Approach To Predict Copolymer Compositions in Case of Variable Monomer Reactivity

Ignacio Rintoul and Christine Wandrey*

École Polytechnique Fédérale de Lausanne, Institut des Sciences et Ingénierie Chimiques, CH-1015 Lausanne, Switzerland

Received May 16, 2005; Revised Manuscript Received July 7, 2005

ABSTRACT: An analytical approach to predict copolymer compositions is presented for the particular case that the reactivity of one monomer (B) alters under the influence of one measurable medium parameter. Terpolymerization mathematical treatment was applied to binary systems (A/B), which turn into ternary systems (M_1, M_2, M_3) in a defined range between two extremes of the medium parameter. The approach needs as input data a relationship describing the coexistence of two derivatives (M_2, M_3) of B as a function of the influencing parameter, knowledge of homopolymerization kinetic data of B, and reactivity ratios, r_A and r_B, only at the extremes of the variable medium parameter. As a case study, the copolymerization of acrylamide/acrylic acid mixtures in aqueous medium was selected with the pH as variable parameter. Good agreement of predicted and experimental data was proved. The approach provides a useful tool to significantly decrease the number of polymerization experiments needed to identify the effect of medium parameters on the polymerization kinetics. The principle of the approach is proposed to treat any set of two monomers if one alters the characteristics under the influence of any measurable medium parameter.

Introduction

Free radical copolymerization is a well-established procedure to modify polymer properties by arranging different monomers in a polymer molecule. It has many advantages due to the versatility, applicability to many functional groups, certain tolerance to impurities, and practicability in both polar and nonpolar media. The final copolymer constitution and configuration primarily result from the reaction kinetics. Nevertheless, in any radical copolymerization process parameters such as pH, ionic strength, solvent composition, or temperature have the potential to influence the reaction path and thus the product characteristics. The influence of these factors and their interrelations may infinitely increase the number of reaction possibilities. Consequently, to evaluate the total number of potential conditions by experimental work can become extremely time-consuming. This situation is always a strong motivation to design models with the scope to better understand the impact of polymerization conditions on the ultimate copolymer properties.

The traditional procedure to predict copolymer compositions is to insert the comonomer feed composition and appropriate monomer reactivity ratios into the instantaneous copolymer composition equation usually referred as Mayo−Lewis equation.[1,2] Clearly, knowledge of the influence of reaction parameters on the monomer reactivity ratios becomes crucial for the determination of copolymer compositions.

First methods to obtain reactivity ratios were proposed by Fineman and Ross[3] and later refined by Kelen and Tüdös.[4] They are based on different approaches to linearize the Mayo−Lewis equation. Further procedures have been elaborated. More recently, a nonlinear approach was developed and extended to an error-in-variables model with the aim to properly treat the error in both the independent and dependent variables. Table 1 alphabetically summarizes methods that are frequently used to calculate monomer reactivity ratios.[5]

All methods require as input data the comonomer feed composition and the resulting copolymer composition. In the case of alterations in the feed under the influence of medium or reaction parameters, other than the concentration, the interdependency between the change of the reactivity and the variation of the parameter must be known. To quantify such dependency, in general, the composition of copolymers synthesized under conditions considering all variations has to be analyzed. This can turn out to be a tremendous expenditure of experiments.

With the aim to minimize experimental work a procedure was developed here applicable to predict the compositions of copolymers synthesized by free radical polymerization of two monomers with one of them changing the reactivity under the influence of one variable medium parameter. The originality of the model is based on the calculation of actual termonomer feed ratios for an initially two-component system if one monomer creates a third component of different reactivity dependent on a physical parameter. In addition to the calculable termonomer feed ratios, knowledge of homopolymerization kinetics of the monomer, which varies the reactivity, and availability of the reactivity ratios, though only at both extremes of the influencing variable medium parameter, were identified as input data required for the model.

The radical copolymerization of acrylamide/acrylic acid (AM/AA) with the pH as medium parameter influencing the feed quality and, consequently, the monomer reactivity was selected as a case study to validate the approach. A number of researchers have investigated the copolymerization of this monomer combination under several conditions.[13−18] Despite the technical importance of AM/AA copolymers, the kinetic

* Corresponding author: EPFL-SB−ISIC-LMRP2, CH J2 494, Station 6, CH-1015 Lausanne, Switzerland. Telephone: +41 21 693 36 72. Fax: +41 21 693 60 30. E-mail: Christine.Wandrey@epfl.ch.

10.1021/ma051010t CCC: $30.25
Published on Web 08/18/2005

Table 1. Methods to Calculate Reactivity Ratios

method	ref
Barson−Fenn	6
Bauduin−Boutevin	7
error-in-variables model	8
extended Kelen−Tüdös	9
Fineman−Ross	3
Kelen−Tüdös	4
Mao−Huglin	10
Mayo−Lewis	1
nonlinear optimization	5
nonlinear least squares	5
Tidwell−Mortimer	11
Yezrielev−Brokhina−Roskin	12

parameters published for this system scatter considerably. Very different AM/AA reactivity ratios have been reported. The effect of the pH on the kinetics and final copolymer constitution has been studied without common agreement. To simplify the designation in subsequent discussion, AM and AA will be named as monomers A and B, respectively. Figure 1 summarizes the reactivity ratios of AM (r_A) and AA (r_B) published by several authors covering the pH range from 2 to 9. At pH = 2, r_A and r_B range from 0.25[13] to 0.6[15] and from 0.79[14] to 1.73,[18] respectively. Examining the pH dependence of the two ratios, no clear dependency can be concluded. This may partly be due to the limited quantification of the additional influence of the ionic strength on the kinetic parameters, which is frequently not considered in the literature.

