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Polymerization of ionic monomers in polar solvents: kinetics and mechanism of the free radical copolymerization of acrylamide/acrylic acid

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Abstract

A precise data set describing the kinetics of the free radical copolymerization of acrylamide/acrylic acid (AM/AA) in the range of low total monomer concentration as a function of the pH, total monomer concentration, initiator concentration, and comonomer ratio is presented. Strong impact on the reactivity ratios has been identified for the pH and total monomer concentration. Specifically, at constant total monomer concentration of 0.4 mol/l and $T = 313$ K the reactivity ratio of AM increases from 0.54 at pH 1.8 to 3.04 at pH 12. Contrarily, the reactivity ratio of AA decreases from 1.48 to 0.32. The crossover occurs at pH ≈ 4.2. Electrostatic effects due to the variation of the degree of ionization of AA are primarily suggested to influence the kinetics. When the total monomer concentration increases from 0.2 to 0.6 mol/l at constant pH = 12, the reactivity ratios of AM and AA decrease from 4.01 to 2.13 and increase from 0.25 to 0.47, respectively. Reduction of electrostatic repulsion between the ionized monomer AA and partially charged growing polymer chain ends due to higher ionic strength at higher total monomer concentration serves as explanation of the effect. The precise data set is the prerequisite for a novel approach to calculate copolymer compositions in case of variable monomer reactivity.

Keywords: Copolymerization; Acrylic acid; Electrostatic influence

1. Introduction

Copolymers of acrylamide with ionic comonomers are of high interest for a multitude of industrial applications, and have been studied by academics [1]. Important application fields are aqueous solid–liquid separation, oil recovery, and water modification. Drag reduction agents, flocculants, thickeners, and friction reduction agents are specific examples [2,3]. Most of the polymers are produced by free radical polymerization. This technology has advantages such as versatility, simplicity, compatibility with many functional groups, tolerance to impurities as well as polar and non-polar polymerization media. As disadvantage, the copolymers obtained are, in general, heterogeneous with very limited control over the molar mass, constitution, and chain architecture. The growing market of well-defined materials has become the driving force for the renaissance to study free radical polymerizations in terms of both synthetic possibilities and mechanistic understanding [4].

Polymerization kinetics, and thus the final product characteristics, is influenced by a number of reaction parameters. Specifically, the pH and ionic strength become important when ionic or ionizable comonomers are involved. Traditional studies of synthetic possibilities and mechanistic understanding evaluate the influencing factors and the interrelations experimentally. Such studies may be time-consuming due to the high number of potential reaction conditions, in particular, when electrostatic influences have to be considered additionally.

Kinetics modeling appears as a useful tool to support the study of free radical polymerizations. It permits to predict final product characteristics, to establish or validate proposed reaction mechanisms, to determine properties unable to be measured directly, and, most importantly, to reduce experimental work. Nevertheless, the outcome of modeling strongly depends on the model quality as well as the quality of input data. Such data are available from the literature for a limited number of comonomer combinations

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only. Moreover, data of extremely broad fluctuation have frequently been reported. The latter is the case for the copolymerization of acrylamide (AM) and acrylic acid (AA) in aqueous media, which is of interest here.

Very different and strongly scattering copolymerization reactivity ratios of both monomers have been reported [5–9]. The effect of the pH on the kinetics and final copolymer structure has been studied without common agreement. Moreover, as to the authors' knowledge, there is no information about the influence of the total monomer concentration, ionic strength, and reaction rate on the kinetic parameters at high pH. Therefore, the paper will first summarize and review existing data in the introduction to reveal the experimental needs, before presenting results and conclusions.

Fig. 1 summarizes the reactivity ratios of AM (r_1) and AA (r_2) published by several authors covering the pH range from 2 to 9. At pH = 2, r_1 and r_2 range from 0.25 [5] to 0.6 [7] and from 0.79 [6] to 1.73 [9], respectively. The fluctuation of the values complicates and even prevents the selection of reliable reactivity ratios, and thus the formulation of recipes to produce polymers of well-defined charge density and homogenous charge distribution. Despite the fluctuations, a trend is visible with increasing pH; r_1 increases whereas r_2 decreases. The variation of the reactivity ratios with the pH is unanimously explained by electrostatic interaction between the partially charged growing polymer chain and the ionized monomer molecules.

