Propagation Rate Coefficient of Non-ionized Methacrylic Acid Radical Polymerization in Aqueous Solution. The Effect of Monomer Conversion

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Summary: The propagation rate coefficient, k_p, of methacrylic acid (MAA) in aqueous solution is strongly dependent on monomer concentration.[1–3] Pulsed laser polymerization (PLP) at 25 °C and ambient pressure in conjunction with polymer analysis via size-exclusion-chromatography (SEC) was used to study whether k_p also depends on monomer conversion. As the applicability of the PLP-SEC method is restricted to polymerization up to a few per cent of monomer conversion, situations of higher monomer-to-polymer conversion were achieved by adding to the MAA solution either (*i*) commercially available high-molecular-weight poly(MAA) or (*ii*) *iso*-butyric acid (IBA), which serves as a model component for an associated polymer with chain length unity. Within these experiments, the overall carboxylic acid concentration has been kept constant at 20 wt.-%. Under these conditions, k_p of MAA turns out to be independent of the relative amounts of MAA and IBA, at least up to MAA:IBA ratios of 1:3, whereas k_p increases by 60 per cent upon replacing half of the MAA content by poly(MAA), which situation corresponds to about 50 per cent monomer conversion in MAA polymerizations with initial MAA contents of 20 wt.-%. This k_p value for 50 per cent conversion is close to the one obtained for PLP-SEC experiments at initial MAA concentrations of 10 wt.-%. The presence of poly(MAA) thus does not affect k_p, whereas the IBA content has a similar effect on k_p as has MAA concentration. The behaviour is understood as a consequence of IBA becoming part of the solvent environment at the radical site within the macroradical coil, whereas addition of poly(MAA) does not affect this intra-coil environment. This finding bears important consequences for the modeling of MAA polymerizations carried out at different initial MAA concentrations and up to different degrees of monomer conversion.

Keywords: conversion dependence; laser-induced polymerization; methacrylic acid; propagation kinetics; water-soluble polymers

Introduction

Free-radical polymerization in aqueous solution is of significant industrial importance. To model polymerization processes and product properties, reliable rate coefficients for the individual reaction steps are required. The propagation rate coefficient, k_p, may be precisely obtained by the PLP-SEC method, which combines pulsed-laser initiated polymerization with subsequent

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analysis of the produced polymer by size-exclusion chromatography.[4] So far, studies into radical polymerizations in aqueous solution resulted in k_p values for non-ionized methacrylic acid (MAA)[1–3] and acrylic acid (AA),[1,5,6] as well as for acrylamide[7] and N-*iso*-propyl acrylamide,[8] but also for ionized AA[9], where the *p*H and hence the degree of ionization was controlled by the addition of sodium hydroxide. As a general trend, k_p of non-ionized monomers dissolved in water was found to decrease toward higher monomer concentration. Association in the aqueous phase,[1] in particular dimerization,[7,8] and local monomer concentrations significantly differing from overall monomer concentration,[6] were proposed as being responsible for the observed behaviour. None of these arguments, however, could provide a satisfactory explanation. MAA polymerization allows for an extended testing of effects on k_p. Particular advantages of this system relate to the fact that PLP-SEC measurements in aqueous phase may be carried out over the full concentration range of non-ionized MAA, between 1 wt.-% MAA up to MAA bulk polymerization, and over a wide temperature range, from 20 to 80 °C.[2] Intermolecular interaction of the transition state structure for MAA propagation with the MAA-water solvent environment was shown to be responsible for the strong effects of MAA concentration on k_p, e.g., for the reduction in k_p by about one order of magnitude in going from very dilute aqueous solution of non-ionized MAA to bulk MAA polymerization. In view of these large changes in k_p with MAA concentration, the question arises whether and to which extent k_p varies during polymerization to higher conversion, which is also associated with large changes in MAA concentration. PLP-SEC studies are restricted to the initial polymerization period up to a very few per cent conversion.[4] As propagation is considered to be chemically controlled, the low-conversion k_p values from PLP-SEC, are assumed to stay constant up to high conversions and viscosities.[10] Via ESR, this assumption has already been proven for styrene[11] and methyl methacrylate[12,13] polymerization in non-polar solutions. Because of the large changes of k_p in aqueous solution of non-ionized MAA, this assumption can not necessarily be adopted for MAA-water systems.