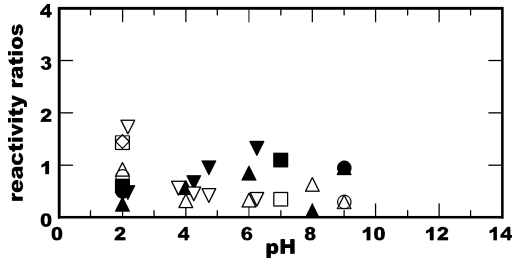

Figure 1. Dependence of the monomer reactivity ratios of acrylamide, r_A, and acrylic acid, r_B, on the pH. Reactivity ratios r_A (full symbols) and r_B (open symbols) were taken from literature data: (▲,△),[12] (●,○),[13] (■,□),[14] (◆,◇),[15] and (▼,▽).[17]

This paper presents a novel approach, the actual reactivity approach (ARA), the idea of which was recently introduced.[19] It is based on the following:

- a physical-chemical law suited to calculate the actual monomer feed composition and the radical chain end state as a function of the variable medium parameter;
- the knowledge of homopolymerization kinetics of the monomer, which is affected by the variation of the medium parameter;
- the availability of the monomer reactivity ratios at the extremes of the influencing variable medium parameter.

Before presenting the model development, the Theoretical Section serves to explain the concept of the ARA and to briefly review electrochemistry and kinetics on which the model is based. The practical applicability will subsequently be demonstrated for the AM/AA copolymerization and include the validation with own experimental data and data published by other authors. As a prerequisite for the intended model, AM/AA copolymerizations at the extremes of the variable parameter, pH = 1.8 and pH = 11.7, were performed to obtain reliable input data at defined reaction conditions. Homopolymerization data of AA were taken from literature.[20]

Table 2. Experimental Conditions of AM/AA Copolymerizations

parameter	range
pH	1.8 and 11.7
comonomer ratio	$0.14 \le [A]/[B] \le 7$
[A]+[B]	0.4 mol/L
$[K_2S_2O_8]$	1.8×10^{-2} mol/L
temp	313 ± 1 K

Table 3. Reactions and Propagation Constants of Terpolymerization Systems

no.	reaction	propagation constant
1	$-M^{\circ}_1 + M_1 \rightarrow -M_1-M^{\circ}_1$	k_{11}
2	$-M^{\circ}_1 + M_2 \rightarrow -M_1-M^{\circ}_2$	k_{12}
3	$-M^{\circ}_1 + M_3 \rightarrow -M_1 -M^{\circ}_3$	k_{13}
4	$-M^{\circ}_2 + M_1 \rightarrow -M_2-M^{\circ}_1$	k_{21}
5	$-M^{\circ}_2 + M_2 \rightarrow -M_2-M^{\circ}_2$	k_{22}
6	$-M^{\circ}_2 + M_3 \rightarrow -M_2-M^{\circ}_3$	k_{23}
7	$-M^{\circ}_3 + M_1 \rightarrow -M_3-M^{\circ}_1$	k_{31}
8	$-M^{\circ}_3 + M_2 \rightarrow -M_3-M^{\circ}_2$	k_{32}
9	$-M^{\circ}_3 + M_3 \rightarrow -M_3-M^{\circ}_3$	k_{33}

Experimental Section

Materials. White crystals of ultrapure AM, four times recrystallized, and ultrapure AA (BASF, Germany) were selected as monomers. Potassium persulfate ($K_2S_2O_8$) puriss. ≥99% was used as initiator. NaOH and HCl served 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.

Polymer Synthesis and Analytics. Copolymerizations were performed in a 100-mL glass reactor. The polymerization procedure, conversion analysis, and calculation of copolymer composition and reactivity ratios have recently been described in detail.[21] Table 2 summarizes the experimental conditions for all AM/AA copolymerizations, which were necessary to obtain copolymerization parameters at the extremes of the reaction conditions. The AM and AA monomer concentrations and the initiator concentration in mol/L are designated as [A], [B], and $[K_2S_2O_8]$, respectively. The Kelen-Tüdös equation was employed to calculate the reactivity ratios,[4,21] which are summarized in Table 7 and used for the model validation.

Theoretical Section

Concept of the Actual Reactivity Approach (ARA). This short paragraph details and explains the idea of the ARA. The basis idea is to transform polymerization systems, for which kinetic parameters, properties, and/or chemical structures depend in a defined manner on secondary reaction conditions, into systems where the relative concentrations but not the properties and structures of the components are affected by this secondary reaction conditions. Secondary may be any reaction conditions such as, for example, pH, ionic strength, and solvent quality. By contrast, the feed composition (total monomer concentration, initiator concentration, initial monomer feed ratio) are considered as primary conditions here.

The concept first requires the selection of the appropriate model basis consisting of two parts, the physical-chemical relationship, which serves to calculate the actual termonomer feed composition as a function of the actual value of the influencing medium parameter, and the kinetic scheme, which defines the reaction steps for the system under investigation (*Model Basis*). Subsequently, discrete regions have to be defined, where

Table 4. Reaction Regions and Their Characteristics

region	pH range	ionization of AA as: monomer α	ionization of AA as: polymer chain end α′	occurrence of AA	pH selected for model
I	pH < 2.2	0	0	AA, -AA	2
II	2.2 < pH < 3.8	0 < α < 1	0	AA, A^-, -AA	3.2
III	3.8 < pH < 6.2	0 < α < 1	0 < α′ < 1	AA, A^-, -AA, -A^-	5.6
IV	6.2 < pH < 8.4	1	0 < α′ < 1	A^-, -AA, -A^-	7.5
V	8.4 < pH	1	1	A^-, -A^-	12

Table 5. Summary of K_p Relationships Adapted to the pH Regions I–V of Table 4 Applying Eq 8b

region	α	α′	K_p
I	0	0	$K_p^{I} = k_{22}$
V	1	1	$Kp^{V} = k_{33}$
II	0 < α < 1	0	$K_p^{II} = k_{22} + (k_{23}\text{-}k_{22})\ \alpha$
IV	1	0 < α′ < 1	$K_p^{IV} = k_{23} + (k_{33}\text{-}k_{23})\ \alpha'$
III	0 < α < 1	0 < α′ < 1	$K_p^{III} = k_{22} + (k_{32}\text{-}k_{22})\ \alpha' + (k_{23}\text{-}k_{22})\ \alpha + (k_{33}+k_{22}\text{-}k_{23}\text{-}k_{32})\ \alpha'\alpha$

