Propagation Kinetics of Free-Radical Methacrylic Acid Polymerization in Aqueous Solution. The Effect of Concentration and Degree of Ionization

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Summary: Propagation rate coefficients, k_p, of free-radical methacrylic acid (MAA) polymerization in aqueous solution are presented and discussed. The data has been obtained via the pulsed laser polymerization – size-exclusion chromatography (PLP-SEC) technique within extended ranges of both monomer concentration, from dilute solution up to bulk MAA polymerization, and of degree of ionic dissociation, from non-ionized to fully ionized MAA. A significant decrease of k_p, by about one order of magnitude, has been observed upon increasing monomer concentration in the polymerization of non-ionized MAA. Approximately the same decrease of k_p occurs upon varying the degree of MAA ionization, α, at low MAA concentration from $\alpha = 0$ to $\alpha = 1$. With partially ionized MAA, the decrease of k_p upon increasing MAA concentration is distinctly weaker. For fully ionized MAA, the propagation rate coefficient even increases toward higher MAA concentration. The changes of k_p measured as a function of monomer concentration and degree of ionization may be consistently interpreted via transition state theory. The effects on k_p are essentially changes of the Arrhenius pre-exponential factor, which reflects internal rotational mobility of the transition state (TS) structure for propagation. Friction of internal rotation of the TS structure is induced by ionic and/or hydrogen-bonded intermolecular interaction of the activated state with the molecular environment.

Keywords: aqueous-phase polymerization; free-radical polymerization; methacrylic acid; PLP-SEC; propagation rate coefficients; pulsed-laser initiation; water-soluble monomers

Introduction

Water-soluble homopolymers and copolymers are of high technical importance because of their wide-spread application in hydrogels, thickeners, viscosifiers, flocculants, membranes, coatings, etc.[1] Mostly, these polymers are obtained from free-radical polymerization in aqueous solution. Water-soluble monomers of particular technical relevance are acrylic acid, acrylamide, 2-acrylamido-2-methylpropane sulfonic acid, *N*-*iso*-propyl acrylamide, *N*,*N*′-dimethylacrylamide, methacrylic acid, dimethylamino-ethyl methacrylate, *N*-vinyl amides, *N*-vinyl pyrrolidone, *N*-vinyl formamide, *N*-vinyl imidazole, *N*-methyl-*N*-vinyl imidazolinium chloride. Investigations into the free-radical rate coefficients for polymerizations of these monomers in aqueous as well as organic solutions are scarce.[2] Significant changes of the rate coefficients are expected as a consequence of the action of hydrogen bonds between monomer, polymer, growing radicals, and water. The complexity may be further

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enhanced in case that ionic interactions come into play which requires to additionally consider the degree of ionization for monomer, polymer, and free-radical species and the associated ionic interactions.

The first studies into the kinetics of free-radical polymerization in aqueous phase date back to the work of Katchalsky and coworkers in the early 1950s.[3] In the 1970s and 1980s, polymerizations in aqueous solution were investigated by the Russian school, as reviewed by Gromov et al.[4,5] Generally, polymerizations in aqueous solution are characterized by strongly enhanced polymerization rates as compared to reactions in organic phase. The higher rates were assigned to the increased reactivity of monomer with a radical upon solvation by water. Also association of species, conformation of polymer coils, and hydrophobic interactions were assumed to govern free-radical polymerization rates in aqueous solutions.[5] The arguments were mostly based on measured overall rates of polymerization. A few individual rate coefficients have been determined by combining stationary methods with the instationary rotating sector technique. The quality of so-obtained data may however be rather insufficient, in particular in cases where the radical concentrations and radical size distributions are clearly different for the underlying two experiments.[6] Reported data thus exhibit an enormous scatter. The propagation rate coefficients for non-ionized acrylic acid (AA) in aqueous solution at ambient temperature that were available in the year 2000, differed by orders of magnitude. A value of $4\,000\ \text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ has been deduced from post-polymerization experiments,[7] whereas $k_p = 27\,000\ \text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ has been obtained via the rotating sector technique,[8,9] and $k_p = 92\,000\ \text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ was determined by pulsed-laser polymerization in conjunction with size-exclusion chromatography (PLP-SEC).[10] Obviously, such a large spread in reported k_p values is undesirable and poses problems for modeling acrylic acid polymerization processes in aqueous solution. The situation for most of the other water-soluble monomers was even worse at that time as no individual free-radical polymerization rate coefficients were available at all.

