

A Kinetic Study of Acrylamide/Acrylic Acid Copolymerization

by

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AUTHOR'S DECLARATION

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Abstract

Homo- and co-polymers of acrylamide (AAm) and acrylic acid (or acrylate salt) (AA) or methacrylic acid (MAA)) are important classes of water-soluble polymers due to their numerous applications in fields such as super absorbents, additives in cosmetics, membrane technology, waste-water treatment and oil field operations. These polymers are generally made by free radical polymerization.

For copolymerization reactions it is extremely important to know the details of reaction kinetics in order to ascertain the kinetic effects of different reaction parameters, which ultimately dictate final copolymer composition, microstructure and properties. The reactivity ratios for copolymerization of AAm and AA have been shown to be dependent on pH and they also change with reaction solvent.

The present experimental investigation has been performed to study the kinetics of copolymerization of these monomers in aqueous and alcoholic media by considering factors such as type of initiator and solvent, and pH, in order to determine how they affect the reactivity ratios of these monomers. Reactivity ratios were determined by non-linear least squares (NLLS) and the error-in-variables-model (EVM) techniques and full conversion range kinetic investigations were carried out to confirm these values.

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Chapter 1 Introduction

Copolymers of acrylamide (AAM) and acrylic acid (AA) are important water-soluble polymers due to their numerous industrial applications in many fields. Polymer properties are strongly influenced by the characteristic charges which are due to the presence of the ionic monomer AA. Typically the resulting polymers have high molecular weights and are hydrophilic.

Copolymers of AAM and AA are prepared by free radical polymerization. It is necessary to study the kinetics of polymerization as the ultimate properties of the polymer depend on molecular weight and microstructure, which are in turn related to relationships that govern the reaction kinetics. On the basis of previous investigations, it is known that reaction kinetics of AAM and AA copolymerization are dependent on many factors, for example, the ionic strength and pH of reaction media^{1, 2}, which is due to the presence of ionic monomer (AA). The reaction kinetics of free radical solution homo- and co-polymerization of both AAM and AA in aqueous media have been studied previously and many authors have attempted to explain the resulting observations. However, there are still several aspects of the reaction kinetics that need to be clarified, especially regarding dependency on monomer concentration, the type of initiator used and the solvent.³ In copolymerizations the reactivity ratios for the monomers involved are key parameters related to reaction kinetics and they influence copolymer composition and microstructure. Reactivity ratios for the copolymerization of AAM and AA have been determined previously. However, the different studies show a wide range of values. The reactivity ratios for copolymerization of AAM and AA have been shown to be

dependent on pH and they also change with solvent. The present experimental investigation has been performed to study some of the reasons for this variability. Thus the goals of the present experimental work described in this thesis were to look at the following:

- a. To study the effect of monomer concentration on reactivity ratios in aqueous media at pH close to 7. Thus the reactivity ratio values for AAm and AA were estimated from feed and copolymer composition data from low conversion copolymerization reactions.
- b. The analysis was done by the error-in-variables-model (EVM) technique, based on the Mayo - Lewis (terminal) copolymerization model.
- c. The determined values of the reactivity ratios were compared with those reported in the literature.
- d. The effect of different initiators and solvents was examined.
- e. The reactivity ratios were confirmed by selected full conversion range experiments.

In Chapter 2 a review of relevant studies by previous investigators for the polymerization of AAm and AA is presented. Chapter 3 presents all the experimental details and steps from monomer purification to drying of polymer, along with relationships used for choosing best monomer feeds for reactivity ratio analysis. The results of the study are presented and discussed in Chapter 4, where the reactivity ratio studies in aqueous systems are described for copolymerizations using potassium persulphate (KPS) and 4,4'-azo-bis-(4-cyanovaleric acid) (ACVA) as initiators. Several

comparisons of the results from the reactivity ratio studies are made, followed by complementary investigations from full conversion experiments. Finally, Chapter 5 presents concluding remarks and some suggestions for further work.

Chapter 2 Literature Review and Background Information

As a general group, water-soluble polymers represent a wide class of polymeric materials ranging from naturally formed polymers that are key elements of living organisms, to a range of synthetic materials of immense practical utility. Synthetic water-soluble polymers are used in many applications such as:

1. Enhanced oil recovery⁴
2. Flocculation in waste treatment⁵
3. Water-soluble gels and viscosity modification
4. Adhesion
5. Coatings
6. Water retention
7. Biomedical, pharmaceutical and high value cosmetic products.

Clearly then such materials have a huge economic impact in terms of their production and use in a wide range of applications. Overall, given the great utility of synthetic water-soluble polymers, it is not surprising that there is a large amount of research describing their production and characterization with respect to selected polymer properties. For example, incorporation of hydrophobic groups into a polymer backbone greatly increases its performance for improvements in oil recovery^{6, 7}. Moreover, interest in the area has expanded with advances in research to synthesize water-soluble polymers having complex architecture for specialized applications, which have been made possible through the use of controlled radical polymerization such as Reversible Addition Fragmentation chain Transfer (RAFT)⁸. This technique has been utilized to make block

copolymers directly in an aqueous medium. Although studies of water-soluble systems have moved into these more specialized areas, there is still much to learn about production of what can be regarded as the most common water soluble copolymer, i.e., the AAm/AA copolymer.

Copolymers of AAm and AA are amongst the most important water soluble polymers due to their numerous industrial applications in many fields. The chemical structures of the monomers are shown in Figures 2-1 and 2-2. The properties of polymers of this type are heavily influenced by the degree and distribution of characteristic charges, which are due to the presence of the ionic monomer AA. Typically they have high molecular weights and are very hydrophilic.

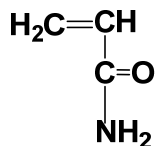


Figure 2-1 Structure of Acrylamide Monomer

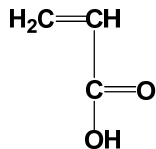


Figure 2-2 Structure of Acrylic Acid Monomer

A general structure of the monomer units in a copolymer chain is shown in Figure 2-3 with the acid group of AA in the ionized form, with a sodium counter-ion (n and m designate general numbers of AAm and AA repeat units, respectively).

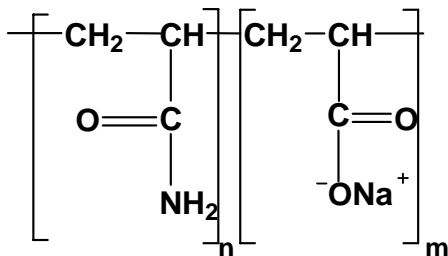


Figure 2-3 AAm/AA Copolymer General Structure

As a result of the importance of AAm/AA copolymers, polymerization of AAm and AA has been widely studied as have the product properties. The polymers are typically formed by free radical polymerization. In practical polymerizations to make such materials a variety of specific methods are possible, for example solution polymerization. Bulk polymerizations are not preferred because the polymers are not soluble in the bulk monomers. Alternatively, a technically more complex process, inverse emulsion radical polymerization, can be used. These processes may be routinely used to make polymers with selected technical specifications but the understanding of the reaction processes is often somewhat empirical.

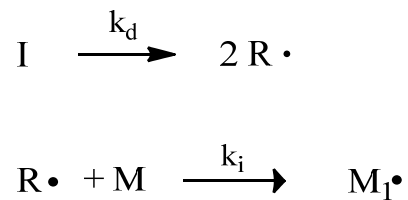
In relation to this, it should be noted that the structure of polymers produced by any free radical polymerization is strongly related to the kinetics of polymerization. A survey of the literature reveals that in the past, despite the amount of research devoted to the

study of water-soluble polymers, there have been only limited studies investigating the details of kinetics for polymers of AAm and AA^{9, 10}. A recent study has highlighted another problem with kinetic studies in the polymerization of these monomers, i.e., the fact that although there have been a number of studies of polymerization for these monomers, key kinetic data are at times contradictory¹¹ and thus of limited use in development of practical processes or for refining kinetic models. This gap in knowledge of these processes can be regarded as a block to the most efficient exploitation of the polymers and so further kinetic studies are warranted to obtain a better understanding. This situation has stimulated the study described below.

In order to highlight terms that will be used in the later discussion it is worth considering some standard arguments in polymerization kinetics. Typically the mechanism for free radical polymerization consists of three distinct steps: initiation, propagation and termination¹².

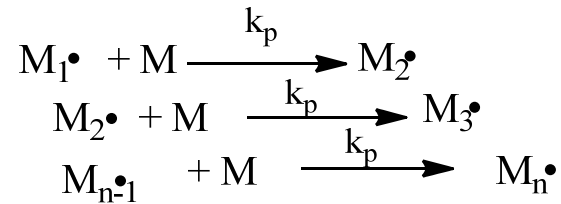
Initiation consists of the breakdown of initiator molecules (I) to make primary radicals ($R\bullet$) which then react with a monomer molecule to start the chain ($M_1\bullet$). The rate constant for initiator decomposition is k_d , and that for the primary addition of radical to monomer is k_i

Initiation



Propagation proceeds by addition of a free monomer unit M to the radical $M_1\bullet$ to produce a radical with two monomer units and so on and so forth, with k_p being the rate constant for propagation.

Propagation



In parallel with initiation and propagation there is the possibility of reaction between radicals, which results in the removal of radicals, called termination. The overall rate constant for termination is k_t . The case below illustrates termination by coupling or combination (essentially the joining of two radicals to make one dead polymer molecule), which is prevalent for most monomers¹². In some systems, termination by disproportionation is also possible and has been suggested as the primary method for AAm homopolymerization^{12, 13}.

Termination



The general kinetic scheme of free radical polymerization has been well studied. In order to develop a kinetic expression for the rate of polymerization (R_p), it is assumed that the reactivities of radicals in long chains are equivalent and there is a steady state radical

concentration¹². Then it can be shown that the ideal rate of polymerization R_p can be represented by equation (1).

$$R_p = k_p [M] \sqrt{\frac{R_i}{2k_t}} \quad (1)$$

R_i in equation (1) is the rate of initiation. From equation (1) it is clear that values of the rate constant for propagation (k_p) and termination (k_t) dictate the rate of polymerization and related kinetics, which will also affect the average molecular weights and molecular weight distribution. Therefore much of the study of polymerization kinetics has been to evaluate these reaction constants.

In copolymerization, the reactions between monomers and the different propagating radicals take place simultaneously for all possible combinations of radicals and monomers. Therefore composition of copolymer cannot be simply obtained by knowing their homo-propagation rates.¹² Over the years the quantification of copolymerization rate has been extensively studied by several workers assuming that the chemical reactivity of the propagating radical chain is dependent on the (terminal) monomer unit at the growing end and not on the adjacent chain or overall chain composition.

