Propagation Rate Coefficient of Free-Radical Polymerization of Partially and Fully Ionized Methacrylic Acid in Aqueous Solution

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ABSTRACT: Pulsed-laser polymerization (PLP) in conjunction with aqueous-phase size-exclusion-chromatography (SEC) was employed to determine the propagation rate coefficient, k_p, of methacrylic acid (MAA) free-radical polymerization in aqueous solution. This was done over a wide range of degree of MAA ionization, at MAA concentrations between 5 and 40 wt %, and at temperatures from 6 to 80 °C. Depending on monomer concentration, the degree of ionization, α, may largely affect k_p. At 5 wt % MAA, k_p is lowered by about 1 order of magnitude in passing from nonionized to fully ionized MAA, whereas the associated decrease in k_p at 40 wt % MAA is only by 20%. The changes of MAA k_p with α are assigned to intermolecular interactions affecting the friction that is experienced by the relevant internal rotations of the transition state structure for propagation. Increasing hindrance of rotational motion is associated with a lowering of the pre-exponential factor, $A(k_p)$. The observed effects are primarily of entropic origin, but slight changes in activation energy, $E_A(k_p)$, also seem to play a role. An expression is given which allows for estimates of MAA k_p as a function of degree of ionization, monomer concentration, and temperature.

Introduction

Improved control of polymerization processes requires a detailed understanding of the polymerization kinetics. The relevant rate coefficients thus need to be known. The advent of pulsed-laser techniques has enormously advanced the quantitative analysis of free-radical polymerization kinetics.[1] Pulsed laser initiated polymerization (PLP) carried out in conjunction with subsequent analysis of the polymeric product by size-exclusion chromatography (SEC)[2] has emerged as the method of choice for measuring propagation rate coefficients, k_p,[3] for homopolymerizations and copolymerizations.[1] In view of the increasing importance of polymerizations in aqueous solution,[4−6] the rather limited availability of rate coefficient data for these systems was surprising. This situation has changed during recent years by pioneering PLP−SEC investigations into aqueous-phase polymerizations of acrylic acid (AA),[7] methacrylic acid (MAA)[7] and N-isopropyl acrylamide,[8] followed by extended studies into k_p of MAA,[9−11] AA,[12−14] acrylamide,[15] and N-vinyl pyrrolidone.[16] For radical polymerization of nonionized MAA in aqueous solution, benchmark k_p values[17] and also termination rate coefficients, k_t, have been collated[18] and used within first modeling studies.[19]

Most of the water-soluble monomers studied so far were nonionized at their natural p*H*. The PLP−SEC experiments carried out at low degrees of monomer conversion reveal that k_p of these monomers strongly decreases toward higher monomer concentration.[7−13,15−17] Studies into nonionized MAA at

temperatures from 20−80 °C showed that k_p for dilute aqueous solution is about 10 times higher than the associated bulk k_p value.[9] This enormous solvent effect is primarily due to the variation in $A(k_p)$, the Arrhenius pre-exponential (or frequency factor), whereas activation energy, $E_A(k_p)$, remains essentially unchanged. The decrease in $A(k_p)$ with increasing monomer concentration has been assigned to an enhancement of the barrier to internal rotational motion of the transition state (TS) structure in passing from a dilute to an MAA-rich environment. This explanation may be generalized for aqueous-phase polymerization of other nonionized monomers, where such strong solvent effects are also observed.[8,13,15,16] With the significant changes of k_p being identified as a genuine kinetic effect, the experimental k_p's may be considered as true k_p values, $k_{p,true}$,[9] rather than apparent k_p values, which latter assignment has been used in earlier studies into the variation of k_p with monomer concentration.[7,8,13] The explanation via apparent k_p values assumes that the "local monomer concentration" at the radical site may differ from the known overall monomer concentration. The insight that measured k_p values are "true" k_p's greatly simplifies the description of propagation rate in aqueous-solution polymerizations.

The variation of p*H* appears to be an obvious way to influence k_p of (meth)acrylic acid in aqueous solution. PLP−SEC studies into k_p of partially or fully ionized monomers are scarce so far. Within an experimental series on acrylic acid (5 wt % AA in aqueous solution) at 6 °C, we found an almost 9-fold decrease of k_p between nonionized AA ($\alpha = 0$) and fully ionized AA ($\alpha = 1$), from 111 000 to 13 000 L·mol^{-1}·s^{-1}.[14] This observation was explained by repulsive interactions between a monomer molecule and a radical chain-end both bearing a negative charge. The same qualitative argument has been put forward in the pioneering

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studies into AA[20] and MAA[20,21] where an approximately 10-fold decrease in the initial rate of polymerization between nonionized and completely ionized monomers has been found. The increase in propagation rate upon further addition of NaOH to fully ionized AA in aqueous solution (k_p = 57 000 L·mol^{-1}·s^{-1} at α = 1.1)[14] was interpreted on the basis of the "ion–pair concept" put forward by Kabanov et al.[20,22−25]

In view of the recent insight into k_p of nonionized methacrylic acid, it appeared rewarding to analyze k_p as a function of the degree of monomer ionization, α, within extended ranges of temperature and monomer concentration. Non-PLP−SEC studies into ionized AA at higher monomer concentrations (up to 37 wt % AA) indicated that the polymerization rate is less dependent on α at higher AA content.[26] Because of the much higher k_p values, the associated higher molecular weights and larger solution viscosities, and, most importantly, because of intra- and intermolecular hydrogen transfer (backbiting) reactions, PLP−SEC studies into AA are less easily carried out than are the ones into MAA.[27] As the effects of acid ionization should be seen with AA and MAA to a similar extent, the dependence of k_p on α has been studied for aqueous solutions of MAA first. A preliminary set of k_p values from PLP−SEC experiments at 40 °C for MAA concentrations, c_{MAA}, from 5 to 40 wt % and α values from 0 to 1,[10] clearly demonstrates that the dependence of k_p on both c_{MAA} and α is not trivial. For partially ionized MAA, the decrease of k_p upon increasing MAA concentration is noticeably weaker than for the nonionized MAA, and the propagation rate coefficient for fully ionized MAA is even slightly increasing with monomer concentration.

The present paper aims at providing a comprehensive picture of k_p for aqueous-solution polymerization of MAA. Via PLP in conjunction with aqueous-phase SEC, k_p has been measured over the full range of MAA ionization, at MAA concentrations between 5 and 40 wt %, and at temperatures from 6 to 80 °C. The effect of added salt (NaCl) was studied within the full range of degrees of MAA ionization for polymerization of 5 wt % MAA. After presenting some experimental details and prior to reporting and discussing the results, some aspects of polyelectrolyte solutions will be highlighted.