During recent years, the PLP-SEC technique has been used extensively for k_p measurements in aqueous phase and reliable k_p values[11] became available for AA,[10,12–14] methacrylic acid (MAA),[10,15,16] *N-iso*-propyl acrylamide (NIPAm)[17] and acrylamide (AAm).[18] The implementation of aqueous-phase SEC into PLP-SEC studies on water-soluble monomers[12] brought a significant improvement of k_p determination, as molecular weight distributions of polymer samples from PLP could be measured directly without the need for carrying out polymer modification reactions to produce samples which may be subjected to SEC analysis in organic phase.[10] Such polymer modification may give rise to changes of the size distribution and thus may result in unreliable k_p values.[12] Such an effect is more likely to occur with acrylates than with methacrylates. Recent PLP-SEC studies into k_p of non-ionized MAA in aqueous solution demonstrated that the k_p data deduced from aqueous-phase SEC[15] are in close agreement with the ones obtained from SEC in tetrahydrofuran on poly(methyl methacrylate) samples produced by methylation of poly(MAA) samples from PLP of MAA.[10] The data sets have been combined to form the first set of benchmark k_p values for a polymerization in aqueous solution.[16]

The PLP-SEC investigations into k_p of free-radical polymerization in aqueous phase suggest that k_p varies strongly with monomer concentration. For MAA,[10] NIPAm[17] and AAm[18] a strong decrease in k_p was found upon increasing monomer concentration. The same trend is seen for AA[13] from monomer concentrations of 3 wt.-% on, whereas at very low AA contents k_p increases with acrylic acid concentration. Attempts to assign the strong solvent effects to associated structures,[10] to dimerization,[17,18] or to local monomer concentrations at the radical site being different from overall monomer concentration[13] were unable to provide a consistent physical picture of the propagation kinetics.

In order to provide a comprehensive understanding of the effects of the solvent environment on k_p in aqueous-phase polymerization, it is highly recommendable to have reliable rate coefficient data for extended ranges of experimental conditions, in particular of temperature, monomer concentration, and degree of ionization. With acrylate-type monomers, PLP-SEC experiments are limited to lower temperatures because of the formation of mid-chain radicals, which disfavor k_p studies at temperatures well above ambient temperature.[19,20] No such restrictions occur with MAA, which appears to be a perfect monomer for fundamental studies into k_p for the following reasons: (*i*) The so-called backbiting reaction, by which mid-chain radicals are produced, does not occur. (*ii*) The k_p values of methacrylate-type monomers are such that suitable laser repetition rates for reliable PLP-SEC experiments are easily available. (*iii*) The poly(MAA) quantities produced during the PLP experiment are soluble within a wide range of MAA concentrations in water, from very dilute MAA solution up to the situation of MAA bulk polymerization. The first PLP-SEC studies into the temperature dependence of k_p for non-ionized MAA dissolved in water[10] were carried out at a single monomer concentration, of 15 wt.-% MAA, and the concentration dependence was mapped out only at 25 °C. Within our earlier work on k_p of non-ionized MAA in aqueous phase, monomer concentration was varied from 1 to 100 wt.-% MAA and the polymerization temperatures covered the range from 15 to 80 °C.[15] The present contribution extends this work to PLP-SEC studies in which, in addition to temperature and MAA concentration, the degree of ionic dissociation of MAA is varied. The experimental details and the extended body of individual k_p data measured under conditions of partial and full ionization will be presented elsewhere.[21]

Propagation Rate Coefficients for Aqueous-phase Polymerizations of Non-ionized Methacrylic Acid