When two types of monomer are involved in a polymerization reaction, their relative tendencies to react together to make copolymer cannot be quantified simply by considering the relative k_p values of the homopolymerizations. Some radicals are actually more reactive toward the other monomer in the system than their own and vice versa. Many systems have been studied and different models have been developed to explain the results of propagation kinetics⁹. The simplest model presented in this regard

is the terminal model of copolymerization¹⁴ developed by Mayo and Lewis in a classic study. This model states that copolymerization of two monomers M_1 and M_2 leads to two types of free radicals M_1^\bullet and M_2^\bullet from monomers M_1 and M_2 , respectively. Therefore there are four reactions possible for the overall propagation step.

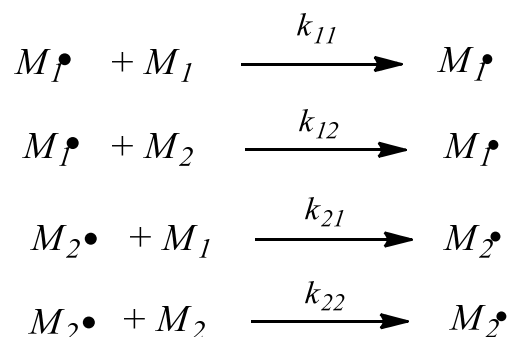


Figure 2-4 Propagation Reactions; Terminal Copolymerization Model¹²

In the above scheme, k_{11} , k_{12} , k_{21} and k_{22} , are rate constants of the individual propagation reactions. It is clear from Figure 2-4 that for the terminal model of copolymerization the propagating radicals having M_1 as the terminal units are involved in the 1st and 2nd reactions, while the propagating radicals ending in monomer unit M_2 are in the last two reactions. Based on Figure 2-4, the reactivity ratios (r_1 and r_2) are therefore defined as the ratios of the rate constants of homopropagation over the corresponding rate constants of cross-propagation for the particular radical. Thus, the reactivity ratios for monomers M_1 and M_2 are designated as r_1 and r_2 , respectively, and are defined as:

$$r_1 = \frac{k_{11}}{k_{12}} \qquad r_2 = \frac{k_{22}}{k_{21}}$$

On the basis of the rate of reaction (either appearance of polymer or disappearance of monomer) for the terminal model equations, Mayo and Lewis derived equation (2) to quantify copolymer composition (in terms of mole fractions) with respect to reactivity ratios and starting monomer mole fractions.

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2} \quad (2)$$

F_1 is the mole fraction of monomer M_1 in the copolymer and f_1 and f_2 are the respective mole fractions of monomers M_1 and M_2 in the feed. This equation applies to the instantaneous copolymer composition and so is valid for running copolymerization reactions to low conversions, where the cumulative copolymer composition and feed composition have little chance to drift from the values obtained at the start of reaction.

2.1 An Overview of Methods for Reactivity Ratios Estimation

A primary target for our study was the examination of the reactivity ratios for AAm / AA copolymerization and so a brief overview will be presented here. A basic requirement for experimental determination of reactivity ratios (r_1 and r_2) is to relate monomer- and copolymer-composition data in relation to the Mayo Lewis equation (2).

The use of the instantaneous copolymer composition equation as shown in the form of equation (2) or as the equivalent differential form (equation 3) along with relevant experimental data is the most common way to evaluate reactivity ratios for a given copolymer system, using copolymer composition data collected at low conversion levels (usually below 5%).

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1](r_1[M_1] + [M_2])}{[M_2]([M_1] + r_2[M_2])} \quad (3)$$

Equation (3) is the differential copolymer equation relating the initial molar concentration of monomers M_1 and M_2 to $d[M_1]/d[M_2]$, the composition (mole ratio of monomers 1 and 2 in copolymer) of the copolymer formed at the initial phase of reaction.

It can be seen that in order to obtain estimates for r_1 and r_2 , it is necessary to have copolymer composition data available for several monomer feeds in conjunction with knowledge of the initial feed compositions and then these data can be fit to equation (2) or (3) by varying r_1 and r_2 . Given that for most copolymerizations the initial monomer feed composition is not the same as the initial copolymer composition (in terms of mole fractions or mole ratios of the two components), this means that both the monomer feed composition and the copolymer composition will drift throughout the reaction. Therefore, traditionally, for determining r_1 and r_2 the copolymerization is carried out to low conversions ($< 5\%$) of monomer in order to minimize drift of feed- and copolymer-compositions. In that way the feed and copolymer compositions can be regarded as essentially those of the initial instant of reaction, within experimental error for the measurements of feed and copolymer compositions¹⁵⁻¹⁷.

Initial feed compositions are easily determined from the amounts of reagents and other reaction components. However, copolymer composition must be found by the most reliable method to distinguish the different monomers for the specific system being studied. There are several different methods to measure copolymer composition either by Infra Red (IR), Ultra Violet (UV)¹⁸, and Nuclear Magnetic Resonance (NMR)¹⁷

spectroscopy, or by elemental analysis¹⁹ (to find the proportion of different elements in a given sample of copolymer). These are direct methods for studying the copolymer composition. Another method is to determine the composition of residual monomers in the reaction mixture at different levels of monomer conversion, for instance, either by High Pressure Liquid Chromatography (HPLC)¹¹ or Gas Chromatography (GC), and then calculate the amount of each monomer in the copolymer based on the amounts of monomers consumed.

2.2 Mathematical Methods for Determining r_1 and r_2

Prior to the wide scale usage of computers as a general laboratory tool, non-linear parameter estimation methods for determining r_1 and r_2 were not easy and so early workers resorted to algebraic (yet incorrect) manipulation of the equations that allowed for the use of linear regression techniques. Mayo and Lewis did this by a graphical method (the method of intercepts) by rearrangement of the copolymer equation into a linear form (equation of a straight line) with respect to the reactivity ratios¹⁴:

$$r_2 = \frac{[M_1]}{[M_2]} \times \frac{d[M_1]}{d[M_2]} \left\{ 1 + \frac{r_1[M_1]}{[M_2]} \right\} - 1 \quad (4)$$

Using this method each experimental point of co-monomer feed and the corresponding copolymer composition was entered in equation (4) and r_2 (y-axis) was plotted as a function of different assumed values of r_1 (x- axis). Based on assumed values of r_1 each set of experimental data yielded a straight line. The intersection point of the various straight lines gave the best estimate of reactivity ratios. Experimental error in copolymer composition data may appear in the form of variation of the intersection point

of these lines. This graphical method can lead to considerable error as it is ultimately subjective in the choice of the best intercept point (see Figure 2-5).

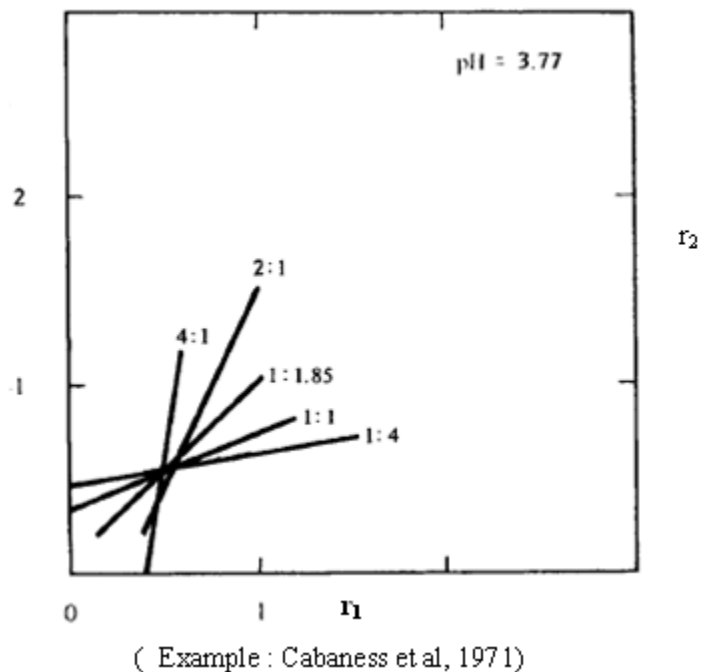


Figure 2-5 Example of Method of Intercepts¹⁹

In order to obtain better values of r_1 and r_2 , Fineman and Ross proposed the rearranging of copolymer equation in terms of mole fraction (Equation 5) in the form of a linear equation with respect to r_1 and r_2 , and applied (incorrectly) linear least squares regression for using copolymer composition data to evaluate reactivity ratios r_1 and r_2 ²⁰.

$$G = r_1 F - r_2 \quad (5)$$

where $G = X(Y-1)/Y$, $F = X^2/Y$, $X = [M_1]/[M_2]$, and $Y = d[M_1]/d[M_2]$

Using this method G is plotted against F to give a straight line with slope = r_1 and y-axis intercept = $-r_2$

The above mentioned methods (and other similar efforts at the time (that rely on approximate linearization techniques) by other researchers) for reactivity ratio determination were critically reviewed by Tidwell and Mortimer²¹. They pointed out that assumptions made about independent and dependent variables in linear regression were not satisfied by equation (5) which leads to a lack of quantitative accuracy in the r_1 and r_2 calculation.

Kelen and Tudos²² attempted to improve this and so presented a modified form of the method based on linearization of the Mayo Lewis equation by introducing an arbitrary positive constant (α) into equation (5). Their equation can be expressed as equation (6):

$$\eta = \left[r_1 + \frac{r_2}{\alpha} \right] \varepsilon - \frac{r_2}{\alpha} \quad (6)$$

$$\text{where: } \eta = \frac{G}{\alpha + F} \text{ and } \varepsilon = \frac{F}{\alpha + F}$$

In using equation (6), plotting η versus ε (G and F are as defined for equation 5) gives a straight line having $(-r_2/\alpha)$ and r_1 as intercepts on extrapolation to $\varepsilon = 0$ and $\varepsilon = 1$ respectively. In the above, $\alpha = (F_m F_M)^{1/2}$, F_m and F_M are lowest and highest values of F respectively, and this distributes the experimental data symmetrically on the plot.

In support of the studies of Tidwell and Mortimer, the drawbacks associated with methods based on linearization were also pointed out by O'Driscoll and Reilly^{23, 24}. In this work the statistical limitations of linear(izing) methods were demonstrated by illustrating that the independent variable in the equation was not really independent, while the dependent variable did not have constant variance as required by linear regression methods.

An excellent solution to these problems was reported by Penlidis et al., who developed a computer program that estimated r_1 and r_2 by the error-in-variables-model (EVM) method²⁵. This method estimates r_1 and r_2 using the appropriate and correct methodology via non-linear regression and EVM, and also gives a measure of uncertainty for the values in the form of a 95% joint confidence region. Given the ready access to microcomputers that can run the software it is a user-friendly method of choice for obtaining reliable reactivity ratios for the terminal model of copolymerization. As such it was used in the analytical section of this research project.