Table 6. Application of the Actual Reactivity Approach to Calculate Kinetic Parameters for Regions I–V

region	pH selected for model	K_p, L/mol s	α	α′	k_{ij}, L/mol s
I	2	$K_p^{I} = 119\,700$	0	0	$k_{22} = 119\,700$
II	3.2	$K_p^{II} = 112\,600$	0.09	0	$k_{23} = 41\,200$
III	5.6	$K_p^{III} = 17\,100$	0.95	0.77	$k_{32} = 51\,200$
IV	7.5	$K_p^{IV} = 13\,000$	1	≈0.77	
V	12	$K_p^{V} = 4800$	1		$k_{33} = 4800$

Table 7. Experimental Monomer Reactivity Ratios of AM/AA at Different pH

pH	r_A	r_B
1.8	$r_{12} = 0.54$	$r_{21} = 1.48$
11.7	$r_{13} = 3.04$	$r_{31} = 0.32$

the reactivity of the participating reactants is different but depends on clearly definable conditions (*System Design*). Then, as the core of the approach, an initially binary system with variable kinetic parameters defined by secondary influences has to be transformed into a ternary system with constant kinetic parameters (*Kinetic Transformation*). On this basis, for all previously defined regions, the terpolymerization problem will be solved substituting the unknown actual concentrations of the coexisting monomers and deriving constant kinetic parameter of partial reactions (*Solution of the Terpolymerization Problem*). Finally, the copolymerization scheme can be reestablished allowing the calculation of r_A and r_B considering the medium influence (*Return to the Copolymerization System*).

Model Basis. With the pH as variable parameter determining the fraction of the ionic monomer component in the monomer feed as well as the reactivity of the monomer and the polymer chain end, electrochemistry and reaction kinetics provide the model basis.

Electrochemistry. In aqueous solution, AA is in equilibrium with the dissociated form, acrylate (A^-) according to eq 1:

$$AA \leftrightarrows A^- + H^+ \tag{1}$$

The acid dissociation constant of AA, K_a, as the equilibrium constant for the reaction in which the acid is in equilibrium with its conjugate base in aqueous solution, is defined by eq 2.

$$K_a = \frac{[A^-][H^+]}{[AA]} \tag{2}$$

where $[A^-]$, $[H^+]$, and [AA] are the concentrations, in mol/L, at the equilibrium of A^-, H^+, and AA, respectively. For weak acids, eq 3 can be derived from eq 2 according to the Henderson–Hasselbalch equation.[22]

$$pH = pK_a^{M} + \log\left(\frac{\alpha}{1-\alpha}\right) \tag{3}$$

In eq 3, α is the fraction of dissociated acidic groups (degree of ionization) and pK_a^M is the negative logarithm of K_a. In the system under study α is the dependent variable, which is adjusted by modifying the pH. Therefore, eq 3 can be rewritten to express α as a function of pH. Rewriting yields eq 4a.

$$\alpha = \frac{10^{(pH-pK_a^{M})}}{1 + 10^{(pH-pK_a^{M})}} \tag{4a}$$

Appropriately, the AA monomer units of the polymer chain, and especially the AA radical chain ends, are able to dissociate, with the degree of dissociation influenced by the pH. However, one has to consider that the anionic charge is fixed at the polymer backbone and the positively charged counterions can freely dissociate only as long as the charge distance remains above the Bjerrum length. In general, the ionization process of polyelectrolyte chains is quite complex.[23] On the other hand, the dissociation of polyelectrolyte chain ends may be treated differently[24] justifying the application of eq 4b where α′ is the degree of ionization of the AA radical end.

$$\alpha' = \frac{10^{(pH-pK_a^{Pend})}}{1 + 10^{(pH-pK_a^{Pend})}} \tag{4b}$$

In eq 4b, pK_a^{Pend} is the negative logarithm of the effective dissociation constant of the chain end. pK_a^{Pend} is assumed to have a value between the pK_a^M and the pK_a of AA units in a poly(acrylic acid) molecule (pK_a^P).

With eqs 4a and 4b the actual pH dependent concentrations in the monomer feed and at the polymer chain end can be calculated from the initial AA concentration [AA] and the total chain end concentration [−AA]

$$[A^-]_\alpha = \alpha[AA] \tag{5a}$$

$$[AA]_\alpha = (1-\alpha)[AA] \tag{5b}$$

$$[-A^-]_\alpha = \alpha'[-AA] \tag{5c}$$

$$[-AA]_\alpha = (1-\alpha')[-AA] \tag{5d}$$

Kinetics. Due to the pH dependent coexistence of AM, AA, and A^- the presented approach is based on a terpolymerization mathematical treatment of the binary system AM/AA. The basic concept and equations describing the simultaneous polymerization of three different monomers (M_1, M_2, M_3) will be exposed here. Table 3 lists the nine propagation reactions, which can occur between the three monomers and appropriate polymer radical chain ends ($-M^\circ_1$, $-M^\circ_2$, $-M^\circ_3$). Each reaction is characterized by one propagation constant. In the subsequent sections it is throughout referred to the number of the reaction presented in the first column of Table 3.

The quantitative terpolymerization treatment is complex due to nine reactions, which may simultaneously occur. In general, the portion of each type of monomer units in the terpolymer can be expressed as a function of the concentration of the monomers in the feed and six reactivity ratios, as it is written in eq 6, parts a−c.[25]

$$[M_1^P] = [M_1]\left\{\frac{[M_1]}{r_{31}r_{21}} + \frac{[M_2]}{r_{32}r_{21}} + \frac{[M_3]}{r_{31}r_{23}}\right\} \times \left\{[M_1] + \frac{[M_2]}{r_{12}} + \frac{[M_3]}{r_{13}}\right\} \quad (6a)$$

$$[M_2^P] = [M_2]\left\{\frac{[M_1]}{r_{12}r_{31}} + \frac{[M_2]}{r_{12}r_{32}} + \frac{[M_3]}{r_{32}r_{13}}\right\} \times \left\{[M_2] + \frac{[M_1]}{r_{21}} + \frac{[M_3]}{r_{23}}\right\} \quad (6b)$$

$$[M_3^P] = [M_3]\left\{\frac{[M_1]}{r_{13}r_{21}} + \frac{[M_2]}{r_{23}r_{12}} + \frac{[M_3]}{r_{13}r_{23}}\right\} \times \left\{[M_3] + \frac{[M_1]}{r_{31}} + \frac{[M_2]}{r_{32}}\right\} \quad (6c)$$

$[M_i^P]$ denotes the instantaneous portion of monomer "i" in the terpolymer. $[M_i]$ are the concentrations of monomer "i" in the feed, and $r_{ij} = k_{ii}/k_{ij}$ are the reactivity ratios with both i and j ranging from 1 to 3. To calculate any terpolymer composition from eq 6a−c, in addition to the monomer feed concentrations of the three monomers, all six reactivity ratios r_{12}, r_{13}, r_{21}, r_{23}, r_{31}, r_{32} have to be known. Usually, they have to be determined experimentally.

