically, to the point of inflection on the low molecular weight side of the major peak of their MWD. This was so under a variety of circumstances. This result, including the extension to 'overtone' peaks, has now been verified in further model calculations using a number of different kinetic models and calculational techniques[5, 6, 17-21]. Additionally, in a few cases[2, 19] it has been possible to compare k_p as accurately measured by other techniques with k_p as measured by PLP-MWD, L_1 having been taken as just described. In all such cases the comparison is remarkably favourable. It therefore can be stated that in using Eq. (1) to determine k_p, inflection points on the low molecular weight sides of MWD peaks should be used as L_i values: this is illustrated in Fig. 1. It is emphasized that such L_i do not correspond *exactly* to k_p as given by Eq. (1), but rather that under normal circumstances[21], these turning points are the MWD features that best *correlate* with k_p. (Indeed, this and SEC calibration are the major sources of error in k_p.) In fact some recent work[21] suggests that under the extreme conditions of very rapid termination and high radical concentrations, the L_i turning points do not correlate optimally with k_p (although the error is still not considerable). Care should therefore be taken to establish that the turning points are really the best measure of k_p (see next section and ref.[21]).

(3 b) There are three common ways of expressing the MWD: $n(M)$, the relative *number* of polymer chains of molecular weight M; $w(M)$, the relative *weight* of polymer $(n(M) \sim M^{-1} w(M)$; and $w(\log M)$. It is noted that $w(M)$ and $w(\log M)$ are not the same, and also that under usual circumstances, SEC gives $w(\log M)$ directly[22, 23]. Specifically, if the SEC calibation curve is linear in the relation between $\log M$ and the elution volume, and the detector is sensitive to total mass, then the intensity of an SEC signal is related to the various distributions by

$$\text{SEC signal} \sim w(\log M) \sim Mw(M) \sim M^2 n(M) \tag{2}$$

(generalizations of Eq. (2) for non-linear calibration curves have been given elsewhere[22, 23]; the constants of proportionality in Eq. (2) are trivially related to the total mass of polymer in the sample). For a PLP sample, values of L_i vary slightly, depending on which type of MWD is used: $n(M)$ gives the lowest values of L_i, $w(\log M)$ the highest[19]. Which type of MWD gives values of L_i that yield k_p most accurately from Eq. (1)? The indications are that either $w(M)$ or $w(\log M)$ should be used[7], but this is not of major significance, for the differences in L_i values from different representations are typically much less than 10%[19]. However in reporting results it should be made clear which sort of MWD has been used for k_p evaluation.

Further, it would be useful to indicate the noise reduction to which the SEC data has been subjected, and also to report how MWD points of inflection were located (e. g., numerical differentiation, or via cubic spline fitting of the MWD). Data reporting should also include both some actual SEC traces and the derivative of the particular MWD used to locate the point of inflection.

It should also be clearly indicated which inflection points have been used to evaluate k_p. In the usual instance the L_1 inflection point is far more evident and precisely locatable than al other inflection points (e. g., Fig. 1). It is therefore sufficient that any
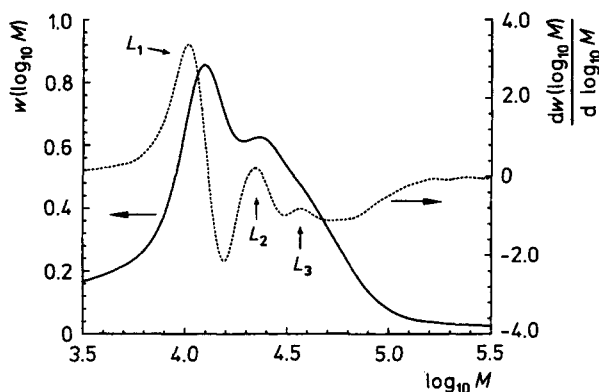