Investigations into k_p of non-ionized MAA were carried out over the entire concentration range, between 1 wt.-% MAA in aqueous solution up to bulk MAA polymerization, at temperatures ranging from 15 to 80 °C.[15] Presented in Figure 1 is the variation of k_p with methacrylic acid concentration, c_{MAA}, at 60 °C. In going from the bulk system to 5 wt.-% MAA, k_p increases by one order of magnitude, from 1 200 to 12 300 $L \cdot mol^{-1} \cdot s^{-1}$. Corresponding changes of k_p with MAA concentration are observed for 25, 40 and 80 °C, where k_p data for several monomer concentrations was collected.[15] Similar trends have been seen with AA, where in experiments at and slightly below ambient temperature,[13] a decrease in k_p by a factor of three was found upon increasing the acrylic acid concentration in aqueous solution, c_{AA}, from 3 wt.-% to the highest experimentally accessible concentration of 40 wt.-%. Within these earlier experiments that were carried out within a narrower monomer concentration range, it appeared justified to assign the observed concentration dependence of k_p to a local monomer concentration at the free-radical site to be different from overall acrylic acid concentration.[13] In case of MAA, k_p could be measured over the entire concentration range from very dilute aqueous solution up to the bulk system. The data convincingly shows that local monomer concentration effects can not be made responsible for the observed order of magnitude change of k_p with MAA concentration.[15]

The extended temperature range of the experiments reported in Ref.[15] allows for reliably deducing Arrhenius factors, $A(k_p)$, and activation energies, $E_A(k_p)$, for a wide range of MAA concentrations. A single (mean) value of $E_A(k_p) = (15.6 \pm 1.1)$ $kJ \cdot mol^{-1}$ affords for a very satisfactory representation of the temperature dependence of k_p for the entire range from dilute aqueous solution (5 wt.-% MAA) to the bulk polymerization system.[15] Replacing

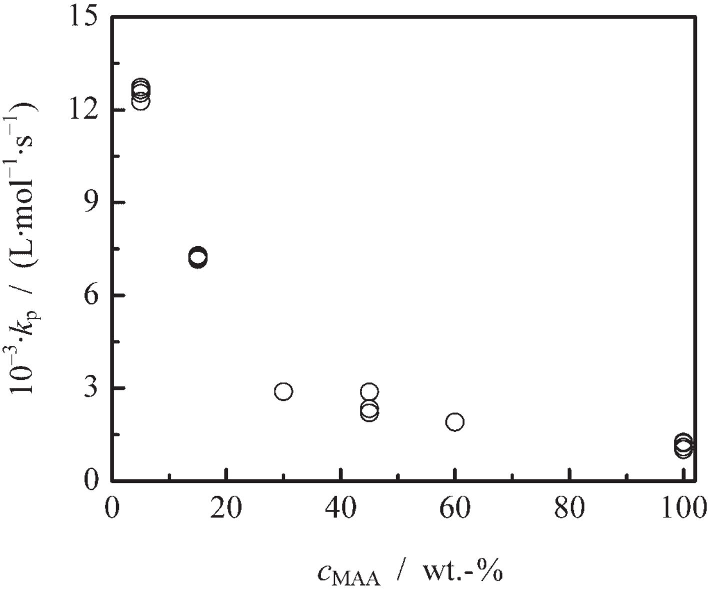

Figure 1.

Variation of k_p for methacrylic acid in aqueous solution as a function of monomer concentration, c_{MAA}. The data is from aqueous-phase PLP-SEC experiments at 60 °C tabulated in Ref. [15]

water molecules by MAA and vice versa thus does not affect the energy barrier for propagation. The large variation of k_p with c_{MAA} may be unambiguously assigned to effects on the pre-exponential factor.

