# Free-Radical Propagation Rate Coefficient of Nonionized Methacrylic Acid in Aqueous Solution from Low Monomer Concentrations to Bulk Polymerization

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ABSTRACT: The propagation rate coefficient, $k_p$, for free-radical polymerization of nonionized methacrylic acid (MAA) in aqueous solution has been studied via pulsed laser polymerization (PLP) in conjunction with aqueous-phase size-exclusion chromatography (SEC). The PLP−SEC experiments were carried out between 20 and 80 °C within the entire concentration range from dilute solution containing 1 wt % MAA up to bulk MAA polymerization. The $k_p$ values which are determined under the assumption that the relevant monomer concentration at the radical site is identical to the known overall MAA concentration decrease by about 1 order of magnitude between 1 and 100 wt % MAA. This significant lowering is almost entirely due to a reduction in the Arrhenius preexponential factor, $A(k_p)$, whereas the activation energy, $E_A(k_p)$, stays essentially constant. The decrease in $A(k_p)$ is assigned to intermolecular interactions between the transition state (TS) structure for MAA propagation and an MAA environment being significantly stronger than the ones between this TS structure and an $H_2O$ environment. In an MAA-rich environment, the barrier to rotational motion of the relevant degrees of motion of the TS thus experiences enhanced friction, which is associated with a lowering of the preexponential factor and thus of $k_p$.

## Introduction

The advent of pulsed laser polymerization (PLP) techniques has enormously improved the understanding of free-radical polymerization kinetics and mechanisms. So far, accurate rate coefficients have primarily been determined for bulk polymerizations, and less effort has been spent on measuring kinetic data for free-radical polymerization in solution.[1] Thus, modeling even of the technically relevant aqueous-phase polymerizations of water-soluble monomers essentially rests on rate coefficients deduced by less reliable techniques.[2] The lack of accurate PLP-derived data also poses problems toward a thorough understanding of individual kinetic processes, such as propagation and termination, in such aqueous-phase hydrogen-bonded systems. For the propagation rate coefficient, $k_p$, the situation has improved during recent years. The IUPAC-recommended PLP−SEC method, in which PLP is carried out in conjunction with size-exclusion chromatography,[3] has been applied toward measuring $k_p$ for water-soluble monomers polymerized in aqueous solution, e.g., for acrylic acid (AA) and methacrylic acid (MAA)[4] and for *N*-isopropylacrylamide.[5] The applicability of the PLP−SEC technique to aqueous systems has been confirmed, e.g., by showing that the consistency criteria may be fulfilled.[6] As a characteristic feature of polymerization in aqueous solution, $k_p$ turned out to significantly decrease toward increasing monomer concentration. This effect is clearly seen in recent studies into AA[7] and acrylamide (AAm).[8] These first PLP−SEC measurements on water-soluble monomers also revealed some problems. A major difficulty is associated with the SEC analysis of polymeric products which may however be overcome by using aqueous-phase SEC.[7−9]

Extensive studies have been carried out on aqueous-phase $k_p$ of AA. The effects of monomer concentration and of temperature as well as of the presence of salts or of propionic acid, the saturated analogue of AA, were investigated for nonionized AA,[7,9] and first PLP−SEC experiments were carried out on partially and fully ionized AA.[10] The polymerization conditions could however not be varied over wide monomer and temperature ranges for reasons which are specific to AA: (i) The solubility of poly(AA) in its own monomer is too poor as to allow for PLP−SEC experiments on AA-rich solutions. (ii) Because of the extremely high $k_p$ values which, e.g., at ambient temperature and AA concentrations around 20 wt %, are of the order of 100 000 L mol$^{-1}$ s$^{-1}$, the propagation rate becomes too fast as to allow for significant molecular weight control by the excimer laser, even at pulse repetition rates as high as 100 Hz. Moreover, higher AA concentrations are associated with significant laser-induced AA conversion, which poses problems toward reliable PLP−SEC experiments (that have to be carried out in the very initial polymerization period). (iii) Intramolecular chain-transfer reactions associated with the α-hydrogen atom at the poly(AA) backbone (that largely affect free-radical polymerization of acrylate monomers[11]) do not allow for PLP−SEC experiments at temperatures above 25 °C.

These problems are not met with methacrylic acid. It thus appears recommendable to use MAA for studies into the $k_p$ behavior of an acid monomer in aqueous solution within extended ranges of temperature and monomer concentration. MAA has no α-hydrogen atom that is susceptible to backbiting reactions and thus to the formation of poorly reactive midchain radicals which disfavor PLP−SEC measurements.[11] Therefore, PLP−SEC experiments on MAA may be carried out up to higher temperatures. Moreover, the $k_p$'s of methacrylates are by about 1−2 orders of magnitude below the ones of corresponding acrylates.[11] PLP−SEC studies into MAA thus should

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not run into problems associated with polymer molecular weights generated in the time interval between two successive laser pulses becoming too high. Poly(MAA), in addition, shows much better solubility in its own monomer. Thus, PLP–SEC measurements may be carried out up to high monomer concentrations. Kuchta et al.[4] have already reported PLP–SEC $k_p$ data for 25 °C and monomer concentrations between 15 and 80 wt % as well as for 15 wt % MAA and temperatures between 18 and 89 °C. Beuermann et al.[12] have identified suitable PLP–SEC conditions for bulk MAA polymerization at 60 °C. Within both the Kuchta et al. and the Beuermann et al. papers, however, the poly(MAA) samples from PLP have been methyl esterified prior to SEC analysis on a conventional setup with tetrahydrofuran being used as the eluent. The esterification route usually requires multiple PLP experiments to provide the amount of sample material that is necessary for the esterification reaction and for the FTIR analysis, by which complete transformation of carboxylic acid groups into ester groups is monitored.[4,12] Moreover, SEC analysis directly on the product from PLP eliminates the risk of side reactions accompanying polymer modification procedures. Such side reactions may affect polymer molecular weight and thus may affect or even invalidate $k_p$ analysis. They presumably play no major role with poly(MAA) but appear to unfavorably contribute to PLP–SEC $k_p$ measurements for AA. This point has been addressed in refs 7, 9, and 10 where aqueous-phase SEC analysis of PLP-prepared poly(AA) has been introduced. It appears to be recommendable to use aqueous-phase SEC also for direct analysis of molecular weight distributions of poly(MAA), as will be done within the present paper.

In PLP–SEC experiments, $k_p$ is determined via the following simple expression

$$L_i = i k_p c_M t_0 \qquad i = 1, 2, 3, ... \tag{1}$$

where $L_1$ is the degree of polymerization at the point of inflection on the low molecular weight side of the MWD peak. $L_1$ is identified with the number of propagation steps occurring in the preselected time interval $t_0$ between two successive laser pulses. $c_M$ is monomer concentration, which quantity is determined as the arithmetic mean of monomer concentrations before and after applying the sequence of laser pulses required for generating the PLP sample. Higher-order inflection points $L_2$, $L_3$, ... are resulting from preferential termination of the propagating radicals after growth periods $2t_0$, $3t_0$, ....

As can be seen from eq 1, the product term $k_p c_M$ is the primary result from PLP–SEC. Actually, $k_p c_M$ should be replaced by $k_{p,true} c_{M,loc}$, where $c_{M,loc}$ is the relevant local monomer concentration at the radical site and $k_{p,true}$ is the associated “true” propagation rate coefficient. In aqueous MAA solutions, where interactions via hydrogen bonds (between monomer, polymer, and water) occur and where also hydrophobic interactions may play a significant role, $c_{M,loc}$ may be different from the known overall monomer concentration, $c_{M,ov}$. As independent information on $c_{M,loc}$ is however not available, $c_M$ in eq 1 is identified with overall monomer concentration, $c_{M,ov}$. The resulting propagation rate coefficient should be referred to as “apparent” propagation rate coefficient, $k_{p,app}$, as has been emphasized within the preceding study into AA $k_p$.[7] Particular attention needs to be paid to the aspect of potential differences of $c_{M,loc}$ and $c_{M,ov}$, within $k_p$ studies in solutions with significant differences in the properties of solvent and monomer. Such situations are met in PLP–SEC experiments on monomers dissolved in carbon dioxide.[13] They may also occur in monomer–solvent systems with strongly interacting groups, as in aqueous-phase polymerizations,[4,5,7–9] in polymerizations of hydroxyl-functionalized monomers in organic solvents,[14,15] and in systems where solvent and monomer are very dissimilar in molecular size and shape.[16] Throughout the present study, $c_M$ in eq 1 will be identified with $c_{M,ov}$. The presented and discussed rate coefficients thus, strictly speaking, are $k_{p,app}$ values. To keep notations simple, the apparent propagation rate coefficients will be referred to as $k_p$.