The use of the differential form of the copolymer equation is not the only possible way to determine reactivity ratios. Sometimes stopping the reaction at very low conversion may lead to some experimental difficulties which may result in a significant source of error. For instance, if the reaction is not stopped soon enough then drift occurs in co-monomer composition towards the less reactive monomer as conversion increases from monomer to polymer. This results in a variation of copolymer composition as reaction proceeds¹². The equations for instantaneous copolymer composition may be integrated as a function of conversion for any given co-monomer feed. Meyer and Lowry determined such an integrated equation (7) into a closed analytical form to express the

relationship of degree of conversion with co-monomer feed composition (f_1)¹² (corresponding to that conversion level) and the initial monomer feed mole fraction (f_{1_0}).

$$X = 1 - \left(\frac{f_1}{f_{1_0}}\right)^\alpha \left(\frac{1-f_1}{1-f_{1_0}}\right)^\beta \left(\frac{f_{1_0}-\delta}{f_1-\delta}\right)^\gamma \quad (7)$$

where X is the fraction of converted monomer,

$$\alpha = \frac{r_2}{1 - r_2}$$

$$\beta = \frac{r_1}{1 - r_1}$$

$$\gamma = \frac{1 - r_1 r_2}{(1 - r_1)(1 - r_2)}$$

$$\delta = \frac{1 - r_2}{2 - r_1 - r_2}$$

This equation can be used to correlate the drift in feed and copolymer composition with conversion.¹²

To overcome difficulties associated with the integrated copolymer equation, Shawki and Hamielec²⁶ developed a non linear least squares algorithm by using both differential and integral forms of the copolymer equation, which required that composition data (f_1 vs F_1) to be firstly fitted to equation (2) and then the composition-conversion data were used in equation (7). This method based on non-linear least squares was found to be very useful for estimating reactivity ratios from composition/conversion data obtained at intermediate conversion levels (i.e., not limited to low conversion levels only). Thus any experimental difficulties and error which arise for low conversion experimentation due to stopping the reaction at low conversion can be avoided.

In our investigations, the primary strategy was to use low conversion copolymerizations to obtain the necessary feed and corresponding copolymer composition data and then use these data within the EVM framework in order to determine r_1 and r_2 for the chosen reaction conditions. To supplement this, full conversion polymerizations were run and the composition data were also examined by integrated methods.

2.3 Factors Affecting Kinetics of Aqueous Polymerization of Acrylic Acid

Previous kinetic studies of AAm and AA polymerization have examined the effects of different reaction parameters with respect to reaction rates and reactivity ratios. Many of these studies show that some unusual effects (compared to standard radical kinetics) are observed. The following sections will describe some of this work.

The kinetics of polymerizations of polar monomers in aqueous media have been shown to be more complex than those observed for common organic monomers (e.g. styrene and methyl methacrylate) in standard organic solvents. The reaction kinetics of water soluble ionic monomers, such as AA or methacrylic acid (MAA), are generally considered as pH- and ionic strength-dependent. This is because of the possibility of H^+ dissociation for the monomers, which changes the nature of groups adjacent to the reactive C=C double bond. These factors therefore act in addition to the standard effects of concentrations of monomer and radicals, expected based on the standard principles of free radical polymerization¹² discussed earlier.

Many past investigators have worked on the polymerizations of AA type monomers and have reported results which support the concept of pH dependent polymerization for

water soluble ionic monomers. The primary investigation in this regard was made by Katchalsky and Blauer who looked at MAA as a model water soluble monomer²⁷. MAA has similar polymerization characteristics to AA as a model monomer but it is easier to handle as reaction rates are typically slower (by an order of magnitude). In their study they looked at the relation between rate of polymerization and pH²⁷. They presented the idea of pH dependency on polymerization rate in terms of reactivity of the monomer and the polymeric chain end radical acid being in dissociated and undissociated forms¹⁰, see Figure 2-6.

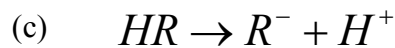
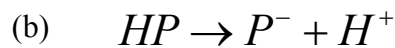
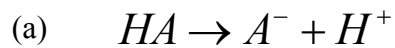


Figure 2-6 Different Dissociating Species for Aqueous Polymerization of Acidic Monomers

HA = Undissociated monomer acid

A^- = Dissociated monomer acid

HP = Undissociated polymer acid

P^- = Dissociated polymer acid

HR = Undissociated polymer acid radical

R^- = Dissociated polymer acid radical

H^+ = Hydrogen cation (proton)

The assumption was made that monomer acid in the undissociated form, which is the major component in a low pH reaction medium, is more reactive than monomer in the dissociated form (at high pH). The situation is more complicated at moderate pH as the

reaction medium will contain both undissociated and dissociated forms of monomer and the concentrations of the two forms will depend upon pH, based on the Henderson-Hasselbach equation (8),

$$pH = pK_a - \log\left(\frac{1-\alpha}{\alpha}\right) \quad (8)$$

Where :

$pH = -\log_{10}[H^+]$, and $[H^+]$ is the concentration of hydrogen ions

$pK_a = -\log_{10}K_a$, K_a is the equilibrium constant for equations , (a), (b) and (c) in Figure 2-6.

α is the degree (fraction) of dissociation of acid.

Therefore the rate of polymerization has a strong dependence on pH. In actual practice the monomer in dissociated form reacts with radicals at a much slower rate than the undissociated form. The assumptions regarding the dependency of polymerization rate presented by Katchalsky are applicable only for the low pH range ($pH < 2.5$), in which most of the monomer acid is in the undissociated form. Thus the overall rate of polymerization is strongly dependent on the concentration of monomer acid in undissociated form or the degree of ionization, α , of the reaction medium, which is a direct function of pH in addition to other factors. The equation developed for the rate of polymerization in which undissociated monomer acid has a dominant role shows the reaction kinetics is pH dependent and is given by equation (9).

$$-\frac{d[M]}{dt} = R_p = k_p \left(\frac{fk_d}{k_t} \right)^{\frac{1}{2}} [I]^{\frac{1}{2}} [M]^{\frac{1}{2}} (1 - \alpha) \quad (9)$$

In equation (10), α is the degree of H^+ dissociation for the monomer, which is a direct function of pH. $[I]$ and $[M]$ are concentrations of initiator and monomer, respectively; k_d , k_p and k_t are the rate constants for initiator decomposition, propagation and termination, respectively. The equation indicates the maximum value for R_p will be when $\alpha = 0$.

The dependency of reaction kinetics of weak-unsaturated acidic monomers (ionic monomers) on pH was studied further by Kabanov et al.^{28, 29}

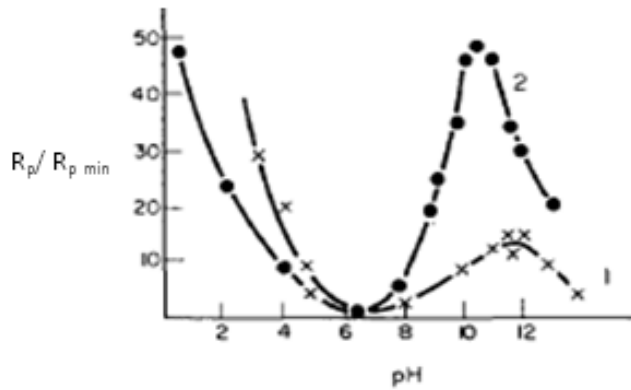


Figure 2-7 Dependence of R_p on pH for Polymerization of MAA (1) and AA (2) at $60^\circ C$.²⁹

Figure 2-7 clearly shows that the relative rates of polymerization ($R_p / R_{p \min}$) have their lowest values at around pH 7 and then they rise again as pH increases towards the basic range. $R_{p \min}$ is the minimum rate of polymerization. The drop of R_p with pH in the range 1 - 6.5 is explained by the increase in α . The increase in R_p at pH > 6.5 was explained as being due to the higher sodium cation (Na^+) concentration, with addition of

sodium hydroxide (NaOH), which leads to ion pair formation. The reaction of different propagating species in aqueous polymerization media with ionic monomers (AA or MAA) over the entire pH range can be explained by the following equations :

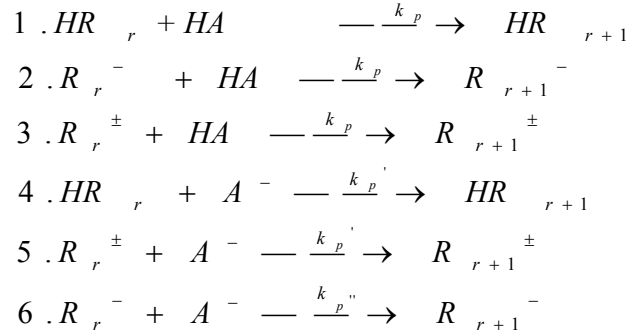


Figure 2-8 Possible Propagation Reactions for Acidic Monomer in Dissociated and Undissociated Forms

HA = Monomer acid in undissociated form

A^- = Monomer acid in dissociated form

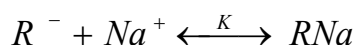
R_r^\pm = Polymeric acid associated with Na^+ of chain length “r”

k_p, k_p' and k_p'' = propagation rate constants

HR_r , and R_r^- are polymer acid radical in undissociated and dissociated forms, respectively. It was assumed that these three types of polymeric radicals in the system possess almost equal reactivity. The rates of propagation in reactions 1, 2 and 3, of Figure 2-8, are assumed to be the same because monomers in undissociated form (at low pH) are reacting with propagating radicals (radicals of same reactivity) and have the same value of the rate constant k_p . In the same way, for reactions 4 and 5, which are possible when the pH is close to neutral, the propagation rates were the same but less than those of the first three reactions due to the lower reactivity of monomer in dissociated form,²⁷ which leads to a lower value of the rate constant ($k_p' < k_p$). In reaction

6, the value of the reaction rate constant k_p'' is approximately zero because both monomer acid and polymer acid radical are in the dissociated form and they both have a negative charge, which leads to electrostatic repulsion between them and results in the slow propagation rate. Based on these assumptions, the increase in polymerization rate at higher pH was possible only if repulsive forces between monomer acid and polymer acid radical were reduced, which would happen due to ion pair formation at high pH where local Na^+ concentration was high.

The ion pair formation takes place according to the following equation:



Where R^- is an anionic polymeric radical and RNa is the equivalent ion paired radical associated with Na^+ and K is the equilibrium constant for the association/dissociation of Na^+ .

Another strong justification of ion pair formation in polymerization of AA and MAA, presented by the same investigators, is the increase in value of the propagation rate constant (k_p), when measured between pH of 7.9 and 13.6. At the same time, they observed that the value of the termination rate constant was not affected by this increase. Hence, the overall polymerization rate increases strongly.