Our preceding kinetic studies into the aqueous-phase polymerization of AA with propionic acid[6] being present and also into the polymerization of 2-acrylamido-2-methylpropane sulfonic acid (AMPS) up to high degrees of monomer conversion[14] provided some indication that k_p depends on the total concentration of carboxylic groups, which may be part of the monomer, the polymer, or a carboxylic acid co-solvent, rather than only on monomer concentration. The PLP-SEC-derived k_p values for AA were lowered upon increasing the concentration of propionic acid[6] and k_p for AMPS, as obtained from a combination of the single pulse (SP)-PLP technique with chemically initiated polymerization, appeared to be independent of monomer conversion.[14]

In order to deduce PLP-SEC-based information on the dependence of k_p on monomer conversion, the present study addresses k_p measurements for MAA in the presence of poly(MAA) and of *iso*-butyric acid (IBA). The latter component represents the saturated analogue of MAA and thus may be looked upon as the associated ''polymer of chain length unity''. The PLP-SEC experiments have been carried out at 25 °C and ambient pressure on aqueous MAA solutions to which different amounts of poly(MAA) or of IBA have been added. The mixtures were prepared such that the overall concentration of carboxylic acid, irrespective of the COOH groups being part of the monomer, the polymer, or the *iso*-butyric acid, is fixed at 20 wt.-%. Within each PLP-SEC experiment, only a small fraction of the MAA is polymerized, such as to obtain an amount of PLP-induced poly(MAA) which is sufficient for SEC analysis.

Experimental Part

Materials

Methacrylic acid (MAA) (Fluka, >98% stabilized with 0.025% hydrochinon monomethylether), the photoinitiator 2,2-dimethoxy-2-phenylacetophenone (DMPA, Aldrich, 99%), poly(methacrylic acid) (poly(MAA), Polysciences, lot# 547 827, 5% water) and *iso*-butyric acid (IBA, Fluka, p.a., >99.5%) were used as supplied. Demineralized water was used for preparing the reaction solutions.

Preparation of Solutions

Solutions with added poly(MAA) were prepared by dissolving poly(MAA) in demineralized water overnight. No such extended pre-mix times were required for addition of IBA. The monomer MAA was added by using a stock solution of DMPA in MAA and pure MAA such as to adjust the DMPA concentration to 2 $\text{mmol} \cdot \text{L}^{-1}$ for all polymerization reactions. Adding up to 10 wt.-% of poly(MAA) yields homogeneous solutions with viscosities being sufficiently low to allow for easy handling.

PLP-SEC Conditions

Details of the PLP experiments on aqueous solutions of non-ionized MAA are reported in ref. [2]. The polymerizations were carried out in a in a QS 110 cell (Hellma-Worldwide) of 10 mm path length. The reaction solutions were purged with nitrogen for 4 min and thermostated for 20 min prior to PLP. For each mixture, at least two PLP experiments were performed. To reach monomer conversions up to 5%, between 25 and 300 pulses were applied. Monomer conversion was determined by weighing the polymer after freeze-drying. The polymer molecular weight distribution was determined via aqueous-phase SEC[2] using two injections for each sample.