Model Development

Following the concept as outlined in the Theoretical Section, the ARA was developed in four consecutive steps, which will now be presented.

System Design. For monomer A only for pH considerably lower than 2 significant change of the reactivity was reported due to protonation. AM becomes neutral at pH above 2.[18] At pH > 2 H-bond interactions are suggested to be responsible for the changes of the AM reactivity.[26] However, interactions between electrical charges are much stronger than H-bonding. Therefore, it is supposed that changes of the AM reactivity due to pH variation in the range 2−12 is negligible compared to changes for AA.[26]

Figure 2 presents the influence of the pH on the kinetic and electrochemical behavior of monomer B. The pK_a^M of AA in aqueous solution has been reported as 4.2[27] and 4.25.[28] Using eq 4a it can be calculated that

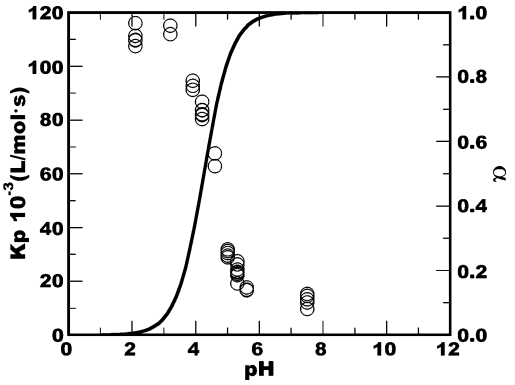

Figure 2. Dependence of the degree of ionization, α, of acrylic acid (—) and the experimental apparent propagation coefficients, K_p, (○)[20] on the pH.

more than 99% of AA occur in neutral form at pH below 2.2, and exclusively in the ionic form at pH higher than 6.2.

The pK_a^P for poly(acrylic acid) has differently been reported, for example, 4.75 and 6.4, respectively.[27,29] The difference was assigned to different molar masses of the homopolymers. In general, higher molar mass polymers have higher pK_a^P.[30] Accordingly, the pK_a^P of AM/AA copolymers will shift depending on the molar mass and copolymer composition. Moreover, also influence of the ionic strength and α on pK_a^P was recently quantified for poly(acrylic acid).[30] From eq 3, nonionized AA can be expected at pH below 2.75 while AA polymer chains with maximum charge density will be present above 8.4. Little is known about differences between pK_a at the polymer backbone, pK_a^P, and the chain end, pK_a^{Pend}. However, from the molar mass dependence strong chain end influences may be concluded. For copolymers of not to high charge density, where no counterion condensation occurs, almost entirely dissociated chain ends may be expected. The different pK_a of the chain end was recently assumed and discussed to affect free-radical polymerization.[20]

With eqs 4 and 5 as well as data taken from the literature and cited above, the pH regions where AA is coexisting with A^-, either as free monomer or as monomer unit at the polymer chain end, have been identified as pH 2.2−6.2 and 3.8−8.4, respectively.

According to the degrees of ionization α and α′, calculated from eq 4, parts a and b, five regions may be defined. The regions are characterized by the presence or absence of potentially reacting species. Within each region the conditions at only one pH value were selected for further model calculations. All regions are summarized in Table 4.

Kinetic Transformation. The core of the ARA is to transform a binary system with variable kinetic parameters into a ternary system defined by secondary influences but having constant kinetic parameters. The ionization of AA is accompanied by a strong decrease of the reactivity of the monomer. Such decrease is the consequence of electrostatic repulsion between the ionized monomer and the equally charged growing polymer chain end. Since AA and A^- possess very different reactivities, they can be treated as two different monomers from the kinetic point of view. Consequently, three differently reacting monomer species and their corresponding chain ends can be defined for the copolymerization of AM/AA at different pH: AM, AA, and A^- as monomers and $-M^\circ_{AM}$, $-M^\circ_{AA}$, and $-M^\circ_{A^-}$ as radical

chain ends. Thus, the copolymerization of AM with AA at different pH values may be interpreted as a terpolymerization of AM, AA, and A^-.

Two different notations of the AM/AA system emphasize the concept. AM and AA are named as monomers A and B when the AM/AA mixture is treated as a binary system with variable monomer reactivity and constant relative concentrations. On the other hand, if the mixture is treated as a tertiary system, AM, AA and A^- will be designated as monomers 1, 2, and 3, respectively. Here, the relative concentration of the monomers will change while their reactivity remains invariable as long as no other parameter than the pH is modified. In the latter case, the reaction scheme presented in Table 3 and eq 6a−c are applicable. Nevertheless, it is important to note that eq 6a−c result from the polymerization of three different monomers while the ARA intends to use the equations with input data of only two monomers for the case that one of them changes the reactivity under the influence of one measurable medium parameter.

For this purpose information on Tables 3 and 4 will be combined and analyzed. In region I, the only reacting species are AM and AA, and thus only reactions 1, 2, 4, and 5 listed in Table 3 are possible. Similarly can be concluded that reactions 1, 3, 7, and 9 are the only possibilities in region V. Consequently, in regions I and V the polymerization can be considered as normal copolymerization with four propagation constants in each region, k_{11}, k_{12}, k_{21}, k_{22} in region I and k_{11}, k_{13}, k_{31}, k_{33} in region V. On the other hand, all characteristics of a terpolymerization are obvious in region III, with all nine propagation reactions of Table 3. In region II, monomer B is partially ionized and can, therefore, react as both M_2 and M_3 either with $-M^\circ_1$ or $-M^\circ_2$. Radical chain ends $-M^\circ_3$ are assumed not to exist in region II. Contrarily, for region IV is derived that only M_3 reacts with either $-M^\circ_1$, $-M^\circ_2$, or $-M^\circ_3$.

