PAPER

Critically evaluated rate coefficients in radical polymerization – 7. Secondary-radical propagation rate coefficients for methyl acrylate in the bulk†

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Propagation rate coefficient (k_p) data for radical polymerization of methyl acrylate (MA) in the bulk are critically evaluated and a benchmark dataset is put forward by a task-group of the IUPAC Subcommittee on *Modeling of Polymerization Kinetics and Processes*. This dataset comprises previously published results from three laboratories as well as new data from a fourth laboratory. Not only do all these values of k_p fulfill the recommended consistency checks for reliability, they are also all in excellent agreement with each other. Data have been obtained employing the technique of pulsed-laser polymerization (PLP) coupled with molar-mass determination by size-exclusion chromatography (SEC), where PLP has been carried out at pulse-repetition rates of up to 500 Hz, enabling reliable k_p to be obtained through to 60 °C. The best-fit – and therefore recommended – Arrhenius parameters are activation energy $E_A = 17.3$ kJ mol^{-1} and pre-exponential (frequency) factor $A = 1.41 \times 10^7$ L mol^{-1} s^{-1}. These hold for secondary-radical propagation of MA, and may be used to calculate effective propagation rate coefficients for MA in situations where there is a significant population of mid-chain radicals resulting from backbiting, as will be the case at technically relevant temperatures. The benchmark dataset reveals that k_p values for MA obtained using PLP in conjunction with MALDI-ToF mass spectrometry are accurate. They also confirm, through comparison with previously obtained benchmark k_p values for *n*-butyl acrylate, methyl methacrylate and *n*-butyl methacrylate, that there seems to be identical family-type behavior in *n*-alkyl acrylates as in *n*-alkyl methacrylates. Specifically, k_p for the *n*-butyl member of each family is about 20% higher than for the corresponding methyl member, an effect that appears to be entropic in origin. Furthermore, each family is characterized by an approximately constant E_A, where the value is 5 kJ mol^{-1} lower for acrylates.

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Introduction

The precise knowledge of rate coefficients for the individual reactions in radical polymerization is crucial for the modeling of polymerization processes and for the understanding and development of new polymerization methodologies. The fundamental reactions governing radical polymerization processes are initiation, propagation and termination, with the propagation reaction taking a prominent role, since it defines the rate of monomer consumption and thus directly affects the overall rate of polymerization. As a consequence, the propagation rate coefficient, k_p, is of utmost importance, and most other rate coefficients, such as those for termination or transfer, are measured relative to it. The IUPAC Subcommittee on *Modeling of Polymerization Kinetics and Processes* recommended the so-called pulsed-laser polymerization-size-exclusion chromatography (PLP-SEC) technique[1] as the method of choice to reliably determine k_p.[2] A series of benchmark papers have reported accurate Arrhenius data for k_p of a broad range of monomers.[2–7] With PLP-SEC, k_p becomes available by the correlation of the time between two consecutive laser pulses with the chain length of the generated polymeric material. This correlation is based on the almost instantaneous initiating and terminating action of each laser pulse, which gives rise to a specific molar-mass distribution (MMD) exhibiting patterns of peaks according to the darktime t_0 and multiples thereof, these reflecting the circumstance that some of the growing radicals survive one or more laser pulses and continue their growth over such an extended time period. k_p is directly accessed from eqn (1):[8]

$$DP_i = i k_p c_M t_0 \qquad (1)$$

Here DP_i refers to characteristic degrees of polymerization outlined above, these manifesting themselves as points of inflection on the MMD, while c_M is the known monomer concentration. The accuracy of the method is limited by problems associated with molar-mass determination. In addition, side reactions such as chain transfer or very rapid radical termination may pose problems.

One family of monomers that has proven to be difficult to access *via* PLP-SEC is the acrylates. Undefined MMDs may occur with these monomers, as well as a dependence of the obtained (apparent) propagation rate coefficient on the pulse-repetition rate. Thus the clear correlation between t and DP_i may be obscured.[9,10] The importance of the transfer-to-polymer reaction in acrylate polymerizations was foreseen by Scott and Senogles.[11–13] However, only after the important finding of Ahmad *et al.*[14] and Chiefari *et al.*,[15] the absence of a characteristic MMD structure was understood to result primarily from the formation of tertiary mid-chain radicals (MCRs). These MCRs exhibit a considerably higher stability and thus lower propagation activity than secondary chain-end radicals (see Scheme 1), thereby broadening the radical MMD and thus invalidating eqn (1).[16] Transfer-to-polymer may occur *via* inter- or intra-molecular reactions.[17] Intermolecular transfer only matters in terms of kinetics of polymerization at higher polymer concentrations, which do not occur in typical PLP-SEC experiments.
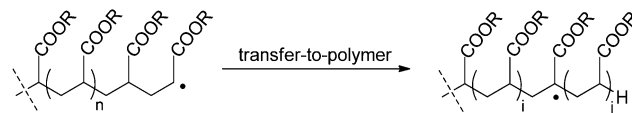
Scheme 1 Formation of mid-chain radicals by the intramolecular transfer-to-polymer reaction of secondary chain-end radicals in acrylate polymerization, where $i + j = n + 1$; for the most favored backbiting process *via* a six-membered ring transition structure, $j = 2$.