Selection of PLP Conditions

The molecular weight distribution (MWD) of the commercial poly(MAA) that was added to the initial solution in some of the PLP experiments is shown in Figure 1. Although the MWD is relatively broad ($M_n = 55\,000$ $\text{g} \cdot \text{mol}^{-1}$, $M_w = 370\,000$ $\text{g} \cdot \text{mol}^{-1}$, polydispersity index = 6.7), inflection points of PLP-produced samples may be clearly identified, if they occur at molecular weights below 30 000 $\text{g} \cdot \text{mol}^{-1}$. According to ref. [2], the molecular weights for the primary inflection points, M_1, in aqueous-phase polymerizations at MAA contents of 20 wt.-% should be located at ~20 000 $\text{g} \cdot \text{mol}^{-1}$ for a pulse repetition rate of 40 Hz. Under such conditions even secondary points of inflection, M_2, may be observed. Also on the basis of the experience from ref.[2], the initial DMPA concentration was chosen to be $c_{\text{DMPA}} = 2$ $\text{mmol} \cdot \text{L}^{-1}$. Within the MAA polymerizations in the presence of IBA, a laser pulse repetition rate of 20 Hz was used.

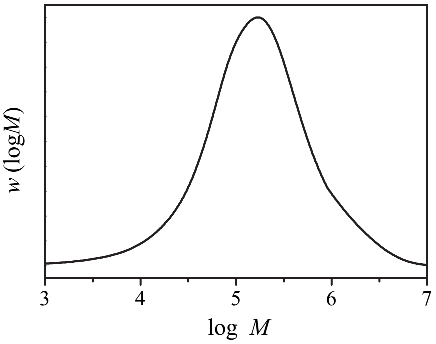

Figure 1.
Molecular weight distribution of the commercial poly(methacrylic acid) which was added to some of the aqueous solutions of non-ionized MAA prior to PLP.

Results and Discussion

The aim of the present work was to study the dependence of the propagation rate coefficient, k_p, of MAA in aqueous solution on monomer conversion. As the powerful SEC-PLP method is restricted to experiments at low degrees of monomer conversion, situations occurring during polymerization were simulated by pre-mixing either poly(MAA) to the initial reaction mixture or by adding IBA, which may be considered as a hypothetical "poly(MAA)" of chain length unity. Both components have been added such as to reach an overall carboxylic acid concentration of 20 wt.-%. The so-prepared solutions are subjected to pulsed laser polymerization such that MAA conversions of a very few per cents are reached. The k_p values were calculated according to:

$$L_1 = k_p \cdot c_M \cdot t_0 \tag{1}$$

where L_1 is the degree of polymerization at the first point of inflection (POI) on the low molecular weight side of the polymer from PLP, c_M is the MAA monomer concentration, and t_0 is the dark-time between two successive laser pulses, which is identical to the inverse of laser pulse repetition rate. The occurrence of at least one higher-order inflection point at about twice the chain length of the first point of inflection serves as a consistency criterion for reliable k_p measurement.[15] Monomer concentrations were calculated from density data as detailed in ref.[2]. It was assumed that the densities of poly(MAA) and monomeric MAA are the same and that the temperature dependence of IBA density is identical to that of MAA. The error in k_p estimates due to these assumptions is small as compared to the accuracy of PLP-SEC determinations, which is illustrated by the scatter of the k_p data reported below.

Aqueous-phase Polymerization of MAA in the Presence of IBA

Table 1 collates the experimental conditions and k_p values obtained for MAA polymerization in aqueous phase with added IBA. The experiments have been carried out at 25 °C and ambient pressure using a laser pulse repetition rate of 20 Hz, an initiator concentration of $c_{\mathrm{DMPA}} = 2\ \mathrm{mmol \cdot L^{-1}}$ and a constant overall acid concentration of 20 wt.-%. The virtual conversion, X_{virtual}, has been estimated under the assumption that the added saturated acid, IBA, has been produced by preceding polymerization of MAA. The PLP-induced conversion, X_{PLP} (in per cent), is always below 6%. To account for changes in MAA concentration during laser pulsing, the relevant monomer concentration in Table 1, c_{MAA}, is calculated as the arithmetic mean of MAA concentrations before and after PLP. The virtual conversion, X_{virtual}, is determined according to Eq. (2):

$$X_{\mathrm{virtual}} = \left(1 - \frac{c_{\mathrm{MAA}}}{c_{\mathrm{MAA}} + c_{\mathrm{IBA}}}\right) \cdot 100\% + \frac{X_{\mathrm{PLP}}}{2} \tag{2}$$