The combination AM/AA has specific and partially unique characteristics. On the one hand, it presents an interesting and useful model for academic copolymerization studies. On the other hand, both the homopolymers and copolymers are of practical interest with productions in the thousands of tons scale. Both homo and copolymers were also subject of characterization studies [10,11]. The AM/AA system is particularly suited for basic studies and modeling. It offers the possibility to study, quantitatively, the effect of the degree of ionization of the monomer on the kinetics and mechanism of free radical polymerization in polar media. Moreover, the system is appropriate to investigate synergistic effects of monomer ionization and ionic strength in the polymerizing batch under variable reaction conditions including different initiator concentrations, total monomer concentrations, and relative monomer ratios. Recently, novel data have been published describing the homopolymerization of AA in detail and with high precision covering the pH range from 2.1 to 13.1 [12].

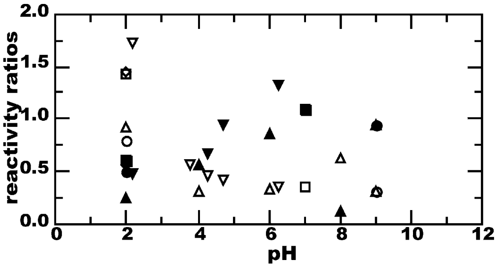

Fig. 1. Summary of published reactivity ratios of AM (full symbols) and AA (open symbols): (▲, △) [5], (●, ○) [6], (■, □) [7], (◆, ◇) [8] and (▼, ▽) [9].

The goal of the research performed here was to fill the existing experimental gap by performing copolymerizations at pH conditions for which data have yet not been reported including the extension of the pH range up to 12. Results will be presented, which, on the one hand, aim to extend the knowledge about the specific system AM/AA and to provide, on the other hand, input data of high reliability for the development of general kinetic models and mechanistic interpretations. More precisely, the data will serve as overall reference for binary monomer systems, which turn into ternary systems in a defined limited range of experimental conditions [13]. Experiments at relatively low monomer concentration appeared advantageous to avoid non-linearity of time-conversion curves in the initial phase and side effects due to viscosity. Finally, the results of this contribution can directly be used to formulate recipes and design charged copolymers.

2. Experimental

2.1. Materials

White crystals of ultra pure AM (monomer 1), four times recrystallized and AA (monomer 2), ultrapure (BASF, Germany), were selected as monomers. Special emphasis was given to the handling of AM, since AM is toxic in contact with skin and inhalation and may cause genetic damage. Potassium persulfate ($K_2S_2O_8$) puriss. >99% was used as initiator. NaOH and HCL were used for pH adjustment. The water had millipore quality (18.2 MΩ/cm), and methanol was HPLC grade. With the exception of AA, all chemicals were purchased from Axon Lab AG-Apply Chem, Switzerland.

2.2. Polymer synthesis

Polymerizations were performed in a 100-ml glass reactor equipped with stirrer, condenser, gas inlet and a heating/cooling jacket. A thermostat adjusted the reaction temperature within ±1 K. Oxygen was removed from the initial monomer solution prior to the polymerization by purging with N_2 during 30 min at 293 K. Afterward, the temperature was increased to 313 K to activate the thermal decomposition of $K_2S_2O_8$ and to initiate the polymerizations, which were performed isothermally at 313 K during 60 min. During the reaction, the reactor was continuously purged with N_2. Samples of 0.1–0.2 g were withdrawn each 5 min during 20 ± 5 s.

The influences of the pH, total monomer concentration ([AM] + [AA]), and initiator concentration ($[K_2S_2O_8]$), on the reactivity ratios of solution free radical copolymerizations of AM with AA have been studied. Table 1 summarizes the experimental conditions for all AM/AA copolymerizations.

2.3. Conversion analysis

The conversion of the copolymerization process was calculated from residual monomer concentration data. The residual monomer concentrations of withdrawn samples were obtained using a HPLC system composed of a L-7110 Merck-Hitachi pump (Hitachi, Japan) and a SP6 Gynkotek UV detector (Gynkotek, Germany) operating at 197 nm. The stationary and mobile phases were LiChrosphere 100 RP-18 (Merck, Germany) and 5 wt% acetonitrile aqueous solution with a flow rate of 1 ml/min. The samples were firstly mixed with a defined amount of methanol to precipitate and isolate the polymer from the solution. The residual monomer remains in solution. A defined portion of the supernatant was injected for HPLC analysis.

The HPLC system was calibrated using AM and AA standard solutions in the concentration range of 7×10^{-4} to 7×10^{-3} mol/l. The standard solutions were prepared by sequential dilutions of 1 mol/l stock solutions of AM and AA. The peak area served as calibration parameter. Fig. 2 shows typical calibration curves for both monomers, with $r^2\geq0.999$.