The present study aims at measuring and discussing $k_p$ for nonionized methacrylic acid in aqueous solution at monomer concentrations between 1 and 100 wt % MAA and at temperatures between 15 and 80 °C. The fraction of MAA dissociating into ions is well below 1% at the polymerization conditions presented in this paper. The large set of experimental data allows for the determination of Arrhenius parameters of $k_p$ as a function of monomer concentration. The kinetic analysis exclusively rests on molecular weight distributions determined directly, via aqueous-phase SEC, on the PLP-prepared poly(MAA) samples.

## Experimental Section

**Chemicals.** Methacrylic acid (Fluka, >98.0%, stabilized with 0.025 wt % hydroquinone monomethyl ether) and the photoinitiator DMPA (2,2-dimethoxy-2-phenylacetophenone, Aldrich, 99%) were used as supplied. Demineralized water was used for preparing the monomer solutions.

**Preparation of Monomer Solutions for PLP.** According to the procedure used for AA,[9] a stock solution of DMPA in MAA was prepared, which was diluted with MAA and water to yield the desired monomer and initiator concentrations. The polymerizations were carried out at DMPA concentrations, $c_{DMPA}$, of the order of $10^{-3}$ mol L$^{-1}$. The MAA concentration, $c_{MAA}$, at a particular polymerization temperature was calculated from the reported density expressions for MAA[4]

$$\rho_{MAA}/\text{g cm}^{-3} = 1.0288 - 5.568 \times 10^{-4}(T/°\text{C}) - 1.1132 \times 10^{-5}(T/°\text{C})^2 + 1.0041 \times 10^{-7}(T/°\text{C})^3$$

and for water[17]

$$\rho_{water}/\text{g cm}^{-3} = 0.9999 + 2.3109 \times 10^{-5}(T/°\text{C}) - 5.44807 \times 10^{-6}(T/°\text{C})^2$$

assuming ideal mixing of MAA and water. The validity of this assumption was tested for selected MAA concentrations and polymerization temperatures by densitometry experiments on the aqueous monomer solutions.

**Pulsed Laser Polymerization.** Pulsed laser polymerizations were performed using an excimer laser (LPX 210i, Lambda Physik) operated on the 351 nm (XeF) line. Pulse repetition rates between 1 and 40 Hz were used, with most of the PLP experiments being carried out at 20 Hz. Incident laser energy was around 10 mJ/pulse. The monomer solutions were either charged into a QS165 cell equipped with a jacket for temperature control or into a QS 110 cell with 10 mm path length (both cells are from Hellma-Worldwide). They were purged with nitrogen for 2–4 min. The cells were closed with a PTFE stopper. Prior to pulsing, the cell was thermostated for about 20 min. The number of pulses was selected to be between about 10 up to a few hundred, such as to reach a monomer conversion of about 5%. Postpolymerization was suppressed by pouring the mixture from PLP into a sample vial containing hydroquinone monomethyl ether. Water and MAA were evaporated under high vacuum at ambient temperature. The degree of monomer conversion was determined by gravimetry on the dry samples.

**Size-Exclusion Chromatography.** The aqueous-phase SEC setup consisted of a Waters in-line degasser, a Waters pump 515 equipped with a plunger washing kit, a Rheodyne 7725i injector, a guard and three Suprema columns (Polymer Standards Service) of particle size 10 $\mu$m and pore sizes of 100, 1000, and 3000 Å (positioned in a Waters column heater module), and a differential refractometer (Waters M2410). The analyses was performed at 60 °C using demineralized water as the eluent which contained 0.1 mol L$^{-1}$ $Na_2HPO_4$ to provide a pH value of 9.0 and 200 ppm of $NaN_3$.[18] The poly(MAA) samples were thus analyzed as poly(sodium methacrylates). The eluent was permanently stirred to avoid concentration changes as a consequence of salt sedimentation. Ethylene glycol was used as the flow marker to adjust eluent flow to a rate of 1 mL min$^{-1}$. The poly(MAA) samples were dissolved in the eluent at a concentration of 2 mg mL$^{-1}$ and filtered through a 0.45 $\mu$m filter. The injected volume was 200 $\mu$L. Calibration of the SEC setup was performed with narrowly distributed poly(sodium methacrylate) standards (Polymer Standards Service) of peak molecular weights between 1250 and 1 027 000 g mol$^{-1}$. Data acquisition and analysis were performed via the WinGPC7.2 software (Polymer Standards Service), which was also used for identification of the position of points of inflection on the MWD (via the maxima of the first derivatives of the MWD curves). These first-derivative curves were smoothed by a Fourier fit contained in the WinGPC7.2 software package.

## Results and Discussion

PLP–SEC experiments for determination of $k_p$ were carried out at MAA concentrations of $c_{MAA} = 1, 2, 3, 5, 10, 15, 20, 30, 40, 45, 60$, and 100 wt % and at ambient temperature as well as at 40, 60, and 80 °C. That the consistency criteria for reliable PLP–SEC experiments[6] were met was verified by using several initiator concentrations and by carrying out part of the PLP experiments under a variation of pulse repetition rate with all other PLP parameters being kept constant. The number of applied laser pulses was varied such as to keep monomer conversion below 5%. Only within the PLP experiments at the lowest MAA concentrations, for $c_{MAA}$ between 1 and 3 wt %, monomer conversion was allowed to be as large as 10% to provide a sufficient amount of polymer for SEC analysis.

Representative molecular weight distribution (MWD) curves and associated first-derivative curves of poly(MAA) samples from PLP of MAA in aqueous solution are shown in Figures 1 and 2. The PLP structure is clearly seen which demonstrates that (i) the PLP conditions have been sensibly chosen and (ii) aqueous-phase SEC is obviously capable of resolving the PLP-induced structure of the MWD. Shown in Figure 1 are MWDs of poly(MAA) samples obtained by PLP at 25 °C for aqueous solutions containing 5 and 40 wt % MAA as well as for bulk MAA polymerization. The experiments were carried out at a pulse repetition rate of 20 Hz. Primary and secondary points of inflection (and even a tertiary inflection point at 5 wt %) on the low molecular weight side of PLP-induced components contributing to the MWD (full lines) are clearly identified from maxima in the associated first-derivative curves (dotted lines). Figure 2A presents examples of MWDs measured on PLP-produced poly(MAA) samples prepared at temperatures from 20 to 80 °C. The associated first-derivative curves are plotted in Figure 2B. The data in Figure 2 refer to $c_{MAA} = 15$ wt %, $c_{DMPA} = 2 \times 10^{-3}$ mol L$^{-1}$, and a pulse repetition rate of 20 Hz. Toward higher MAA concentration (Figure 1) and toward higher temperature (Figure 2), the amount of high-molecular-weight "background" poly(MAA) increases. For the PLP conditions of Figures 1 and 2 this high-molecular-weight material, however, does not affect the quality by which the $M_1$ and $M_2$ inflection point positions may be determined.