The first two entries in Table 1 refer to polymerizations without pre-mixed IBA. The virtual conversion, X_{virtual}, thus is given by 50 per cent of the monomer conversion due to laser pulsing, X_{PLP}. The ratios of the peak positions of the first and second POI, and thus M_1/M_2 in Table 1, are mostly close to 0.5, indicating the reliability of k_p determination. Only at the highest virtual conversion, of about 75%, the M_1/M_2 ratio differs by more than 20% from 0.5. Within part of these experiments at high IBA content, no second maximum in the first-derivative curve of the MWD is seen but only a shoulder. The first POI of the MWD is significantly reduced toward increasing X_{virtual}, that is toward lower MAA concentration. The k_p values are however more or less independent of virtual conversion.

Aqueous-phase Polymerization of MAA in the Presence of Poly(MAA)

Within the PLP-SEC experiments on non-ionized MAA in the presence of poly(MAA), the determination of points of inflection, via the maxima in the associated first-derivative curves of the MWD, is complicated by the pre-mixed polymer which obviously can not be removed prior to SEC analysis. Figures 2 and 3 depict MWDs (A) and the associated first-derivative curves (B) of polymer samples obtained by PLP-induced polymerizations of 15 wt.-% MAA dissolved in water containing 5 wt.% of pre-mixed polymer and of 10 wt.-% MAA dissolved in water containing 10 wt.-% of pre-mixed polymer, respectively. The full lines (a) represent the polymer sample after pulsed laser polymerization, whereas the dashed

Table 1.
Experimental details of pulsed-laser induced polymerizations of methacrylic acid (MAA) in aqueous solution with *iso*-butyric acid (IBA) being added. The IBA content is expressed by a virtual conversion, X_{virtual}, which considers the amount of IBA as being produced from MAA by polymerization. The overall concentration of MAA + IBA is 20 wt.-% in all these experiments. Pulsed-laser polymerizations were performed at 25 °C and ambient pressure using a photoinitiator (DMPA) concentration of $c_{\text{DMPA}} = 2$ mmol · L^{-1} and a laser pulse repetition rate of 20 Hz. Listed in the columns are the virtual degree of monomer conversion, X_{virtual}, the MAA concentration, c_{MAA}, (see text), the number of applied laser pulses, the PLP-induced monomer conversion, X_{PLP}, the molecular weight at the first point of inflection (POI), M_1, the ratio of MWs at the first and second POIs, and the resulting propagation rate coefficient, k_p.

X_{virtual}/%	c_{MAA}/mol · L^{-1}	*number of laser pulses*	X_{PLP}/%	M_1/g · mol^{-1}	M_1/M_2	k_p/L · mol^{-1} · s^{-1}
2.6	2.29	150	5.2	35 890	0.50	2 903
2.6	2.29	150	5.2	38 370	0.50	3 104
15.7	1.99	150	6.0	33 730	0.50	3 133
15.7	1.99	150	6.0	33 650	0.50	3 126
13.6	2.04	75	1.9	32 810	0.49	2 983
13.6	2.04	75	1.9	34 120	0.49	3 102
13.5	2.04	50	1.6	33 810	0.49	3 070
13.5	2.04	50	1.6	34 120	0.50	3 098
27.5	1.73	100	5.1	29 920	0.50	3 203
27.5	1.73	100	5.1	29 850	0.50	3 195
27.4	1.73	70	3.3	29 040	0.49	3 113
27.4	1.73	70	3.3	30 340	0.51	3 252
27.1	1.73	45	2.6	29 440	0.51	3 144
27.1	1.73	45	2.6	29 040	0.49	3 101
38.3	1.46	40	1.6	25 760	0.49	3 277
38.3	1.46	40	1.6	25 650	0.49	3 262
38.1	1.46	60	1.3	25 820	0.49	3 280
38.1	1.46	60	1.3	25 700	0.49	3 265
50.6	1.17	40	1.4	21 430	0.48	3 400
50.6	1.17	40	1.4	20 510	0.47	3 255
51.1	1.16	60	2.4	20 940	0.48	3 339
51.1	1.16	60	2.4	20 650	0.49	3 293
77.6	0.57	50	5.3	10 330	0.41	3 348
77.6	0.57	50	5.3	10 140	0.40	3 287
77.2	0.57	70	4.5	9 860	0.40	3 184
77.2	0.57	70	4.5	10 020	0.39	3 236
75.9	0.59	25	2.6	10 160	SH	3 190
75.9	0.59	25	2.6	10 450	SH	3 279