2.4. Calculation of copolymer compositions

The copolymer compositions were calculated from residual monomer concentration data. Statistic and chemically controlled copolymerizations follow the instantaneous copolymer composition equation, usually referred to as Mayo–Lewis equation, Eq. (1). The equation is accomplished by running polymerizations at low conversions, where the reaction conditions are assumed to be constant, i.e. minor changes of the monomer concentration can be neglected [14].

$$\frac{M_{\mathrm{AM}}^{\mathrm{P}}}{M_{\mathrm{AA}}^{\mathrm{P}}}=\frac{[\mathrm{AM}]\cdot(r_1\cdot[\mathrm{AM}]+[\mathrm{AA}])}{[\mathrm{AA}]\cdot([\mathrm{AM}]+r_2\cdot[\mathrm{AA}])} \tag{1}$$

Here, [AM] and [AA] are concentrations of AM and AA in the comonomer solution in mol/l. $M_{\mathrm{AM}}^{\mathrm{P}}$ and $M_{\mathrm{AA}}^{\mathrm{P}}$ are the molar fractions of the corresponding monomer units in the copolymer.

The incorporation of monomer units into the copolymer chains causes the loss of monomer molecules. If $[\mathrm{AM}]_i$ is the initial concentration of AM in the monomer solution and $[\mathrm{AM}]_\tau$ is the corresponding monomer concentration at a reaction time τ, the number of AM mols incorporated into the copolymer at τ is given by:

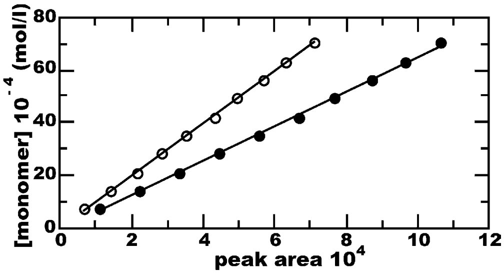

Fig. 2. HPLC calibration curves. The concentrations of standard solutions of AM (●) and AA (○) were plotted as a function of the corresponding HPLC peak areas.

$$[\mathrm{AM}]_\tau^{\mathrm{P}}=[\mathrm{AM}]_i-[\mathrm{AM}]_\tau \tag{2}$$

Differentiation of Eq. (2) yields:

$$\mathrm{d}[\mathrm{AM}]_\tau^{\mathrm{P}}=\frac{\mathrm{d}[\mathrm{AM}]_\tau}{\mathrm{d}t}\cdot\mathrm{d}t \tag{3}$$

Eq. (3) provides the instantaneous incorporation of AM monomer units into the copolymer at the reaction time τ. A corresponding expression can be derived for AA.

By definition, $M_{\mathrm{AM}}^{\mathrm{P}}$ is the number of AM units in the copolymer chain divided by the total number of monomer units:

$$M_{\mathrm{AM}}^{\mathrm{P}}=\frac{[\mathrm{AM}]^{\mathrm{P}}}{[\mathrm{AM}]^{\mathrm{P}}+[\mathrm{AA}]^{\mathrm{P}}} \tag{4}$$

Combining Eqs. (3) and (4), the instantaneous molar fraction of AM in the copolymers produced at the reaction time τ, can be expressed as a function of the actual rate of consumption of AM and AA from the solution:

$$M_{\mathrm{AM}}^{\mathrm{P}^\tau}=\frac{\mathrm{d}[\mathrm{AM}]_\tau/\mathrm{d}t}{(\mathrm{d}[\mathrm{AM}]_\tau/\mathrm{d}t)+(\mathrm{d}[\mathrm{AA}]_\tau/\mathrm{d}t)} \tag{5}$$

The residual monomer concentration in the withdrawn samples at different reaction times yields d[AM]/dt and d[AA]/dt. Consequently, the actual copolymer composition can be determined at any time of the copolymerization. The procedure is based on the assumption that side reactions have no considerable influence on the kinetics and copolymer composition.

Table 1
Copolymerization conditions

Series	[AM]+[AA] (mol/l)	[$K_2S_2O_8$] (mol/l)	pH
1	0.4	1.8×10^{-2}	$1.8\leq$pH≤12
2	$0.2\leq$[AM]+[AA]≤0.6	3.6×10^{-3}	12
3	0.4	$3.6\times10^{-3}\leq[K_2S_2O_8]\leq3.6\times10^{-2}$	12

Variation of the comonomer ratio: $0.14\leq$[AM]/[AA]≤7, with 7 different comonomer ratios for each series; reaction temperature: 313 K.