Table 1 summarizes the measured values of $k_p$ for MAA in aqueous solution at 25 °C and MAA concentrations between 1 and 100 wt %, corresponding to molar concentrations between 0.12 and 11.88 mol L$^{-1}$, respectively. Also given in Table 1

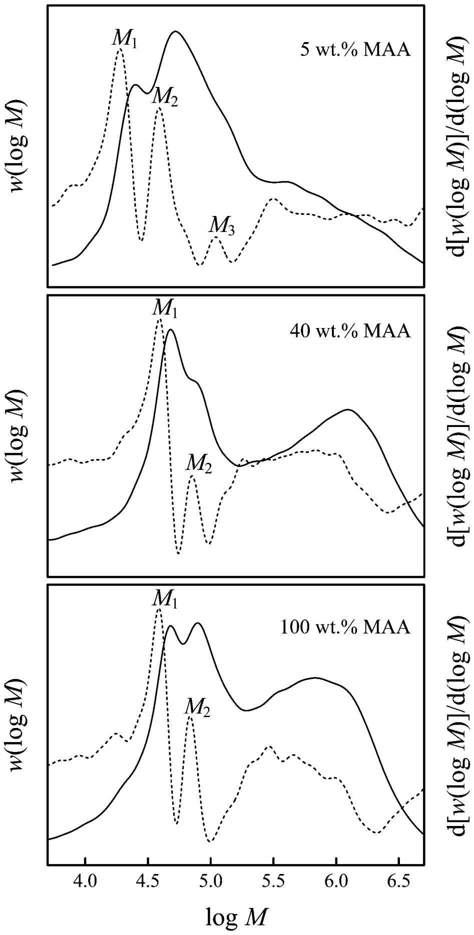

**Figure 1.** Molecular weight distributions (solid lines) and associated first-derivative curves (dashed lines) obtained from polymerizations of methacrylic acid (MAA) dissolved in water at two MAA concentrations and from bulk MAA polymerization at 25 °C; laser repetition rate: 20 Hz.

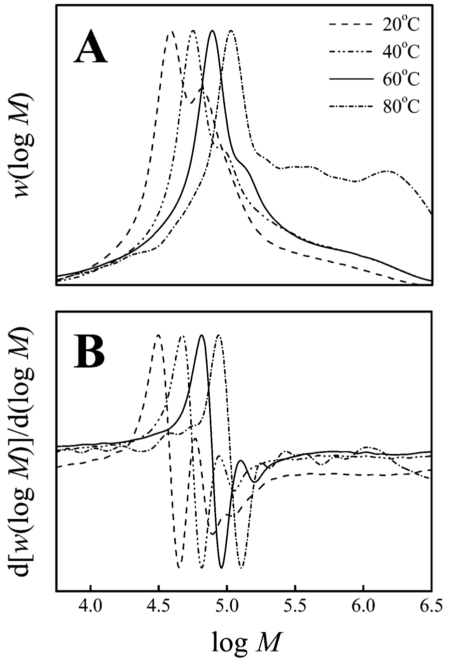

**Figure 2.** Molecular weight distributions (A) and associated first-derivative curves (B) obtained from polymerizations at various polymerization temperatures on methacrylic acid (MAA) in aqueous solution; MAA concentration: $c_{MAA} = 15$ wt %; photoinitiator concentration: $c_{DMPA} = 2 \times 10^{-3}$ mol L$^{-1}$; pulse repetition rate: 20 Hz.

**Table 1. Polymerization Conditions and (Apparent) Propagation Rate Coefficients ($k_p$) for Methacrylic Acid (MAA) Polymerized in Aqueous Solution at 25 °C and Various MAA Concentrations ($c_{MAA}$)[a]**

| $c_{MAA}$ | | $c_{DMPA} \times 10^3$ | pulse rep | no. of | $M_1 \times 10^{-3}$ | $M_2 \times 10^{-3}$ | | $k_p$ |
|---|---|---|---|---|---|---|---|---|
| (mol $L^{-1}$) | (wt %) | (mol $L^{-1}$) | rate (Hz) | pulses | (g $mol^{-1}$) | (g $mol^{-1}$) | $M_1/M_2$ | (L $mol^{-1}$ $s^{-1}$) |
| 0.12 | 1 | 0.1 | 20 | 300 | 4.3 | 11.0 | 0.39 | 7000 |
| | | 0.2 | 20 | 200 | 4.4 | 10.0 | 0.43 | 6979 |
| 0.23 | 2 | 0.3 | 20 | 200 | 8.6 | 18.2 | 0.47 | 6993 |
| | | 0.3 | 20 | 200 | 8.7 | 18.2 | 0.48 | 7093 |
| | | | | | 8.8 | 18.2 | 0.48 | 7126 |
| | | 0.3 | 20 | 200 | 8.5 | 18.2 | 0.47 | 6772 |
| | | 0.3 | 20 | 200 | 8.9 | 17.7 | 0.50 | 7134 |
| | | 0.3 | 20 | 220 | 9.0 | 19.3 | 0.47 | 7167 |
| 0.35 | 3 | 0.6 | 20 | 150 | 11.9 | 26.2 | 0.45 | 6330 |
| | | | | | 12.1 | 25.6 | 0.47 | 6433 |
| | | 0.6 | 20 | 120 | 12.0 | 26.7 | 0.45 | 6359 |
| | | | | | 12.2 | 25.5 | 0.48 | 6462 |
| | | 0.4 | 20 | 160 | 12.1 | 26.7 | 0.45 | 6439 |
| | | 0.4 | 20 | 160 | 12.0 | 26.0 | 0.46 | 6363 |
| | | 0.4 | 20 | 180 | 12.1 | 26.0 | 0.47 | 6436 |
| 0.59 | 5 | 0.7 | 20 | 140 | 19.0 | 38.8 | 0.49 | 6093 |
| | | 0.7 | 20 | 140 | 18.6 | 38.0 | 0.49 | 5933 |
| | | 0.7 | 20 | 140 | 18.5 | 38.1 | 0.49 | 5879 |
| | | 0.7 | 20 | 140 | 18.4 | 37.5 | 0.49 | 5868 |
| 1.17 | 10 | 1.3 | 20 | 120 | 31.4 | 61.0 | 0.51 | 5034 |
| | | 1.3 | 20 | 120 | 30.5 | 59.8 | 0.51 | 4865 |
| | | | | | 30.4 | 61.2 | 0.50 | 4849 |
| 2.35 | 20 | 2.7 | 20 | 90 | 37.6 | 70.5 | 0.53 | 2997 |
| | | 2.7 | 20 | 90 | 36.6 | 71.1 | 0.51 | 2911 |
| | | | | | 37.5 | 71.9 | 0.52 | 2938 |
| | | 2.7 | 10 | 80 | 64.1 | 127.1 | 0.50 | 2550 |
| | | 2.7 | 10 | 80 | 64.0 | 124.5 | 0.51 | 2544 |
| | | 2.7 | 20 | 110 | 37.1 | 70.0 | 0.53 | 2958 |
| | | 2.7 | 20 | 110 | 36.1 | 68.4 | 0.53 | 2865 |
| | | 2.7 | 20 | 110 | 36.5 | 69.7 | 0.52 | 2915 |
| | | 2.7 | 20 | 110 | 36.6 | 69.2 | 0.53 | 2904 |
| | | 2.7 | 40 | 90 | 19.1 | 39.3 | 0.49 | 3034 |
| | | 2.7 | 40 | 90 | 18.6 | 38.6 | 0.48 | 2960 |
| 3.53 | 30 | 3.9 | 20 | 160 | 36.5 | 68.7 | 0.53 | 1955 |
| 4.72 | 40 | 5.3 | 20 | 30 | 39.0 | 71.0 | 0.55 | 1539 |
| | | 5.3 | 20 | 35 | 38.8 | 78.8 | 0.54 | 1531 |
| 5.31 | 45 | 2.1 | 20 | 140 | 37.0 | 71.9 | 0.51 | 1318 |
| 7.09 | 60 | 8.0 | 20 | 50 | 37.4 | 80.2 | 0.47 | 982 |
| | | | | | 37.8 | 78.3 | 0.48 | 993 |
| | | 8.0 | 20 | 50 | 38.2 | 83.2 | 0.46 | 1002 |
| | | | | | 37.9 | 78.0 | 0.49 | 994 |
| | | | | | 39.4 | 81.1 | 0.49 | 1034 |
| 11.88 | 100 | 13.3 | 20 | 25 | 38.8 | 68.8 | 0.57 | 608 |
| | | 13.3 | 20 | 30 | 38.6 | 69.2 | 0.56 | 605 |

[a] $c_{DMPA}$: photoinitiator concentrations; $M_1$ and $M_2$: molecular weights at the primary and secondary point of inflection of the molecular weight distribution, respectively.