Experimental Section

Chemicals. Methacrylic acid (Fluka > 98%, stabilized with 0.025% hydroquinone monomethylether), the photoinitiator DMPA (2,2-dimethoxy-2-phenylacetophenone, Aldrich, 99%), and sodium hydroxide (Scharlau, > 99%) were used as supplied. Demineralized water was used as the eluent for aqueous-phase SEC and for preparation of monomer and NaOH solutions.

Preparation of Solutions for Polymerization. The solutions were prepared according to the procedure detailed for ionized AA[14] using aqueous NaOH solutions. The pH value of the mixtures was measured prior to polymerization via a Methrom 602 pH meter (Switzerland) or an EcoScan pH 5 instrument (Eutech Instruments, Singapore).

Pulsed Laser Polymerization. Sample preparation and pulsed laser polymerization were performed as described elsewhere.[9,14] The polymerization experiments were carried out in two laboratories: at the University of Göttingen using an excimer laser (LPX 210i, Lambda Physik) operated on the 351 nm (XeF) line with an energy of 10 mJ per pulse at pulse repetition rates of 10, 20, or 40 Hz, and at the International Laser Centre at Bratislava using a Solar LQ129 (Minsk, Belarus) with a lamp-pumped Nd:YAG laser employing second and third harmonics for operation at 355 nm with an energy of 12 mJ per pulse at pulse repetition rates of 10, 20, and 30 Hz. Depending on α, MAA concentration and temperature, a few tens up to several hundreds of pulses were applied to yield monomer conversions up to 5%. After polymerization, the mixture was poured into a sample vial

containing hydroquinone to prevent postpolymerization. Residual sodium methacrylate unfavorably affects gravimetric conversion detection as well as SEC determination of the molecular weight distribution (MWD). Therefore each polymer sample was dialyzed against demineralized water using a dialyzing tube with the molecular weight cutoff below 3000 g/mol and an internal diameter of 11.5 mm (Spectra/Por Spectrum Laboratories, Inc.). It was verified by comparing the MWDs of dialyzed and of nondialyzed samples of nonionized polyMAA with PLP-structured MWD that dialysis leaves the SEC traces unchanged at least above ~2000 g·mol^{-1}. After dialysis, polymer was isolated by freeze-drying and monomer conversion was determined gravimetrically.

Size-Exclusion Chromatography. The aqueous-phase SEC of polyMAA samples was performed as detailed in our paper on k_p of nonionized MAA polymerized in aqueous solution.[9]

Features of Polymerizing Polyelectrolyte Systems

By increasing the pH value and hence the degree of ionization of weak carboxylic acids, the propagation reaction may be affected by electrostatic interactions, in particular between the negatively charged carboxylate groups on both the ionized monomer and the macroradical. The counterions reduce the repulsive electrostatic interactions that are responsible for polyelectrolyte chain expansion and dynamics.[28] The ionic strength of the polymerizing solution is determined by the concentration of ionized monomer. At high ionic strengths which, in the area of aqueous-phase polyelectrolyte solutions, refer to concentrations between 10^{-3} and 10^0 mol·L^{-1}, the screening of charges results in a conformation of the polyelectrolyte chain that is close to the one of nonionized polymer.[29,30] Thus, at typical monomer concentrations of ~1 mol·L^{-1}, the polymerization of an ionized monomer at α > 0.1 proceeds at high ionic strengths in terms of the polyelectrolyte solutions. A substantial screening of the charges on the polyion chain may thus be expected to occur under typical polymerization conditions of ionized monomers. As monomer is consumed during polymerization, the ionic strength may vary during the course of a polymerization to high degrees of monomer conversion. This effect, however, plays no role with PLP−SEC experiments, which are carried out at low conversion. The interaction of charged groups on the polymer chain with water molecules, which is a particular feature of polyelectrolyte solutions,[4] may affect the TS structure for propagation.[9]

The acid−base characteristics of monomeric and polymeric species may add complexity to the polymerization kinetics. An exchange of protons and/or counterions may take place between the carboxylic groups of the monomer and the macroradical because of differences in pK_a value. Moreover, the pK_a value of polyelectrolyte chains depends on molar mass, degree of ionization and ionic strength[31] and thus may change with monomer conversion and even during the growth of a polymer chain.

The conformation of ionized polyMAA and polyAA chains depends on the degree of ionization.[32−36] In case of polyMAA, hydrophobic attractive interactions, giving rise to the lower-critical-solution-temperature behavior of polyMAA in aqueous solution,[37] compete with repulsive electrostatic interactions at low degrees of polymer ionization, e.g., at α < 0.2. It is not clear so far, whether chain conformation will significantly affect k_p, but conformational dynamics does so by influencing the internal rotational motion of the TS structure.

The effective charge on the ionized poly(M)AA chain does not reflect the degree of monomer ionization. Whereas the degree of ionization is identical to the degree of neutralization for the monomeric species, this correlation is not valid for polymeric species. This is due to different pK_a values and hence to different degrees of ionization at a given pH (see the titration curves in Figure 1 of ref 14), but also due to counterion condensation, i.e.,

to an accumulation of counterions close to the surface of the polyanion.[38−40] For example, the maximum degree of ionization for polyMAA in aqueous solution is $\alpha \sim 0.36$ with monovalent counterions in the absence of added salt.[41] In the case that the degree of polyMAA neutralization exceeds this value, polyMAA does not exhibit an enhancement of effective charge and the intramolecular and intermolecular electrostatic interactions remain constant.[41]

In summary, the kinetics of radical polymerization of partially or fully ionized MAA at different MAA concentrations may be affected by the specific features of polyelectrolyte systems which are not yet fully understood. Additional difficulties are associated with (*i*) the relative amounts of monomeric and polymeric ions which may change during polymerization[28,42] depending on initial monomer concentration, monomer conversion, degree of monomer ionization and polymer molecular weight, (*ii*) the fact that each individual polymerization does not proceed in a well-defined solvent because the solvent quality varies depending on the initial composition of the polymerization system as well as during polymerization, and (*iii*) the polymeric product being polydisperse.

Results and Discussion

The reported PLP−SEC experiments fulfill the consistency criteria for reliable k_p measurement.[43] Shown in Figure 1 are the molecular weight distributions and associated first-derivative curves for aqueous-solution polymerizations of 5 wt % MAA

at 6, 40, and 80 °C and degree of MAA ionization $\alpha = 0.3$. Corresponding data for several MAA weight percentages at $\alpha = 0.7$ and 40 °C are given in Figure 2. The primary and secondary inflection points on the MWD are found from the maximum positions, M_1 and M_2, respectively, of the first-derivative curves (dotted lines in Figures 1 and 2). With some of these first-derivative curves, even a third maximum, M_3, can be seen.