Intramolecular transfer, on the other hand, which occurs either *via* a random transfer step or, more frequently, *via* a six-membered cyclic transition state, is an important process even at low degrees of monomer conversion. The latter reaction is referred to as backbiting.[18,19]

The impact of intramolecular chain transfer on PLP was suggested[16] and the consequences were addressed in an IUPAC benchmark paper on k_p of *n*-butyl acrylate (BA).[6] Reliable k_p values of secondary BA radicals were determined at low temperatures (<20 °C), where laser pulsing could be applied at repetition rates that are sufficiently high to minimize the occurrence of MCR formation. As Arrhenius parameters for k_p of BA were reported, propagation rate coefficients could be extrapolated to technically relevant temperatures. It is, however, important to note that such an extrapolation yields k_p data of secondary chain-end macroradicals, whereas actual polymerizing systems at these higher temperatures contain a mixture of secondary and (much more slowly propagating) tertiary radicals. The propagation rate of secondary radicals should thus not be confused with the effective rate of propagation that applies in acrylate polymerization above low temperatures and refers to the joint action of propagating secondary and tertiary radicals.[9,20]

Significant advances have been made in the understanding of acrylate (transfer) kinetics since the benchmark report on BA.[6] Online discrimination and quantification of MCRs and secondary propagating radicals (SPRs) became available *via* electron paramagnetic resonance (EPR) spectroscopy.[21–23] Rate coefficients for backbiting have been reported and the rate of monomer addition to BA MCRs has been studied in detail.[10,22,23] With the advent of pulse lasers with repetition rates as high as 500 Hz, successful PLP-SEC experiments on BA were carried out up to 60 °C.[24] The resulting values are in excellent agreement with the ones extrapolated from the previously reported benchmark data determined at lower polymerization temperatures, underpinning the quality of both datasets. The results, however, also indicated another limitation, namely β-scission of the MCRs.[25,26] At temperatures above 60 °C, a deviation from Arrhenius behavior of the evaluated rate coefficients was observed. This could not be explained by transfer-to-polymer steps, but was attributed to β-scission of MCRs.[24] This scission reaction, which is associated with a relatively high activation energy,[27] yields significant amounts of unsaturated macromonomer species at temperatures above 100 °C, especially during polymerizations at low radical concentrations.[15,28] Each β-scission step is preceded by a transfer-to-polymer step. The scission step poses additional problems for PLP-SEC experiments, as radicals are formed that are smaller than the

preceding MCR. However, at moderate temperatures the impact of β-scission may be neglected and, as was demonstrated for BA, k_p of SPRs may be deduced by extrapolation.

In conclusion, the understanding of acrylate kinetics has advanced significantly during recent years, and although some uncertainties still exist, propagation rate coefficients of secondary chain-end radicals may be accurately measured. The present report focuses on providing benchmark data for bulk polymerization of methyl acrylate (MA), a monomer that is of both application-oriented and academic interest.

Collation of data

Due to the inherent difficulties in the determination of reliable acrylate propagation rate coefficients, only a limited number of k_p datasets exist for MA. Earlier data from methods other than PLP-SEC exhibit a large scatter and are not considered for the present evaluation. The following groups have provided the critically evaluated k_p data for bulk MA that are collated in Table 1:

van Herk and co-workers (Eindhoven laboratories)

The group of van Herk reported two datasets, one of which was measured by Manders *via* classical PLP-SEC at a pulse repetition rate of 100 Hz and temperatures from −20 to +30 °C.[29] Bulk polymerization of MA was investigated with 2,2-dimethoxy-2-phenylacetophenone (DMPA) as the photoinitiator at concentrations from 0.00045 to 0.0024 mol L^{-1}. For analysis of molar mass distributions from SEC, the Mark–Houwink–Kuhn–Sakurada (MHKS) values provided by Hutchinson *et al.*,[30] $\alpha = 0.66$ and $K = 19.5 \times 10^{-5}$ dL g^{-1}, were employed. In the more recent study of this group, molar masses of poly(MA) from PLP were analyzed by the matrix-assisted laser-desorption ionization-time of flight (MALDI-ToF) technique. The latter method, which avoids the band broadening problems of SEC, was used between −30 and +40 °C by Willemse *et al.*,[31] with PLP repetition rates up to 100 Hz. The advantages of MALDI-ToF over SEC for determination of DP$_i$ and the resulting accuracy of k_p data will be addressed below.