The dependency of kinetics of aqueous polymerization of acrylic acid on pH followed by an ion pair formation was also studied by Manickam et al. (1979)³⁰. This group studied the rate of polymerization and other kinetic parameters both at low pH ($\cong 1$), when monomer acid was in the completely undissociated form, and at high pH (pH =

11) when monomer acid was in the completely dissociated form (acrylate), initiated by persulphate initiator. Their investigation seemed to show that:

1. The rate of polymerization was proportional to 0.5 order of radical initiator (persulphate) concentration, $[S_2O_8^{2-}]$
2. The rate appeared to be proportional to 1.5 order of monomer concentration both at low and high pH for undissociated and dissociated forms of AA, respectively
3. Little difference in activation energies was noted. The activation energies for low pH polymerization and high pH range were found to be 22 and 23.5 kcal/mol, respectively.
4. The reaction mechanism of AA polymerization gave similar kinetic equations for both undissociated and dissociated AA despite the charge difference on polymer acid radical due to the acrylate anion $[CH_2 = CHCOO^-]$.
5. No clear evidence of incorporation of sulphate radical ion as end group was found.

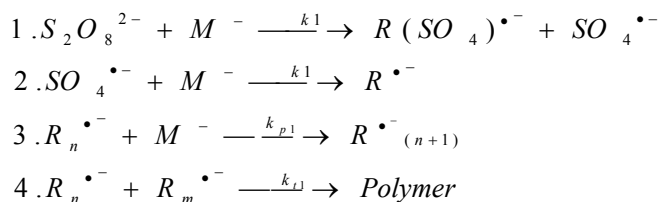


Figure 2-9 Reactions of Persulphate with Monomer³⁰

In the light of these reactions, Manickam et al. explained the reasons as promoted chain propagation due to electron transfer from monomer to $SO_4^{\bullet-}$ resulting in the

formation of a radical cation which may be neutralized by reaction with water molecules present in the system. The expression given for the rate of polymerization was given by equation (10):

$$R_p = \frac{\sqrt{2}k_p k_d^{1/2}}{k_t^{1/2}} [S_2O_8^{2-}]^{1/2} [M^-]^{3/2} \quad (10)$$

Such a mechanism leads to ion formation and an increase in the ionic strength of the reaction medium, which increases the value of the propagation rate constant in reactions (1) and (2) of Figure 2-9 due to decreasing interionic repulsion.

In the low pH range (<1) when the polymerization was performed in the presence of 0.1 M perchloric acid, so that all monomeric acid remained in undissociated form, the rate of polymerization was dependent on the same order of $[S_2O_8^{2-}]$ and monomer but was not affected by changing the ionic strength of the media. It was postulated that the undissociated forms of monomer and polymeric radical dominate the reaction media and no increase in rate of polymerization was observed even after increasing the ionic strength, which also supported the absence of ion pair formation or salt effects in this situation.³⁰

The study³⁰ concluded that the rate of polymerization in acidic media will always be higher than in alkaline media, unless the ionic strength of the medium is increased up to a maximum value where ion pair formation or salt effects can be observed. They also tried to investigate effects of pH on polymerization rate by considering the arguments presented by Katchalsky and Blauer on the basis of different reactions of monomer in acidic (undissociated) and in acrylate ion (dissociated) form. They compared the propagation rate constant (k_p) and termination rate constant (k_t) values for polymerization

of AA for different reactions between pH ranges 2-7 and confirmed that rate of polymerization was proportional to the degree of ionization of AA at practical values of pH.

According to their studies, the rate of polymerization at pH above 7 becomes complicated because of ion pair formation with monomer due to increasing cation (Na^+) concentration by addition of sodium hydroxide. It was concluded that a decrease in electrostatic repulsion due to increasing degree of ion association after pH 7 leads to an increase in polymerization rate.

As has been shown from the early studies, the degree of ionization (α) of ionizable groups such as carboxylic acids has an influence on the value of k_p in free radical polymerization of acrylic acid. In addition there was an unusual kinetic dependency for the reaction with respect to monomer concentration. The results from the early studies showed that the degree of ionization affects the value of k_p in free radical polymerization of acrylic acid. This was further investigated in the most recent studies by Lacik and coworkers³¹, who confirmed some of the previous findings about AA polymerization, regarding rates of polymerization, but their overall conclusions as to the reasons were a bit different. Their studies were performed using Pulse Laser Polymerization – Size Exclusion chromatography (PLP-SEC). Currently, this method is widely regarded as the best way of determining polymerization rate constants.

In the work by Lacik and coworkers, a series of different experiments was performed at monomer concentrations equivalent to 20 and 40 wt % of monomer, in the temperature range of 2.6 to 28.5°C. Firstly, the results of their study showed that there is significant

variation in k_p values with monomer concentration. The value of k_p decreased with increasing concentration of acrylic acid from 20 to 40 wt %, at each temperature studied. The value of k_p for 20 wt % AA is almost 60 % higher than that for 40 wt % of AA, with other reaction conditions kept the same. In addition, the activation energy for k_p was found to be independent of concentration variations.

The k_p values for AA polymerization were also evaluated by using the same technique at fixed concentration of 0.69 M and 6 °C while degree of ionization was varied between minimum ($\alpha = 0$) to maximum ($\alpha = 1$)². At these degrees of ionization, the values of k_p decreased from 111,000 L.mol⁻¹.sec⁻¹ to 13,000 L.mol⁻¹.sec⁻¹. This implies that the apparent value of k_p decreased by one order of magnitude. This again confirmed the trend for AA polymerization for different pH values suggested by Kabanov et al. 1975,²⁹ that the k_p value decreased to a minimum at pH close to 7 when almost all monomer was in the dissociated form. An increase in k_p value was observed if “ $\alpha > 1$ ”, which was achieved by adding more NaOH past the neutralization point. Again it was assumed that the resulting ion pair formation reduced repulsion between reacting species present in the system. An expression was developed for the non-linear dependence of k_p on degree of ionization (α), expressed by equation (11):

$$k_p = \alpha^2 k_{p(\alpha=1)} + (1-\alpha)^2 k_{p(\alpha=0)} + 2\alpha(1-\alpha)k_{p,ionic/non-ionic} \quad (11)$$

In the most recent study by the same group, the k_p of partially and fully ionized MAA in aqueous solution was investigated over a wide range of experimental conditions regarding different concentration, degree of ionization and temperature³². The MAA was chosen for this most comprehensive study because it gave a better behaved

polymerization reaction for a fundamental study. It had been found that there were some inconsistencies in the earlier studies working with AA because of its extremely high k_p values making accurate and repeatable measurement difficult. MAA was also a better system because AA has a significant tendency to transfer reactions which affect the molecular weight measurements that are an essential part of PLP-SEC results. In the study they chose MAA concentrations equivalent to 5 %, 20 % and 40 % (by weight) and studied the effects on k_p by looking at four degrees of ionization ($\alpha = 0, 0.3, 0.7$ and 1) at five different temperatures (6, 20, 40, 60 and 80°C).

The values of k_p were determined at all sets of experimental conditions. MWD data for selected conditions gave consistent results which showed the values of k_p were reliable and were not affected by other parameters in the PLP method, like photo-initiator concentration, pulse repetition rate, number of applied laser pulses and the overall PLP set up. The study gave a comprehensive understanding of how the different reaction variables affected the measured k_p 's. It was found that for fixed other conditions, the values of k_p varied significantly with changing monomer concentration. However, the degree of that variation was different for each of the MAA concentrations used at all temperatures. At the lowest concentration (5% MAA), the values of k_p were about 10 times greater for $\alpha = 0$ as compared to those for when $\alpha = 1$. At the highest MAA concentrations (40%), k_p values were of the same order of magnitude for all values of α (see Figure 2-10). It was decided that this was due to the variation of hydrogen bonding interactions which may arise for different amounts of monomer (acid content) in water.

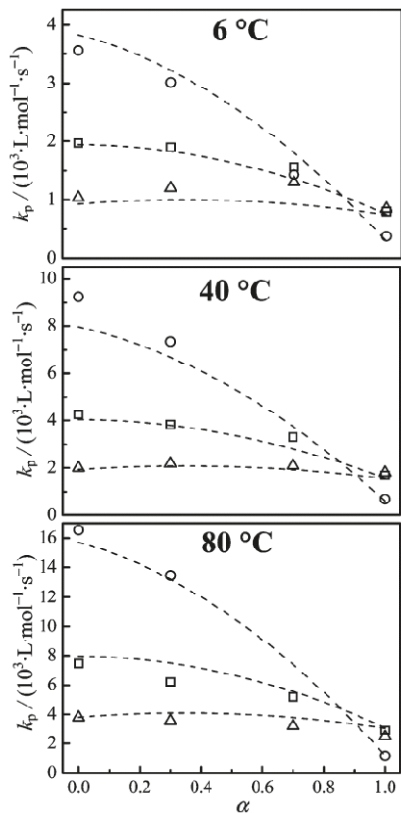


Figure 2-10 Variation of k_p for MAA with α ³². (Symbols for MAA different mass percentage concentrations: 5% = \circ , 20%= \square and 40%= Δ)

The results also showed that the reduced k_p values ($k_{p(\alpha)}/k_{p(\alpha=0)}$) for MAA followed the same trends as seen for those of AA.

An additional effect on k_p was also analyzed. The effect of addition of NaCl was examined over the same range of degrees of ionization at 40° C. This study showed that k_p did not change significantly either with or without added NaCl . This did not follow what was expected by the classical mechanism of polymerization of ionized MAA and AA, as suggested by Kabanov et al.²⁹, in that it was expected that with extra Na^+ ion present the k_p would increase because of ion pair formation. The authors suggested that

the traditionally accepted mechanism should therefore be reconsidered to explain the results.

Lacik et al. have postulated that the differences observed for k_p for the different monomer concentrations stem from changes in the Arrhenius frequency factor with monomer concentration.

$$k = Ae^{-E_a/RT} \quad (12)$$

The Arrhenius equation (12) is normally used to show the dependency of rate constants with temperature, with constant A (pre-exponential or frequency factor) and activation energy (E_a). However, it is clear from equation (12) that variations in A will also lead to changes in k_p . In the polymerization of MAA, the dependency of k_p on T showed that E_a was essentially constant at all concentrations but the A values were higher at low concentrations. It is believed that a higher value of A (k_p) for dilute solutions of MAA was due to less resistance to the internal rotational motion of the monomer. On increasing concentration the resistance or barrier for rotational motion also increased, which resulted in lower value of A and therefore in k_p .

The studies of homopolymerizations of AA (and similar monomers) show clearly that many factors can affect the rate of polymerization. This complexity is compounded by the fact that during the course of reaction the pH conditions may change since AA monomer is a stronger acid than AA in the polymer chain. This can also have an effect on the overall polymerization reaction³³.

2.4 Factors Affecting Kinetics of Aqueous Polymerization of Acrylamide

As with AA, a considerable amount of research has also been devoted to understanding the polymerization kinetics for AAm. It has also been found that this

system often shows kinetic relationships that differ from those of “ideal” radical polymerizations.

Many early studies looked at the persulphate initiated polymerization of AAm and tried to explain apparently anomalous kinetic dependencies with respect to the reaction components in different ways. An early study by Riggs and Rodriguez (1947)³⁴ looked at this complex polymerization system and found an unusual rate dependence with respect to monomer and initiator concentrations. This is shown in equation (13) for M =AAm.

$$R_p = k_p [M]^{1.25} [I]^{0.5} \quad (13)$$

This relationship shows that R_p was apparently proportional to the monomer concentration to the 1.25 order rather than 1, as expected from the general theory of free radical polymerization. The authors concluded that the higher rate order is the result of influence of monomer on rate of initiation (formation of free radicals by promoted decomposition of the persulphate).