Fig. 1. Molecular weight distribution (MWD) of the polymer formed in a pulsed-laser-initiated polymerization of styrene at 30 °C and 1 bar[29]. The MWD is given as $w(\log_{10}M)$, where w is weight fraction and M is molecular weight in $g \cdot mol^{-1}$. The L_i points of inflection can clearly be identified as maxima in the derivative $dw(\log_{10}M)/d(\log_{10}M)$ of the MWD; from the chain lengths L_i corresponding to these points of inflection, the value of the propagation rate coefficient k_p is derived. Notice how the L_1 point of inflection is most reliably located, and how it lies on the low molecular weight side of the major MWD peak

'overtone' inflection points — at most L_2 and L_3 will be evident in practice — be used merely as self-consistency checks (see next section A), and that k_p be determined employing only

$$L_1 = k_p \cdot [M] \cdot t_d \qquad (3)$$

The physical meaning of Eq. (3) is that L_1 is the number of monomer units that a radical adds in the time between laser pulses; if a radical formed by a pulse is terminated instantly by a radical formed by the subsequent pulse, then a dead chain of degree of polymerization L_1 results. What is crucial for determining k_p is how this characteristic chain length manifests itself in an MWD.

4. Criteria for reliability

We now outline the measures that should be taken to ensure that a PLP-MWD experiment is in fact yielding a *reliable* value of k_p:

(1) Duplicate runs must be performed in order to assess instrumental reproducibility, since both laser pulse profiles and SEC measurements can vary from day to day.

(2) It is considered essential that there be at least a first overtone inflection point evident, and this be such (see Eq. (1)) that $L_2 \approx 2L_1$: this is illustrated in Fig. 1. This criterion gives confidence that the MWD turning point at chain length L_1 is really a manifestation of the occurrence of termination between radicals from successive pulses.

(3) Also considered essential is that the experimentally-measured k_p be shown to be independent of changes in the pulse which controls the radical concentration. This is best done by variation of the initiator concentration or the incident pulse energy. By varying the radical concentration in this way, the *rate* of termination is varied; while this should affect the relative intensity of the L_1 inflection point, it should not affect its location, which simply reflects the chain length grown in the time between pulses. If there is such an effect, then a value of k_p cannot be obtained from the data through Eq. (1).

(4) It is also highly recommended that k_p be shown to be independent of variation of either or both pulse repetition rate and duration of irradiation. If in addition the value of k_p is independent of monomer concentration (i. e., by addition of a solvent), then that functions as another consistency check, as well as showing that the solvent employed does not affect k_p (if however the value of k_p varies with addition of solvent, that indicates a significant solvent effect, provided that the other consistency checks are satisfied). Another useful consistency check is to vary photoinitiator and laser wavelength. One thereby checks that there are no adventitious photochemical processes occurring: such might result in the L_1 inflection point not giving k_p. The additional consistency checks listed here are especially useful for monomers such as acrylates or vinyl acetate, for which it has been found difficult to use the PLP-MWD technique [19, 20, 24, 25].

(5) To be encouraged are attempts to ratify k_p values through simulation of experimentally obtained MWDs. In so doing one reaches beyond the semi-empirical nature of Eq. (1) and uses all the information in an MWD in order to evaluate k_p. Exact reproduction of an experimental MWD from a PLP has not yet been achieved (largely beause of gaps in our present understanding of polymerization mechanisms, amongst which is included the chain length dependence of termination, and of k_p for very short chains). However simulation methods are still helpful for verifying k_p values [5, 20, 21].

In reporting results, complete details should be given of whichever consistency checks have been performed. None of the above checks is of itself an absolute guarantee that an L_1 inflection point is yielding an accurate value of k_p. However by carrying out an appropriate number of the above checks, a 'critical evaluation' of both experimental method and apparatus is effectively carried out. Such critically evaluated k_p values for styrene are presented in the section that now follows.

5. Typical results and benchmark values

In reporting results, *truly representative* MWDs, and the derivatives thereof, should be given. This is exemplified by the typical styrene results of Fig. 1, in which the L_i inflection points are clearly evident as turning points in $dw(\log_{10}M)/d(\log_{10}M)$. In presenting data, k_p from *each* run should be specified as well as the values of all the quantities used in Eq. (1). Apart from facilitating easier comparison of experimental results in the event of discrepancies emerging, such data presentation also enables re-evaluation of results, e.g. should more accurate Mark-Houwink constants become available if universal calibration had been used to specify L_i.