Details about the experimental conditions and the complete list of obtained k_p values are provided in the Supporting Information, Tables S1−S3. The large data set was obtained from PLP experiments in two laboratories, at Göttingen and Bratislava. The aqueous-phase SEC analyses have exclusively been performed at the Bratislava Polymer Institute of the Slovak Academy of Sciences. That the consistency criteria for reliable k_p determination are met, is seen from (a) the ratio of molecular weights at the first and second point of inflection, M_1/M_2, being close to 0.5 and (b) the obtained k_p values not being dependent on photoinitiator concentration, pulse repetition rate, the number of applied laser pulses, and the different PLP set-ups used at the two laboratories. The criterion of k_p being independent of monomer concentration is not applicable in the aqueous solvent system, as the strength of the different types of hydrogen-bonded interactions varies with acid content. From the individual experimental k_p values in Tables S1−S3 of the Supporting Information, arithmetic mean values, k_p, for experiments carried out under ostensibly the same conditions, are calculated and listed in Table 1
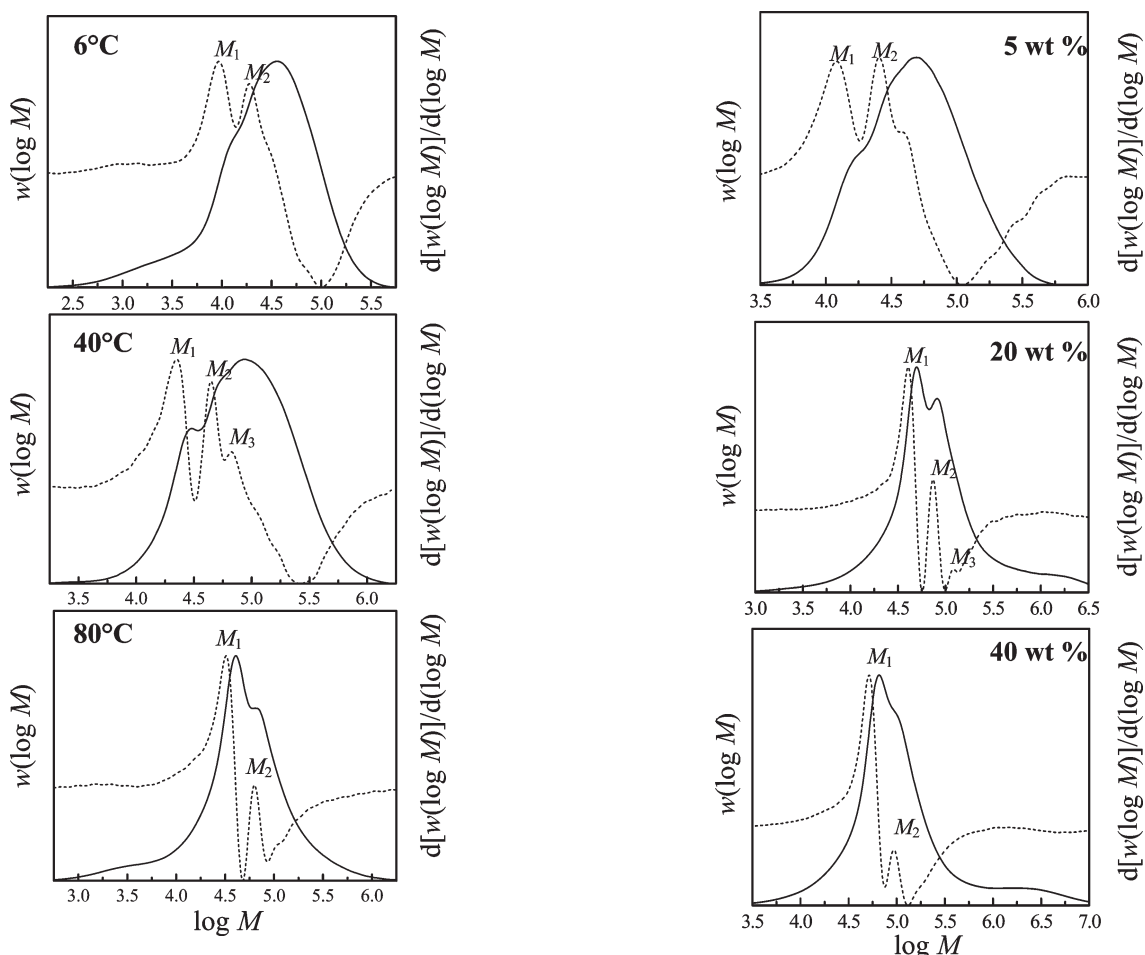

Figure 1. Molecular weight distributions (full lines) and associated first-derivate curves (dotted lines) obtained from pulsed laser induced polymerizations of 5 wt % methacrylic acid in water at temperatures of 6, 40, and 80 °C and a degree of monomer ionization of $\alpha = 0.3$. The laser repetition rate was 20 Hz and the photoinitiator concentration, c_{DMPA}, was $1 \cdot 10^{-3}$ mol·L^{-1}.

Figure 2. Molecular weight distributions (full lines) and associated first-derivate curves (dotted lines) obtained from pulsed laser induced polymerizations of 5, 20, and 40 wt % of methacrylic acid in water at 40 °C and a degree of monomer ionization of $\alpha = 0.7$; the laser repetition rate was 20 Hz.

Table 1. Arithmetic Mean Values, k_p, Deduced from the Individual k_p Data in Tables S1−S3 for Aqueous Solution Polymerizations of Methacrylic Acid, MAA, at Various MAA Concentrations, c_{MAA}, Degrees of Ionization, α, and Temperatures.[a]