2.5. Calculation of reactivity ratios

Several authors have noted that the values of copolymerization reactivity ratios depend on the mathematical treatment of raw data [8]. In this contribution, the calculations of the reactivity ratios r_1 and r_2 were carried out using the Kelen–Tüdös equation [15]:

$$\frac{f\cdot(F-1)}{\alpha\cdot F+f^2}=\left(r_1+\frac{r_2}{\alpha}\right)\cdot\frac{f^2}{\alpha\cdot F+f^2}-\frac{r_2}{\alpha} \tag{6}$$

It is in Eq. (6) $\alpha=\sqrt{(f^2/F)_{\max}(f^2/F)_{\min}}$. For the system studied here, $f=M_{AM}/M_{AA}$ and $F=M^P_{AM}/M^P_{AA}$ are the molar ratio of the monomers in the comonomer solution and the molar ratio of the monomer units in the copolymer, respectively. M^P_{AM} and M^P_{AA} are defined by Eq. (4). M_{AM} and M_{AA} correspond to the experimental conditions selected.

3. Results

Three series of copolymerizations have been performed in the range of experimental conditions listed in Table 1. For each series one reaction parameter was varied, the pH, the total monomer concentration, or the initiator concentration, while copolymerizations were carried out at various monomer ratios.

3.1. Conversion analysis

Fig. 3 presents, exemplary, the experimental conversion analysis for AM/AA copolymerizations at pH = 12, [AM] + [AA] = 0.4 mol/l, $[K_2S_2O_8]=1.8\times10^{-2}$ mol/l, $T=313$ K, and four selected comonomer ratios. The residual monomer concentration is plotted as a function of the reaction time. For better visualization, only four monomer ratios have been selected out of seven performed under these reaction conditions. The continuous but different consumption of both monomers is clearly visible. At pH 12, whatever the monomer ratio is, it is obvious that AM is consumed much faster than AA.

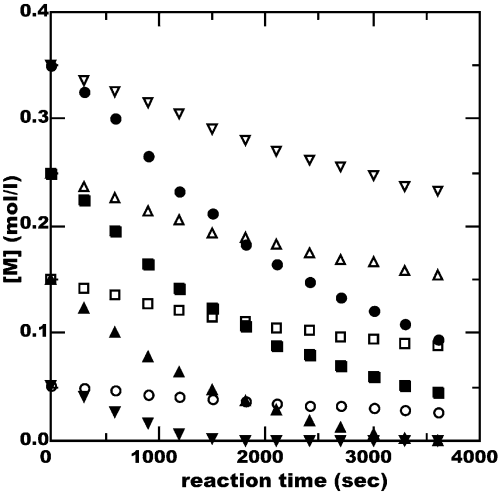

Fig. 3. Conversion analysis. Residual monomer concentration, [M] vs. reaction time curves. Residual [AM] (full symbols) and [AA] (open symbols) concentrations of polymerizations at different comonomer ratios (AM/AA) are plotted as a function of the reaction time. AM/AA = 0.14 (▼, ▽), 0.6 (▲, △), 1.66 (■, □), and 7(●, ○); $T=313$ K; pH = 12; [AM] + [AA] = 0.4 mol/l; $[K_2S_2O_8]=1.8\times10^{-2}$ mol/l.

3.2. Copolymerization diagrams and reactivity ratios

The acrylamide content of copolymers, M^P_{AM}, for all experimental M_{AM} has been calculated from the initial part of monomer conversion curves (Fig. 3) with the aim to plot copolymerization diagrams. Analyzing the monomer consumption allows the calculation of instantaneous copolymer compositions. Fig. 4 shows copolymerization diagrams at four different pH conditions. Appropriate Kelen–Tüdös plots are presented in Fig. 5, demonstrating good linearity as a prerequisite for the calculation of reliable reactivity ratios. All reactivity ratios r_1 and r_2 were calculated from linear regression of plots such as in Fig. 5 according to Eq. (6).

3.3. Influence of the pH

It is already qualitatively visible from the four selected copolymerization diagrams shown in Fig. 4 that the pH strongly influences the kinetics and, consequently, the copolymer composition. Table 2 summarizes the values of reactivity ratios for all nine pH conditions experimentally investigated sorted with increasing pH.