Although $E_A(k_p)$ and $A(k_p)$ are determined as correlated parameters from Arrhenius fitting of experimental rate coefficient data, both parameters constitute independent physical quantities and may be separately deduced from transition state theory. The pre-exponential factor is determined by the geometry of the rotating groups and by the rotational potentials of the relevant internal motions of the transition state structure.[22,23] These internal motions of the transition state structure are schematically represented by the arrows in Figure 2. There is an internal rotational motion around the terminal C–C bond of the macroradical, a rotation around the C–C bond that is formed during the propagation step, and a bending motion associated with this new C–C bond. The shaded area represents the environment consisting of varying amounts of MAA and water molecules which may interact with the internal motions of the TS structure via hydrogen bonds. The pre-exponential factor, $A(k_p)$, of MAA free-radical propagation in dilute aqueous solution is significantly higher than in MAA bulk polymerization, e.g., is $4.62\cdot10^6$ L·mol^{-1}·s^{-1} for 5 wt.-% MAA as compared to $0.38\cdot10^6$ L·mol^{-1}·s^{-1} in case of bulk MAA polymerization

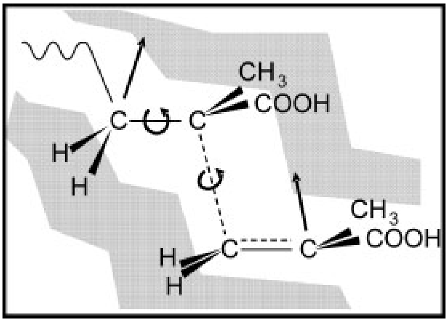

Figure 2.

Illustration of the transition state (TS) structure for the propagation step in MAA polymerization. The arrows indicate rotational and bending motions of the TS structure. The internal rotational motions of the TS structure are affected by hydrogen bonded interactions with the molecular environment (shaded area).

Table 1.
Arrhenius parameters, $A(k_p)$ and $E_A(k_p)$, for bulk polymerizations of methacrylic acid (MAA), methyl methacrylate (MMA) and methyl acrylate (MA) and for polymerizations of MAA and AA in aqueous solution. Bulk polymerizations are indicated by monomer concentrations of $c_M = 100$ wt.-%.

	c_M/wt.-%	$E_A(k_p)$/kJ · mol^{-1}	$A(k_p) \cdot 10^{-6}$/L · mol^{-1} · s^{-1}	Ref.
MAA	5	16.5	4.62	[15]
MAA	15	14.5	1.33	[15]
MAA	100	16.1	0.38	[15]
MMA	100	22.4	2.67	[24]
AA	20	11.9	12.0	[12]
AA	40	12.2	8.9	[12]
MA	100	17.7	16.6	[25]

(see Table 1). This comparison indicates that the internal rotational mobility of the transition state for propagation is higher at larger water contents. The lower rotational mobility in case of bulk polymerization is indicative of stronger hydrogen bonding interactions of the transition state structure with an environment that essentially consists of MAA molecules.

It is instructive to compare the Arrhenius parameters for k_p of MAA in bulk and in aqueous solution with the corresponding parameters for methyl methacrylate (MMA) and methyl acrylate (MA) bulk polymerizations as well as for AA polymerizations in aqueous solution. Listed in the upper part of Table 1 are the numbers for the methacrylic monomers, MAA and MMA, whereas the values for AA and MA are given in the lower part.

The first three entries in Table 1 illustrate that the activation energy for MAA propagation, $E_A(k_{p,MAA})$, is almost insensitive toward the molecular environment, whether the solvent is pure MAA (entry 3) or whether it is mostly water (entry 1). The pre-exponential factor, $A(k_{p,MAA})$, on the other hand, is enhanced by about one order of magnitude in passing from pure MAA to an environment essentially consisting of water. The pre-exponential, $A(k_{p,MAA})$, at low MAA concentrations, in between 5 and 15 wt.-% is close to the pre-exponential reported for methyl methacrylate bulk polymerization, $A(k_{p,MMA})$, listed as entry 4 in Table 1. Taking MAA bulk polymerization as a reference, this finding indicates that the pre-exponential factor and thus internal rotational motion are enhanced to similar extents by either changing the environment of the TS structure from pure MAA to an H_2O/MAA mixture containing about 10 wt.-% MAA or by methyl esterifying all carboxylic acid groups and thus transfer an MAA bulk polymerization into an MMA bulk polymerization in which hydrogen bonds will be absent. Despite the similarity in pre-exponential factor, the latter two systems, bulk MMA and aqueous solution MAA (10 wt.-%) polymerization clearly differ in activation energy, which is by about 6 kJ · mol^{-1} lower with the MAA system(s).