Buback and co-workers (Göttingen laboratories)

Buback *et al.* investigated k_p of MA under high-pressure conditions between −15 and −28 °C with DMPA as the photoinitiator.[32] Consistent k_p data adhering to the criteria for reliable k_p determination were obtained. The pressure dependence of k_p is associated with an activation volume of (11.7 ± 0.4) cm^3 mol^{-1} at −28 °C and (11.2 ± 0.7) cm^3 mol^{-1} at −15 °C. Extrapolation of the k_p data to ambient pressure yields 3360 L mol^{-1} s^{-1} for −28 °C and 5270 L mol^{-1} s^{-1} for −15 °C. The MHKS parameters provided by Hutchinson *et al.*[30] were used for SEC analysis.

Barner-Kowollik, Junkers, Castignolles and co-workers (Karlsruhe laboratories)

Junkers *et al.*[33] provided data from DMPA-initiated PLP-SEC of MA in the range from 11.3 to 81.2 °C. To successfully carry out measurements up to the highest temperatures, fast pulsing with a 500 Hz laser was applied in order to largely eliminate the influence of backbiting on the resulting molar mass distributions. Excellent repeatability of MMDs, including higher-order inflection points, was observed at all temperatures. In order to stay on the safe side, Junkers *et al.*[33] used only the restricted temperature range up to 60 °C for deriving Arrhenius parameters of k_p. Above 60 °C, a leveling-off of k_p was seen and was attributed to the influence of β-scission on the polymer MMD,[15,25] an effect that would lead to underestimation of k_p due to an increased polymer background in the sample stemming from the scission fragments.[9,10] MHKS parameters for a broad temperature range using PLP-generated poly(MA) samples were determined to be: $\alpha = 0.74$ and $K = 10.2 \times 10^{-5}$ dL g^{-1} (THF, 30 °C). Additionally, all samples were assessed with respect to the error margins associated with size-exclusion chromatography and to the local dispersity profile resulting from multiple detection analysis of branched polymer. Relatively homogeneous branching distributions were observed, confirming that SEC can indeed be used with high accuracy for determination of MMDs of poly(MA), as was also found for BA. However, this finding must not necessarily hold true for other acrylates, such as 2-ethylhexyl acrylate[34] or *tert*-butyl acrylate.[35]

Stach and Lacík (Bratislava laboratories)

In the framework of the current k_p collation, a new dataset for bulk MA polymerization has been compiled by Stach and Lacík, also using high pulse repetition rates of 250 and 500 Hz. Temperatures from −26 to +80 °C were covered (see the ESI† for experimental details) with 0.0005, 0.005 and 0.020 mol L^{-1} DMPA as the photoinitiator. The same MHKS parameters as in the study of Junkers *et al.*[33] were used for SEC analysis. Also in this study a leveling-off of k_p data was observed at temperatures above 60 °C, although points of inflection for both $i = 1$ and 2 in eqn (1) could be seen even at 70 °C. In addition to producing polymer by a single sequence of laser pulses applied at high repetition rate, in a second type of experiment polymer samples were made by applying several sequences of laser pulses with a reduced number of pulses per sequence. With this second approach, the reaction mixture can equilibrate back to the thermostat temperature during an experiment, meaning that any enhancement of temperature as a consequence of rapid pulsing (and hence rapid polymerization) should become visible from comparison of k_p values obtained by the two pulsing strategies. It is gratifying to note that no significant difference in k_p has been found upon applying the two pulsing procedures (see Table 1 for the comparison).

Deriving benchmark values

The k_p datasets in Table 1 were estimated using slightly different monomer densities (for the calculation of bulk monomer concentration). In addition, different MHKS parameters were applied for SEC analysis depending on the type and temperature of the eluent. The associated error is small compared with the limits of accuracy of size-exclusion chromatographic analysis. Thus, as within the previous benchmark report on BA, no recalculation of k_p data has been performed.

Table 1 Critically evaluated values of propagation rate coefficient, k_p, for bulk methyl acrylate polymerization at ambient pressure measured as a function of temperature, θ, laser pulse repetition rate, f, average laser-pulse energy, E_p, and initiator concentration, c_I. Values of k_p for $T > 60$ °C were not used for deducing Arrhenius parameters and are given only in the ESI†