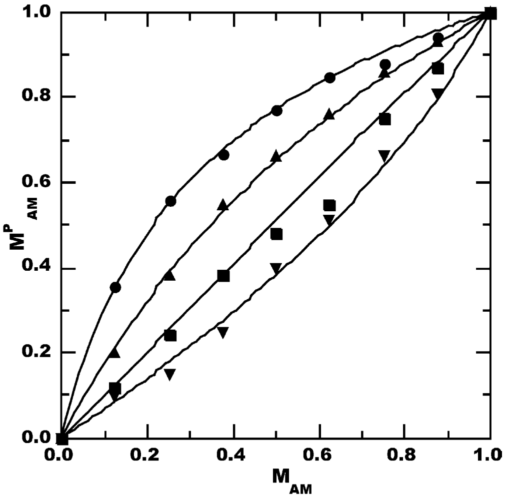

Fig. 4. Copolymerization diagram of AM and AA at different pH. Mol fraction of AM units in the copolymers (M^P_{AM}) plotted vs. the corresponding concentration of AM in the comonomer feeds (M_{AM}). pH = 1.8 (▼), 4.4 (■), 5.3 (▲), and 12 (●); $T=313$ K; [AM] + [AA] = 0.4 mol/l; $[K_2S_2O_8]=1.8\ 10^{-2}$ mol/l.

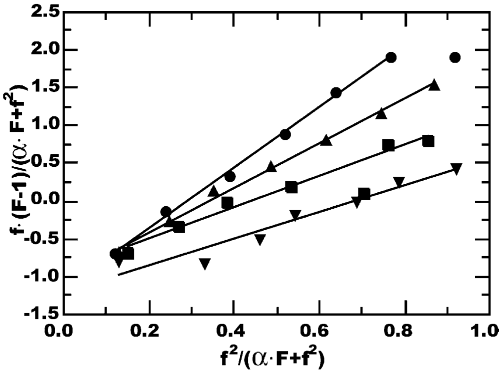

Fig. 5. Determination of reactivity ratios by the Kelen–Tüdös equation, Eq. (6). pH = 1.8 (▼), 4.4 (■), 5.3 (▲), and 12 (●) (highest value not used for regression); $T=313$, $[AM]+[AA]=0.4$ mol/l; $[K_2S_2O_8]=1.8\ 10^{-2}$ mol/l.

3.4. Influence of the total monomer concentration

A further dependency, which has been identified from series 2 in Table 1, concerns the influence of the total monomer concentration on the reactivity ratios. Fig. 6 summarizes results for five different total monomer concentrations in the range of 0.2–0.6 mol/l. Clearly, r_1 decreases and r_2 increases with the total concentration. Increasing the monomer concentration to study the influence of the ionic strength required the reduction of the initiator concentration for accurate analysis of the initial polymerization phase.

3.5. Influence of the initiator concentration

Despite it is well known that, in general, modification of the initiator concentration has no influence on the reactivity ratios, the copolymerization series 3 in Table 1 was performed. The initiator concentration was varied with the purpose to demonstrate the absence of any concentration dependent interaction of the ionic initiator with the fully ionized monomer. Moreover, the precision of the data analysis at considerably different reaction rate in the experimental range should be shown. As it was expected only fluctuations within the error range, but no systematic variation of the reactivity ratios has been found (Fig. 7) confirming the absence of initiator concentration influences.

Table 2
Reactivity ratios of AM (r_1) and AA (r_2) at different pHs. Reaction conditions: $T=313$ K, $[AM]+[AA]=0.4$ mol/l, and $[K_2S_2O_8]=1.8\times10^{-2}$ mol/l

pH	Reactivity ratios	
	r_1	r_2
1.8	0.54	1.48
2.7	0.69	1.34
3.6	0.82	1.28
4.4	1.27	0.91
5.3	1.83	0.51
6.2	2.50	0.39
7.8	2.95	0.42
8.8	3.05	0.42
12	3.04	0.32

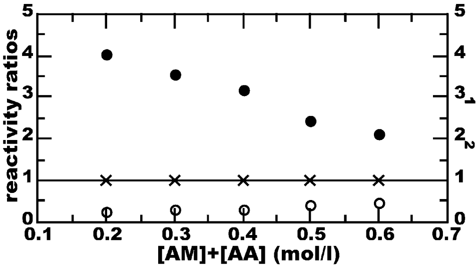

Fig. 6. Reactivity ratios, r_1 (●) and r_2 (○), and the product $r_1\times r_2$ (×) as a function of the total monomer concentration $[AM]+[AA]$. $T=313$ K, pH = 12, $[K_2S_2O_8]=3.6\times10^{-3}$ mol/l.

4. Discussion

The experimental findings summarized above will be analyzed and discussed in detail in the subsequent paragraphs. The pH dependence and data precision will be examined prior to focusing on the specific copolymerization behavior at pH 12.