For AA, bulk polymerization parameters are not accessible because of the insolubility of poly(AA) in its own monomer. The $E_A(k_{p,AA})$ values for polymerization in aqueous solution containing 20 and 40 wt.-% AA (entries 5 and 6 in Table 1), respectively, are both close to 12 kJ · mol^{-1}. It appears reasonable to assume that a value of this size should also apply to bulk AA polymerization. Thus, also with the acrylic systems, the value of the acid monomer, $E_A(k_{p,AA})$, would be by about 6 kJ · mol^{-1} below the methyl ester value, $E_A(k_{p,MA})$, which indicates a similar effect of the hydrogen bonded interactions on the activation barrier for the propagation reaction upon passing from MAA to MMA and from AA to MA. It should be noted that the quantum-chemical calculations in Ref.[26] predicted a lowering of $E_A(k_{p,AA})$ upon introducing a water solvent field as compared to $E_A(k_{p,AA})$ in the gas phase. These calculations, however, did not consider the influence of the monomer solvent field nor of mixed water/monomer solvent fields. Our experimental data indicates that the acid monomer is capable of lowering the reaction barrier by approximately the same extent as do water molecules. Also for the AA polymerizations in aqueous solution, the pre-exponential largely increases toward lower monomer concentration (see entries 5 and 6 in Table 1). At AA concentrations below 20 wt.-%, the pre-exponential factor may approach the value reported for bulk methyl acrylate polymerization, in close agreement with the observation for $A(k_p)$ of bulk MMA polymerization and polymerization of MAA in aqueous solution at MAA contents of about 10 wt.-%. The similarity seen with the propagation rate coefficients of the two carboxylic acid monomers in aqueous solution provides further support for assigning the change in k_p to the internal rotational mobility of the TS structure due to friction induced by hydrogen bonding interactions with the molecular environment.

In MMA and MA no such hydrogen bonds are operative. The distinct difference in the pre-exponential for bulk polymerization of these two monomers (see entries 4 and 7 in Table 1), however also originates from effects on internal rotational mobility. The lower value of $A(k_{p,MMA})$ is due to enhanced *intramolecular* friction induced by the α-methyl groups on the polymer backbone.

The studies into k_p of non-ionized MAA suggest that the strong dependence of k_p values on monomer concentration that has been observed for other water-soluble monomers in aqueous-phase polymerization [10,13,17,18] is most likely also a genuine kinetic effect. The measured propagation rate coefficients should be regarded as "true" k_p values rather than as "apparent" rate coefficients which are associated with local monomer concentrations being largely different from the easily accessible overall monomer concentrations. It goes without saying that no firm conclusions about the k_p behavior of other water-soluble monomers can be drawn on the basis of the MAA data. For example, the observed insensitivity of $E_A(k_{p,MAA})$ toward the MAA to water ratio of the polymerizing system must not hold for other water-soluble monomers, as the interactions of the TS structure with monomer molecules and with water molecules may be rather different. The variation of $E_A(k_p)$ and $A(k_p)$ thus needs to be separately investigated for each monomer system by careful PLP-SEC measurements within extended temperature and concentration intervals.

Having realized that k_p varies with the MAA to H_2O ratio, immediately raises the question whether and to which extent the change in monomer concentration during polymerization to higher degrees of monomer conversion may affect k_p. As PLP-SEC experiments have to be carried out at low degrees of monomer conversion, the situation of high conversion has to be simulated by adding polymer to the PLP system prior to laser pulsing. The data from such experiments on methacrylic acid polymerization in aqueous solution are presented and discussed in another paper contained in this volume.[27]

The following section addresses the impact of ionic dissociation of MAA on the propagation kinetics in aqueous solution at different monomer concentrations. The primary intention of these studies is to find out whether the preceding kinetic analysis, which assumes *intramolecular* rotational mobility of the TS structure and thus the pre-exponential factor being affected by strong *intermolecular* interactions, is also suitable for interpreting free-radical propagation of ionized MAA in aqueous solution.