Unusual R_p dependency with monomer concentration in the case of solution polymerizations of styrene and methyl methacrylate had been explained on the basis of a hypothesis known as the cage effect theory.¹² The theory postulated that a solvent or a monomer-swollen solvent boundary surrounds the initiator; further aspects of the theory include complex formation due to some association between monomer and initiator, postulating that a reversible complex can be formed between monomer and initiator. The decomposition of such complex yields a primary radical and a macroradical.

For AAm, the cage hypothesis did not provide a valid explanation for the higher rate order with respect to monomer. For example, Riggs and Rodriguez³⁴ opposed the

explanation of complex formation between AAm and persulphate in terms of the activation energy for the process. In their study of AAm polymerization, they reported the overall activation energy of AAm polymerization in aqueous media was 1690 cal/mol. However, the value of the activation energy for thermal decomposition of persulphate initiator was 1680 cal/mol, which means that complex formation did not affect the activation energy significantly because a change in activation energy would be expected if that were true.

Later, Hunkeler proposed that the mechanism leading to the unusually high rate order for monomer (AAm) concentration was the result of enhancement of persulphate decomposition by monomer (monomer induced decomposition of the persulphate, a fact well known from emulsion polymerization observations), in addition to thermal decomposition of initiator³⁵. He presented a hybrid cage-complex theory which postulated that in an aqueous medium hydrogen bonding creates strong association between AAm and persulphate. He further explained that the unusual (high) rate order was constant for low and moderate AAm concentrations and remained constant for AAm concentrations up to its solubility limit in water.

The mechanism of hybrid cage complex seemed to give the best fit to reaction kinetic data for AAm polymerization initiated by persulphate in aqueous media. The interaction proposed was between monomer and initiator by hydrogen bonding due to the presence of water. The extent of this interaction or association between AAm and persulphate was dependant on the hydrogen bonding strength of reacting species which promoted electron transfer from AAm (donor) to the acceptor (persulphate). This then leads to higher initiator decomposition and in the rate order of monomer exceeding one.

In another investigation related to the kinetic mechanism of AAm polymerization, performed by Giz et al.¹³, the online and automatic continuous monitoring of reaction parameters was done to collect data at various conditions of temperature and initiator. This yielded information about molecular weight distribution (MWD) polydispersity and this was then related to a kinetic scheme. The data for monomer conversion vs time for several AAm polymerizations at 70° C followed first order kinetics over a major fraction of conversion, which indicates standard free radical polymerization kinetics. The overall reaction behavior followed the ideal kinetic scheme of free radical polymerization. The MW and initiator decay rate were inversely and directly proportional to the square root of initiator concentration, respectively. This allowed the application of a quasi steady state assumption (QSSA) for evaluating rate constants. Values of k_p^2/k_t for different temperatures were also evaluated for three temperatures and were 16.7 ± 0.95 , 14.7 ± 1.05 and $10.6 \pm 0.75 \text{ Lmol}^{-1} \text{ s}^{-1}$ for 70, 60 and 50 °C, respectively. .

The most recent study of this system has suggested that the unusual kinetics do not stem from variation of reaction order with respect to monomer concentration. Instead, Seabrook et al. have shown that k_p changes with variation in monomer concentration³³⁶ (as has been observed for AA and MAA³²). In their study, Seabrook and Gilbert have examined the polymerization of AAm in aqueous medium using PLP -SEC methodology using three different initiators, including azo and persulphate initiators^{37,38}. They showed that polymerization of AAm in water followed standard free radical kinetics for their dependencies with respect to monomer and initiator concentrations, but k_p changed with monomer concentration [AAm]. Figure 2-11 shows that first order dependence on

monomer concentration is maintained for a given initial concentration of AAm because of the linear relationship for $\ln[\text{AAm}]/[\text{AAm}]_0$ versus time.

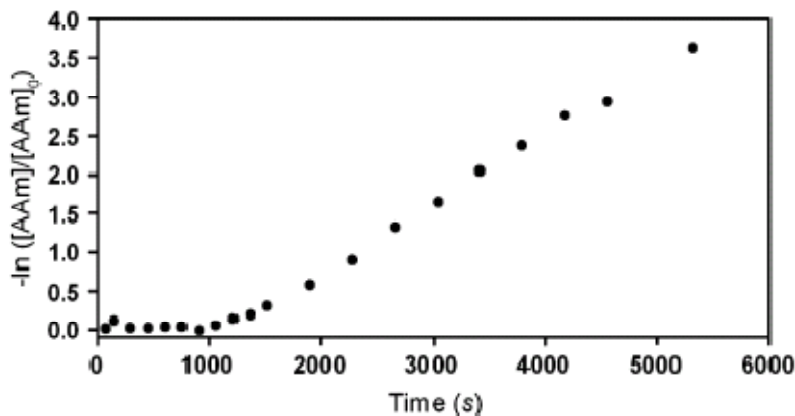


Figure 2-11 Data Showing First Order Kinetics with Respect to [AAm] for AAm Polymerization³⁶ (10% (1.41M) Solution of AAm and 0.0069 M $\text{K}_2\text{S}_2\text{O}_8$)

They explained that the earlier models would not agree with such results. However, they did suggest that there could be a number of explanations for the results and stated the need to obtain more data on the rate constants for the different steps within the overall kinetic mechanism (i.e., for termination, propagation and transfer) on monomer, polymer and added salt concentrations. They concluded that a complete understanding is beyond current fundamental theories and the high sensitivity of all the fundamental rate coefficients in such reaction systems makes accurate measurement difficult. However, it is possible that the reasoning used by Lacik et al. to explain the variability of k_p with [AA] also applies to AAm.

In relation to the work carried out in our study it is important to note in practical terms that the k_p values for the polymerizations of AA and AAm have been shown to be

sensitive to many aspects of the reaction system and this will have an effect on copolymerizations also. This should be noted when considering the copolymerization of AA and AAm.

2.5 Effects of Solvent on Polymerization of AAm and AA

As would be expected given the sensitivity of AA and AAm polymerizations to changes in the reaction medium, the nature of solvent has a considerable effect on reaction kinetics in free radical solution polymerization.

An early investigation to find the effect of different solvents (polar and non-polar) on polymerization of acrylic acid was carried out by Chapiro and Dulieu³⁹. They investigated the effects of two types of solvents; one was a group of polar solvents, water, methanol and dioxane (note also that these solvents can dissolve polyacrylic acid), while the others were non-polar solvents (these solvents cannot dissolve polyacrylic acid). The polar solvents were known to have a strong association with AA due to its carboxyl group that can associate with polar solvents by hydrogen bonding. As a result of this molecular association, the above group of solvents tend to form cyclic dimers or linear oligomers (open dimer), where each carboxyl group was linked to two neighbours. It was assumed that some unusual kinetics of polymerization arise due to such molecular association (complex formation).

An extensive study in this regard was performed by Gromov et al.⁴⁰ who studied the effect of single and combinations of polar solvents on AA and AAm polymerization. A significant decrease in k_p value was noted for AAm polymerization at 40° C for DMSO and tetrahydrofuran (THF), which was, respectively, 5 and 12 times less than that of

AAm polymerization in aqueous medium at the same temperature. The increases in k_p for more polar solvents was attributed to increases in polarity and hydrogen bonding affinity of AAm.

The trends observed for the different solvent's effects on values of k_p and $k_t^{1/2}$ for AA polymerization were similar those for AAm. The values of k_p of AA reported at 30°C for water and DMSO were 31900 ± 1000 and 760 ± 70 L/mol⁻¹ s, respectively, and those for k_t were 1.8 ± 0.05 and 0.20 ± 0.02 L/mol⁻¹ s for water and DMSO for the same temperature. Overall the studies in different solvents show that the intermolecular interactions between AA and AAm monomers have big effects on the monomer reactivity. Given that the interactions are minimized in a highly polar hydrogen bonding solvent like water, it was shown that these interactions slow down polymerizations of AA and AAm. This should therefore also carry over into the copolymerization of AA and AAm, where interactions among all components of the reaction mixtures may affect how the monomers behave in the polymerization reaction.

2.6 Copolymerization of AAm /AA and Reactivity Ratios

As defined in the introduction, reactivity ratios of two monomers M_1 and M_2 , according to the terminal model of copolymerization, are based on the kinetic balance of four possible propagation reactions. We have described in the sections above that the kinetics of homopolymerization of the two monomers are heavily dependent on various reaction operating conditions. It is therefore expected that the reactivity ratios would also be affected by the same factors; like pH, degree of ionization, ionic strength, monomer concentration, solvent and co-monomer ratios, as all of these factors influence the reaction kinetics by affecting the magnitudes of k_p .

It has been proposed in the terminal model of copolymerization by Mayo and Lewis,¹⁴ that the reactivity of the propagating chain only depends on the monomer unit at their growing end. If highly polar or ionic monomer species are involved in copolymerization, the reactivity of the terminal units are significantly changed due to the presence of varying charge characteristics of the monomers. Thus copolymerization of the ionic monomer AA with AAm needs to be assessed with respect to the different degrees of charge distribution, which is a direct function of pH when reactions are in aqueous media. Therefore the copolymer composition can be tuned by changing the pH of the reaction media. In reality the system can be regarded, at some pH values, as a terpolymerization since the AA monomer may have two interchangeable forms.

The pioneering investigators, in the study of AA/AAm copolymerization, were Cabaness et al.¹⁹, who performed detailed experimental studies to evaluate the relationship of reactivity ratios and pH for copolymerization of AAm and AA in aqueous media, initiated by KPS, at 60° C. They studied the copolymerization system over a range of pH from 2.17 to 6.25, which, because of the nature of the H⁺ dissociation mechanism, means that the reacting species were in different forms (see Figure 2-12).

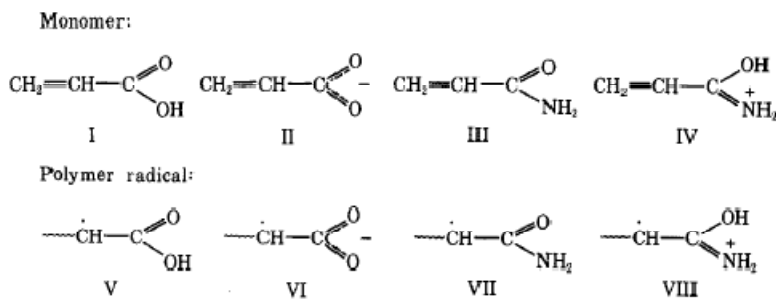


Figure 2-12 Different Forms of Monomer and Monomer Repeat Units for AA and AAm Copolymerization between pH 2 – 6¹⁹.