c_{MAA}			k_p/ L·mol^{-1}·s^{-1}				
wt %	mol·L^{-1}	α	6 °C	20 °C	40 °C	60 °C	80 °C
5	0.59	0	3556 (3831; 8%)	5986 (5284; −11%)	9243 (7958; −14%)	12856 (11412; −11%)	16544 (15709; −5%)
		0.3	3017 (3222; 7%)	4433 (4444; 0%)	7346 (6693; −9%)	10432 (9589; −8%)	13468 (13212; −2%)
		0.7	1433 (1806; 26%)	2911 (2491; −14%)	4631 (3752; −19%)	6602 (5380; −19%)	8719 (7409; −15%)
		1.0	*372 (291; −22%)*	*474 (402; −15%)*	682 (605; −11%)	862 (868; 1%)	1158 (1195; 3%)
20	2.35	0	1969 (1944; −1%)	2933 (2681; −9%)	4257 (4038; −5%)	5787 (5790; 0%)	7697 (7971; 4%)
		0.3	1897 (1829; −4%)	2735 (2523; −8%)	3800 (3758; −1%)	5020 (5449; 9%)	6228 (7501; 20%)
		0.7	1566 (1353; −14%)	2523 (1867; −26%)	3311 (2812; −15%)	4229 (4032; −5%)	5170 (5550; 7%)
		1.0	802 (755; −6%)	1306 (1041; −20%)	1691 (1568; −7%)	2389 (2248; −6%)	2908 (3094; 6%)
40	4.72	0	*1037 (928; −11%)*	1428 (1280; −10%)	2023 (1929; −5%)	2923 (2765; −5%)	3950 (3807; −4%)
		0.3	*1196 (997; −17%)*	1507 (1376; −9%)	2168 (2072; −4%)	2873 (2971; −3%)	3568 (4090; 15%)
		0.7	*1300 (925; −29%)*	1587 (1276; −20%)	2098 (1922; −8%)	2702 (2755; 2%)	3230 (3793; 17%)
		1.0	852 (747; −12%)	1426 (1030; −28%)	1803 (1552; −14%)	2263 (2226; −2%)	2477 (3064; 24%)

[a] The standard deviations of the k_p values are below 10%. The values in italics have been estimated via Arrhenius fits (see Table 2) of k_p data measured at identical c_{MAA} and α, but different temperatures. The numbers in brackets are propagation rate coefficients, k_p*, estimated from eq 7. Also listed in brackets are the percentage differences between k_p* and k_p: $100(k_p* - k_p)/k_p$.
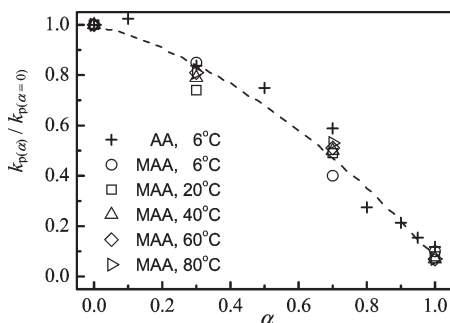
Figure 3. Dependence of reduced propagation rate coefficient $k_{p(\alpha)}/k_{p(\alpha=0)}$ on the degree of ionization of methacrylic acid (MAA, data from Table 1) and acrylic acid (AA, data from ref 14) for aqueous solution polymerization at $c_{(M)AA}$ = 5 wt % and different polymerization temperatures. The dashed line represents k_p values for MAA estimated from eq 7.

(the entries in brackets are discussed further below). The standard deviations are below ~10%.

The k_p data for the lowest MAA content, 5 wt %, will be discussed first. As has been seen in our study into acrylic acid at 6 °C,[14] k_p decreases by about 1 order of magnitude in passing from nonionized to fully ionized AA. With MAA, the variation of k_p with degree of monomer ionization has been monitored up to 80 °C. The associated (arithmetic mean) k_p values for nonionized and fully ionized monomer at 5 wt % MAA are around 9200 and 700 L·mol^{-1}·s^{-1} at 40 °C, 12 700 and 900 L·mol^{-1}·s^{-1} at 60 °C, and 16 500 and 1200 L·mol^{-1}·s^{-1} at 80 °C, respectively. The decrease in MAA k_p between α = 0 and α = 1 thus slightly exceeds 1 order of magnitude at 5 wt % MAA. It should be noted that the early literature k_p data for fully ionized MAA (~1000 to 2000 L·mol^{-1}·s^{-1}) deduced via the rotating sector technique for 0.92 mol·L^{-1} MAA at 23 °C[20] are close to the numbers from the PLP−SEC experiments (see Table 1).
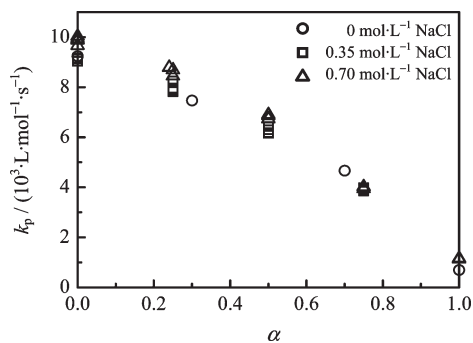
Shown in Figure 3 is the variation of the reduced propagation rate coefficient, $k_{p(\alpha)}/k_{p(\alpha=0)}$, as a function of the degree of monomer ionization, α, for 5 wt % MAA in water at several temperatures. Also included in Figure 3 are reduced k_p values from the earlier study into k_p of AA.[14] The similarity in $k_{p(\alpha)}/k_{p(\alpha=0)}$ vs α behavior of AA and MAA is remarkable in view of the fact that the absolute k_p's of AA and MAA under otherwise identical conditions are largely different, by about 1.5 orders of magnitude. This similarity further suggests that electrochemical equilibration is faster than the time period required for a propagation step. If this were not the case, the much faster propagation with AA should give rise to a behavior that deviates from that of MAA.

The correlation of $k_{p(\alpha)}/k_{p(\alpha=0)}$ with α appears to be insensitive toward temperature, which indicates that entropic rather than enthalpic effects are controlling this change of k_p. Whereas the activation energy, $E_A(k_p)$, should not largely vary with degree of MAA ionization, the variation of k_p with α should be associated with changes in the pre-exponential factor $A(k_p)$, as has been found for MAA[9] and NVP[16] propagation in aqueous solution upon changing the monomer concentration. The Arrhenius parameters will be detailed further below.

Intuitively, the decrease in k_p with increasing degree of ionization may be assigned to repulsive interactions between equally charged monomer and growing radical chain-end. This argument has been used in the classical papers on polymerization of ionized unsaturated carboxylic acids,[20,21] and has been adopted in our earlier work to explain the decrease in k_p between α = 0 and α = 1 at 5 wt % AA.[14] Repulsive interactions may be screened by the addition of a low-molecular-weight electrolyte, e.g., of NaCl. In case that repulsive interactions diminish k_p, the addition of NaCl to aqueous solutions of partially or fully ionized MAA should result in enhanced k_p values. Such experiments have now been carried out for 5 wt % MAA polymerized at 40 °C and two NaCl concentrations, 0.35 and 0.70 mol·L^{-1}, within the range from α = 0 to α = 1. Higher NaCl concentrations were not applied, as the system may turn inhomogeneous.[44−46] The obtained k_p values together with the experimental conditions are shown in Table S4 of the Supporting Information.