are the photoinitiator concentration, $c_{DMPA}$, the pulse repetition rate, the number of applied laser pulses, the molecular weights at the primary ($M_1$) and at the secondary ($M_2$) points of inflection of the MWD, the ratio of these positions, $M_1/M_2$, and the resulting apparent $k_p$ value. According to eq 1, $k_p$ is obtained from the degree of polymerization at the primary point of inflection, $L_1 = M_1/M_0$, where $M_0$ is the molecular weight of the monomeric unit which, because of SEC analysis being carried out at pH 9, is $M_0 = 108$ g $mol^{-1}$ of sodium methacrylate. The entries in Table 1 confirm that the PLP−SEC consistency criteria recommended by the IUPAC "Subcommittee on Modeling of Polymerization Kinetics and Processes"[6] are met: The $M_1/M_2$ ratios are close to 0.5, and $k_p$ is not significantly (by no more than 15%) affected by varying either photoinitiator concentration or, as studied at 20 wt % MAA, pulse repetition rate. The reproducibility of $k_p$ measurements is excellent, as can be seen from the various duplicate experiments. The right-hand side column in Table 1 shows the enormous reduction in apparent $k_p$, by about 1 order of magnitude, in going from highly dilute solution of MAA in water to bulk MAA polymerization.

Listed in Table 2 are the $k_p$ data obtained at 80 °C for MAA concentrations up to $c_{MAA} = 45$ wt %. The pulse repetition rate used within the underlying PLP experiments was 20 Hz. Again, a pronounced decrease of $k_p$ toward higher MAA concentration is seen. Collected in Table 3 are $k_p$ values for temperatures other than 25 and 80 °C (with the exception of an experiment at 80 °C/40 Hz which is not contained in the 80 °C data of Table 2 that exclusively refers to a pulse repetition rate of 20 Hz). Most of the $k_p$ data in Table 3 have been determined for the intermediate temperatures of 40 and 60 °C. Table 3 includes several data points from experiments where the secondary point of inflection was only reflected as a shoulder (indicated by SH) in the first-derivative curve of the MWD. The $k_p$ values deduced from primary points of inflection of such experiments are nevertheless considered reliable, as the positions of these primary points of inflection were identical to the ones observed in polymerizations which were run at the same or very similar PLP conditions, but resulted in both primary and secondary points of inflection.

Plotted in Figure 3 is $k_p$ as a function of $c_{MAA}$ for 25 °C. The very extended concentration range of the data from Table 1

**Table 2. Pulsed Laser Polymerization (PLP) Conditions and (Apparent) Propagation Rate Coefficients ($k_p$) for Methacrylic Acid (MAA) Polymerized in Aqueous Solution at 80 °C and Various MAA Concentrations ($c_{MAA}$)[a]**

| $c_{MAA}$ (mol L$^{-1}$) | $c_{MAA}$ (wt %) | $c_{DMPA} \times 10^3$ (mol L$^{-1}$) | no. of pulses | $M_1 \times 10^{-3}$ (g mol$^{-1}$) | $M_2 \times 10^{-3}$ (g mol$^{-1}$) | $M_1/M_2$ | $k_p$ (L mol$^{-1}$ s$^{-1}$) |
|---|---|---|---|---|---|---|---|
| 0.11 | 1 | 0.1 | 240 | 12.9 | 28.9 | 0.45 | 21 324 |
| | | | | 12.9 | 29.2 | 0.44 | 21 068 |
| | | 0.2 | | 11.8 | 30.4 | 0.39 | 19 361 |
| | | | | 12.6 | 28.5 | 0.44 | 20 590 |
| 0.23 | 2 | 0.2 | 120 | 25.6 | 50.8 | 0.50 | 20 959 |
| | | 0.2 | | 26.2 | 52.7 | 0.50 | 21 312 |
| | | 0.4 | | 24.7 | 50.0 | 0.49 | 20 380 |
| 0.34 | 3 | 0.4 | 80 | 37.9 | 69.3 | 0.55 | 20 772 |
| | | 0.4 | | 36.0 | 67.9 | 0.53 | 19 698 |
| | | 0.4 | | 36.1 | 69.2 | 0.52 | 19 777 |
| | | 0.6 | | 35.6 | 68.9 | 0.52 | 19 446 |
| 0.57 | 5 | 0.7 | 50 | 51.5 | 97.7 | 0.53 | 16 923 |
| | | 0.7 | | 52.6 | 101.4 | 0.52 | 17 293 |
| | | 1.0 | 120 | 47.3 | 110.7 | 0.43 | 15 883 |
| | | 1.0 | | 47.6 | 109.1 | 0.44 | 15 993 |
| 1.14 | 10 | 1.3 | 25 | 76.00 | 164.4 | 0.46 | 12 426 |
| | | 1.3 | | 74.30 | 156.7 | 0.47 | 12 148 |
| | | 1.3 | | 77.50 | 161.8 | 0.48 | 12 728 |
| 1.71 | 15 | 2.0 | 20 | 87.3 | 179.5 | 0.49 | 9 536 |
| | | 2.0 | | 88.7 | 192.3 | 0.46 | 9 733 |
| | | 2.0 | | 82.4 | 194.1 | 0.42 | 9 131 |
| 2.27 | 20 | 3.0 | 20 | 94.0 | 202.0 | 0.47 | 7 717 |
| | | 3.0 | | 93.1 | 213.8 | 0.44 | 7 675 |
| 3.41 | 30 | 11.6 | 7 | 83.6 | 195.0 | 0.43 | 4 517 |
| | | 1.3 | 30 | 89.5 | 225.9 | 0.40 | 5 013 |
| 4.55 | 40 | 4.0 | 18 | 95.9 | 219.3 | 0.44 | 4 003 |
| 5.11 | 45 | 1.0 | 30 | 100.0 | SH | | 3 683 |
| | | 2.0 | 16 | 88.7 | 208.0 | 0.43 | 3 281 |

[a] $c_{DMPA}$: photoinitiator concentration; $M_1$ and $M_2$: molecular weights at the primary and secondary point of inflection of the molecular weight distribution (MWD), respectively. PLP was carried out at a laser pulse repetition rate of 20 Hz. SH: the secondary point of inflection occurs only as a shoulder in the first-derivative curve of the MWD.

illustrates the enormous advantage of studying MAA rather than AA propagation in aqueous solution. $k_p$ for AA in aqueous solution could only be measured up to about 40 wt % monomer. The AA literature values[7] for $k_p$ are plotted in the inset to Figure 3. The maximum in apparent $k_p$ which is found with AA aqueous-phase polymerization at monomer concentrations between 1 and 3 wt % is not seen with MAA. The origin of the peculiar $k_p$ maximum in aqueous-phase polymerization at low AA concentrations is not yet fully understood. It may reflect preferential solvation at low monomer concentrations in systems with strong intermolecular interactions.[19] The different behavior at low monomer concentration of apparent $k_p$ for AA and MAA may be due to the fact that water is a better solvent for poly(AA) than for poly(MAA).[20−22] Thus, an increased local monomer concentration may occur in the vicinity of growing MAA macroradicals. Another explanation for the maximum in apparent $k_p$ of AA may be that AA forms complexes with polymer molecules and macroradicals, thus reducing the AA concentration that is available for propagation, which effect may result in a lowering of apparent $k_p$. As the amount of such "adsorbed" monomer is small, this effect may only be detected at very small monomer concentrations, as is the case with AA.[7] MAA may be less efficient in producing such tightly adsorbed monomer layers. Alternative explanations for the $k_p$ maximum assume the formation of self-assembled monomer structures.[23] None of these "explanations" are fully convincing. The assumption that an "adsorbed" monomer layer is responsible for the "maximum $k_p$ anomaly" at low AA contents, however, appears to be the most likely one. As no maximum in $k_p$ vs $c_M$ occurs in low-concentration aqueous MAA solutions, it appears to be beyond the scope of this paper to further speculate about the origin of this peculiar effect in aqueous-phase AA polymerization.