They stated that varying reactivity of end units affects reaction kinetics and therefore reactivity ratios of AAm and AA in copolymerization because the proportions of the different types of units would vary with pH.

For low pH (< 2), all acrylic acid monomer is in fully non-ionized form, hence reaction medium comprises acrylic acid and partially protonated acrylamide, as pure acids are proton donors (H^+) according to the traditional theory by Bronsted – Lowry. At low pH monomer acrylic acid and protonated acrylamide or acrylate anion and acrylamide essentially undergo a simple copolymerization reaction. The system turns to terpolymerization in the pH range from 2 to 6 due to the presence of acrylic acid, acrylate and acrylamide monomer and their respective propagating chains.

The early results showed that the reactivity ratio of AA (r_1) decreases and that of AAm (r_2) increases with an increase in pH. Thus the content of both monomers AA and AAm or copolymer composition can be tuned by regulating the pH of the reaction media. Figure 2-13 shows a plot of the reactivity ratios versus pH and it shows their cross-over point at pH 3.77, which is at $r_1 = r_2 = 0.56$. It should be noted that Cabaness et al. used the method of intercepts for their evaluation of r_1 and r_2 and that no replication was done in their polymerizations so the absolute reliability of the values should be questioned.

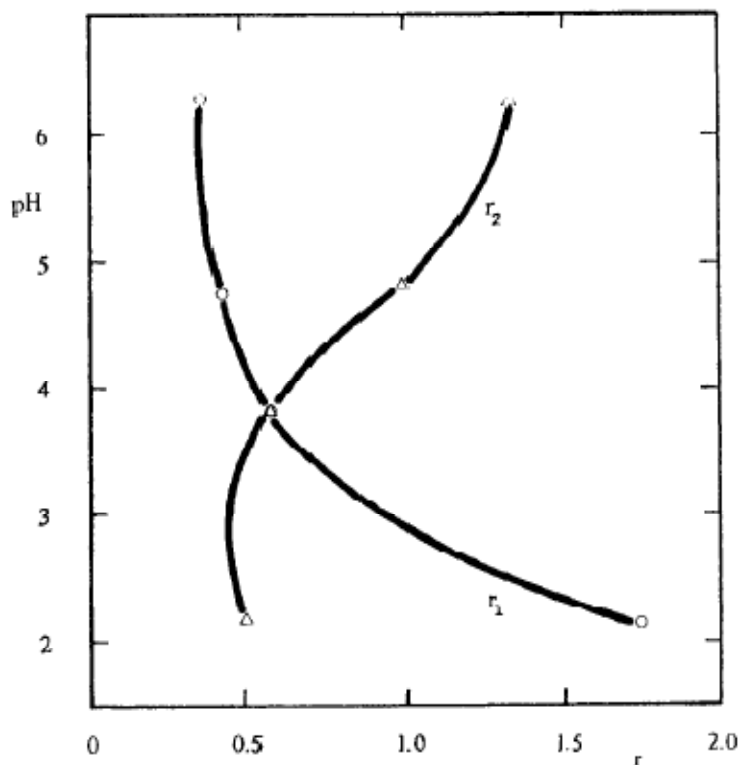


Figure 2-13 Reactivity Ratio Change with pH for AA/AAm Copolymerization¹⁹ (r_1 is for AA)

In another study, conducted by Shawki and Hamielec²⁶, the reactivity ratios of AAm and AA at 40° C (using KPS as initiator) were evaluated from copolymer composition – conversion data from several monomer feeds by an improved non-linear least squares method (NLLS). In the paper, there was no information available for other reaction conditions like pH and ionic strength in their study. They highlighted that the use of NLLS on the integrated copolymer equation and the Mayo Lewis equation (2) overcomes the error related to dependent and independent variable in linearized forms of equation (2). This NLLS method was very helpful for reactivity ratio estimation from composition – conversion data at intermediate conversions and avoided the need for

stopping the reaction at very low conversion, which can lead to significant error due to practical difficulties during the experiment to control the extent of reaction. The reported values for the reactivity ratios are shown in Table 2-1.

Table 2-1 Reactivity Ratios for AAm/AA Copolymerization

Ref	Initiator	Solvent	Temp (°C)	pH	r ₁ (AAm)	r ₂ (AA)
⁴¹	K ₂ S ₂ O ₈	H ₂ O	25	No data	0.6±0.02	1.43±0.03
⁴²	AIBN	C ₆ H ₆	60	No data	1.38	0.36
19	K ₂ S ₂ O ₈	H ₂ O	60	2.17	0.48±0.06	1.73±0.21
				3.77	0.56±0.09	0.56±0.09
				4.25	0.67±0.04	0.45±0.03
				4.73	0.95±0.03	0.42±0.02
				6.25	1.32±0.12	0.35±0.03
⁴³	No data	H ₂ O	No data	6	0.85±0.62	0.33±0.20
				2	0.25±0.36	0.92±0.82
24	K ₂ S ₂ O ₈	H ₂ O	40	No data	0.57±0.04	1.45±0.33

Rintoul and Wandrey have carried out the most extensive investigation describing the free radical copolymerization of AAm and AA in aqueous media¹¹. Their studies were done at 40° C using persulphate initiator over an extended pH range. They also looked at the effects on reactivity ratios of varying such factors as ionic strength, total monomer concentration and initiator concentration. The experimental results yielded useful information in understanding the effect of pH on reactivity ratios for selected reaction conditions and these are summarized in Table 2-2.

Table 2-2. Variation of Reactivity Ratios with pH for AAm/AA Copolymerization from Rintoul and Wandrey¹¹ (Temperature = 40° C, [AAm] + [AA]= 0.4 M, [K₂S₂O₈] = 1.8 × 10⁻³ M)

pH	r ₁ (AAm)	r ₂ (AA)
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

The table entries show a similar trend of reactivity ratio variation with pH as noted in previous literature values reported by Cabaness et al.¹⁹ Both studies showed that reactivity ratios of AAm (r₁) increase with increasing pH (from 1 to 12) (see Tables 2-1 and 2-2), whereas reactivity ratios of AA (r₂) decrease for the same pH range, at the

chosen total monomer concentration. The values for the two studies at equivalent pH are however different, possibly due to different reaction conditions and primarily due to methods of data analysis.

It was also shown by Rintoul and Wandrey that reactivity ratios change with changing monomer concentration (see Figure 2-14).

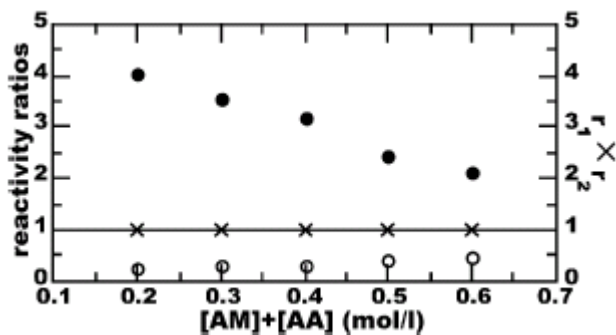


Figure 2-14 Variation in Reactivity Ratios (r_1 ●; r_2 ○, ($r_1 \times r_2$) ×) for AAm/AA Copolymerization at pH = 12¹¹

This was related by the authors to an increase in ionic strength due to an increase in total monomer concentration. It can be seen that for the reaction at pH = 12, r_1 drops significantly but r_2 increases. These effects are not unexpected given that recent studies have shown that k_p 's for both AAm and AA homopolymerization are somewhat sensitive to the monomers' concentrations in solution^{2,36}. The increase in ionic strength due to the increase in total monomer concentration at fixed pH has opposite effects on the reactivity ratios of AAm and AA, which may reflect the influence of electrostatic interactions when an ionic monomer is present in the system. It should be noted that this study on the

effects of concentration was done at only one pH value and it is possible that different trends would be observed at other pH values.

It should also be noted that despite the thoroughness of this study, the reactivity ratios were calculated using the Kelen–Tudos method, which, as explained earlier, uses a linearized form of the differential copolymer equation (and hence ignores the change in error structure, thus violating one of the basic hypothesis for the validity of linear least squares). As a result, it is not the best way to determine reactivity ratios. So the results should probably be re-assessed by using EVM or at least non-linear regression methods. Other investigators have applied the Fineman-Ross method to calculate reactivity ratios, which is also based on a linearization of the differential copolymer equation. The erroneous nature of using linear methods to solve for r_1 and r_2 has been discussed previously and is unnecessary these days since non-linear regression methods can be handled routinely on modern desktop computers.²⁵

In the most recent work on AA/AAm copolymerization, reactivity ratios of AAm and AA were evaluated at pH = 2 and pH = 5 using online monitoring of AAm and AA monomer consumption in a continuous reactor system. Automatic Continuous Online Monitoring of Polymerization (ACOMP) allowed for the direct and continuous monitoring of reaction parameters, e.g., viscosity, conversion of both monomers by UV measurement, and ionic strength and pH during different stages of reaction¹⁸. The polymerization was initiated by 4,4'-azo-bis-(4-cyanovaleric acid) and the reaction temperature was 60°C. On the basis of the copolymer composition data collected a fit to the Mayo-Lewis equation was made using a non-linear technique.^{18, 44} The values obtained are shown in Table 2-3.

Table 2-3 Reactivity Ratios for AAm/AA Copolymerization¹⁸

pH	r ₁ (AAm)	r ₂ (AA)
2	0.16 ± 0.04	0.88 ± 0.08
5	1.88 ± 0.17	0.80 ± 0.07

The values obtained are quite different from those obtained by Rintoul and Wandrey for similar pH values. This could stem again from differences in experimental conditions and/or differences in the methods of analysis.

Finally, Chapiro et al.⁴⁵ studied AAm and AA polymerizations in different solvents, and their results are shown in Table 2-4 ; the results show different behaviour to different solvent dielectric characteristics. They related the differences in reactivity ratio values to changes in the degrees of association between monomers in the different solvents. The higher degrees of monomer association are seen with less polar solvents.

Table 2-4 Reactivity Ratios for AAm/AA Copolymerization in Different Solvents⁴⁵

Solvent	r ₁ (AAm)	r ₂ (AA)
Bulk monomer	0.60	0.57
Benzene	1.0	0.30
Dioxane	1.02	0.35
Methanol	0.84	0.75
Acetic Acid	0.55	0.75
Dimethylformamide	0.52	1
Water	0.47	1.3

Overall, it can be seen from this survey that the homo- and co-polymerizations with AAm and AA are very complex with many interacting variables. Therefore, in order to understand the copolymerization systems well, a carefully designed study is needed to obtain the best understanding of all the effects. The current study was therefore initiated to try and accomplish this.