θ/°C	f/Hz	E_p/mJ	c_I/mmol L^{-1}	k_p/L mol$^{-1}\cdot$s^{-1}	Ref.
−28	100	4	5	3300	32
−26.4	250	3.0	0.5	2992	This work
−25.8	250	3.0	5	3166	This work
−25.5	250	3.0	5	3359	This work
−25	60	60	5	3290	31[a]
−25	60	40	5	3321	31[a]
−25	500	3.0	5	3378	This work
−24.6	250	3.0	20	3684	This work
−24.2	500	3.0	20	3553	This work
−19.3	100	25	5.3	3790	29
−19.1	100	25	5.3	3740	29
−18.5	100	25	5.3	3680	29
−17.9	100	25	5.3	3860	29
−17.5	100	25	5.3	3920	29
−17.1	100	25	5.3	3870	29
−16.6	100	25	5.3	3930	29
−16.3	100	25	5.3	4060	29
−16.2	100	25	5.3	4120	29
−16.0	100	25	5.3	3930	29
−15.8	500	3.0	5	4135	This work[b]
−15.7	80	60	5.00	4643	31[a]
−15.6	80	40	5.00	4567	31[a]
−15	100	4	5.00	5300	32
−11.3	100	25	1.1	5410	29
−11.3	100	25	1.1	5370	29
−11.3	100	25	1.1	5290	29
−11.3	80	25	1.1	5060	29
−11.3	100	25	2.4	5240	29
−11.3	100	25	2.4	5200	29
−11.3	100	25	2.4	5340	29
−8	100	60	5.00	5788	31[a]
−8	100	40	5.00	5797	31[a]
−2.9	100	25	2.4	6560	29
−2.7	100	25	1.1	6600	29
−2.7	100	25	2.4	6540	29
−2.5	100	25	1.1	6680	29
−1.9	100	25	1.1	6790	29
−0.5	100	25	2.4	6790	29
−0.3	80	25	1.1	6170	29
0	250	3.0	5	7031	This work
0	250	3.0	5	7198	This work
0	500	3.0	5	7655	This work
0	500	3.0	5	7421	This work
0	250	3.0	20	7523	This work
0	250	3.0	20	7322	This work
0	500	3.0	20	7286	This work
0	500	3.0	20	7725	This work
0.1	500	3.0	5	7325	This work[b]
0.9	100	60	5.00	7593	31[a]
0.9	100	40	5.00	7619	31[a]
1.9	100	20	1.2	6170	29
2.2	100	20	1.2	6370	29
3.8	100	25	1.0	6130	29
3.8	100	25	1.0	6740	29
4.0	100	25	1.0	6530	29
4.2	100	20	1.2	5990	29
7.8	100	60	5.00	9308	31[a]
7.8	100	40	5.00	9299	31[a]

Table 1 (Contd.)

θ/°C	f/Hz	E_p/mJ	c_I/mmol L^{-1}	k_p/L mol$^{-1}\cdot$s^{-1}	Ref.
11.3	500	1.5	5.00	9401	33
11.9	500	1.5	5.00	10 320	33
12.4	100	25	1.1	9740	29
15	100	30	5.00	11 397	31[a]
15	100	15	5.00	11 397	31[a]
19.8	500	1.5	5.00	13 011	33
19.8	500	3.0	5	11 578	This work[b]
20	250	3.0	0.5	10 892	This work
20	500	3.0	0.5	11 812	This work
20	250	3.0	5	10 850	This work
20	250	3.0	5	11 054	This work
20	500	3.0	5	11 842	This work
20	500	3.0	5	12 046	This work
20	250	3.0	20	10 924	This work
20	250	3.0	20	11 004	This work
20	500	3.0	20	11 792	This work
20	500	3.0	20	12 101	This work
20.4	500	1.5	5.00	12 826	33
21.8	100	30	5.00	13 727	31[a]
22.3	100	15	5.00	13 808	31[a]
25.0	100	20	0.45	14 600	29
25.0	100	20	0.45	13 800	29
25.0	100	20	0.45	14 000	29
25.0	100	10	0.45	14 000	29
25.0	100	10	0.45	13 500	29
25.0	100	10	0.45	14 000	29
25.0	80	20	0.45	13 400	29
25.0	80	20	0.45	12 900	29
29.7	500	1.5	5.00	15 851	33
29.8	100	30	5.00	16 461	31[a]
29.9	100	30	5.00	16 317	31[a]
30.8	500	1.5	5.00	13 944	33
32.0	100	2	1.2	15 100	29
32.0	100	2	1.2	14 700	29
35.7	500	3.0	5	16 796	This work[b]
36.5	100	30	5.00	19 376	31[a]
37.2	100	15	5.00	19 578	31[a]
40	500	3.0	0.5	17 756	This work
40	500	3.0	5	17 419	This work
40	500	3.0	5	17 379	This work
40	500	3.0	20	17 244	This work
40	500	3.0	20	17 499	This work
40	500	3.0	5	17 900	This work
40	500	3.0	5	18 151	This work
40.3	500	1.5	5.00	21 079	33
40.3	500	1.5	5.00	21 480	33
50.2	500	1.5	5.00	26 041	33
50.4	500	1.5	5.00	26 297	33
60	500	3.0	20	24 211	This work
60	500	3.0	20	23 930	This work
60	500	3.0	5	25 019	This work
60	500	3.0	5	25 740	This work
60.5	500	1.5	5.00	31 654	33
60.6	500	1.5	5.00	31 965	33

[a] Characteristic MMDs were determined *via* MALDI-ToF rather than by SEC. [b] PLP experiments performed with interrupted sequences of laser pulses (see text).