Propagation Rate Coefficient in Aqueous Solution of Partially and Fully Ionized Methacrylic Acid

Methacrylic acid in aqueous solution is a weak acid with a pK_a value of ~4.36.[3] Thus, the degree of ionization, α, is below 1 mol.% within the entire range of MAA concentrations. Adding a base, e.g., sodium hydroxide, to the system enhances the p*H* and produces anionic carboxylate groups. Thus, MAA is an excellent candidate for studying radical propagation rate coefficients at different extents of ionic dissociation. Charged carboxylate groups may occur with the monomer, the polymer, and the growing radicals. In addition, the system contains counter-ions, e.g., sodium cations, in case of using NaOH for partial or complete neutralization. Depending on the molar ratio of the base and the monomeric acid, PLP-SEC experiments may be carried out over an extended range of degrees of ionization, from $\alpha = 0$ to $\alpha = 1$. Neutralization appears to be a rather simple procedure, but it needs to be taken into account that the pK_a values of MAA and poly(MAA) are different. Thus, full ionization of the monomer does not necessarily mean that also poly(MAA) is fully ionized. Moreover, the effects of counter-ions are difficult to be adequately described for the high molecular weight polymer. In addition, the structure and the dynamics of charged macroradical species may significantly affect the polymerization kinetics.

Until recently, the knowledge about the polymerization kinetics and mechanism of ionized (meth)acrylic acid was based on a very limited set of rate coefficients from the pioneering studies,[3,28] in which the rate of polymerization was measured for various p*H* values. Only recently, the first PLP-SEC study was carried out for 5 wt.-% acrylic acid at 6 °C over the full range from $\alpha = 0$ to $\alpha = 1$.[14] In going from non-ionized to fully ionized AA, an approximately ten-fold decrease in k_p, from 111 000 to 13 000 $L \cdot mol^{-1} \cdot s^{-1}$, was observed. The lowering in k_p was explained by repulsive interactions between negatively charged macroradicals and monomer molecules, following the line of arguments put forward earlier.[3,28] It was, however, clear[14] that this limited set of PLP-SEC data will not be sufficient to answer the various questions concerning the effects on k_p due to ionic speciation, to counter-ions, to electrochemical equilibria, to acid-base properties of monomer, macroradical, and polymer, to the ionic strength, and perhaps to local monomer concentration.

Obviously, more experimental data for wider ranges of temperatures and monomer concentrations are required to arrive at a better understanding of the mechanism of free-radical polymerization in partially and fully ionized systems. Acrylic acid is no perfect monomer for kinetic studies in wide ranges of experimental conditions. As in the case of PLP-SEC studies into k_p of non-ionized monomers, methacrylic acid is a better choice also for investigations into ionized systems within extended temperature and monomer concentration ranges. For MAA, k_p values were measured at monomer concentrations, c_{MAA}, between 5 and 40 wt.-% and at temperatures from 6 to 80 °C over the entire range of MAA ionization, between $\alpha = 0$ and $\alpha = 1$.[21] The experimental procedure is similar to the one used in the experiments on aqueous solutions of AA at different degrees of ionic dissociation.[14]