[SH] The overtone position, L_2, only shows up as a shoulder in the first-derivative curve of the MWD.

lines (b) are MWDs measured on the commercial (pre-mix) poly(MAA). Subtraction of MWD (b) from (a), which was carried out via the WinGPC®7.20 software employed for SEC data acquisition and evaluation, yields polymer trace (c) as the MWD of the PLP-produced sample. The MWD (c) in Figure 2 shows a typical PLP-type structure. Also with the PLP-SEC data depicted in Figure 3, the PLP structure is better seen from curve (c) obtained by the subtraction procedure. The improved detection of PLP-induced structure from MWD curves after applying the subtraction procedure is also evidenced by the first-derivative plots shown in Figures 2B and 3B. In case of 50% virtual conversion (Figure 3), subtraction of the MWD for the pre-mixed polymer is necessary for identification of the POIs.

Table 2 summarizes the experimental results for polymerizations of MAA in the presence of pre-mixed poly(MAA) at 25 °C and ambient pressure, a laser repetition rate of 40 Hz, an initiator concentration of $c_{\text{DMPA}} = 2$ mmol · L^{-1}, and a constant overall acid concentration of 20 wt.-%. Subtraction of the MWD for the pre-mixed polymer from the overall MWD measured on the sample from PLP allows for precisely detecting the M_1 and M_2 positions. The propagation rate coefficient clearly

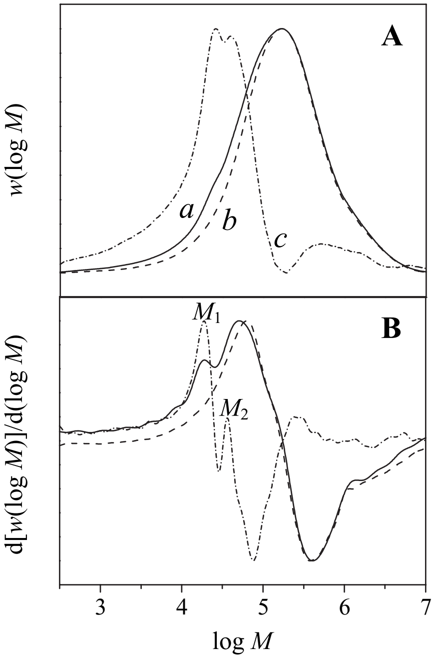

Figure 2.
Molecular weight distributions (MWD) **(A)** and associated first-derivative curves **(B)** for samples from PLP-induced polymerization (at 25 °C and 40 Hz) of 15 wt.-% of non-ionized methacrylic acid (MAA) in aqueous solution containing 5 wt.-% poly(MAA). The full line (a) refers to the polymer sample from PLP-SEC, the dashed line (b) represents the pre-mixed poly(MAA), and the dashed-dotted line (c) is obtained by subtracting (b) from (a).