Toward higher monomer concentration, both MAA and AA show a pronounced drop in apparent $k_p$. This strong effect is not or not significantly dependent on the absolute size of $k_p$, which differs for the two monomers by more than 1 order of magnitude, as can be seen from the ordinate scales in Figure 3. The $k_p$ values, e.g., at 25 °C and at a monomer concentration of 1.4 mol L$^{-1}$, are around 4000 and 140 000 L mol$^{-1}$ s$^{-1}$ for MAA and AA, respectively. The resulting ratio of apparent AA and MAA $k_p$ values is 35, which number is close to the ratios observed for $k_p$'s of acrylate and methacrylate monomers (with identical alkyl ester moiety) in the organic bulk phase.[1,11]

Before discussing the large body of $k_p$ data (Tables 1−3) in more detail, our values have to be compared with the earlier results by Kuchta et al.,[4] who reported one data set for both the dependence of $k_p$ on MAA concentration (at 25 °C) and the dependence of $k_p$ on temperature (for $c_{MAA} = 15$ wt %). Figure 4 illustrates the excellent agreement of $k_p$ data from the two sources, which is particularly pleasing, as Kuchta et al.[4] employed the esterification route with subsequent conventional SEC analysis of the polymer using tetrahydrofuran as the eluent, whereas aqueous-phase SEC without preceding polymer modification has been applied in the present study. The almost perfect agreement of the data demonstrates that poly(MAA) esterification does not significantly affect MWD, whereas changes of MWD occur in esterifying poly(AA), as has been shown in ref 9. As all $k_p$ values in Tables 1−3 have been determined according to the same procedure as used for measuring the data in Figure 4 which are from the present study, the agreement in Figure 4 suggests that the entire set of $k_p$ data reported in Tables 1−3 may be considered reliable. The full data set will now be discussed with particular emphasis on the dependence of $k_p$ on MAA monomer concentration and on polymerization temperature. One example for each of these dependencies has already

**Table 3. Polymerization Conditions and (Apparent) Propagation Rate Coefficients ($k_p$) for Methacrylic Acid (MAA) Polymerized in Aqueous Solution at Several Temperatures between 15 and 80 °C and Various MAA Concentrations ($c_{MAA}$)**[a]

| $c_{MAA}$ (wt %) | $T$ (°C) | $c_{DMPA} \times 10^3$ (mol $L^{-1}$) | pulse rep rate (Hz) | no. of pulses | $M_1 \times 10^{-3}$ (g $mol^{-1}$) | $M_2 \times 10^{-3}$ (g $mol^{-1}$) | $M_1/M_2$ | $k_p$ (L $mol^{-1}$ $s^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| 5 | 60 | 1.0 | 20 | 100 | 37.5 | 76.7 | 0.49 | 12268 |
| | | 1.0 | 20 | 100 | 38.3 | 78.3 | 0.49 | 12524 |
| | | 1.0 | 20 | 140 | 38.3 | 76.4 | 0.50 | 12639 |
| | | 1.0 | 20 | 140 | 38.5 | 77.8 | 0.50 | 12727 |
| 15 | 20 | 2.0 | 20 | 400 | 31.6 | 58.7 | 0.54 | 3447 |
| | | 2.0 | 20 | 800 | 31.7 | 58.5 | 0.54 | 3552 |
| | | 2.0 | 20 | 150 | 32.1 | 59.7 | 0.54 | 3418 |
| | | 2.0 | 20 | 110 | 32.1 | 59.7 | 0.54 | 3435 |
| | 40 | 2.0 | 20 | 200 | 47.3 | 87.9 | 0.54 | 5158 |
| | | 2.0 | 20 | 160 | 47.8 | 88.5 | 0.54 | 5183 |
| | | 2.0 | 20 | 95 | 48.6 | 89.1 | 0.55 | 5274 |
| | | 2.0 | 20 | 70 | 47.9 | 90.8 | 0.53 | 5194 |
| | 60 | 2.0 | 20 | 200 | 65.0 | 126.2 | 0.52 | 7202 |
| | | 2.0 | 20 | 240 | 65.6 | 126.8 | 0.52 | 7161 |
| | | 2.0 | 20 | 75 | 66.4 | 128.8 | 0.52 | 7285 |
| | | 2.0 | 20 | 50 | 66.1 | 125.0 | 0.53 | 7215 |
| 30 | 23 | 1.0 | 40 | 160 | 18.7 | 37.4 | 0.50 | 2003 |
| | | 1.0 | 20 | 160 | 36.5 | 68.4 | 0.53 | 1953 |
| | 26 | 11.9 | 20 | 40 | 35.6 | 66.4 | 0.54 | 1871 |
| | | 4.0 | 20 | 80 | 35.4 | 70.6 | 0.50 | 1896 |
| | 40 | 3.9 | 20 | 60 | 46.6 | SH | | 2512 |
| | | 1.3 | 20 | 120 | 46.0 | 100.5 | 0.46 | 2446 |
| | | 1.0 | 20 | 120 | 46.1 | 100.0 | 0.46 | 2485 |
| | 60 | 1.0 | 40 | 120 | 26.9 | 52.7 | 0.51 | 2884 |
| | 80 | 1.0 | 40 | 80 | 37.2 | SH | | 4033 |
| 45 | 23 | 1.0 | 20 | 160 | 35.6 | 68.9 | 0.52 | 1273 |
| | | 1.0 | 40 | 150 | 18.8 | 37.4 | 0.50 | 1354 |
| | 40 | 1.0 | 20 | 120 | 47.4 | SH | | 1718 |
| | | 1.0 | 40 | 110 | 26.3 | 52.5 | 0.50 | 1909 |
| | | 2.0 | 20 | 100 | 48.4 | 109.4 | 0.44 | 1741 |
| | | 17.7 | 20 | 25 | 43.1 | SH | | 1548 |
| | 60 | 1.0 | 20 | 80 | 64.0 | SH | | 2330 |
| | | 1.0 | 40 | 70 | 39.2 | 88.3 | 0.44 | 2875 |
| | | 17.4 | 20 | 15 | 60.1 | SH | | 2192 |
| 60 | 15 | 1.3 | 20 | 400 | 30.8 | 55.0 | 0.56 | 815 |
| | | 1.3 | 20 | 400 | 30.3 | 53.1 | 0.57 | 804 |
| | | 2.6 | 20 | 200 | 29.9 | SH | | 789 |
| | | 2.6 | 20 | 200 | 29.4 | SH | | 777 |
| | 24 | 1.3 | 20 | 280 | 36.3 | SH | | 967 |
| | | 1.3 | 20 | 280 | 37.6 | 75.9 | 0.50 | 1000 |
| | | 2.6 | 20 | 140 | 34.4 | SH | | 920 |
| | | 2.6 | 20 | 140 | 35.2 | SH | | 939 |
| | 40 | 1.3 | 20 | 200 | 50.1 | SH | | 1349 |
| | | 1.3 | 20 | 200 | 50.0 | SH | | 1346 |
| | | 2.6 | 20 | 100 | 47.2 | SH | | 1274 |
| | 60 | 1.3 | 20 | 120 | 69.8 | SH | | 1905 |
| 100 | 40 | 10 | 10 | 12 | 87.7 | 200.4 | 0.45 | 695 |
| | | | | | 88.1 | 193.2 | 0.46 | 698 |
| | | 10 | 20 | 10 | 54.0 | 104.7 | 0.52 | 855 |
| | | | | | 52.4 | 112.2 | 0.47 | 830 |
| | | 20 | 10 | 8 | 87.9 | SH | | 697 |
| | | | | | 87.5 | 214.8 | 0.41 | 694 |
| | | 20 | 20 | 8 | 52.1 | 117.0 | 0.45 | 827 |
| | | | | | 53.0 | 110.9 | 0.48 | 840 |
| | 60 | 10 | 10 | 7 | 134.9 | 298.5 | 0.45 | 1089 |
| | | 10 | 20 | 7 | 75.9 | SH | | 1224 |
| | | | | | 77.8 | SH | | 1255 |
| | | 20 | 10 | 7 | 125.9 | 331.1 | 0.38 | 1018 |
| | | | 10 | | | | | 1190[b] |
| | | | 10 | | | | | 1167[b] |

[a] $c_{DMPA}$: photoinitiator concentration; $M_1$ and $M_2$: molecular weight at the primary and secondary point of inflection of the molecular weight distribution (MWD), respectively. SH: the secondary point of inflection occurs only as a shoulder in the first-derivative curve of the MWD. [b] $k_p$ values taken from Beuermann et al.[12]

been reported in ref 4 (see Figure 4), where however no attempt was made to provide a detailed kinetic interpretation.