4.1. Comparison of experimental results and literature data

Fig. 8 visualizes quantitatively the influence of the pH on the reactivity ratios with the aim to facilitate the comparison, data analysis, and interpretation. For better comparison the same scale as in Fig. 1 was applied.

Comparing the data of Figs. 1 and 8, similar trends for r_1 and r_2 as already published become visible. The new data clearly identify and confirm non-linearity for both the increase of r_1 and decrease of r_2 with the pH. Both reactivity ratios level off with increasing pH, in particular at pH > 8 for

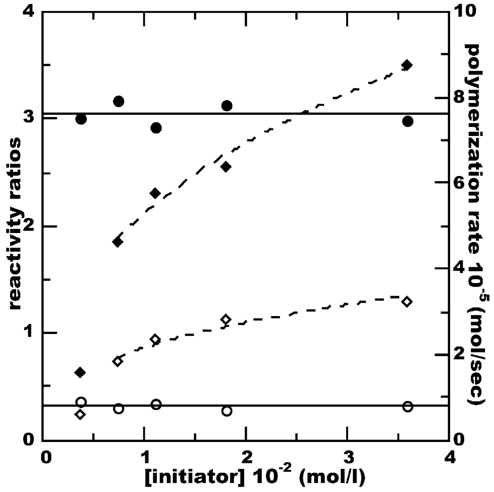

Fig. 7. Reactivity ratios, r_1 (●) and r_2 (○), as well as polymerization rates of AM (◆) and AA (◇) as a function of the initiator concentration. $[AM]=[AA]=0.2$ mol/l, $T=313$ K, and pH = 12. (The dashed lines are added to guide the eyes; full lines represent the average values).

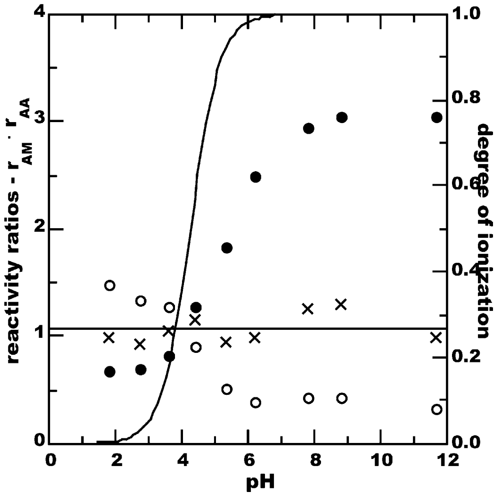

Fig. 8. pH dependence of the reactivity ratios, r_1 (●) and r_2 (○), the product $r_1 \times r_2$ (×), as well as the degree of ionization of AA (—). $T=313$ K, [AM]+[AA]=0.4 mol/l, $[K_2S_2O_8]=1.8 \times 10^{-2}$ mol/l. (The full line related to the product represents the average value).

r_1 and pH > 6 for r_2. Moreover, r_1 seems to reach constancy at pH < 3, too. The difference between the reactivity ratios at high pH is almost three times that at low pH. Both monomers present similar reactivity ratios at pH ≈ 4.2.

4.2. Experimental precision

High precision is claimed in the introduction. Therefore, experimental accuracy including error sources is briefly discussed. The residual monomer concentrations is affected by the following error sources: the preparation of AM and AA stock solutions, filling the reactor, withdraw of samples, addition of MeOH, dilution of the supernatant, and injection in the HPLC system. Considering all error sources, the relative errors of the residual monomer concentration values were estimated to be less than 2%. Consequently, the errors associated with comonomer and copolymer compositions were 0.15 and 3%, respectively. Propagation by the Kelen–Tüdös equation yields relative errors of 8.5% for r_1 and 3.8% for r_2. The error of r_1 is higher due to the higher polymerization rate of AM compared to AA, and thus the determination of d[AM]/dt becomes less precise.

Other error sources are comparably negligible. The solutions were freshly prepared and degassed at 293 K during 30 min to avoid initiator decomposition. The heating velocity was 10 K/min. Moreover, the batches were rigorously agitated during the reactions in a reactor having an area/volume ratio of 1.7 cm^{-1}. Good heat transfer guaranteed the absence of temperature gradients. The samples withdrawn from the reactor were immediately diluted in MeOH to terminate all reactions.