For polymerizations at 40 °C, the dependence of k_p on monomer concentration, between 5 and 40 wt.-% MAA, is illustrated for different degrees of monomer ionization ($\alpha = 0$, 0.7, and 1.0) in Figure 3. The concentration dependence of k_p for non-ionized MAA (that is moving along line 1 in Figure 3) has been discussed in the preceding section. At $\alpha = 0.7$, the decrease of k_p with c_{MAA} is much weaker than at $\alpha = 0$. For $\alpha = 1.0$ (that is along line 3 in Figure 3), the situation is reversed in that k_p even increases with c_{MAA}. This effect is weak but can be safely established. The approximately ten-fold decrease in k_p from $\alpha = 0$ to $\alpha = 1$ at c_{MAA} of 5 wt.-% is indicated by the arrow (2) in Figure 3. An analogous order-of-magnitude change of k_p upon passing from the non-ionized to the fully ionized acid monomer has been observed for acrylic acid polymerization in aqueous solution at 5 wt.-% AA.[14] The lowering of k_p with α becomes less pronounced toward higher c_{MAA}, and k_p is insensitive toward the degree of ionic dissociation at 40 wt.-% MAA, as is indicated by point (4) in Figure 3. In view of the strong variations

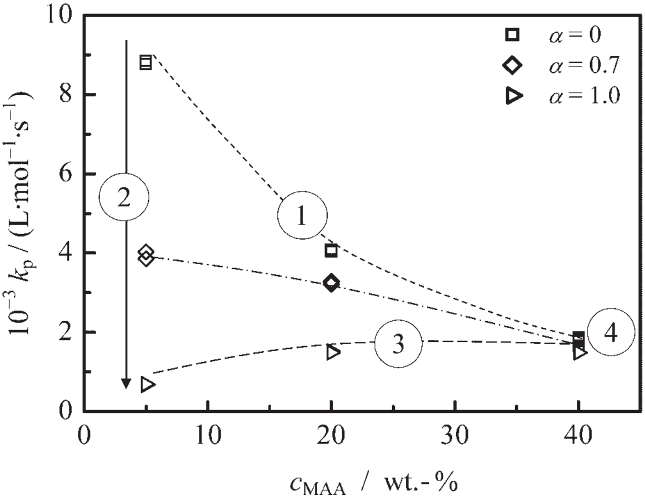

Figure 3.
Dependence of the free-radical propagation rate coefficient, k_p, of methacrylic acid polymerization in aqueous solution on monomer concentration, c_{MAA}, between 5 and 40 wt.-%. Data are presented for three degrees of monomer dissociation, $\alpha = 0$, 0.7, and 1. The polymerization temperature was 40 °C. The numbers 1, 2, 3 and 4 in the figure are referred to in the text.

of aqueous-phase k_p as a function of both α and c_{MAA} monomer concentration, this latter observation appears to be particularly noteworthy. It says that introducing negative charges on the monomer and on the growing radicals does not lower k_p due to increasing repulsive interactions, what one would intuitively assume.

Attempts to quantitatively determine the extent of ionic dissociation of all relevant species including macroradicals and polymer molecules and to correlate such speciation with the variations observed for k_p is difficult, if not impossible, in view of the complex acid-base properties and polyelectrolyte behavior as well as the coupled electrochemical equilibria.[21] Studies into polyelectrolyte behavior in aqueous solution carried out so far,[1,29] have been performed at conditions precisely defined with respect to solvent composition, ionic strength, concentration regime, and molecular weight. These conditions differ from the ones met in the actual free-radical polymerization experiments presented in Figure 3 and in Reference [21]. Despite this complexity, it has been realized[21] that with all the aqueous solutions of partially and fully ionized MAA under investigation the concentration of ionized monomer providing the ionic strength is above 0.1 mol · L^{-1}. According to the existing knowledge about polyelectrolytes in aqueous solution, such an ionic strength is sufficient to effectively screen ionic interactions.[30] As a consequence, repulsive interactions should not result in a distinct decrease of k_p toward higher degrees of ionization. This conclusion is supported by the experimental observation that an increase of ionic strength, by adding sodium chloride to an aqueous solution of 5 wt.-% MAA, does not affect the k_p.[21]