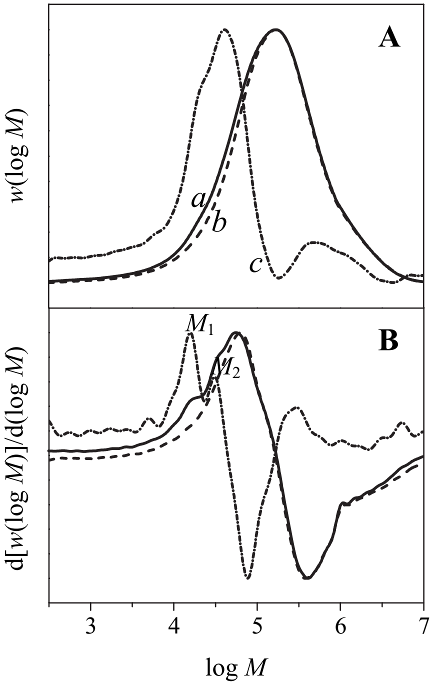

Figure 3.
Molecular weight distributions (MWD) **(A)** and associated first-derivative curves **(B)** for samples from PLP-induced polymerization (at 25 °C and 40 Hz) of 10 wt.-% methacrylic acid (MAA) in aqueous solution containing 10 wt.-% poly(MAA). The full line (a) refers to the polymer sample from PLP-SEC, the dashed line (b) represents the pre-mixed poly(MAA), and the dashed-dotted line (c) is obtained by subtracting (b) from (a).

increases toward higher degrees of (virtual) monomer conversion, by about a factor of 1.6 in going from 0 to 10 wt.-% pre-mixed poly(MAA) at constant overall concentration of MAA units. This behavior is in contrast to what has been observed in the experiments with pre-mixed IBA, where no significant change of k_p was seen.

Discussion

The numbers in Tables 1 and 2 demonstrate that under conditions of constant overall acid concentration (20 wt.-%), which closely corresponds to a constant overall content of (non-ionized) carboxylic acid groups, the replacement of MAA monomer by IBA leaves k_p of MAA constant, whereas the replacement of MAA monomer by poly(MAA) enhances k_p. The latter observation is consistent with the finding from PLP-SEC experiments on aqueous MAA solutions (without any added carboxylic acid groups), that lowering the MAA content results in a higher k_p.[2] The experimental findings are illustrated in Figure 4, where k_p of MAA is plotted vs. virtual MAA conversion for a constant overall acid concentration of 20 wt.-%. This unusual way of representing k_p solution data requires some further explanation. The k_p data for values of X_{virtual} around 2 to 3 per cent (diamonds) are from experiments on aqueous MAA solutions containing 20 wt.-% MAA, but no added further carboxylic acid groups (as are contained in IBA or in poly(MAA)). The

Table 2.

Experimental details of pulsed-laser induced polymerizations of methacrylic acid (MAA) in aqueous solution with poly(MAA) being added. The overall concentration of MAA + poly(MAA) is 20 wt.-% in all experiments. Pulsed-laser polymerizations were performed at 25 °C and ambient pressure using a photoinitiator (DMPA) concentration of $c_{DMPA} = 2$ mmol · L^{-1} and a laser pulse repetition rate of 40 Hz. Listed are the virtual degree of monomer conversion, $X_{virtual}$, the MAA concentration, c_{MAA}, the number of applied laser pulses, the molecular weight (MW) at the first point of inflection (POI), M_1, and the ratio of MWs at the first and second POI. The final column contains the resulting propagation rate coefficients, k_p.