Figure 4 shows the comparison of k_p values with and without NaCl being added. Irrespective of the degree of ionization, the addition of NaCl does not result in any clearly detectable effect on k_p. This experimental data indicates that the charges on the polyelectrolyte are already significantly screened by the ionized MAA in the absence of NaCl. Figure 4 suggests that there is the necessity to reconsider the classical mechanism for polymerization of ionized (M)AA in aqueous phase.[20,21] Hence, the repulsive interactions between charged monomer and the growing radical chain-end do not play the dominant role in determining the propagation rate in free-radical polymerization of ionized monomers.
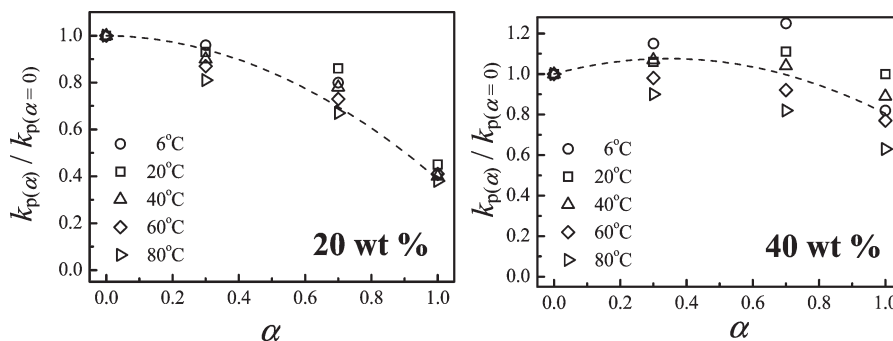
Shown in Figure 5 is the dependence of the arithmetic mean k_p values (listed in Table 1) on the degree of monomer ionization, α, for polymerizations at 6, 40, and 80 °C in aqueous MAA solutions containing 5, 20, and 40 wt % monomer, respectively. Whereas k_p at 5 wt % MAA steadily and substantially decreases with α, by 1 order of magnitude up to α = 1.0, the k_p values for 20 wt % MAA are only weakly decreasing up to α = 0.7 and k_p of fully ionized MAA is only by a factor of 2.5 below the associated k_p value at α = 0. This trend continues in that k_p at the highest experimental MAA content of 40 wt % appears to be more or less

Figure 4. Dependence of k_p on the degree of ionization, α, of MAA for aqueous-solution polymerizations at c_{MAA} = 5 wt % (0.59 mol·L^{-1}) and 40 °C in the presence of two concentrations of sodium chloride.
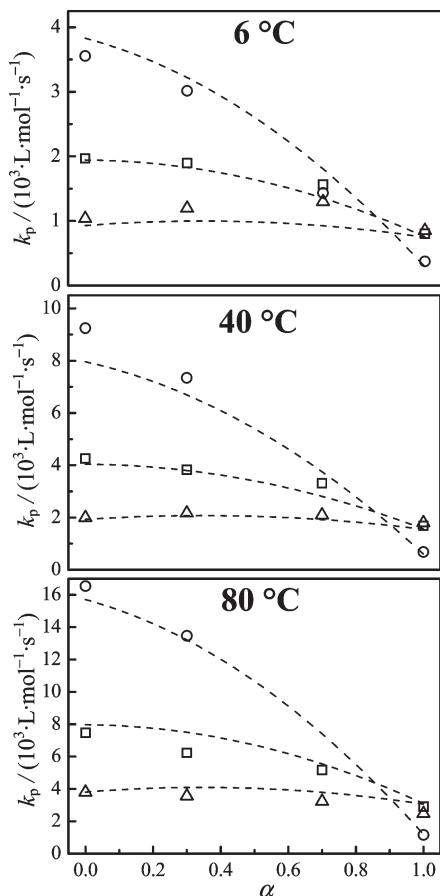
Figure 5. Variation of the propagation rate coefficient, k_p, of MAA polymerization in aqueous solution as a function of the degree of monomer ionization, α, for MAA concentrations of 5 (circles), 20 (squares), and 40 wt % (triangles) at 6, 40, and 80 °C. Dashed lines represent k_p values estimated from eq 7.

insensitive toward the degree of ionization over most of the α range with a slight decrease, by about 20%, in the range close to full MAA ionization. The dashed lines in Figure 5 are calculated from eq 7, as will be described further below. Interestingly, the k_p values under conditions of full MAA ionization (α = 1) are higher at larger MAA content. The general trends of k_p dependence do not appear to be very sensitive toward polymerization temperature, as is indicated by the plot of reduced propagation rate coefficient, $k_{p(\alpha)}/k_{p(\alpha=0)}$, vs the degree of monomer ionization (Figure 6) for temperatures from 6 to 80 °C and MAA concentrations of 20 and 40 wt %.

Arrhenius fits of the primary experimental k_p data from Tables S1−S3 yield the activation energy and the pre-exponential factor, $E_A(k_p)$ and $A(k_p)$, respectively. The numbers so obtained are listed in Table 2 for each MAA content and degree of ionization. Part of the data at higher MAA content and at higher α has been deduced from fitting over a reduced temperature range (40−80 °C), as the experimental data at lower temperature show significant scatter. In order to indicate that for some of the Arrhenius parameters so obtained, the uncertainty is relatively high, these less reliable numbers of Table 2 are given in italics.

It is known from quantum chemical studies into AA, that $E_A(k_p)$ in a water solvent field is significantly below the associated gas phase value.[47] The same should be true for MAA. Our previous paper into the solvent dependence of k_p for nonionized MAA showed that varying the solvent environment from pure MAA to an aqueous environment does not affect $E_A(k_p)$.[9] Inspection of the $E_A(k_p)$ values in Table 2, however, suggests that there is a slight decrease of activation energy toward increasing ionic strength (IS) of the polymerization medium (IS = αc_{MAA}, with c_{MAA} being the molar MAA concentration). This lowering of $E_A(k_p)$ may be attributed to the polarity of the polymerization medium due to the presence of ionized MAA. This effect may be similar to the one observed for polymerization of methacrylates in ionic liquids, where $E_A(k_p)$ was found to be below the bulk polymerization value by a few kJ·mol^{-1}.[48−50] The $E_A(k_p)$ values from Table 2 (with the exception of the value for 40 wt % MAA and α = 1) can be fitted by an exponential function against ionic strength (Figure 7). The resulting expression reads:

$$E_A^*(IS)/kJ\cdot mol^{-1} = 4.554 \exp[-1.14\alpha(c_{MAA}/mol\cdot L^{-1})] + 10.34 \quad (1)$$

At ionic strengths above 0.6 mol·L^{-1}, the activation energy is by more than 2 kJ·mol^{-1} below the number measured at IS < 0.6 mol·L^{-1}, in particular at small MAA weight fractions and at α = 0.