The model intends to predict the instantaneous copolymer composition at any pH. Despite the claim to develop a monotonic approach, it will be demonstrated that calculations at only five pH values, one per region, are sufficient to obtain the kinetic parameters for the construction of copolymerization diagrams at any pH. The five pH values were chosen at the extremes and approximately in the middle of the pH ranges for regions II−IV in Table 4.

Solution of the Terpolymerization Problem. To calculate any instantaneous terpolymer composition from eq 6a−c, the monomer feed concentrations of the three monomers and six monomer reactivity ratios have to be known. Their calculation is here presented.

Applying the notation introduced above as well as eq 5, parts a and b, leads to eq 7a−c yielding the unknown feed concentrations of M_2 and M_3.

$$[M_1] = [A] \tag{7a}$$

$$[M_2] = (1 - \alpha)[B] \tag{7b}$$

$$[M_3] = \alpha[B] \tag{7c}$$

From the AM/AA copolymerization experiments performed at pH = 1.8 (region I) and pH = 11.7 (region V), r_{12}, r_{21}, r_{13}, and r_{31} are accessible. More precisely, regions I and V yield $r_{12} = r_A^{pH=2}$ and $r_{21} = r_B^{pH=2}$ for I and $r_{13} = r_A^{pH=12}$ and $r_{31} = r_B^{pH=12}$ for V, respectively.

To obtain r_{23} and r_{32}, the homopolymerization of AA at different pH must be interpreted as a copolymerization of AA and A^-. The ARA of the current paper proposes K_p as the overall contribution of all propagation reactions participating in the consumption of AA and A^- during the homopolymerization of AA. In other words K_p summarizes the contributions of reactions 5, 6, 8, and 9 presented in Table 3. The mathematical expression for K_p is given by eq 8a. K_p stands for the summation of the corresponding propagation constants (k_{ij}) weighted by the molar fractions of the "*i*" radical chain end (F°_i) reacting with a "*j*" monomer (f_j). The summation indices *i* and *j* start from 2 to present a consistent notation. Since AM is absent during the homopolymerization experiments of AA, the indices 2 and 3 indicate the contribution of all reactions involved.

$$K_p = \sum_{i=2,j=2}^{i=3,j=3} k_{ij} F_i^\circ f_j \tag{8a}$$

Equation 8a can be rewritten as a function of the degrees of ionization of the monomer (α) and the radical chain end (α′), yielding eq 8b. The Supporting Information presents the derivation in detail.

$$K_p = k_{22} + (k_{32} - k_{22})\alpha' + (k_{23} - k_{22})\alpha + (k_{33} + k_{22} - k_{23} - k_{32})\alpha'\alpha \tag{8b}$$

Table 5 summarizes the relationships of K_p adapted to the pH regions of Table 4 and derived from eq 8b. K_p^I and K_p^V directly yield k_{22} and k_{33}. k_{23} can be calculated from K_p^{II} with α at one appropriate pH value, 5.6 here. Introducing the value 5.6 into eq 4a, the corresponding value of α is obtained, which is then inserted in the expression for K_p^{II} yielding k_{23}. Finally, k_{32} can be calculated by the following procedure: pH conditions are selected for region III where α approaches 1, for example α = 0.95. Then, it is assumed that $\alpha'_{\alpha=0.95} \approx \alpha'_{\alpha=1}$ and, consequently, $\alpha'_{\alpha=1}$ is obtained from K_p^{IV}. Inserting this α′ value, α = 1, and the already known propagation constants into K_p^{III} yields k_{32}. Finally, $r_{23} = k_{22}/k_{23}$ and $r_{32} = k_{33}/k_{32}$ are obtained.

Return to the Copolymerization System. The binary system may be reconstructed due to the fact that AA and A^- represent portions of the same monomer the amount of which is known from the batch recipe as $[B] = [M_2] + [M_3]$ defined by eq 7, parts b and c, and the amount of AA units in the copolymer $[M^P_B] = [M^P_2] + [M^P_3]$ defined by eq 6, parts b and c. The amount of AM as monomer and polymer unit remains invariable as $[A] = [M_1]$ and $[M^P_A] = [M^P_1]$ defined by eqs 7a and 6a. Now, all data are available to plot diagrams showing the dependence of the instantaneous copolymer composition $F_A = F_1$ on the initial comonomer feed composition $f_A = f_1$ at any pH in the range from 2 to 12.

The reconstruction of the binary system is further reflected by the transformation of the invariable reactivity ratios r_{12}, r_{21}, r_{13}, r_{31}, r_{23} and r_{32} into the pH-dependent reactivity ratios r_A and r_B. By definition, it is $r_A = k_{AA}/k_{AB}$ and $r_B = k_{BB}/k_{BA}$. The values of k_{AA}, k_{AB}, k_{BB}, and k_{BA} are obtained from eqs 9a−d. The equations reflect the pH dependence, which is inherent in α and α′.

$$k_{AA} = k_{11} \tag{9a}$$

$$k_{AB} = (1 - \alpha)k_{12} + \alpha k_{13} \tag{9b}$$

$$k_{BB} = k_{22} + (k_{32} - k_{22})\alpha' + (k_{23} - k_{22})\alpha + (k_{33} + k_{22} - k_{23} - k_{32})\alpha'\alpha \tag{9c}$$

$$k_{BA} = (1 - \alpha')k_{21} + \alpha' k_{31} \tag{9d}$$

Applying the definition of monomer reactivity ratios to eq 9a−d, parts a and b of eq 10 are obtained for the calculation of r_A and r_B. See Supporting Information for details of the derivation.