The most striking feature of MAA apparent $k_p$ is the enormous reduction toward high $c_{MAA}$. Within the preceding study into aqueous-phase $k_p$ of acrylic acid, the range of monomer concentrations was restricted.[7] It appeared justified to assign the observed variation in apparent $k_p$ up to 40 wt % AA, by about a factor of 3, primarily to changes in "local" monomer concentration. The wide concentration range, from 1 wt % up to bulk polymerization, that is accessible in aqueous-phase polymerization of MAA, however, demonstrates that the assumption of the "true" propagation rate coefficient, $k_{p,true}$, being constant would require that "local" monomer concentration differs from overall $c_{MAA}$ by up to a factor of 10. Such enormous differences between "local" and overall monomer concentration are very unlikely, as they would require MAA at low monomer

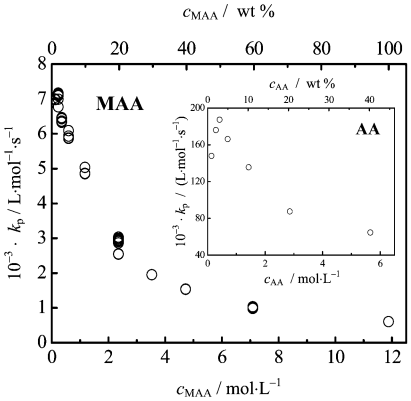

**Figure 3.** Variation with monomer concentration of apparent propagation rate coefficient ($k_p$) of methacrylic acid (MAA) in aqueous solution at 25 °C. The inset shows apparent $k_p$ values for the aqueous phase polymerization of acrylic acid (AA) as a function of acrylic acid concentration at 25 °C (values taken from ref 7).

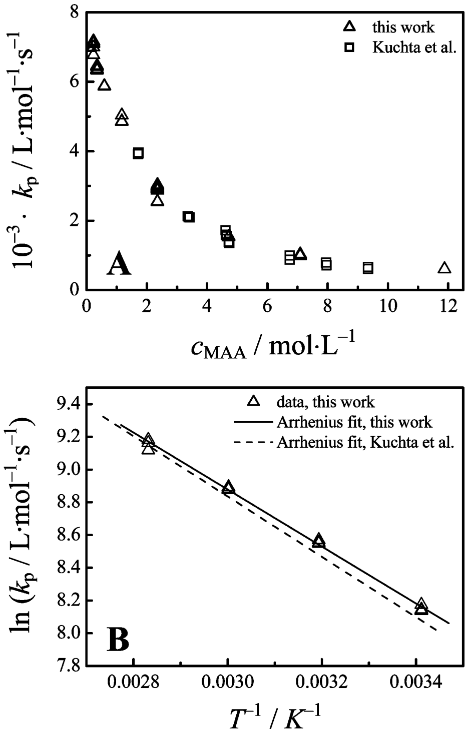

**Figure 4.** Comparison of apparent propagation rate coefficients ($k_p$) for methacrylic acid (MAA) polymerization in aqueous phase with data reported by Kuchta et al.[4] Variation of $k_p$ with methacrylic acid concentration at 25 °C (A); temperature dependence of $k_p$ for 15 wt % MAA (B).

concentrations to be almost exclusively located in the immediate vicinity of polymeric species with these monomer-saturated macromolecule and macroradical coils being contained in almost pure water. No reason is seen for such an effect, as both MAA and water are capable of interacting via hydrogen bonds and thus are too similar as to undergo any such poly(MAA)-induced separation in the liquid state. Specific association of MAA to poly(MAA) would also be in conflict with the good solubility of poly(MAA) in aqueous phase, and it is hard to imagine that any kind of demixing would become dominant toward very low $c_{MAA}$. Moreover, changes of $k_p$ resulting from specific interactions between poly(MAA) and MAA, which are not or not to a significant extent occurring between poly(MAA) and water molecules, should give rise to differences in the dependence of $k_p$ on $c_{MAA}$ for different temperatures. This is obviously not what the measured data tell, as can be seen from a comparison of apparent $k_p$ values for 25 and 80 °C. In Figure 5, reduced propagation rate coefficients, $k_p/k_{p,max}$ (with $k_{p,max}$ referring to the $k_p$ value extrapolated for $c_{MAA} = 0$), are plotted vs $c_{MAA}$. Within the region of the steep decrease of $k_p$, up to 5.11 mol $L^{-1}$ (45 wt % MAA), where data for both temperatures are available, $k_p/k_{p,max}$ for 25 and 80 °C may be adequately represented by a single line (dotted line in Figure 5, which actually is an exponential function). This observation may be taken as a strong argument against the occurrence of any significant selective enhancement of either monomer or water in the immediate vicinity of poly(MAA) molecules or macroradicals. Moreover, this finding is in conflict with assuming special types of association, e.g., dimerization, of MAA molecules being responsible for the dramatic drop in apparent $k_p$ upon enhancing $c_{MAA}$.

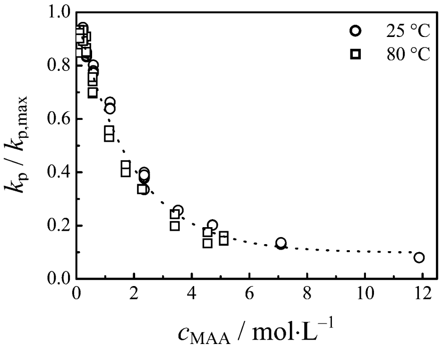

**Figure 5.** Dependence of reduced propagation rate coefficients, $k_p/k_{p,max}$ (with $k_{p,max}$ referring to the $k_p$ value extrapolated for a methacrylic acid (MAA) concentration of $c_{MAA} = 0$), on overall methacrylic acid concentration, $c_{MAA}$, at 25 and 80 °C for MAA polymerization in aqueous phase ($k_{p,max}$ values are 7600 L mol$^{-1}$ s$^{-1}$ at 25 °C and 22 840 L mol$^{-1}$ s$^{-1}$ at 80 °C).

To summarize the discussion on local vs overall monomer concentration: Both quantities may differ to some extent with this potential difference, however, being far too small to account for the variation seen with the primary experimental quantity $k_p c_M$. Thus, to a good approximation, $c_{M,loc}$ may be identified with $c_{M,ov}$, and the propagation rate coefficient is significantly enhanced toward increasing MAA concentration, as a consequence of a genuine kinetic effect.

A kinetic explanation for the dependence of $k_p$ on $c_{MAA}$ may assume that the activation energy, $E_A(k_p)$, varies as a function of water content. Via quantum-chemical calculations at different levels of theory, Thickett and Gilbert[24] recently demonstrated that the introduction of a water solvent field lowers the activation energy for addition of AA to an "acrylic acid radical", $E_A(k_p)$, by about 10 kJ mol$^{-1}$ relative to the associated gas-phase value, whereas $E_A(k_p)$ in a toluene solvent field is not significantly different from the gas-phase value. One might argue that $E_A(k_p)$ is also varied in MAA polymerizations, with the activation energy being smaller at higher water content, thus enhancing $k_p$ toward lower $c_{MAA}$. This possibility cannot be tested on the basis of the Thickett and Gilbert paper,[24] as the solvent field of the acid monomer has not been considered there. Inspection of the activation energies deduced from our apparent $k_p$ data should, however, allow for the detection of a variation of $E_A(k_p)$ with $c_{MAA}$ and thus with water content.