Equation 1 has been set up in an attempt to deduce pre-exponential factors, $A^*(IS)$, on the basis of the $E_A^*(IS)$ values represented by eq 1. The attempts to provide a reasonable fit of

Figure 6. Dependence of the reduced propagation rate coefficient, $k_{p(\alpha)}/k_{p(\alpha=0)}$, on the degree of monomer ionization, α, of methacrylic acid for aqueous solution polymerizations between 6 and 80 °C for 20 and 40 wt % MAA. The dashed lines represent k_p values estimated from eq 7.

Table 2. Arrhenius Parameters $E_A(k_p)$ and $A(k_p)$ for k_p of Methacrylic Acid (MAA) Polymerization in Aqueous Solution at Different Initial MAA Concentrations and Various Degrees of MAA Ionization (See Text)[c]

	5 wt % MAA		20 wt % MAA		40 wt % MAA	
α	$E_A(k_p)/\text{kJ·mol}^{-1}$	$A\cdot10^{-6}/\text{L·mol}^{-1}\cdot\text{s}^{-1}$	$E_A(k_p)/\text{kJ·mol}^{-1}$	$A\cdot10^{-6}/\text{L·mol}^{-1}\cdot\text{s}^{-1}$	$E_A(k_p)/\text{kJ·mol}^{-1}$	$A\cdot10^{-6}/\text{L·mol}^{-1}\cdot\text{s}^{-1}$
0	15.0 ± 0.3^b	2.78^b	14.1 ± 0.3^b	0.92^b	14.8 ± 0.5^b	0.61^b
0.3	15.8 ± 0.4^b	3.03^b	11.3 ± 0.3^a	0.29^a	11.5 ± 0.3^a	0.18^a
0.7	15.3 ± 0.9^b	1.62^b	10.3 ± 0.3^a	0.17^a	9.9 ± 0.5^a	0.10^a
1.0	*11.8 ± 1.2^a*	*0.06^a*	12.4 ± 0.6^a	0.20^a	*8.0 ± 2.1^a*	*0.04^a*

[a] Temperature range 40−80 °C [b] Temperature range 20−80 °C [c] Numbers given in italics are deduced from a small data set. They exhibit considerable uncertainty.
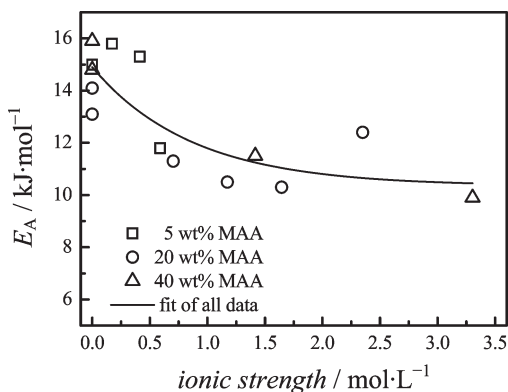
Figure 7. Dependence of $E_A(k_p)$ on ionic strength (IS) as obtained from Arrhenius fitting of individual k_p data sets for identical α and MAA content. The full line represents the variation of $E_A(k_p)$ with ionic strength, $E_A^*(\text{IS})$, of solution given by the concentration of ionized MAA expressed as $E_A^*(\text{IS})/\text{kJ·mol}^{-1} = 4.554 \exp[-1.14\alpha(c_{\text{MAA}}/\text{mol·L}^{-1})] + 10.34$.

the experimental data using $E_A^*(\text{IS})$ from eq 1 and adopting $A^*(\text{IS})$ to be the single adjustable parameter however failed. The estimates of k_p from an Arrhenius expression with the parameters $E_A^*(\text{IS})$ and $A^*(\text{IS})$ resulted in values which largely differed from the experimental ones.

Therefore, another approach has been used. An empirical expression (eq 7) has been derived for representing the variation of k_p within the entire range of polymerization conditions covered within the present study. Equation 7, which will now be presented, has been used to construct the dashed line k_p curves in Figures 3, 5 and 6.

In our earlier study into k_p of partially and fully ionized AA at 5 wt %,[14] the experimental data have been fitted to eq 2, which considers propagation steps of monomer and a macroradical chain-end being either ionized or nonionized:

$$k_{p(\alpha)}/\text{L·mol}^{-1}\cdot\text{s}^{-1} = k_{p(\alpha=0)}(1-\alpha)^2 + k_{p(\alpha=1)}\alpha^2 + 2\alpha(1-\alpha)k_{p(\alpha=0)}f \quad (2)$$

with f being the only adjustable parameter.

The picture underlying eq 2 is oversimplified in that the screening of the net charge on the macroradical chain-end is not taken into account. The reasonable fitting capacity seen with this earlier attempt, however, made us stay with a parabolic function (eq 3) as the basis for fitting attempts of k_p as a function of degree of monomer ionization, α. Within a second step, the fitting was extended such as to additionally take the effect of initial weight faction of MAA in water, w_{MAA}^0, into account.

$$k_{p(\alpha)}/k_{p(\alpha=0)} = a\alpha^2 + b\alpha + c \quad (3)$$

The boundary condition: $k_{p(\alpha)}/k_{p(\alpha=0)} = 1$ for $\alpha = 0$ requires $c = 1$, and $k_{p(\alpha)}/k_{p(\alpha=0)}$ at $\alpha = 1$ results in $a = k_{p(\alpha=1)}/k_{p(\alpha=0)} -$

$b -1$. The modified eq 3 thus reads:

$$k_{p(\alpha)}/k_{p(\alpha=0)} = (k_{p(\alpha=1)}/k_{p(\alpha=0)} - b - 1)\alpha^2 + b\alpha + 1 \quad (4)$$