$$r_A = \frac{r_{12}r_{13}(10^{pK_a^M} + 10^{pH})}{r_{13}10^{pK_a^M} + r_{12}10^{pH}} \tag{10a}$$

$$r_B = \frac{k_{22}10^{pK_a^M}10^{pK_a^{Pend}} + (k_{32}10^{pK_a^M} + k_{23}10^{pK_a^{Pend}})10^{pH} + k_{33}10^{2pH}}{\frac{k_{22}}{r_{21}}10^{(pK_a^M + pK_a^{Pend})} + \left(\frac{k_{33}}{r_{31}}10^{pK_a^M} + \frac{k_{22}}{r_{21}}10^{pK_a^{Pend}}\right)10^{pH} + \frac{k_{33}}{r_{31}}10^{2pH}} \tag{10b}$$

It is visible that the calculation of r_A and r_B requires values for r_{12}, r_{13}, r_{21}, r_{31}, k_{22}, k_{23}, k_{32}, k_{33}, pK_a^M, and pK_a^{Pend}. Essentially, it was shown that all parameters, with the exception of pK_a^{Pend}, can be calculated or are experimentally accessible. To obtain a value for pK_a^{Pend}, first, eq 8b was transformed into eq 11, which yields α', and with that and eq 4b, finally, pK_a^{Pend} from eq 12.

$$\alpha' = \frac{K_p - k_{22} + \alpha(k_{22} - k_{23})}{(k_{32} - k_{22}) + \alpha(k_{22} + k_{33} - k_{23} - k_{32})} \tag{11}$$

$$10^{pK_a^{Pend}} = \frac{10^{pH}(1 - \alpha')}{\alpha'} \tag{12}$$

All data are now available to calculate r_A and r_B dependent on pH.

Model Application and Discussion

In this section the model developed above will be applied to calculate the propagation constants and reactivity ratios for the copolymerization of AM/AA under conditions where the initial total monomer concentration was constant. Variation of the total monomer concentration modifies the ionic strength in the case of ionic or ionized monomers. The ionic strength is known and was proved to influence the copolymerization kinetics.[21] It varies with the AA concentration and the pH, however, it becomes significant only at the very extremes of the pH where high amounts of HCl or NaOH are required to adjust the pH.[20,21]

Determination of Propagation Constants and Reactivity Ratios. Experimental data of the homopolymerization of AA at different pH were taken from the literature.[20] There, apparent propagation coefficients (K_p) of AA were determined applying pulsed laser technique combined with size exclusion chromatography. The pH dependent values are plotted in Figure 2 for the pH range of interest herein. A dramatic decrease of K_p is observed when the pH increases, in particular for $3 < pH < 7$. This decrease of K_p is accompanied by the ionization of AA confirming the altered reactivity of AA to be a consequence of the ionization processes. The contribution of the ionic strength to the K_p caused by the addition of NaOH can be neglected in this range of pH. However, it was found to become significant at $pH > 12$.[20] Considering recent information on monomer concentration effects on K_p,[31] it is justified to note that such effects may be neglected for the source of the data where the pH influnce was studied for AA solutions of 5 wt % = 0.7 mol/L.[20] Comparison of K_p obtained for 0.42 mol/L[31] reveals a difference of only about 2% what is within the experimental error. Consequently, application to 0.4 mol/L, the total monomer concentration selected for the model is justified. The same holds for AM for which deviations within the experimental error range were reported in the concentration range 0.32−0.7 mol/L.[32] Nevertheless, it is known from other ionic monomers that the monomer concentration influence can become significant in particular at higher monomer concentration.[33]

K_p values for the calculations were obtained from fitting the values in Figure 2. Because of fitting the values of K_p^{II}, K_p^{III}, and K_p^{IV} differ slightly from those published by Lacik et al.[20] Table 6 summarizes the values calculated.

k_{22} and k_{33} were directly obtained from K_p^I and K_p^V after fitting. Analyzing region II at pH = 3.20 and using eq 4a reveals $\alpha = 0.09$. Subsequently, k_{23} was calculated from K_p^{II}. For region IV, knowing k_{33}, k_{23}, and K_p^{IV}, the value of α' was approximated as 0.77. Finally, assuming that $\alpha'_{\alpha=1} \approx \alpha'_{\alpha=0.95}$ and applying K_p^{III}, k_{32} was determined. With the knowledge of k_{22}, k_{23}, k_{32}, and k_{33} the monomer reactivity ratios $r_{23} = 2.90$ and $r_{32} = 0.094$ were calculated. The values confirm that homopolymerization of M_2 is favorable compared with cross-propagation with M_3. Contrarily, cross-propagation of 3 and 2 is preferred compared with homopolymerization of M_3.

From AM/AA copolymerizations carried out under conditions described in Table 2, at the two extremes of the pH range investigated here, the monomer reactivity ratios r_{12}, r_{21}, r_{13}, and r_{31} were obtained as reported in Table 7.

Now all data are available to calculate terpolymer compositions from eq 6a−c.

Model Validation. In Figures 3 and 4, model curves are compared with experimental data. The experimental data at different pH were taken from the literature.[14−18] In each case, both experimental points and model curves present the molar fraction of AM in the copolymer (F_A) as a function of the molar fraction in the monomer feed (f_A).

There is, in general, good agreement between predicted curves and experimental data though differences for various data sources are visible. Comparing model predictions and experimental data maximum deviations are observed for data at pH = 4.7[18] and at pH = 2.5[14] as 28% and 13.5%, respectively. This may likewise serve to explain scattering in Figure 1.

For the validation of eq 10b, the pK_a^{Pend} value was calculated as follows: Calculating α for different pH conditions according to eq 4a and introducing corresponding experimental values of K_p[20] into eq 11, a series of α' values was obtained. Subsequently, the value of pK_a^{Pend} was calculated as average $pK_a^{Pend} = 5.29 \pm 0.42$. As expected, the value is higher than pK_a^M but within the range reported for pK_a^P.[27,29] Table 8 contains all values.