The styrene k_p given in Tab. 1 are all from PLP-MWD investigations of bulk systems [19, 21, 26–31] at ambient pressure (note that the PLP-MWD method has recently been used to determine styrene k_p up to 3 kbar [29]). Solution polymerization values have not been included in this benchmark set of data, even though a PLP-MWD investigation [27] found no evidence of a significant solvent effect on k_p for styrene. Also not included amongst the values of Tab. 1 are k_p obtained using the same method as that discussed here but with non-laser means of intermittent initiation.

The benchmark styrene results of Tab. 1 are presented graphically in Figs. 2 and 3, in Fig. 2 as $\ln k_p$ versus $1/T$, where T is the absolute temperature, in Fig. 3 as k_p versus T. It is clear that the k_p values from many different laboratories agree excellently with each other, even though experimental conditions were different, as is detailed in Tab. 1. These data cover a wide range of the conditions which were stated above to be desirable/essential to vary.

Fig. 2.   Fig. 3.
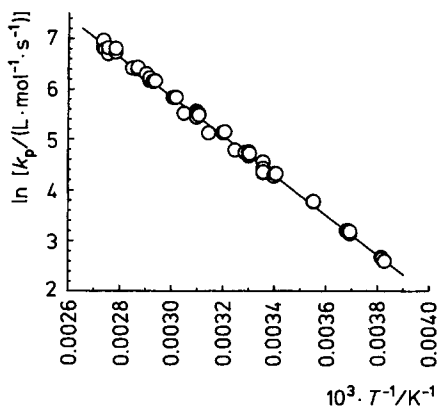
Fig. 2.   Arrhenius plot of the propagation rate coefficient k_p for styrene. Points: data from Tab. 1; line: best fit (Eq. (4b)) of Arrhenius equation (Eq. (4a)) to points
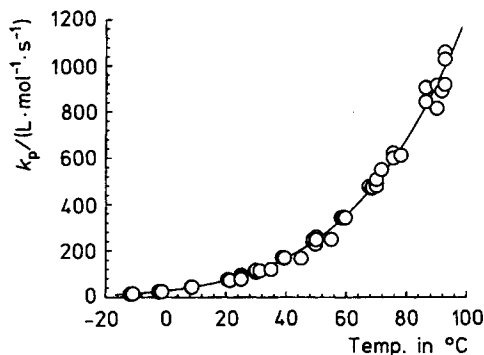
Fig. 3.   Values of the styrene propagation rate coefficient k_p from Tab. 1 as a function of temperature. Points: data from Tab. 1; line: best fit (Eq. (4b)) of Arrhenius equation (Eq. (4a)) to points

Tab. 1.   Critically evaluated values of the propagation rate coefficient k_p for styrene as a function of temperature