$X_{virtual}$/%	c_{MAA}/mol · L^{-1}	*number of laser pulses*	M_1/g · mol^{-1}	M_1/M_2	k_p/L · mol^{-1} · s^{-1}
1.0	2.35	150	19 815	0.52	3 120
1.0	2.35	150	20 370	0.53	3 208
1.7	2.35	300	20 464	0.53	3 223
1.7	2.35	300	20 606	0.53	3 245
27.5	1.76	150	18 967	0.52	3 983
27.5	1.76	150	19 364	0.53	4 066
27.5	1.76	300	18 707	0.51	3 928
28.3	1.76	300	18 793	0.52	3 946
56.4	1.18	150	16 181	0.53	5 096
57.1	1.18	300	15 740	0.51	4 958
57.1	1.18	300	16 144	0.52	5 085

associated value of $X_{virtual}$ is thus given by 50 per cent of the MAA conversion brought upon by pulsed laser polymerization.

The triangles refer to PLP-SEC experiments on aqueous MAA solutions with different amounts of added IBA. The $X_{virtual}$ values around 75% refer to experiments on 1:3 mixtures of MAA:IBA at an overall concentration of 20 wt.-% carboxylic acid (MAA + IBA). The virtual conversion thus is made up of a conversion of MAA to an associated "polymer of chain-length unity" plus a small poly(MAA) production by PLP. Toward increasing IBA

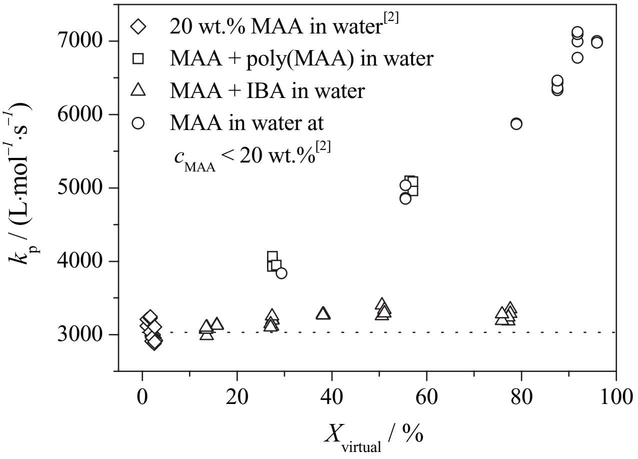

Figure 4.

Dependence of k_p on virtual conversion, $X_{virtual}$, for polymerizations of methacrylic acid in water at 25 °C and ambient pressure. The diamond symbols refer to polymerization of MAA (20 wt.-%) in aqueous solution without any added carboxylic acid groups (partially taken from ref.[2]). The squares and the triangles represent aqueous-phase polymerizations of MAA in the presence of poly(MAA) and IBA, respectively, at overall concentration of 20 wt.-% carboxylic acid. The k_p values indicated by the circles are taken from ref.[2]. They refer to polymerization of MAA in aqueous solution at concentrations below 20 wt.-% (for a more detailed explanation see text). The dotted line indicates the mean value of low conversion k_p at 20 wt.-% MAA in aqueous solution (this work and ref.[2]).

content, k_p slightly increases. This effect however occurs within the accuracy of PLP-SEC measurements which is estimated to be ±15 per cent for this particular system.

The k_p values of MAA measured in the presence of poly(MAA), indicated by the square symbols, grow significantly with $X_{virtual}$. Within this series of experiments, conversion during an MAA polymerization in aqueous solution of MAA, is simulated by pre-mixing poly(MAA) and by simultaneously lowering MAA monomer concentration of the solution subjected to PLP such that the overall content of MAA units stays at 20 wt.-%.

Also included in Figure 4, as circles, are propagation rate coefficients from ref.[2] for aqueous MAA solutions without added acid. These values are truly virtual in that they are estimated for the hypothetical situation that conversion is only reflected in a reduction of MAA monomer concentration without any polymeric MAA units being produced. Virtual conversion was calculated such that the MAA to water ratio is identical to the one of a reference experiment for an initial monomer concentration of 20 wt.-% in which MAA is actually transformed into polymeric MAA units. Thus the virtual conversion for a PLP-SEC experiments on an aqueous solution containing 10 wt.-% MAA slightly exceeds 50 per cent, as otherwise the MAA monomer to water weight ratio would be 1:9 instead of 1:8, which is the ratio for a polymerization to 50 per cent conversion starting from an initial concentration of 20 wt.-% MAA. The three types of experiments, indicated by the triangles, squares, and circles, have in common, that identical virtual conversion is associated with the same MAA to water ratio. The circles demonstrate that the reduction in MAA concentration significantly enhances k_p.