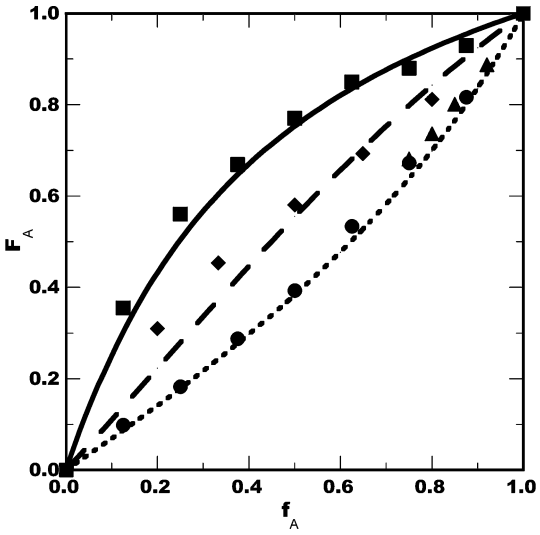

Figure 3. Dependence of the instantaneous copolymer composition F_A on the initial comonomer feed composition f_A. Comparison of model prediction (lines) and experimental data (symbols). pH = 12: (—, ■).[21] pH = 4.7: (- - -, ◆).[18] pH = 1.8: (···, ●,[15] ▲).[16]

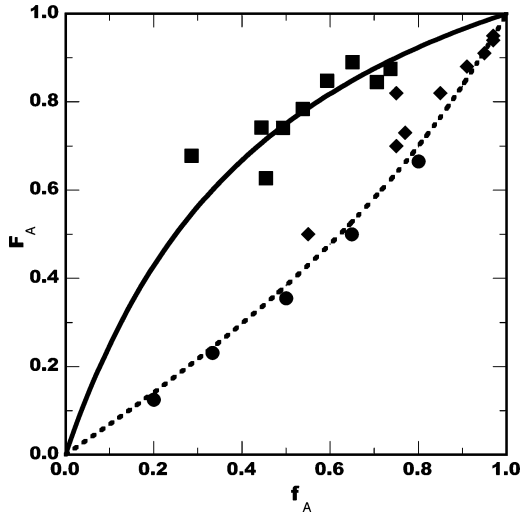

Figure 4. Dependence of the instantaneous copolymer composition F_A on the initial comonomer feed composition f_A. Comparison of model prediction (lines) and experimental data (symbols). pH = 7.1: (—, ■).[17] pH = 2.5: (- - -, ◆).[14] pH = 2.17: (···, ●).[18] (Note that the curves calculated for pH = 2.5 and pH = 2.17 overlay due to the very similar r_A and r_B values. Only the latter is therefore printed here.)

Table 8. Determination of pK_a^{Pend}

pH	α	K_p, L/mol s	α′	pK_a^{Pend}
3.2	0.08	112 600	0.01	5.18
3.9	0.31	92 900	0.04	5.24
4.2	0.47	81 000	0.03	5.68
4.6	0.69	62 300	0.07	5.74
5.0	0.85	30 400	0.55	4.91
5.3	0.92	23 600	0.62	5.10
5.6	0.96	17 100	0.73	5.17
				av: 5.29 ± 0.42

With the availability of r_{12}, r_{13}, r_{21}, r_{31}, k_{22}, k_{23}, k_{32}, k_{33}, and pK_a^M, pH dependent reactivity rations r_A and r_B could be calculated at any pH in the range 2−12. Figure 5 shows how the monotonic functions of calculated r-parameters adjust to experimentally obtained values.[21] Figure 5 may contribute to evaluate the data of Figure 1.

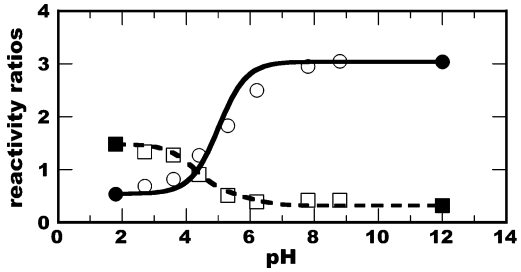

Figure 5. Dependence of the monomer reactivity ratios r_A and r_B on the pH. Comparison of model prediction (lines) and experimental data[21] (symbols). AM (—, ●, ○) and AA (- - -, ■, □). Full symbols indicate input data used to calculate the model.

Table 9. Sensitivity of r_B to Variation of pK_a^{Pend}

pH	$pK_a^{Pend} = 4.87$	$pK_a^{Pend} = 5.71$
1.8	1.48	1.48
2.7	1.45	1.45
3.6	1.29	1.3
4.4	0.87	0.91
5.3	0.49	0.57
6.2	0.36	0.45
7.8	0.32	0.33
8.8	0.32	0.32
11.7	0.32	0.32

The predicted r_A increases faster than the experimental data when the pH increases from 4 to 8. The reason for the difference could be associated with changes in the reactivity of AM with the pH due to protonation or formation of dimers,[18,26,32] which was not yet considered.

The sensitivity of the model to the variable parameter pK_a^{Pend} was evaluated calculating r_B (eq 10b) for the error limits of the pK_a^{Pend} average value of Table 8. Table 9 lists the minimum and maximum values for the entire pH range.

Conclusions

The actual reactivity approach (ARA) provides a procedure how to treat secondary influences on the reactivity of one monomer in the kinetic scheme of copolymerizing systems initially consisting of a mixture of two monomers. To the authors' knowledge, it is the first approach that considers electrochemical behavior for the calculation of copolymer compositions and reactivity ratios. Here the applicability was demonstrated for the case that the pH alters the monomer reactivity due to coexistence of two species, a neutral one and a charged one, of a one monomer structure in a defined pH range. The system AM/AA was selected to demonstrate the principle of the approach. Good correlation of the results from analytical expressions to calculate copolymer compositions with experimental data was proved. In addition, an estimation of the pK_a of an AA ending radical chain end became accessible.

In the case of AM protonation the initial AM/AA copolymerization system would transform to a polymerization of four different monomers AM, AM^+, AA, and A^- resulting in a pH dependent scheme co-ter-tetra-terco polymerization. The approach may also be extended to any other monomer such as methacrylic acid or polymerizable amines, which are ionizable in a certain pH range. Moreover, also other medium parameters, which cause secondary effects on the monomer reactivity, may be subject of similar approaches, for example ionic strength or solvent polarity. The relative simplicity of the model permits including the analytical procedure into chemical engineering and process control software.

Acknowledgment. The Swiss National Science Foundation is gratefully acknowledged for the financial support (Grants 2000-63395 and 200020-100250).