Furthermore, Fig. 9 illustrates the impact of the instantaneous monomer concentrations and monomer ratios on the calculation of the instantaneous copolymer composition and construction of the copolymerization diagrams. It

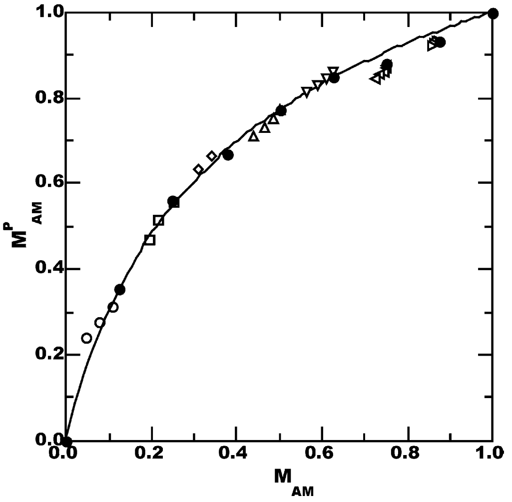

Fig. 9. Copolymerization diagram of AM and AA considering the instantaneous comonomer feed composition at various conversion. Mol fractions of AM in the copolymers (M^P_{AM}) plotted vs. the concentration of AM in the feeds (M_{AM}). Conversion: 0 (●), 0.05, 0.10, 0.15 and 0.20 (open symbols) for different initial AM/AA = 0.14 (○), 0.33 (□), 0.60 (◇), 1.00 (△), 1.66 (▽), 3.00 (◁), and 7 (▷), $T=313$ K; pH = 12; [AM]+[AA] = 0.4 mol/l; $[K_2S_2O_8]=1.8 \times 10^{-2}$ mol/l.

justifies the applicability of the calculation procedure considering the extrapolation from the initial phase based on analytical data such as presented in Fig. 3. The values plotted in Fig. 9 cover a conversion range up to 20% for each initial comonomer ratio. The deviations are acceptable as they are in the range of the general experimental error.

4.3. Influence of the pH

Strong influence of the pH on both reactivity ratios is clearly visible from Fig. 8. The main impact is expected from the degree of protonation/ionization of the monomers and the polymer chain units. In principle, three pH ranges may be distinguished.

Starting from low pH, it is $r_1 < r_2$, the values seem to level off, at least for r_1, at the lowest pH. Monomer solutions of pH lower than 1.8 could not be polymerized due to precipitation of AA. r_1 increases already at pH unessential higher than two whereas r_2 decreases. Crossover of both is observed at pH ≈ 4.2. It was reported at pH = 3.77 by Cabaness et al. [9]. Fig. 8 shows, in addition, the degree of ionization of the AA monomer as a function of the pH. The pK_a of AA (pK_a^{AA}), which has been reported as 4.25 in aqueous solution [16], corresponds to the crossover point. At this pH and polymerization conditions, the copolymerization may be classified as statistical due to $r_1 = r_2 = 1$ [14]. In the third range it becomes $r_1 \gg r_2$ for the total monomer concentration of 0.4 mol/l with both values leveling off.

Although not quantitatively understood, an explanation of the copolymerization behavior based on electrochemistry is offered. Employing the Henderson/Hasselbalch equation [17], the calculation yields that more than 99% of AA are neutral at pH below 2.2, and exclusively ionized, A^-, at $pH > 6.2$. In the medium range, pH 2.2 to 6.2, AA is coexisting with A^-. The range corresponds to the pH dependent variation of r_2 visible in Fig. 8, with the onset of constancy at $pH > 6$.

AM is coexisting with its protonated form at $pH < 2.0$ and seems to become fully neutral at $pH > 2.0$, likewise as polymer chain unit [9].

The pK_a of poly(acrylic acid) (pK_a^P) has differently been reported as 4.75 [18] and 6.40 [19], respectively. The difference may be due to different molar masses of the homopolymers analyzed. In general, higher molar mass AA homopolymers possess higher pK_a^P. Accordingly, the pK_a^P of AM/AA copolymers will shift depending on the molar masses and copolymer composition. Less ionized polymer chains can be expected at lower pH. Appropriately, the copolymers are assumed to reach the maximum ionization at pH above 8.4. Coexistence of AA and A^- as chain units can be concluded for $4.4 < pH < 8.4$ [17].

By definition, the reactivity ratios are $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$, the ratios of the rate constants of homopropagation (k_{11} and k_{22}) over the rate constants of cross-propagation (k_{12} and k_{21}). Electrostatic repulsion between protonated AM and the growing polymer chain are suggested to be the reason of the reduced reactivity of the macroradical towards AM in comparison to AA at low pH [9]. It is $k_{11} < k_{21}$ and $r_1 < 1$. Even $k_{22} > k_{12}$ and, therefore, $r_2 > 1$ may be concluded due to penultimate and antepenultimate effects, which have been reported for growing polymer chains containing protonated or ionized groups [20].