The close agreement of the MAA k_p values in the presence of poly(MAA) with the ones in aqueous MAA solution of identical monomer concentration (without added carboxylic acid groups, circles in Figure 4) indicates that polymeric MAA units do not contribute to changes of k_p. As has been detailed in ref. [2], the propagation rate coefficient of non-ionized MAA in aqueous solution is strongly enhanced toward lower monomer concentration due to weaker intermolecular interactions of the transition state structure with a molecular environment in which carboxylic acid groups are replaced by water molecules. The lower friction of internal rotational motion of the transition state structure in more dilute MAA solution is associated with a higher pre-exponential factor. In an MAA-rich environment, on the other hand, the strong hydrogen-bonded interactions between the carboxylic acid groups lead to significant friction and to a lowering of the pre-exponential factor in the Arrhenius expression for k_p. IBA which is structurally rather close to MAA, obviously has a similar effect on k_p of MAA as has MAA itself. Thus replacing MAA by IBA at constant overall acid concentration has no significant effect on MAA k_p. That poly(MAA) has not the same effect on MAA k_p as has IBA and, to be more precise, has no detectable effect on MAA k_p, indicates that the addition of poly(MAA) is not felt at the reactive site, which is the free-radical functionality of a growing macroradical. The free-radical site is imbedded into the solvent-swollen macroradical coil, which is not or not to a significant extent penetrated by another polymeric coil. Thus the solvent environment of the radical site is not affected by adding polymer. As a consequence, also the effect of solvent friction on the transition structure for propagation remains unchanged. On the other hand, changing the reacting system by adding monomeric carboxylic acid, e.g. MAA or IBA, changes the solvent quality and thus the microscopic environment within the coil. If the two acids are of similar structure, as is the case with MAA and IBA, the k_p value, to a first approximation, depends on overall carboxylic acid concentration, but is insensitive toward the relative amounts of two such acids.

These findings have particularly important consequences for the modeling of polymerization kinetics in aqueous solution, where the concentration dependence of k_p is pronounced. For an estimate of the impact of carboxylic acid concentration on k_p of MAA it needs primarily to be considered whether the carboxylic acid groups (other than of the MAA monomer) are capable of affecting the intra-coil environment of the radical site. Along these lines, k_p of MAA may have a specific chain-length dependence and may be affected by the MWD of produced polymer, in particular by the amount of oligomeric products that may contribute to the intra-coil environment of the growing macroradicals. If an MAA polymerization exclusively produces high molecular weight material, only monomer concentration needs to be taken into account for assessing k_p. It appears to be a matter of priority to carry out further PLP-SEC experiments with different types of carboxylic acids being added and to extend the studies to other acid monomers, with particular interest in acrylic acid.

Conclusion

The propagation rate coefficient, k_p, of methacrylic acid (MAA) in aqueous solution is known to strongly depend on MAA concentration. Within the present study, PLP-SEC experiments have been carried out on aqueous solutions of non-ionized MAA to which either *iso*-butyric acid (IBA) or poly(methacrylic acid) have been added. Enhancement of overall acid concentration by adding low molecular weight IBA lowers k_p of MAA, whereas the addition of poly(MAA) has no significant effect on k_p. The different impact of low and high molecular weight carboxylic acid species on MAA k_p is understood as being due to IBA becoming part of the solvent environment at the radical site of the growing chain, whereas the addition of poly(MAA), is not reflected in the intra-coil solvent environment. This finding has important consequences for modeling the kinetics of MAA solutions at different initial monomer concentrations and degrees of monomer conversion.

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