Chapter 3 Experimental

3.1 Chemicals

AA (inhibited by 200 ppm hydroquinone) and AAm were supplied by Sigma-Aldrich. Potassium persulphate was used as received and supplied by EMD. The initiator, 4,4'-azo-bis-(4-cyano valeric acid) (ACVA) and 'Nochromix' (Godax Laboratories Inc.) were used as obtained from Sigma-Aldrich. Ultrapure water HPLC-grade was obtained from B & J for polymerization reactions and GPC polymer sample characterization analyses. Nitrogen gas was supplied by Praxair (grade 4 PP).

AAm was used as received. AA was purified by distillation under vacuum at a temperature of about 40°C. Vacuum was maintained at 10 Torr throughout the distillation process by regulating the downstream inlet valve. The initial few mL of AA collected were discarded and only the middle fraction was collected for reactions.

Elemental analyses of polymer samples were done by Guelph Chemical Laboratories Ltd., Guelph, Ontario.

3.2 Equipment

The pH meter used was an Orion 520 A. The pH meter was calibrated periodically with buffers at pH = 5, 6 and 7, in order to ensure consistent pH measurement for reaction solutions. Calibration was performed according to typical instructions in the instrument manual. For calibration standards, typical pH buffer solutions, supplied by BDH chemicals, were used.

For polymerizations in vials flat bottom Wheaton vials (20 ml), supplied by VWR, were used with appropriate sealable caps.

3.3 Cleaning of Glassware

Glass crucible filters, used for collecting precipitated polymer, were soaked in 'Nochromix' cleaning solution for at least 24 hrs before use. The cleaning solution was prepared by adding one packet of 'Nochromix' crystals in 2.5L of sulphuric acid (98 %). The 'Nochromix' effectively cleaned and removed contaminants from the sintered glass of the filters. The filters were then rinsed thoroughly with de-ionized water and dried thoroughly before reusing.

3.4 Stock Solution Preparation

Primary stock solutions of monomer with a total monomer concentration of 2 mol/L were prepared (proportions of the 2 monomers depended on the particular experiment) by mixing given amounts of AAm and AA in water (see more details in Chapter 4). For a given experiment the appropriate amount of AAm was first dissolved in a small quantity of water in a flask, and subsequently the required amount of AA was added to it to give the appropriate molar ratio of monomers. For a given experiment, 25ml of the stock solution was taken and the required amount of initiator (persulphate $K_2S_2O_8$ or azo initiator ACVA) was then added to the solution. The pH of the reaction solution was then adjusted to the desired pH by adding the necessary amount of sodium hydroxide solution from a burette and finally the solution was further diluted to a volume of 50 mL of a volumetric flask to give the total monomer concentration of 1 mol/L. The stock solution was kept in the refrigerator prior to use to avoid the chance of premature polymerization.

When ACVA initiator was used, a stock solution was prepared as the sodium salt by neutralization with sodium hydroxide because the initiator in the acidic form was not completely soluble in the initial monomer/aqueous solutions.

3.5 Reactivity Ratio Experiments

In principle, the measurement of reactivity ratios is straightforward; the Mayo-Lewis equation linking feed and copolymer compositions can be fitted to the measured compositions of different copolymers formed from several solutions with different monomer proportions. The nature of the Mayo-Lewis equation means that respective copolymer compositions for a set of different monomer feeds will give the data needed to solve for r_1 and r_2 by suitable regression techniques. For many studies researchers use a large number of feed compositions and obtain the necessary data¹¹. Depending on the number of feeds studied this can be experimentally very time consuming and wasteful in resources if a large number of feeds are used, or it can lead to imprecise results if few feeds are used and they are not the best ones for the reactivity ratio estimation of the chosen copolymer system. The Tidwell-Mortimer criterion gives a method for choosing the optimal two feeds for reactivity ratio estimation by utilizing prior estimates of r_1 and r_2 (normally taken from previous studies) in equations (14) and (15) shown below. The Tidwell-Mortimer criterion was used to determine the optimal feeds needed in the estimation of the reactivity ratios.^{21, 46}

$$(f_1')_o = \frac{r_2}{2 + r_2} \quad (14)$$

$$(f_1'')_o = \frac{2}{2 + r_1} \quad (15)$$

In equations (14) and (15) $(f'_1)_0$ and $(f''_1)_0$ are the two initial feeds of monomer 1 in the copolymerization reactions.

The application of the criterion by Tidwell and Mortimer¹⁹, based on a D- optimal design of experiments, gives optimal values of monomer feeds for obtaining corresponding copolymer compositions needed to relate to the Mayo-Lewis copolymer equation (2). Hence, it gets around the need to perform numerous experimental feeds and obtaining the corresponding copolymer compositions for best fit in the copolymer equation.

For our study, the initial estimates of r_1 and r_2 were taken from previously published data by Rintoul and Wandrey¹¹ (see Table 3-1) for their measurements at pH 6.2, which is close to our experimental pH value of 6.3.

Table 3-1 Reactivity Ratios for AAm/AA Copolymerization at pH =6.2¹¹

r_1	r_2
2.5	0.39

For the values of reactivity ratios used this gave suggested mole fractions for the two experimental feeds as $(f'_1)_0 = 0.163$ and $(f''_1)_0 = 0.444$, and these were used as the basis for planning feeds in the experiments to determine reactivity ratios.

3.6 Adjustment of pH

Before polymerization, the pH of reaction solutions had to be adjusted to obtain the selected experimental conditions. For example, when a stock solution (typically for 50/50 mixtures of monomer) with the appropriate monomer ratio was prepared, 25 mL of

each initial mixture of monomer feed (total monomer concentration in the stock was 2 mol/L) were put together with the required amount of initiator (the amounts appropriate for the correct concentrations of reagents in 50 mL reaction solution) in a 50ml beaker. The beaker was then placed on a stirrer plate along with a small stirrer bar. The tip of the pH meter electrode was immersed in the solution and placed so that it did not strike the stir bar. 3M sodium hydroxide solution was added dropwise from a burette into the beaker while stirring. The pH of solution was noted and NaOH was added until the required pH was obtained. The amount of added NaOH varied depending on the proportions of AAm and AA.

For other reactions, the correct amounts of AAm and AA to make 50mL of solution with a total monomer concentration of 1 mol/L were dissolved in water and then initiator was added. Following this, the pH was adjusted to the correct level by the method above. The solution was transferred to a 50 mL volumetric flask (with rinsing of the beaker to ensure complete transfer of contents) and the solution was then made up to the mark.

3.7 Polymerization Procedures

3.7.1 Low Conversion Polymerization

Prior to reaction, empty vials (with their aluminum/rubber seal caps) were weighed to four decimal places of 1g. The empty weight was noted. Approximately 15mL of reaction solution was placed in each of vials with assigned numbers to ensure identity of vials. The gross weights of the vials plus contents were noted. The vials were then sealed by using a sealing crimper and put into the fridge until the next step in the procedure.

Oxygen is considered a major source of inhibition in free radical polymerization. The presence of oxygen suppresses polymerization by reacting with both initiating and propagating radicals. Therefore it is very important to remove oxygen efficiently from polymerization reactors in order to obtain consistent reactivity in free radical polymerizations. Therefore the reaction vials were thoroughly purged with N₂ to remove oxygen prior to reaction. Each vial was purged by N₂ through needles which were connected to a N₂ gas cylinder assembly, which allowed for degassing of 3 vials at one time. Each of the three vials was fitted with bleed needles, which were inserted before the main needle used for the N₂ feed. The N₂ supply needle was properly inserted down to the bottom of each vial through the rubber seal and the tip of the bleed needle was placed above the liquid level. The flow rate of N₂ was maintained at a fairly fast level that was a compromise between efficient purging and forcing solution out of the bleed needle. The vials were purged with nitrogen for at least 30 minutes. Once the purging was completed, the vials were isolated from possible oxygen re-contamination from air by putting a small amount of grease around the rubber seal of the vial cap.

Note that for the reactivity ratio analysis it was essential to keep monomer conversion at a low level (preferably at or below ca 5%). Since the reaction rates varied with each feed composition, it was necessary to do screening runs which tracked conversion with time for each feed. This was done using procedures similar to those described below for full conversion polymerization. These runs were utilized to decide the time of reaction for the vials used in the subsequent reactivity ratio analysis.

Once these times of reactions were obtained, for each set of experiments for a particular monomer feed, at least three replicate vials were prepared by the procedure

described above. These preparations represented completely independent trials (and hence replicates, as everything was done from scratch). The vials were placed into a temperature controlled shaker bath at 40° C (Grant OLS 200), with the shaking speed set at 110 rpm. The temperature setting was checked by using a manual thermometer, and if there were significant differences between the readings, the bath set temperature was adjusted to give the desired thermometer temperature. Each of three vials was put into the shaker bath sequentially, at two minute intervals; times were noted so that each vial stayed in the water bath for the same time. After completing the assigned reaction time, each vial was taken out of the shaker bath and a few drops of water/ tertiary butyl catechol (TBC) mixture was syringed into the vial to stop polymerization at that instant (TBC is an inhibitor and stops the polymerizations). The vial cap was then opened by using a seal opener and one or two drops of 3M NaOH solution were added to ensure that all AA was converted into the acrylate salt form (to get better precipitation of the polymer) and then vial contents were transferred into a 250 ml conical flask already containing 150 ml of methanol (ca 10 times more of the polymerization solution in reaction vials) to isolate the polymer. Each vial had to be thoroughly rinsed and washed with plenty of methanol to ensure that all of the polymer produced was removed from the vial. The flasks containing the mixtures were then shaken to ensure complete precipitation of polymer products. Polymer products were then filtered through sintered glass crucibles and washed with methanol before transferring to a vacuum oven (at 50°C) for drying.

3.7.2 Full Conversion Range Experiment

For full conversion range reactions, solutions made as described above, of 0.5 mol/L of each monomer AAm and AA, were utilized with the appropriate concentration of initiator (4×10^{-3} mol/L). For each experimental run, multiple vials were prepared and allowed to react in the shaker bath for different time intervals between 10 to 300 minutes, according to the procedure described for low conversion experiments.

3.7.3 Calculation of Conversion

Conversion of monomer to polymer was determined gravimetrically by comparing the mass of isolated polymer to the mass of monomer in a reaction vial.

$$\text{Conversion}\% = \text{mass of polymer} / \text{mass of initial monomer feed} \times 100\%$$

Before the conversion calculation was made, polymer samples were dried for at least 48 hrs in a vacuum oven at 60° C.

3.7.4 Calculation of Copolymer Composition (F₁)

The constituents of copolymer that could be analyzed were carbon, hydrogen and nitrogen. In addition, oxygen and sodium were also present. The molar fraction of monomer in the copolymer (hence, copolymer composition) was calculated from the percentages of C, H and N. Example calculation data are shown in Appendix B and C.