Rather than trying to assign the measured changes in k_p to the complex polyelectrolyte behavior and in particular to repulsive interactions, it seems recommendable to follow the line of arguments presented in the section on k_p of non-ionized MAA. In the preceding section, variations by one order of magnitude of k_p have been assigned to different extents of attractive intermolecular interactions between the TS structure for propagation and the molecular environment. These changes essentially affect the pre-exponential factor, whereas the activation energy within the limits of experimental accuracy remains constant. It appears reasonable to assign the variations induced by ionizing MAA, which at low c_{MAA} also extend over one order of magnitude, to the same genuine kinetic effect. This strategy is supported by the fact that, at least up to $\alpha = 0.7$, the activation energy, $E_{\mathrm{A}}(k_{\mathrm{p}})$, is not significantly changed by the degree of MAA ionic dissociation and stays close to the value obtained for non-ionized MAA.[21]

Within the framework of the kinetic analysis applied to non-ionized MAA, which assigns the change in k_{p} essentially to an effect on the pre-exponential, $A(k_{\mathrm{p}})$, the significant drop in k_{p} upon increasing α at 5 wt.-% MAA (see Figure 3), is attributed to an increased friction to internal rotation of the relevant degrees of rotation in the TS structure for MAA due to attractive interactions of the anionic carboxyl groups with the counter-ions in the molecular environment. Toward increasing c_{MAA}, this effect becomes less pronounced because of increasing ionic strength (at identical α). The slight increase with MAA concentration of k_{p} for $\alpha = 1$ (along line 3 in Figure 3) may be understood as resulting from an increased flexibility of polymer chains upon increasing the ionic strength in passing from 5 to 40 wt.-%, which reduces friction of internal rotational motion. The interesting situation met at 40 wt.-% MAA, where k_{p} is more or less independent of the degree of ionization (point 4 in Figure 3) suggests that, with reference to propagation of non-ionized MAA in dilute aqueous solution, an aqueous-phase environment containing 40 wt.-% fully ionized MAA has the same effect on the (ionized) TS structure for propagation as has an environment of 40 wt.-% non-ionized MAA on the associated non-ionized TS structure.

Because of solubility restrictions, PLP-SEC experiments on aqueous solutions of MAA at concentrations above 40 wt.-% and α approaching unity were not successful so far. Within further experiments attempts will be made to extend the $c_{\mathrm{MAA}} - \alpha$ range for PLP-SEC experiments. Of particular interest are polymerization conditions under which an increase of ionic dissociation of MAA, at constant overall c_{MAA}, may enhance k_{p}. Such kind of investigations should help to provide a general understanding of the k_{p} behavior of water-soluble monomers in aqueous solution.

Conclusions

PLP-SEC studies into the propagation rate coefficient of MAA in aqueous solution at 40 °C reveal that starting from a dilute solution of non-ionized MAA ($\alpha = 0$) both an increase of MAA concentration up to MAA bulk polymerization, at $\alpha = 0$, as well as an increase of the degree of ionic dissociation up to $\alpha = 1$, at 5 wt.-% MAA, result in a significant drop of k_{p}, by about one order of magnitude. Under conditions of full ionization of MAA, $\alpha = 1$, k_{p} slightly increases upon enhancing MAA concentration. At an MAA concentration of 40 wt.-%, within experimental accuracy, k_{p} is insensitive toward the degree of ionic dissociation of MAA. The experimental findings on the influence of c_{MAA} and α on k_{p} of MAA may be consistently interpreted within the framework of transition state theory. The effects are primarily assigned to interactions of the transition state structure for propagation with the molecular environment. Ionic interactions as well as hydrogen-bonded interactions significantly affect the pre-exponential factor, $A(k_{\mathrm{p}})$, whereas the activation energy, $E_{\mathrm{A}}(k_{\mathrm{p}})$, remains almost constant. The availability of reliable k_{p} values for MAA in aqueous solution at widely differing concentrations and degrees of ionization allows for estimating additional rate coefficients from coupled kinetic parameters (such as termination and transfer coefficients), for describing and optimizing polymerization kinetics, and for predicting polymer properties. Studies into the free-radical polymerization of other water-soluble monomers, which are currently underway, will reveal whether and to which extent the variations of k_p measured for MAA generally apply for free-radical polymerization of water-soluble monomers in aqueous solution.

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