Increasing the pH suggests decrease of k_{12} and increase of r_1 while k_{11} can be assumed as constant. The decrease of k_{12} may be due to increasing electrostatic repulsion between the increasingly ionized AA monomer molecules and chain units. Although the effect is also expected to depend on the chain composition, i.e. penultimate and/or antepenultimate effects have to be considered, as it was found for the copolymerization of AM with other permanently charged monomers [20].

Considerable decrease of k_{22} with increasing pH is obvious and serves as explanation for the decrease of r_2. The strongest electrostatic repulsion and, therefore, hindrance is expected for the reaction between a fully ionized radical polymer chain end and A^-. Minor impact is expected on k_{21}, but it cannot completely be excluded [20].

The product of r_1 and r_2, with values equal or close to one, additionally plotted in Fig. 8, allows concluding ideal copolymerization behavior [14] independent of the pH. The deviations at $pH = 7.8$ and $pH = 8.8$ may result from slightly higher r_2 values at these pH. Ideal copolymerization does not imply homogeneous copolymer composition. Homogenous composition is only expected in the case of statistical copolymerization with $r_1 = r_2 = 1$, which was identified at $pH \approx 4.2$.

4.4. Influence of the total monomer concentration at pH = 12

The variation of r_1 and r_2 with the total monomer concentration at $pH = 12$ was presented in Fig. 6. Monomer solutions of concentrations higher than 0.6 mol/l exhibited strong increase of the viscosity already at low conversion preventing precise withdraw of small samples during the reaction. Therefore, copolymerization studies were limited to the range reported here.

Increasing the total monomer concentration, likewise the ionic strength of the medium becomes higher. Higher ionic strength is accompanied by lower Debye length with consequences for electrostatic interactions. Both the monomer and polymer chain unit charges become electrostatically more screened leading to reduction of electrostatic repulsion during chain propagation. r_1 decreases since k_{12} is expected to increase, and r_2 increases due to increasing k_{22}. Nevertheless, r_1 remains higher than r_2 and > 1 whereas r_2 does not exceed 1. As conclusion, $k_{11} > k_{12}$ and $k_{22} < k_{21}$ should further be valid. The total monomer concentration will consequently have a considerable impact on the copolymer composition.

The plot of the product $r_1 \times r_2 \approx 1$ clearly identifies the copolymerization as ideal for all monomer concentrations. This supports the conclusions from the appropriate plot in Fig. 8.

4.5. Influence of the initiator concentration at pH = 12

Generally, propagation may be initiator dependent during the addition of the first monomer units, but it becomes usually initiator independent as the polymer grows. This is confirmed in Fig. 7. Constant reactivity ratios with average values of $r_1 = 3.04$ (standard deviation 0.10) and $r_2 = 0.32$ (standard deviation 0.03) were obtained. Again, the product of the average reactivity ratios is close to one demonstrating no unusual influence of the initiator concentration.

5. Conclusions

The experimental results quantitatively reveal strong electrostatic influence on the free radical solution copolymerization of AM/AA over the total pH range where the system was polymerizable. Partial ionization of AA and the AM/AA copolymer in a defined range of the pH turns the system into a terpolymerization in that range. Demonstrating not only the influence of the pH but also the influence of the ionic strength provides information to which extent the copolymer composition can be modified varying the latter parameter. Moreover, as a general conclusion, the addition of low molar mass salt is recommended to cause decrease of r_1 and increase of r_2 in the high pH range. Simultaneously, the viscosity of the polymerizing system is expected to be lower, which will technologically be advantageous.

As to the authors' knowledge, the present work is the first study that reports quantitatively how r_1 and r_2 are affected by changes of the pH and total monomer concentration at very high pH. Despite r_1 and r_2 clearly level off in the range $8 < \mathrm{pH} < 12$, further variation of the reactivity ratios at $\mathrm{pH} > 12$ is expected due to considerable increase of k_{22}, the rate constant of A^- homopolymerization caused by addition of NaOH necessary to adjust the high pH [12]. Nevertheless, no effect of NaOH was confirmed up to pH 12. Overall, the data extend the knowledge about the copolymerization of AM/AA and provide input values for recipe formulations, further scientific studies, and process modeling [13]. Comparing the copolymerization of AM/AA with copolymerization of AM and other ionic comonomers [21–23] confirms its suitability as unique model system. The particularity is due to the precise adjustability of $r_1 > r_2$, $r_1 = r_2$, or $r_1 < r_2$ over a wide range by varying reaction conditions such as the pH and/or the ionic strength. Further studies have to quantify the impact of the ionic strength.

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