Abbreviations and Symbols

A = monomer with constant reactivity
B = monomer with variable reactivity
M_1 = first monomer for terpolymerization analysis
M_2 = second monomer for terpolymerization analysis
M_3 = third monomer for terpolymerization analysis
AM = acrylamide
AA = acrylic acid
A^- = acrylate
−AM = AM terminal chain unit
−AA = AA terminal chain unit
$-A^-$ = A^- terminal chain unit
$-M^\circ_{AM}$ = −AM growing radical
$-M^\circ_{AA}$ = −AA growing radical
$-M^\circ_{A^-}$ = $-A^-$ growing radical
K_a = dissociation constant
pK_a^i = negative logarithm of K_a (i = M, P, or Pend)
α = degree of ionization of AA
α′ = degree of ionization of −AA
r_A = reactivity ratio: k_{AA}/k_{AB}
r_B = reactivity ratio: k_{BB}/k_{BA}
r_{ij} = reactivity ratio: k_{ii}/k_{ij} (i, j = 1, 2, 3)

Supporting Information Available: Text giving the derivation of eq 8b from eq 8a and calculation of pH dependent monomer reactivity ratios. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Mayo, F. R.; Lewis, F. M. *J. Am. Chem. Soc.* **1944**, *66*, 1594−1560.
(2) Alfrey, T., Jr.; Goldfinger, G. *J. Chem. Phys.* **1944**, *12*, 115, 205−209, 332.
(3) Fineman, M.; Ross, S. D. *J. Polym. Sci.* **1950**, *5* (2), 259−262.
(4) Kelen, T.; Tüdös, F. *J. Macromol. Sci. Chem.* **1975**, *A9* (1), 1−27.
(5) Polic, A. L.; Duever, T. A.; Penlidis, A. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36* (5), 813−822.
(6) Barson, C. A.; Fenn, D. R. *Eur. Polym. J.* **1989**, *25* (7−8), 719−720.
(7) Bauduin, G.; Boutevin, B. *Makromol. Chem. Rapid Commun.* **1991**, *12* (3), 197−201.
(8) Dube, M. A.; Sanayei, R. A.; Penlidis, A.; Odriscoll, K. F.; Reilly, P. M. *J. Polym. Sci., Polym Chem.* **1991**, *29*, 703−708.
(9) Tüdös, F.; Kelen, T.; Foldesberezsnich, T.; Turcsanyi, B. *J. Macromol. Sci. Chem.* **1976**, *A10*, 1513−1540.
(10) Mao, R. S.; Huglin, M. B. *Polymer* **1993**, *34*, 1709−1715.
(11) Tidwell, P. W.; Mortimer, G. A. *J. Polym. Sci., Polym. Chem.* **1965**, *3* (1PA), 369.
(12) Yezrielev, A. I.; Brokhina, E.; Roskin, Y. S. *Vysokomol. Soedin.* **1969**, *A11*, 1670−1676.
(13) Ponratnam, S.; Kapur, S. L. *Makromol. Chem.* **1977**, *178*, 1029−1038.
(14) Truong, N. D.; Galin, J. C.; Francois, J.; Pham, Q. T. *Polymer* **1986**, *27*, 467−475.
(15) Bourdais, *Bull. Soc. Chim. Fran.* **1955**, *93*, 485−490.
(16) Shawki, S. M.; Hamielec, A. E. *J. Appl. Polym. Sci.* **1979**, *23*, 3155−3166.
(17) Kurenkov, V. F.; Myagchenkov, V. A. *Eur. Polym. J.* **1980**, *16*, 1229−1239.
(18) Cabaness, W. R.; Lin, T. Y. C.; Parkanyi, C. *J. Polym. Sci., Part A-1.* **1971**, *9*, 2155.
(19) Rintoul, I.; Wandrey, C. Presented at the 40th IUPAC International Symposium on Macromolecules, Macro2004, Symp.1.1.7. www.e-polymers.org/paris/.
(20) Lacik, I.; Beuermann, S.; Buback, M. *Macromol. Chem. Phys.* **2004**, *205*, 1080−1087.
(21) Rintoul, I.; Wandrey, C. *Polymer* **2005**, *46,* 4525−4532.
(22) Alexandrowicz, Z.; Katchalsky, A. *J. Polym. Sci., Part A-1.* **1963**, *1*, 3231.
(23) Wandrey, C.; Hunkeler, D. In *Handbook of Polyelectrolytes and Their Applications*; Tripathy, S. K., Kumar, J., Nalwa, H. S., Eds.; American Scientific Publishers: Los Angeles, CA, 2002; Chapter 5, p 147.
(24) Manning, G. S.; Mohanty, U. *Physica A* **1997**, *247*, 196−204.
(25) Odian, G. In *Principles of polymerization.*; McGraw-Hill: New York, 1970; Chapter 6, p 387.
(26) Pascal, P.; Napper, D. H.; Gilbert, R. G.; Piton, M. C.; Winnik, M. A. *Macromolecules* **1990**, *23*, 5161−5163.
(27) Serjeant, E. P.; Dempsey, B. In *CRC Handbook of Chemistry and Physics*, 81st ed.; Lide, D., Ed.; CRC Press LLC: Boca Raton, FL, 2000−2001; Chapter 8, p 47.
(28) Kabanov, V. A.; Topchiev, D. A.; Karaputadze, T. M. *J. Polym. Sci., Polym. Symp.* **1973**, *42*, 173−183.
(29) Scott, R. A.; Peppas, N. A. *AIChE J.* **1997**, *43*, 3 (1), 135−144.
(30) De Stefano, C.; Gianguzza, A.; Piazzese, D.; Sammartano, S. *React. Funct. Polym.* **2003**, *55*, 9−20.
(31) Lacik, I.; Beuermann, S.; Buback, M. *Macromolecules* **2003**, *36*, 9355−9363.
(32) Seabrook, S. A.; Tonge, M. P.; Gilbert, R. G. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 1357−1368.
(33) Wandrey, C.; Hernàndez-Barajas, J.; Hunkeler, D. *Adv. Polym. Sci.* **1999**, *145*, 123−182.

MA051010T