Temp. in °C	$\dfrac{k_p}{\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}}$	t_d/s	Initiator [a]	$\dfrac{\text{[initiator]}}{\text{mmol} \cdot \text{L}^{-1}}$	Pulse energy in mJ	Reference
−11.8	13.5	0.5	DMPA	5	30	31)
−11.7	13.5	0.5	DMPA	5	30	31)
−11.2	14.2	1	DMPA	5	30	31)
−10.9	14.62	1	DMPA	5	30	31)
−2.3	23.2	0.5	DMPA	5	30	31)
−2.3	24.1	1	DMPA	5	30	31)
−1.9	24.5	1	DMPA	5	30	31)
−1.3	24.6	0.5	DMPA	5	30	31)
8.5	43.9	0.5	DMPA	5	30	31)
8.5	43.2	0.5	DMPA	5	30	31)
8.7	43.8	1	DMPA	5	30	31)
8.7	43.8	1	DMPA	5	30	31)
20.6	75.5	0.5	DMPA	5	30	31)
21	75.9	0.5	DMPA	5	30	31)
21.3	71.9	0.2	DMPA	5	30	31)
25	77 [b]					26)
25	78 [b]	0.2−8	AIBN	1−5	35	28)
25	84 [b]	0.2	AIBN	5	35	27)
25	78.6 [b]	0.2−8	AIBN	1	35	30)
25	95 [b]	0.1	DMPA	5	varied	21)
29.7	112	0.1	DMPA	5	30	31)
29.8	113	0.2	DMPA	5	30	31)
30	107 [b]	0.1	benzoin	5	40	19)
30	116 [b]	0.1	DMPA	10	3	29)
31.3	114	0.5	DMPA	5	30	31)
35	120 [b]	0.1−10	AIBN, benzoin	5	35	28)
38.8	172	0.2	DMPA	5	30	31)
39.4	168	0.1	DMPA	5	30	31)
39.5	170	0.2	DMPA	5	30	31)
45	168 [b]	0.1−10	AIBN, benzoin	5	35	28)
48.9	240	0.1	DMPA	5	30	31)
49	248	0.2	DMPA	5	30	31)
49.8	229	0.1	DMPA	5	30	31)
50	260 [b]	0.1	benzoin	5	40	19)
50	248 [b]	0.2	DMPA	8	3	29)
50	248	0.2	DMPA	5	30	31)
55	249 [b]	0.1−10	AIBN, benzoin	5	35	28)
58.3	343	0.3	DMPA	5	30	31)
58.4	343	0.1	DMPA	5	30	31)
59.1	344	0.1	DMPA	5	30	31)
59.3	341	0.1	DMPA	5	30	31)
59.7	342	0.1	DMPA	5	30	31)
67.5	477	0.1	DMPA	5	30	31)
68.4	469	0.2	DMPA	5	30	31)
68.6	473	0.2	DMPA	5	30	31)

Tab. 1.   Continued

Temp. in °C	$\dfrac{k_p}{\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}}$	t_d/s	Initiator [a]	$\dfrac{\text{[initiator]}}{\text{mmol} \cdot \text{L}^{-1}}$	Pulse energy in mJ	Reference
70	507	0.1	DMPA	5	30	[31]
70	479 [b]	0.1	benzoin	5	40	[19]
70	490 [b]	0.1	DMPA	10	3	[29]
71.6	550	0.1	DMPA	5	30	[31]
75.5	622	0.1	DMPA	5	30	[31]
75.6	600	0.2	DMPA	5	30	[31]
78.1	612	0.2	DMPA	5	30	[31]
86.3	904	0.1	DMPA	5	30	[31]
86.3	905	0.1	DMPA	5	30	[31]
86.3	843	0.2	DMPA	5	30	[31]
90	915 [b]	0.1	DMPA	10	3	[29]
90	815 [b]	0.1	benzoin	5	40	[19]
91.6	889	0.2	DMPA	5	30	[31]
92.6	918	0.2	DMPA	5	30	[31]
92.6	1 060	0.1	DMPA	5	30	[31]
92.6	1 028	0.1	DMPA	5	30	[31]

[a]   DMPA = 2,2-dimethoxy-2-phenylacetophenone; AIBN = 2,2'-azoisobutyronitrile.
[b]   These values included three-fold in the data fitting of the text.

It is conventional to fit the temperature variation of a rate coefficient to the Arrhenius equation

$$\ln k_p = \ln A - \frac{E_A}{R \cdot T} \qquad (4a)$$

where A is the frequency factor and E_A the activation energy.

Fig. 2 shows the result of a linear fit to the $\ln k_p$ versus $1/T$ data:

$$\ln \left(\frac{k_p}{\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}} \right) = \ln (10^{7.633}) - \frac{32.51 \text{ kJ} \cdot \text{mol}^{-1}}{R \cdot T}$$

$$- 12\,^\circ\text{C} \leq \text{temperature} \leq 93\,^\circ\text{C} \qquad (4b)$$

Because the majority of the Tab. 1 values stem from one laboratory[31], all other [19, 21, 26-30] k_p values were weighted three-fold in carrying out the above fit (and that which follows). Although somewhat arbitrary, this weighting is justifiable, because most of these other k_p were reported as the average value of serveral runs. Besides, fitting without this weighting gives only negligible different Arrhenius parameters.