The Arrhenius plots constructed from the $k_p$ data in Tables 1−3 are presented in Figure 6. Depicted in the upper part (Figure 6A) are the $k_p$ data for MAA concentrations of and below 15 wt %. Figure 6B shows $k_p$ for MAA concentrations of and above 15 wt % including $k_p$ for bulk MAA polymerization. Also contained in Figure 6B are the bulk MAA $k_p$ values reported

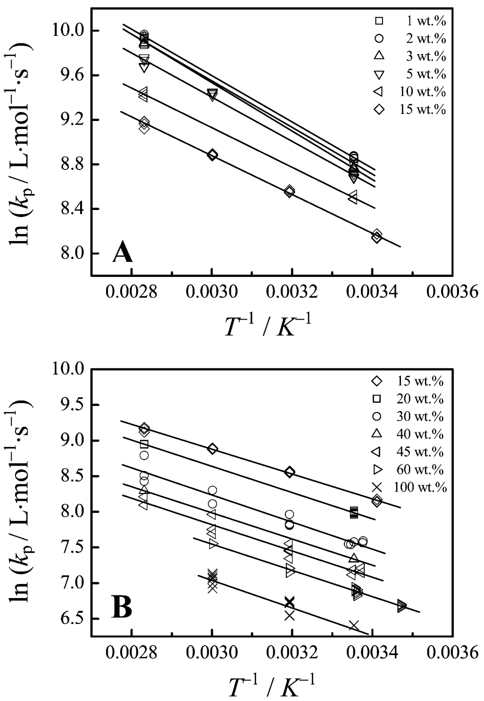

**Figure 6.** Arrhenius plots of apparent propagation rate coefficients ($k_p$) for methacrylic acid (MAA) polymerizations in aqueous solution at MAA concentrations from 1 to 15 wt % (A) and from 15 to 100 wt % (B); bulk polymerization data reported by Beuermann et al.[12] are included in (B).

by Beuermann et al.,[12] which are in close agreement with the data of the present study (see Table 3).

The Arrhenius plots for the different MAA concentrations, in particular the ones for $c_{\mathrm{MAA}}$ of and above 15 wt % (Figure 6B), are more or less parallel lines, which says that $E_A(k_p)$ is insensitive toward MAA concentration. The observed variation of apparent $k_p$ with $c_{\mathrm{MAA}}$ thus results from changes in the preexponential factor, $A(k_p)$. Only at the lowest monomer concentrations, below 5 wt % MAA, the slope of the Arrhenius lines appears to be somewhat steeper. This may indicate that a weak "low-concentration anomaly", as with AA, occurs also with MAA. For AA in aqueous phase, the numbers deduced for $E_A(k_p)$ at low monomer concentrations, e.g. below 10 wt %, are clearly above the activation energies obtained at higher $c_{\mathrm{AA}}$.[7] The variation with $c_{\mathrm{MAA}}$ of $E_A(k_p)$, depicted in Figure 6A, is too weak as to allow for deducing any firm conclusion on such a special behavior of apparent $k_p$ for MAA in highly dilute aqueous solution. The subsequent discussion of Arrhenius parameters will be restricted to MAA concentrations between 5 and 100 wt %, in which extended region $k_p$ drops by about 1 order of magnitude (see Table 1).

Plotted in Figure 7 are the 95% joint confidence intervals (JCIs) associated with the Arrhenius plots in Figure 6. The JCIs were estimated according to the procedure suggested by van Herk assuming constant relative uncertainties of the individual data points.[25] The JCIs for the two correlated Arrhenius parameters, $E_A(k_p)$ and $A(k_p)$, have been constructed for the MAA weight percentages (indicated by the number at each JCI) for which $k_p$ data are available for at least three temperatures. The size of the individual JCIs reflects the number of underlying $k_p$ data and the scatter of these data points. The JCI for MAA bulk polymerization is rather extended which results from the fact that three types of data contribute to the relatively small overall number of data points: data from PLP experiments at 10 and 20 Hz carried out within the present study and data from ref 12. Irrespective of the significant extension of some of the JCIs, the data in Figure 7 clearly support the observation from Figure 6, that the activation energy is more or less insensitive toward MAA concentration, whereas the Arrhenius preexponential factor is strongly diminished toward larger $c_{\mathrm{MAA}}$.

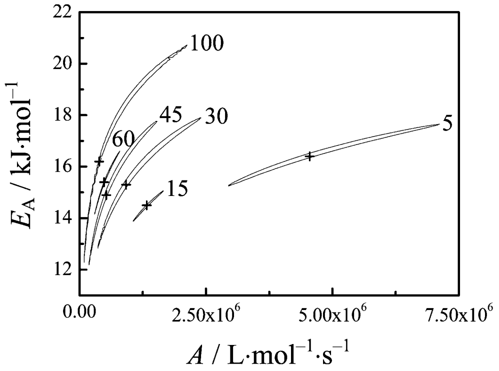

**Figure 7.** 95% joint confidence intervals (JCIs) associated with the Arrhenius plots in Figure 6 for apparent propagation rate coefficient ($k_p$) of methacrylic acid (MAA) in aqueous solution at quite different MAA weight percentages (indicated by the numbers at the JCIs) and of MAA bulk polymerization. Confidence intervals have been constructed only for MAA concentrations with $k_p$ being available for at least three temperatures.

**Table 4. Arrhenius Parameters, Activation Energy ($E_A$), and Preexponential ($A$) for Apparent Propagation Rate Coefficients ($k_p$) of Methacrylic Acid (MAA) in Aqueous Solution at Different Concentrations, $c_{\mathrm{MAA}}$, and in Bulk**

| $c_{\mathrm{MAA}}$ (wt %) | $E_A$ (kJ mol$^{-1}$) | $A \times 10^{-6}$ (L mol$^{-1}$ s$^{-1}$) | temp interval (°C) | $k_p$(25 °C) (extrapolated) (L mol$^{-1}$ s$^{-1}$) |
|---|---|---|---|---|
| 5 | 16.5 ± 0.5 | 4.62 | 20−80 | 5940 |
| 15 | 14.5 ± 0.4 | 1.33 | 20−90 | 3830 |
| 30 | 15.8 ± 1.1 | 1.13 | 23−80 | 1930 |
| 45 | 15.3 ± 1.1 | 0.63 | 23−80 | 1320 |
| 60 | 15.3 ± 0.5 | 0.48 | 15−60 | 1000 |
| 100 | 16.1 ± 1.6 | 0.38 | 25−60 | 574 |

The activation energies and preexponentials listed for the individual MAA concentrations in Table 4 were determined from fits to the logarithmic form of the Arrhenius equation. The activation energy shows a minor, but nonsystematic, variation with MAA concentration. A mean value of $E_A(k_p) = 15.6 \pm 1.1$ kJ mol$^{-1}$ encompasses the entire set of individual activation energies obtained in the extended range between dilute aqueous solution containing 5 wt % MAA and MAA bulk polymerization. Within this range of MAA contents, the preexponential, $A(k_p)$, decreases by slightly more than 1 order of magnitude. Listed in the last column of Table 4 are apparent $k_p$ values for 25 °C estimated from the individual Arrhenius parameters. As is to be expected, the numbers are in close agreement with the experimental values in Table 1, which provided the basis for obtaining $E_A(k_p)$ and $A(k_p)$.

The results in Figures 6 and 7 together with the data in Table 4 unambiguously show that a variation of $E_A(k_p)$ with MAA content cannot be made responsible for the enormous drop in $k_p$ toward higher $c_{\mathrm{MAA}}$. There is definitely no indication of any lowering in activation energy toward smaller $c_{\mathrm{MAA}}$, as would be required for assigning the observed changes in $k_p$ to a variation in $E_A(k_p)$. With reference to the analysis presented by Thickett and Gilbert[24] (for AA), one would assume very similar effects of MAA and of water solvent fields on the activation energy of the MAA propagation rate coefficient.