The k_p data in Table 1 refer to different temperatures, laser repetition rates, f, average laser pulse energies, E_p, and initiator concentrations, c_I. All data were obtained using the
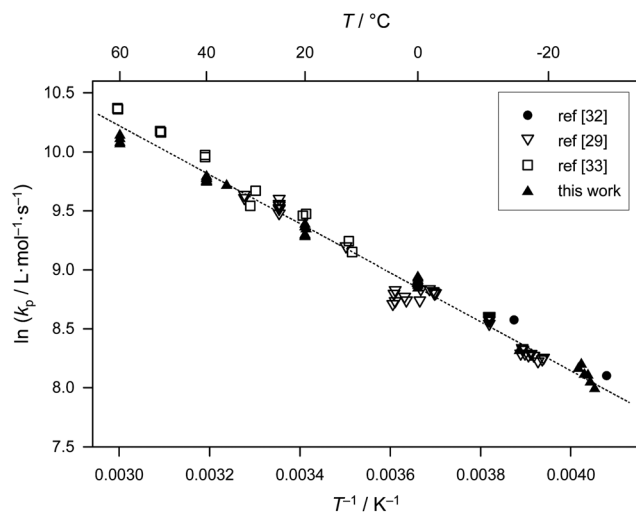
Fig. 1 Arrhenius plot of values of propagation rate coefficient, k_p, for bulk methyl acrylate from Table 1. Eqn (2), the best-fit line to all the points, is also shown.

Fig. 2 95% joint-confidence interval for the Arrhenius parameters for k_p of bulk MA, as estimated from fitting of the data in Fig. 1 (see text).

photoinitiator DMPA, which has proven to be an excellent choice for acrylate PLP-SEC experiments. In fulfillment of the IUPAC reliability criteria,[2] close matching of data obtained at different laser pulse energies is observed. Consistent k_p values are thus derived upon variation of initial radical concentrations. The combined datasets display good agreement and exhibit very satisfactory Arrhenius-type behavior, as depicted in Fig. 1. The scatter of the k_p data provided by the different groups is relatively small and well within the general error margin of 20 per cent that is associated with PLP-SEC measurements.

The unweighted Arrhenius fit of the k_p data in Fig. 1 is given as:

$$\ln(k_p/\text{L mol}^{-1}\text{ s}^{-1}) = 16.46\,(\pm 0.11) - 2080\,(\pm 30)\,K/T \quad (2)$$

where T is the absolute temperature.

Eqn (2) gives activation energy $E_A = 17.29$ kJ mol^{-1} and frequency (pre-exponential) factor $A = 1.41 \times 10^7$ L mol^{-1} s^{-1}. The error margins of both Arrhenius parameters are represented *via* the 95% confidence interval in Fig. 2. The estimate is made on the assumption of a constant relative error of 20% for each individual k_p value. The resulting uncertainties amount to 16.3 kJ mol^{-1} < E_A < 18.2 kJ mol^{-1} and 0.9×10^7 L mol^{-1} s^{-1} < A < 2.0 $\times 10^7$ L mol^{-1} s^{-1}. These error margins are very close to the ones of the benchmark k_p dataset for BA.[6] The error limitations obtained from the joint confidence interval mostly depend on the scatter of the data, whereas trying different relative errors of 10, 15 and 20% in k_p yielded very similar contour plots.