It has recently been pointed out[31] that $k_p(T)$ data can also be analyzed by non-linear fitting to the Arrhenius equation itself:

$$k_p = A \cdot \exp\left(\frac{-E_A}{R \cdot T}\right) \tag{5a}$$

A good method for carrying out such fitting is the error-in-variables (EVM) method[31]. An EVM fit of the Tab. 1 data was therefore performed. An absolute uncertainty of ± 0.5 K in T and a relative uncertainty of $\pm 10\%$ (arising mostly from Eq. (1) and from SEC calibration) was assumed for all k_p values. The result,

$$k_p = 10^{7.630} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1} \exp\left(\frac{-32.51 \text{ kJ} \cdot \text{mol}^{-1}}{R \cdot T}\right)$$

$$-12\,°C \leq \text{temperature} \leq 93\,°C \tag{5b}$$

is essentially identical to that of the linear fit. The 95% joint confidence interval from our EVM fit (constructed using the method of Hautus et al.[32]) is given in Fig. 4. It is stressed that values of A and E_A are highly correlated: it is incorrect to assign individual uncertainties to these parameter values.
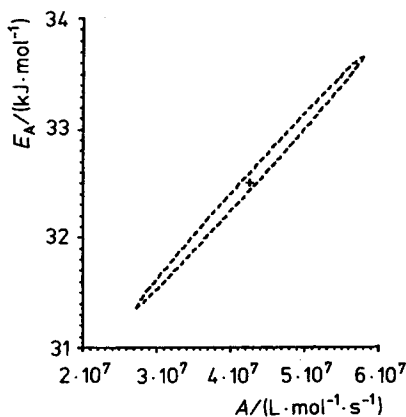

Fig. 4. 95% joint confidence ellipsoid for the frequence factor A and the activation energy E_A from error-in-variables fitting of propagation rate coefficient data for styrene (see text); the "+" is the value with least residual

The results of this section serve three purposes. (I) The k_p values given by Eqs. (5b) or (4b) are recommended for modeling low and intermediate conversion styrene polymerizations carried out at ambient pressure; this supersedes our earlier benchmark results[1]. (ii) Those seeking to measure k_p, for whatever monomer, are encouraged first of all to see if their experimental method gives Arrhenius parameters for styrene that lie within the joint confidence interval of Fig. 4. The necessity of appraising a method through determination of both A and E_A is emphasized: it is not sufficient merely to show that there is agreement between measured and benchmark k_p at one temperature only. (iii) Reproducing the Arrhenius parameters found here should be the aim of microscopic modeling of the propagation process (e. g., quantum mechanical calculations).

6. Comparison with values of k_p from other methods

We now exemplify how the benchmark k_p values may be used to appraise other experimental results.

(a) Electron paramagnetic resonance (EPR) spectroscopy

EPR (or electron spin resonance, ESR) spectroscopy in principle should be a good technique to measure k_p at high polymer fraction, when the propagation reaction becomes diffusion controlled. This method requires simultaneous measurements of the radical monomer concentrations and of the polymerization rate. The concentration of radicals is given by the double integral of the EPR signal, combined with calibration of the signal against an internal standard to convert the signal to an absolute radical concentration. Inferring a value of k_p assumes *inter alia* that there is only one type of radical species in the system (suggestions[33] that there are two distinct types of free radicals in ordinary methyl methacrylate polymerizations have been refuted[34]).