The preceding analysis demonstrates that the pronounced changes in $k_p$ which accompany the gradual replacement of an aqueous solvent environment by an MAA one have to be assigned to effects operating on the preexponential factor. Although $E_A(k_p)$ and $A(k_p)$ are correlated parameters, due to their simultaneous determination from experimental $k_p$ data measured at various temperatures, they are independent physical quantities, which may be separately accessed by transition state theory, e.g., in conjunction with ab initio quantum-chemical calculations, as has been illustrated for propagation reactions in free-radical polymerization by Heuts et al.[26] The preexponential is essentially determined by the geometry of the rotating groups in the reactants and in the transition state (TS) and by the rotational potentials of the relevant internal (hindered) motions in the TS,[26] as has been demonstrated for $A(k_p)$ by Heuts et al.[27]

Applying the knowledge from transition state theory to the $k_p$ data of MAA in bulk and in aqueous phase leads to the conclusion that replacing MAA by $H_2O$ modifies the environment of the transition structure for addition of MAA to a poly(MAA) radical such that the chain-end region experiences a higher degree of rotational freedom. Or, stated otherwise, gradually replacing $H_2O$ by MAA enhances the friction felt by the relevant degrees of freedom of the transition structure for propagation. Along this line of arguments, it appears rewarding to compare the Arrhenius parameters, $E_A(k_p)$ and $A(k_p)$, of MAA and methyl methacrylate (MMA) bulk polymerizations:

$$\text{MAA: } E_A(k_p) = 16.1 \text{ kJ mol}^{-1}; \quad A(k_p) = 0.38 \times 10^{-6} \text{ L mol}^{-1} \text{ s}^{-1}$$

$$\text{MMA:}^{1}\ E_A(k_p) = 22.4 \text{ kJ mol}^{-1}; \quad A(k_p) = 2.67 \times 10^{-6} \text{ L mol}^{-1} \text{ s}^{-1}$$

The numbers for $E_A(k_p)$ demonstrate that MAA does not behave like a typical methacrylate monomer, in that the activation energy is clearly below the corresponding MMA value. $E_A(k_p)$ values in the range 21−23 kJ mol$^{-1}$ are characteristic for the entire family of alkyl methacrylates, but also for several functionalized and cyclic methacrylates.[1] The lower $E_A(k_p)$ of MAA most likely results from effects of hydrogen-bonded interactions on the reaction barrier of the propagation process. As $E_A(k_p)$ of MAA does not change upon replacing MAA by $H_2O$ (see Table 4), hydrogen-bonded interactions with $H_2O$ molecules appear to have a similar effect on the reaction barrier as have MAA molecules. The change in $E_A(k_p)$ seen in going from non-hydrogen-bonded systems, such as alkyl methacrylates, to a hydrogen-bonded one, such as MAA polymerization, is consistent with the trend described in ref 24 for propagation of AA in an $H_2O$ and in a toluene environment.

As an even more remarkable feature, the comparison of Arrhenius parameters for MAA and MMA reveals a large difference in the preexponential factors: $A(k_p)$ for MMA exceeds $A(k_p)$ for MAA by about 1 order of magnitude, which is surprising in view of the fact that the two monomers (and thus also the repeat units of the polymeric species) are of similar size. On the other hand, the $A(k_p)$ values obtained for MAA in dilute aqueous solution, e.g., in the 5−15 wt % MAA region (see Table 4), are close to $A(k_p)$ for MMA. According to transition state theory and with special emphasis on the rotational partition function of the TS structure, this observation suggests that the relevant degrees of motion of the TS for MAA propagation experience a reduced barrier to rotation in the dilute aqueous state as compared to bulk MAA polymerization. It is interesting to note that intermolecular interactions via hydrogen bonds to either $H_2O$ or MAA affect the activation barrier for MAA propagation to approximately the same extent, as is demonstrated by the similarity of $E_A(k_p)$ for polymerization in bulk and in aqueous solution, whereas the relevant rotational potentials of the TS are affected to very different extents by an $H_2O$ and by an MAA environment. A higher barrier to internal rotational motion of the TS structure for MAA propagation in an MAA environment is not unexpected, as carboxylic acid moieties are strongly interacting. The enthalpy of formation of the cyclic dimer of two MAA molecules has been IR spectroscopically measured[28] to be as high as 46.7 kJ mol$^{-1}$ (in an environment of fluid ethene). This interaction energy exceeds the one between MAA and $H_2O$ molecules. That the difference in interaction energies of the TS structure for MAA propagation with either an $H_2O$ or an MAA environment affects $A(k_p)$ to such an extent is probably due to the fact that the relevant TS structure may include several units at the macroradical terminus, e.g., penultimate, pen-penultimate, and perhaps even further units, which enhances the effect of hydrogen-bonded interactions on the rotational barriers of the TS.

The similarity in $A(k_p)$ for MAA propagation in dilute aqueous solution and for MMA in bulk polymerization ($2.67 \times 10^6$ L mol$^{-1}$ s$^{-1}$), with these two monomers being structurally close to each other, is consistent with the results for AA obtained by Thickett and Gilbert,[24] if one assumes a similar effect on $A(k_p)$ of the two non-hydrogen-bonded environments, toluene and MMA. These authors reported $A(k_p)$ for AA propagation to be more or less the same in a water and in a toluene environment. The water environment thus appears to offer a similar hindrance to internal rotational motion of the TS as does the MMA environment in MMA bulk polymerization. As compared to bulk MAA polymerization, the water environment provides enhanced internal rotational mobility to the TS structure for MAA propagation, such as water allows a fish to swim and move around.

The number of repeat units at the macroradical terminus that contribute to the effect of molecular environment on $A(k_p)$ is not known. This poses problems toward attempts of quantitatively analyzing the effect of intermolecular interactions on $A(k_p)$ in terms of transition state theory. We will therefore restrict ourselves to the qualitative statement that the stronger interactions between the TS for MAA propagation with an MAA environment as compared to interactions of the TS with an $H_2O$ environment are the main reason behind the enormous reduction in $k_p$ in moving from MAA polymerization in dilute aqueous solution to MAA bulk polymerization.

It should finally be pointed out that such effects of intermolecular interactions on $k_p$ operating via influences on the barriers of hindered rotation in the TS structure may also affect propagation rate in other systems. Within a very recent study into the free-radical polymerization kinetics of 2-acrylamido-2-methylpropanesulfonic acid (AMPS) in aqueous solution,[29] apparent $k_p$ turned out to decrease by about a factor of 4.5 between 20 and 50 wt % AMPS. The direction of change and the size of the effect suggest that, also with this fully ionized monomer, intermolecular interactions have a strong impact on rotational barriers of the TS for propagation. Additional information from this AMPS study says that, despite the strong variation with (initial) AMPS concentration, $k_p$ is more or less insensitive toward the degree of monomer conversion. $k_p$ thus depends on the overall content of strongly interacting moieties, irrespective of these groups being part of monomer or polymer molecules (or of macroradicals). This observation is fully consistent with what is to be expected from the above argument of $A(k_p)$ being determined by intermolecular interactions.

Also, the weak increase of $A(k_p)$ seen in bulk polymerization of both the acrylate and methacrylate families upon increasing the size of the alkyl ester group may at least partly be assigned to intermolecular interactions and their effect on TS rotational barriers. Longer alkyl groups are capable of more effectively shielding the polar interactions of the carbonyl groups, thereby reducing rotational barriers for the relevant motions of the TS structure for (meth)acrylate propagation.

The assignment of strong $k_p$ dependences on molecular environment to the impact of intermolecular interactions on rotational barriers of transition structures and thus on preexponential factors needs to be tested for other polymerizations, including copolymerizations. Special interest will be devoted to the dependence on monomer concentration of $k_p$ in aqueous solution of partially and fully ionized monomers. Part of such studies into MAA is already underway.[30]

## Conclusions

The PLP−SEC study into $k_p$ of nonionized methacrylic acid in aqueous solution, with both MAA concentration and polymerization temperature being widely varied, reveals that $k_p$ decreases significantly, by about 1 order of magnitude, between dilute aqueous solution and bulk. This enormous drop is essentially due to changes in the Arrhenius preexponential factor, $A(k_p)$, whereas the activation energy, $E_A(k_p)$, remains more or less constant. The experimental observations are explained by differences in the strength of intermolecular interactions between either $H_2O$ or MAA and the TS structure for propagation of MAA. The intermolecular interactions most likely affect the barriers to internal rotational of this TS. An enhanced friction toward rotational motion in MAA bulk polymerization is associated with a lowering of $k_p$. The observed large variation of propagation rate coefficient with MAA content is a genuine kinetic effect, and the apparent $k_p$ values discussed in this work should be close to “true” $k_p$. Effects on $k_p$ resulting from the impact of intermolecular interactions on rotational barriers of the TS appear to be of general relevance for the understanding of propagation kinetics.

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