The k_p data of Willemse and van Herk in Table 1 play a special role, as these values were determined *via* MALDI-ToF analysis of MMDs, and thus should not suffer from the SEC problems of imperfect calibration and band broadening. On the other hand, features in the measured number distributions may not always be unambiguously identified. Additional uncertainties exist with regard to the question of whether the distribution from MALDI-ToF reflects the true distribution, as mass spectrometry is inherently prone to mass discrimination effects,
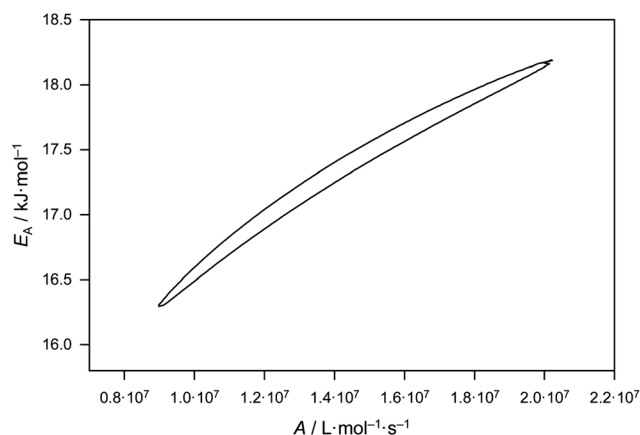
especially for higher molar masses and broad distributions,[36] as occur in PLP experiments. It is gratifying to note that, irrespective of these limitations of PLP–MALDI-ToF, very pleasing agreement of the data from the two methods of molar mass analysis is seen: plotting the PLP-SEC data together with the PLP–MALDI-ToF data yields excellent agreement of the k_p values deduced from the two PLP-based methods (Fig. 3), with the Arrhenius parameters being more or less identical. One remark can be made at this point; because band broadening in SEC systematically underestimates the k_p-values (taking the low-molecular weight inflection point, this point is shifted to lower values due to band broadening) the MALDI-ToF data are systematically slightly higher than the SEC data, as observed in Fig. 3. These statements do not, however, prove the general applicability of the PLP–MALDI-ToF method. Nevertheless, the close agreement hints at the good applicability of the MALDI-
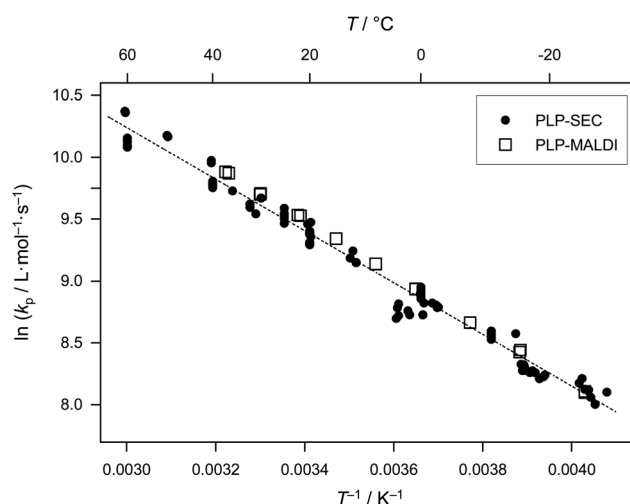

Fig. 3 Comparison of literature k_p data for bulk MA obtained *via* PLP–SEC (data from Fig. 1, full circles) and PLP–MALDI-ToF (data from Willemse *et al.*,[31] open squares); the dashed line represents the Arrhenius fit (equation not given) to the combined dataset, *i.e.*, from both PLP-based methods.

ToF approach. This notwithstanding, and in order to follow the IUPAC suggestion of using PLP-SEC for reliable k_p determination, the values provided by Willemse *et al.* were not included in the joint fit shown in Fig. 1.

Discussion

Benchmark data are of more than just empirical use. For example, they may serve to definitively elucidate mechanistic trends, and also to establish the utility of predictive calculation methodologies.

Comparison with quantum-chemical calculations

With increasing computational power and ongoing refinement of models, it seems worthwhile to compare the experimental benchmark data with results from quantum-chemical (QM) calculations, as were performed for k_p of bulk MA by Coote and co-workers.[37] Using the G3(MP2)-RAD methodology for calculation of gas-phase rate coefficients and accounting for solvation effects by applying the COSMO-RS model, an activation energy of 21.8 kJ mol^{-1} and a frequency factor of $A = 3.2 \times 10^7$ L mol^{-1} s^{-1} were obtained for the addition of a dimer radical to the monomer in bulk monomer solution. The absolute k_p at 20 °C calculated from these parameters underestimates the value from the benchmark dataset (eqn (2)) by a factor of 2.8. The agreement of the quantum-chemically estimated k_p and Arrhenius parameters to better than one order of magnitude of the experimental benchmark values indicates the improvements made with such computational methods in recent times. Nevertheless, the approximations required for the QM calculations do not yet allow for *ab initio* calculations of benchmark k_p values.[38]

Comparison with benchmark k_p data for other monomers

Benchmark k_p values for a series of methacrylate monomers as well as for BA have previously been published.[2–7] Largely based on the more extensive results for methacrylate monomers, a family-type behavior was proposed, this being that within a family of monomers, k_p shows a minor but systematic increase with the size of the alkyl ester group due largely, perhaps entirely, to A variation. The observed trends may help to predict k_p values of family members which have been less thoroughly studied. The comparison of benchmark values for bulk BA and bulk MA with the corresponding values for *n*-butyl methacrylate (BMA) and methyl methacrylate (MMA) is illustrated in Fig. 4.