The parameter b is found from fitting the experimental $k_{p(\alpha)}/k_{p(\alpha=0)}$ data obtained for different w_{MAA}^0 (Figures 3 and 6) and the measured $k_{p(\alpha=1)}/k_{p(\alpha=0)}$ values of 0.07, 0.40, and 0.80 for $w_{\text{MAA}}^0 = 0.05$, 0.20, and 0.40, respectively. The b parameters so obtained can be linearly fitted against w_{MAA}^0, yielding $b = -0.475 + 2.283 w_{\text{MAA}}^0$ ($R^2 = 0.963$) as shown in Figure 8a, to be used with eq 3 for estimates of $k_{p(\alpha)}/k_{p(\alpha=0)}$ at arbitrary (initial) MAA contents in the range from 5 to 40 wt % MAA. The $k_{p(\alpha=1)}/k_{p(\alpha=0)}$ vs w_{MAA}^0 values allow for a straight line fit (Figure 8b), which enables interpolation of $k_{p(\alpha=1)}/k_{p(\alpha=0)}$ data for MAA fractions other than the experimentally investigated ones: $k_{p(\alpha=1)}/k_{p(\alpha=0)} = -0.0276 + 2.081 w_{\text{MAA}}^0$ ($R^2 = 0.999$). The fits illustrated in parts a and b of Figure 8 may be used with eq 4 to yield an expression of the following type:

$$k_{p(\alpha)}/k_{p(\alpha=0)} = (Aw_{\text{MAA}}^0 + B)\alpha^2 + (Cw_{\text{MAA}}^0 + D)\alpha + 1 \quad (5)$$

with $A = -0.202$, $B = -0.553$, $C = 2.283$, and $D = -0.475$.

Within a final step, the previously established[18] variation of $k_{p(\alpha=0)}$ as a function of temperature and initial MAA weight fraction is introduced:

$$\begin{aligned} k_{p(\alpha=0)} &= k_p(w_{\text{MAA}}^0, T) \\ &= 4.1 \times 10^6 \exp\left(\frac{1.88 \times 10^3}{(T/\text{K})}\right) \\ &\quad (0.08 + (1-0.08)\exp(-5.3w_{\text{MAA}}^0)) \end{aligned} \quad (6)$$

Equations 5 and 6 result in eq 7, which allows for calculation of k_p values, k_p^*, as a function of initial MAA concentration, degree of MAA ionization, and temperature.

$$\begin{aligned} k_p^* &= k_p(\alpha, w_{\text{MAA}}^0, T) \\ &= 4.1 \times 10^6 \exp\left(-\frac{1.88 \times 10^3}{(T/\text{K})}\right)(0.08 + (1-0.08) \\ &\quad \exp(-5.3w_{\text{MAA}}^0))[(-0.202w_{\text{MAA}}^0 - 0.553)\alpha^2 \\ &\quad + (2.283w_{\text{MAA}}^0 - 0.475)\alpha + 1] \\ &\quad 0 \le \alpha \le 1; \ 0.05 \le w_{\text{MAA}}^0 \le 0.40; \ 6 \le T/°C \le 80 \end{aligned} \quad (7)$$

The associated k_p^* value is listed in brackets behind each experimental k_p value in Table 1. Also given in brackets is the percentage difference between estimated and experimental propagation rate coefficient: $100(k_p^* - k_p)/k_p$. These deviations are mostly below 15%, which is considered to be the typical uncertainty associated with PLP−SEC measurements. The square-root mean deviation $(k_p^* - k_p)/k_p$ of the data set measured at
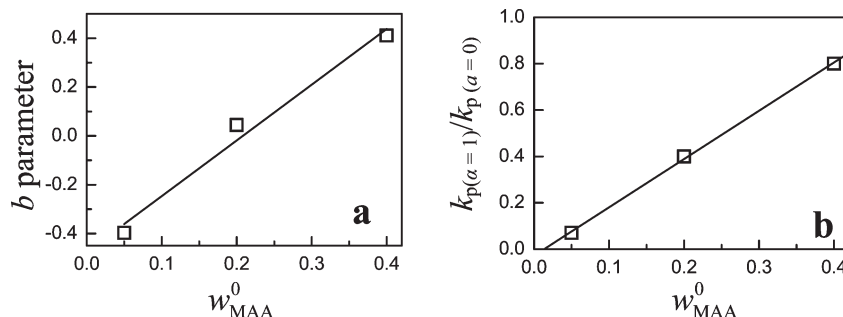
Figure 8. Correlation of (a) the fitting b parameter and (b) the ratio $k_{p(\alpha=1)}/k_{p(\alpha=0)}$ with initial weight fraction of MAA in water, w_{MAA}^0, respectively.
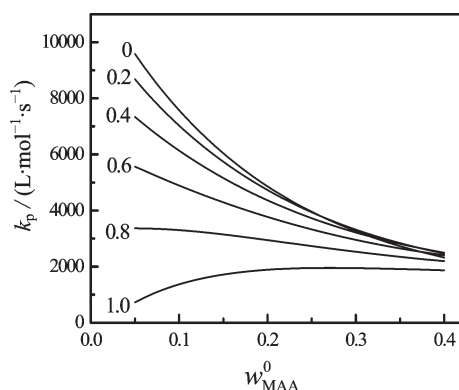
Figure 9. k_p values estimated from eq 7 for various α values and initial weight fractions of MAA in water, w_{MAA}^0, at 50 °C.

constant temperature for $\alpha = 0, 0.3, 0.7$, and 1.0 and initial MAA weight factions in water $w_{MAA}^0 = 0.05, 0.20$, and 0.40 amounts to 12.9% at 6 °C, 14.2% at 20 °C, 9.4% at 40 °C, 5.8% at 60 °C, and 10.2% at 80 °C with each of these isothermal data sets comprising 12 different experimental conditions (see Table 1). The square-root mean deviation of the entire data set encompassing 60 different experimental conditions, between $0 \leq \alpha \leq 1$, $0.05 \leq w_{MAA}^0 \leq 0.40$, and $6 \leq T/°C \leq 80$, amounts to 10.5%. This rather satisfactory representation of the large data set demonstrates the suitability of eq 7 to estimate k_p values within the range of experimental conditions of the present study, as is shown by dashed lines in Figures 3, 5, and 6.

As an illustration of applying eq 7, k_p data have been estimated as a function of MAA weight percentage content for $\alpha = 0, 0.2, 0.4, 0.6, 0.8$, and 1.0 at 50 °C (Figure 9). A strong decrease of k_p with MAA content is seen at low values of α. At around $\alpha = 0.8$, k_p is more or less insensitive toward MAA content. At $\alpha = 1.0$, k_p even increases toward higher monomer content.

It should be noted that eq 7, together with the entire set of k_p data reported in the present study, holds for low-conversion conditions. As has been detailed for nonionized MAA[11] and for N-vinylpyrrolidone,[16] the size of k_p depends on the actual monomer-to-water ratio, which changes with monomer consumption during polymerization. The procedure by which this effect has been taken into account for the propagation rate coefficient of nonionized MAA[11] should also be applicable for estimating k_p of partially or fully ionized MAA as a function of monomer conversion. The data in Figure 9 indicate that the impact of monomer conversion on k_p should diminish toward higher α, as k_p is less sensitive toward monomer concentration in polymerizations of partially and fully ionized MAA.