In view of the applicability of EPR to obtain values of k_p at high polymer fraction, it is important to see if the method, as applied at low polymer fraction, can yield values in accord with those given here. If agreement is obtained, the techniques used to obtain the EPR data at low polymer fraction can be applied with greater confidence at higher polymer fraction. Fig. 5 compares values of k_p obtained by EPR for styrene at low polymer fraction[35] with those from PLP-MWD listed in Tab. 1. It seems that it is possible to obtain consistent k_p values from EPR, at least at the higher temperature range shown. The results shown in Fig. 5 indicate the reliability of using EPR under appropriate conditions, given careful attention to the calibration technique (that used by Yamada et al.[35] is recommended).
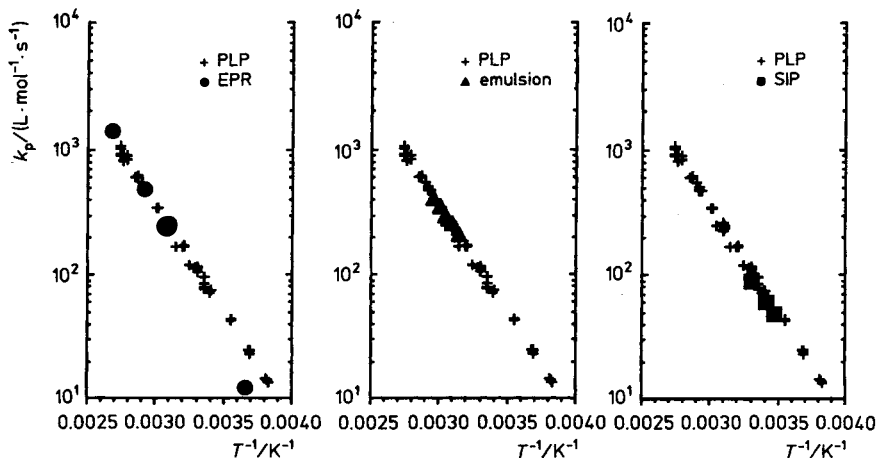

Fig. 5. Comparison of benchmark PLP-MWD k_p values and k_p from some other techniques: EPR[35], emulsion polymerization[36, 37], and spatially intermittent polymerization[38, 39] (SIP) see text

(b) Emulsion polymerization

Emulsion polymerization systems can yield values of k_p under the very special circumstance of accurately knowing the radical concentration, expressed as the average number of radicals per particle ($\bar{n}$). One also needs to know the overall polymerization rate (R_p), the monomer concentration in the locus polymerization ([M]), and the number of latex particles per unit volume (N_c). In practice, this can only be applied when $\bar{n} = 1/2$; however, in contradiction to what is stated in many texts, this value of $\bar{n}$ is only rarely attained. One system in which it was claimed[36,37] that there was considerable evidence for this limiting value of $\bar{n}$ was for styrene latex particles of ca. 70 nm swollen radius at sufficiently high radical flux. Kinetic studies on this system[36,37] gave values of k_p which were stated in the first report of this IUPAC Working Party as being consistent with those from other techniques[1]. This claim can be tested against the more extensive and more reliable data now available; such a test is shown in Fig. 5. It can be seen that the agreement is excellent. However, it must be emphasized that systems which can be unambiguously identified as having $\bar{n} = 1/2$ are very rare, and moreover that a rigorous demonstration of this is very difficult. In short, the emulsion polymerization method is only applicable under special circumstances.

(c) Spatially intermittent polymerization (SIP)

This technique[38,39] is a variant of the rotating sector method. This IUPAC Working Party had reported previously[1] that values obtained by this method appear reliable. The more complete data now available enable a more rigorous examination to be made. A comparison with the PLP-MWD and SIP values of k_p for styrene is given in Fig. 5. It can be seen that the values obtained by SIP are in moderate but imperfect accord with the data collected here: although the k_p values from SIP deviate by only about 15% from the PLP-MWD ones, the SIP Arrhenius factors ($10^{7.04}$ dm$^3 \cdot$ mol$^{-1} \cdot$ s^{-1}, 29.5 kJ $\cdot$ mol^{-1}) are both outside the joint confidence limits of Fig. 4). The discrepancy can probably be assigned to the assumptions made about termination in SIP and related techniques[2].

7. Conclusions

The PLP-MWD method appears to be the best available for measuring k_p, especially because the technique enables one to carry out a variety of self-consistency checks, the fulfilment of which gives a high level of confidence that an accurate value of k_p is being measured. The method is not without limitation — it has not been used to measure k_p at intermediate and high conversion — and nor is it without blemish — it has proven very difficult to use for systems with high k_p, e. g., when T is high, and far more so, when the monomer is one with a high k_p (e. g., the acrylates). This paper sets out in detail what are considered to be optimal means of reporting PLP-MWD data, and essential consistency checks which should be performed for any PLP-MWD

study. PLP-MWD k_p data for styrene from a wide variety of studies and laboratories show excellent consistency, and together may be said to constitute benchmark k_p values for free-radical polymerization.

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