Fig. 4 undoubtedly represents a very significant achievement of experimental science in the way it neatly establishes both family behavior and at the same time the differences between families: the methyl and *n*-butyl members of each family are close to each other while the differences between families are distinct. The activation energies of MMA and BMA differ by only 0.5 kJ mol^{-1} and the frequency factor only by about 40%, which poses problems toward safely establishing whether one or the other or both Arrhenius parameters are different. On the other hand, it is clearly established that bulk k_p of BMA is above the associated value for MMA, *e.g.*, for 20 °C the numbers are 272 L mol^{-1} s^{-1} (MMA) and 314 L mol^{-1} s^{-1} (BMA). The ratio of these
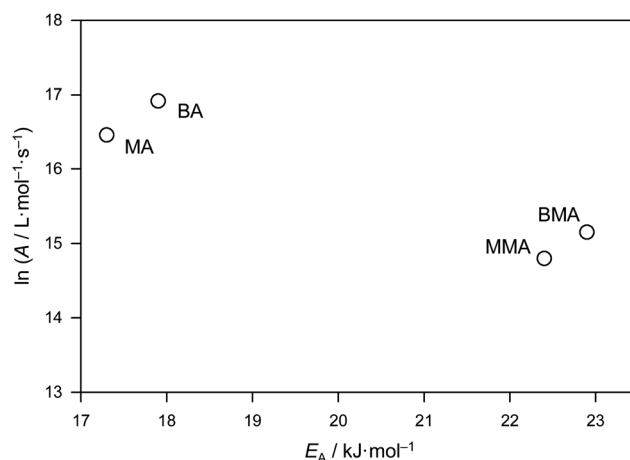
Fig. 4 Arrhenius parameters for the benchmark propagation rate coefficients of bulk methyl acrylate (MA), *n*-butyl acrylate (BA), methyl methacrylate (MMA) and *n*-butyl methacrylate (BMA).[5,6]

values, k_p(MMA)/k_p(BMA), is 0.87. The benchmark data for MA enable a similar comparison for MA and BA. Both acrylates exhibit lower activation energies than the corresponding methacrylates, but differ marginally from each other, *i.e.*, by 0.6 kJ mol^{-1}, which is within the limits of experimental accuracy. The frequency factors for bulk BA and MA are also close to each other. Again, the *n*-butyl member exhibits higher k_p than the methyl member of the same family, *e.g.* at 20 °C it is found that k_p(MA)/k_p(BA) = 0.81. The systematic effect of ester chain length on k_p of bulk (meth)acrylic esters is a genuine kinetic one, as is explained in more detail elsewhere.[39] Also pointed out in ref. 39 is the fact that the increase of k_p with the size of the ester group, which is seen with bulk radical polymerization of alkyl acrylates and alkyl methacrylates, may not occur in solution polymerization or may even be inverted, *e.g.*, in toluene solution, as might be seen from the data provided by Couvreur *et al.*,[40] although the accuracy of the k_p is not established in this latter case due to multiple-detection SEC not having been available to use. Theoretical studies of MA polymerization indicate that intramolecular hydrogen bonding plays a greater role in low polarity environments compared with bulk monomer,[37] and this may provide an explanation for the differing behavior.

Future activities of our IUPAC Subcommittee will focus on the quantitative analysis of the effects of substituents and molecular environment on k_p.[41] These effects are basically related to the extent of internal rotational freedom of the transition state for propagation, as was first pointed out by Heuts *et al.*[42] Significant hindrance to such internal rotational motion is associated with a lower pre-exponential factor and thus with lower k_p, which effect also explains the large difference between acrylate and methacrylate k_p (although this is also due to the difference in E_A). As compared with acrylates, methacrylates suffer from severe hindrance to rotational mobility because of the α-methyl groups present on the polymer backbone.

Given the above-mentioned kinetic argument, which is a purely entropic one, the BA and MA k_p data are fitted in Fig. 5 assuming identical E_A, *viz.* 17.6 kJ mol^{-1}, the arithmetic mean
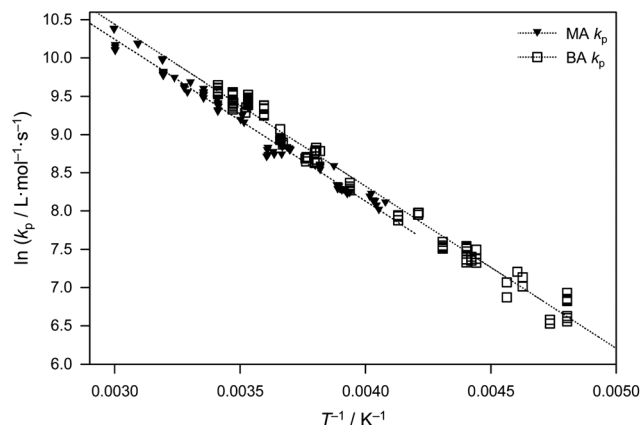
Fig. 5 Arrhenius plot comparing benchmark k_p data for methyl acrylate (present work) and n-butyl acrylate,[6] where each dataset has been fitted using $E_A = 17.6$ kJ mol^{-1} (see text).