The variation of k_p with MAA content and degree of MAA ionization is rather insensitive toward polymerization temperature (see Figures 3 and 6). Thus the dependence of k_p on monomer weight percentage and on α may be discussed via the k_p data for one particular polymerization temperature, e.g., via the 50 °C data in Figure 9. The striking observations are: (*i*) both w_{MAA}^0 and α largely affect k_p, and (*ii*) the dependence of k_p on w_{MAA}^0 is particularly strong at small α and, vice versa, the dependence on α is very pronounced at low w_{MAA}^0.

This inverse type of behavior suggests that the physical reason behind the variation of k_p of nonionized MAA with MAA content may also provide the explanation for the variation of k_p with degree of monomer ionization. The dependence of k_p on w_{MAA}^0 in nonionized MAA was understood in terms of strong hydrogen-bonded intermolecular interactions (between carboxylic acid moieties of the transition state structure for propagation and of MAA molecules in the immediate environment of the TS), which affect hindrance to internal rotational motion of the TS. It appears reasonable that in partially and fully ionized systems similar such interactions may occur between charges on the TS structure and on moieties in the environment of the TS structure.

Other than with nonionized MAA, aqueous systems containing partially or fully ionized MAA together with partially ionized polyMAA species may be rather complex due to the simultaneous occurrence of electrostatic interactions, effects of ionic strength, the impact of electrochemical equilibria, and the action of hydrophobic forces. Increasing friction of internal rotational motion may result from several types of attractive interactions: Electrostatic forces between the radical chain-end and counterions condensed in the vicinity of a polyion may enhance hindrance of the TS rotational modes and thus contribute to a lowering of the pre-exponential factor.[51,52] Ionized MAA may be strongly hydrogen bonded to surrounding molecules and to polyMAA species, including radicals. The strength of hydrogen bonding between an ionized and a nonionized carboxylic acid moiety may exceed the one between such two nonionized moieties.[32] Attractive electrostatic interactions may occur in between polyelectrolyte chains, *e.g.*, under conditions of overcharging of polyions, which may lead to charge inversion of the polymeric species.[53,54] Hydrophobic interactions among methyl groups of polyMAA, which are enhanced at higher ionic strengths and higher amounts of charges on the polymer chain, may also contribute to some enhanced friction within the TS species.

On the other hand, reduced friction of internal rotational motion of the TS may result from solubilization of polyions by water. Moreover, the flexibility of polyions may be enhanced toward increasing ionic strength as a result of the screening of charges.[28] At high monomer contents and high degrees of ionization, the presence of large amounts of counterions may lower the impact of attractive interactions and enhance internal rotational mobility and thus k_p.

The individual contribution of these charge-related effects on k_p within the extended range of experimental conditions is extremely difficult to be properly assigned. The observation from Figure 3 and 6, that the significant variation of $k_{p(\alpha)}/k_{p(\alpha=0)}$ with MAA concentration and the degree of monomer ionization occurs to very similar extents at all polymerization temperatures

under investigation, suggests that the origin behind the effects of MAA concentration and MAA is similar and is of entropic nature. This view is further supported by the similarity of the effect of α on k_p of both AA and MAA at low monomer contents. Thus, in case of ionized monomer, charged TS species (for propagation) interact with the charged environment such as to induce hindrance to rotational motion of the TS structure. The effect is particularly pronounced at low MAA-in-water concentrations. Other than with the situation of nonionized MAA in aqueous solution, high contents of ionized MAA, which are associated with high concentrations of counterions, give rise to a screening of charges that is accompanied by a reduction of the hindrance to rotational motion and thus by an increase of k_p toward higher MAA content at $\alpha = 1$. Propagation with ionized MAA additionally differs from the one with nonionized MAA in that the activation energy, $E_A(k_p)$, tends to decrease toward higher ionic strengths.

The MAA data should provide a sound basis for analysis of k_p of acrylic acid in aqueous solution upon variation of α, weight fraction of AA, and polymerization temperature. Propagation with acrylic acid is further complicated by the occurrence of 1,5-hydrogen shift reactions,[27] which are associated with changing a secondary chain-end radical into a tertiary midchain radical. The reverse process occurs by addition of a monomer molecule to a midchain radical. Both types of radicals largely differ in propagation rate coefficient. They are simultaneously present at typical reaction temperatures with their relative amounts varying as a function of polymerization conditions.

Conclusion

The propagation rate coefficient, k_p, for the initial low-conversion period of aqueous-solution polymerizations of methacrylic acid has been measured for MAA weight percentages up to 40%, for degrees of monomer ionization between zero and unity, and at temperatures from 6 to 80 °C by pulsed laser polymerization in conjunction with aqueous-phase size-exclusion chromatographic analysis of polyMAA. Starting from dilute solution (5 wt %) of nonionized MAA, k_p may be reduced by approximately 1 order of magnitude by either increasing MAA up to bulk MAA polymerization conditions or by passing to fully ionized MAA (but remaining at 5 wt % MAA). The variation of k_p with degree of ionization, α, at each of the three MAA contents under investigation (5, 20, and 40 wt %) is almost insensitive toward polymerization temperature, which suggests that the reason behind the enormous effects of monomer concentration and monomer ionization is mostly of entropic origin. The pre-exponential factor in the Arrhenius expression is affected by intermolecular interactions giving rise to a hindrance of internal rotational mobility of the transition state structure for propagation. Such hindrance can be induced by both intermolecular hydrogen-bonded interactions (in nonionized MAA) and electrostatic attractive interactions of partially and fully ionized carboxylic acid groups in the MAA moieties. The influence of dissociation is primarily discussed with respect to ionic dissociation of the MAA monomer. The dissociation state of partially ionized polyMAA under the influence of the attached counterions has not been considered in any detail, as this aspect is difficult to be understood at the polymerization conditions investigated in this work.

The k_p data for an extended range of polymerization conditions, $0 \le \alpha \le 1$, $0.05 \le w_{MAA}^0 \le 0.40$, and $6 \le T/°C \le 80$, have been fitted to an empirical expression, which allows for representation of the experimental k_p values measured at 60 different reaction conditions within the extended α, w_{MAA}^0, and T range with a square-root mean deviation of 10.5%, which is below the uncertainty associated with PLP–SEC determinations.

Supporting Information Available: Tables of propagation rate coefficients. This material is available free of charge via the Internet at http://pubs.acs.org.

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