Table 2 Benchmark Arrhenius parameters and 20 °C values for bulk k_p of the methyl and butyl esters of acrylic and methacrylic acid

Monomer	A/L mol^{-1} s^{-1}	E_A/ kJ mol^{-1}	k_p(20 °C)/ L mol^{-1} s^{-1}	Ref.
Methyl methacrylate	2.67×10^6	22.4	270	3
n-Butyl methacrylate	3.78×10^6	22.9	310	4
Methyl acrylate	1.41×10^7	17.3	11 660	This work
n-Butyl acrylate	2.24×10^7	17.9	14 480	6

of the BA value from ref. 6 (17.9 kJ mol^{-1}) and the present MA value (17.3 kJ mol^{-1}). This yielded frequency factors of A(MA) = 1.6×10^7 L mol^{-1} s^{-1} and A(BA) = 2.0×10^7 L mol^{-1} s^{-1}, *i.e.*, a difference of 20%. Certainly to the naked eye it would seem that this fitting approach is perfectly adequate, and therefore the value $E_A = 17.6$ kJ mol^{-1} may be cautiously recommended for secondary-radical propagation of all n-alkyl acrylates, with A varying along the indicated lines between family members.

The increase of k_p with alkyl ester chain length is illustrated by the numbers in Table 2 for both acrylates and methacrylates. The higher degree of rotational freedom of the transition-state structure for the butyl esters is understood as being a consequence of the more efficient shielding of dipolar interactions by the larger side chain, perhaps associated with some better internal solubilizing effect of butyl as compared to methyl moieties. Variations of k_p with solvent environment have been explained *via* this kind of argument.[43,44]

Effective propagation rate coefficient

As mentioned above, under typical conditions of acrylate radical polymerization, both secondary chain-end and tertiary mid-chain radicals occur. It cannot be overemphasized that the benchmark k_p values reported in the present study entirely refer only to propagation of the secondary radicals. Monomer

addition to mid-chain radicals takes place with a much lower rate coefficient, k_p^{tert}. The major effect of mid-chain radicals on the overall propagation rate thus results from the loss of secondary radicals due to their transformation into mid-chain radicals. To account for the presence of two types of radicals, an effective propagation rate coefficient k_p^{eff} has to be defined, and can be shown to be given by[6,9,20]

$$k_p^{\text{eff}} = \frac{k_p}{1 + \dfrac{k_{\text{bb}}}{k_p^{\text{tert}} c_M}} \qquad (3)$$

where k_p is the propagation rate coefficient of secondary radicals (*e.g.* the values reported here), k_{bb} refers to the rate coefficient of backbiting (see Scheme 1) and c_M is the monomer concentration. For MA, reliable values of k_p^{tert} and k_{bb} are not yet available, whereas such data do exist for BA.[9,10,23,45] Based on the observation that under PLP conditions almost identical amounts of MCRs are observed for MA and BA polymerizations at the same temperature,[46] it may be assumed that k_{bb} is similar for both monomers, *e.g.*, it is close to 10^2 s^{-1} at 60 °C. On the basis of existing data for BA as well as from homopropagation rates of the MA-dimer and MA trimer,[27] which may serve as a model for MCR propagation, k_p^{tert} can be estimated by the approximation $k_p^{\text{tert}} = k_p/1000$. Both k_p^{tert} and k_{bb} should be precisely determined for MA within forthcoming studies. However, even without accurately knowing these parameters, the current approximate knowledge allows for an adequate estimate of the effective propagation rate coefficient of MA bulk polymerization. The resulting value for 60 °C is 8200 L mol^{-1} s^{-1}, which is about one third of the benchmark value, according to eqn (2), for secondary propagating radicals at the same temperature.

Conclusions

Benchmark data have been collected and analyzed for the chain-growth kinetics of bulk MA secondary propagating radicals at temperatures from −28 to 61 °C. The availability of commercial pulse lasers with pulse repetition rates as high as 500 Hz allows for PLP-SEC studies up to temperatures as high as shown here, for the unfavorable effect of backbiting is largely eliminated by not allowing sufficient time between pulses for it to occur to any significant extent. However, at the highest temperatures the impact of β-scission reactions on the MMD of PLP-structured poly(MA) must be carefully considered. The k_p values from PLP-SEC and from PLP–MALDI-ToF are in good agreement, which suggests that the latter technique may also be suitable for reliable k_p determination.

The Arrhenius pre-exponential factor and activation energy of secondary propagating MA radicals were obtained by fitting of the benchmark dataset to be $A = 1.41 \times 10^7$ L mol^{-1} s^{-1} and $E_A = 17.3$ kJ mol^{-1} respectively. These numbers are close to the associated ones of n-butyl acrylate (BA). At 20 °C, bulk BA propagates faster than bulk MA by 24%, which difference is close to the one seen between BMA and MMA. Thus, family type behavior of alkyl (meth)acrylate k_p is confirmed.

Overall propagation of acrylates may be estimated *via* effective propagation rate coefficients which, in addition to k_p,

requires accurate knowledge of k_p^{tert}/k_{bb}. So far, the latter two rate coefficients have been determined only for BA. Subsequent activities of our IUPAC Subcommittee may focus on the measurement of these rate coefficients for other acrylates, including MA, on the development of standard protocols for determination of such coefficients, and on solvent effects on (meth)acrylate propagation. With all this information at hand, a complete picture of the propagation kinetics for the acrylate family will be available.

Acknowledgements

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