Chapter 4 Results and Discussion

4.1 Screening Studies

The experimental work started with an investigation of AAm/ AA copolymerization at 40° C with a $K_2S_2O_8$ concentration of 0.001 mol/L and $f_{AAm} = 0.5$ (feed mole fraction of AAm). This was done to obtain an understanding of how to work safely with the monomers and to refine procedures needed to be able to carry out reproducible studies of the polymerizations. Preliminary work was done in a 250 mL reaction flask heated in a water bath at 40°C. The solutions were degassed by bubbling N_2 for 1 hour at 0°C prior to warming the reaction flask to the reaction temperature. The solutions were stirred using a magnetic stir bar. Using this method, inconsistent rates of polymerization were noted (variable induction periods and rates) and reproducibility of results in terms of monomer consumption with respect to time was poor. In order to achieve targeted levels of conversion for the reactivity ratio determination it is necessary to have predictable conversion levels and it was clear that this could not be routinely achieved using this method.

Therefore it was decided to switch to a method whereby stock solutions of AAm/AA and initiator were made up and the pH adjusted to the appropriate level and after this, portions of stock solutions were transferred to vials (ca 20 mL maximum volume); these were then sealed with rubber-lined crimp caps. The smaller amount of liquid in the vials could be purged more efficiently than a larger amount in a flask. The vials prepared in this way were then placed in a temperature controlled shaker bath, which again gave better temperature control than that obtained using the flask method. So overall, this method led to far better experimental reproducibility in terms of reaction kinetics, which

is an essential factor for a project such as this one. Even with this modified experimental procedure, it was found that many factors affected the consistency of results obtained for the kinetic studies. Key aspects to be maintained were:

- a) Consistency in degassing solutions. Time and flow rate of N₂ in the purging of the vials had to be kept consistent.
- b) Vials had to be maintained at low temperature during the purge to minimize loss of contents due to evaporation and to prevent early initiation of reaction.
- c) The time that the stock solution sat prior to reaction (especially when using KPS as the initiator) was also a factor. It was likely that promoted dissociation of KPS occurred to some extent. Therefore, if the time that the solution was standing was not kept consistently, then inconsistent final results were obtained.

Initial screening of the copolymerization reactions took place at pH 4 - 5 in order to check whether low conversion could be achieved consistently (< 5 %). The rates of polymerization using this pH range were found to be too fast; leading to conversions of more than 5% in very short periods of time. Given the experimental methods, consistency for equivalent reactions could not be ensured for such fast rates. As was discussed in Chapter 2, reaction kinetics of homopolymerization of AA shows that the relative rate of polymerization (R_p / R_{pmin}) continuously decreases as pH increases from pH ≈ 2 to a pH close to 7^{2, 31}. Hence it was decided for this system, in order to achieve low conversion within a convenient sampling time, that the pH range 6.3 – 6.4 would be used. Once these factors were taken into account, the actual study of AAm/AA copolymerization to assess the reactivity ratios was undertaken.

4.2 Estimation of Reactivity Ratios for AAm/AA Copolymerization with Persulphate Initiator

The nature of the Mayo-Lewis equation dictates that one should obtain copolymer compositions for the copolymer products from the polymerization run at a range of monomer feeds of varying compositions. The data obtained can be used to determine r_1 and r_2 by suitable regression techniques applied to the Mayo-Lewis equation. For many studies, researchers use a large number of feed compositions and obtain the related data¹¹. Depending on the number of feeds used, this can be (unnecessarily) very time consuming and resource intensive if a large number of feeds are used, or it can lead to imprecise results if few feeds are used and they are not the optimal ones for the reactivity ratios under study. As was outlined earlier in the experimental section, the Tidwell Mortimer criterion gives a method for choosing two optimal feeds for reactivity ratio analysis by utilizing prior estimates of r_1 and r_2 . For our study, the optimal values for feeds to be studied were $f_{1(AAm)0} = 0.163$ and 0.444 . In addition, a feed was run with about $f_{AAm} = 0.5$ to obtain extra data for further confirmations.

The experimental studies were run at a temperature of 40°C, the pH was set at about 6.2 and the KPS initiator concentration was 4×10^{-3} mol/L. The details of planned feed compositions used for AAm and AA concentrations are given in Table 4.1. Since the total monomer concentrations were 1 mol/L these were also the numerical values for the mole fractions to be used. These were the ones based on the Tidwell-Mortimer criterion plus another feed to obtain additional data and information. In running the experiments, multiple replicate vials were run for each of the selected feeds, in order to obtain better estimates of the experimental reproducibility (and hence, of the underlying (inherent, intrinsic) overall error). This is very important in kinetic studies of any kind, as without

independent replication, one cannot make comparative statements with any confidence, and yet (surprisingly) very few researchers follow this practice.

Table 4-1 Planned Monomer Concentrations for AAm/AA Reactivity Ratio Experiments with KPS as Initiator

[AAm] (mol/ L)	[AA] (mol/ L)
0.500	0.500
0.163	0.837
0.444	0.556

The actual initial monomer mole fractions (monomer feeds) used are shown in Table 4-2. The table indicates the actual initial mole fraction of Aam $(f_1)_0$ used in the reaction along with the corresponding copolymer compositions (F_1) (mole fraction of AAm in the copolymer) and the monomer conversion levels obtained (uncertainties in percentage conversion levels for a given run were estimated to be about ± 0.5). It can be seen that for most of the reactions the conversion levels were around 5%, thus indicating that they would be acceptable for the reactivity ratio analysis. The samples obtained for higher conversion levels gave similar compositions to those obtained for lower conversions (notable for samples for $(f_1)_0 = 0.4902$), so drift in composition was not significant. Molar copolymer compositions were obtained from elemental analysis (C, H, N analysis) of the samples. The molar proportion of AAm was calculated directly from the percentage of N in the samples and the molar equivalent of AA was calculated from the amounts of C, after the carbon from AAm was deducted from the total C in the samples.

Table 4-2 Results of Low Conversion AAm/AA Copolymerization with KPS as Initiator

$(f_1)_0$ (AAm)	$F_{I(AAm)}$	Conversion (%)
0.4902	0.696	5.4
0.4902	0.688	6.3
0.4902	0.678	7.1
0.4902	0.694	5.9
0.4902	0.622	6.1
0.4902	0.680	9.8
0.1664	0.349	7.4
0.1664	0.333	4.9
0.1664	0.330	5.3
0.4423	0.644	5.7
0.4423	0.649	5.1
0.44223	0.657	5.2

The data for $(f_1)_0$ and F_1 were used to calculate r_1 and r_2 . The copolymer composition and feed data for each set of low conversion experiment calculated from elemental analysis results were used in the micro computer program developed by Dube et al. for using the EVM technique to calculate reactivity ratios²⁵. In order to use EVM there is a need to properly address all sources of experimental error specifically related to monomer feed and copolymer composition. The error involved with monomer feed composition $(f_1)_0$ in the present investigation was calculated as 1% due to different experimental steps having potential error sources from weighing and other procedures, used in making the stock solutions and also during nitrogen purging of vials, which may lead to escape of

monomer solution from the bleed needle. For the copolymer mole fraction, the error was initially considered as 5%, this being typical for different types of copolymer analysis⁴⁷. This seemed reasonable for our results, as the standard deviation for F values from multiple replicate vials using $(f_1)_0 = 0.4902$ was about 0.03 for an average value of $F_1 = 0.676$. In addition, initial estimates for the reactivity ratios have to be used to start the iteration. The values chosen were from Rintoul and Wandrey for pH = 6.2 ($r_1 = 2.50$ and $r_2 = 0.39$). After running the RREVM computer program, the point estimates obtained were $r_1 = 2.0066$ and $r_2 = 0.3234$. In order to quantify the level of uncertainty in these values the EVM program produces 95% joint confidence regions (contours). Figure 4.1 shows the reactivity ratio point estimates obtained, along with confidence regions calculated assuming 5 and 10% error in the F_1 values. The error encountered in copolymer composition (F_1) was taken up to 10%. This was thought reasonable because some copolymerizations were run to conversion levels greater than 5%, which indicated less precision in terms of composition drift, and so the compounded uncertainty for composition was assumed larger than normal.

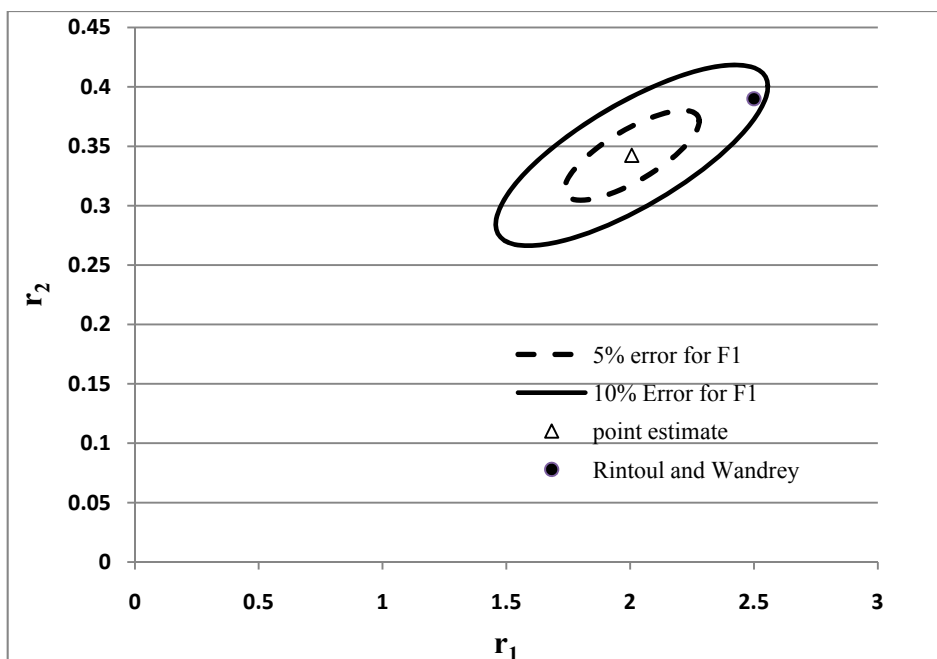


Figure 4-1 Reactivity Ratios for AAm/AA Copolymerization with KPS as initiator

The results in Figure 4-1 show that the literature values for r_1 and r_2 at pH = 6.2 for both AAm and AA were not included in the 95% confidence contour for the values when the error in F was assumed to be 5%. However, the literature estimates from Rintoul and Wandrey were closer to the upper limit of the contour, particularly the value for r_1 . The values from the Rintoul and Wandrey study were found to be inside the contour when the error in F was set at 10%. For this case both calculated and literature values of reactivity ratios were situated within the 95 % posterior probability contour, which shows that the calculated values could be regarded as the same at the given pH range.

The predicted f_1 versus F_1 plots were determined using the reactivity ratios obtained in the two studies and the Mayo Lewis equation (2); these plots are shown in Figure 4-2 (M-L curves). It can be seen that the experimental data do have some overlap with the

predicted curve using the Rintoul and Wandrey estimates. Essentially only one point is significantly different. This point may be an outlier since it is outside the standard deviation for the feed where $(f_1)_0 = 0.4902$. So possibly the one point could have skewed the estimation values for our study.

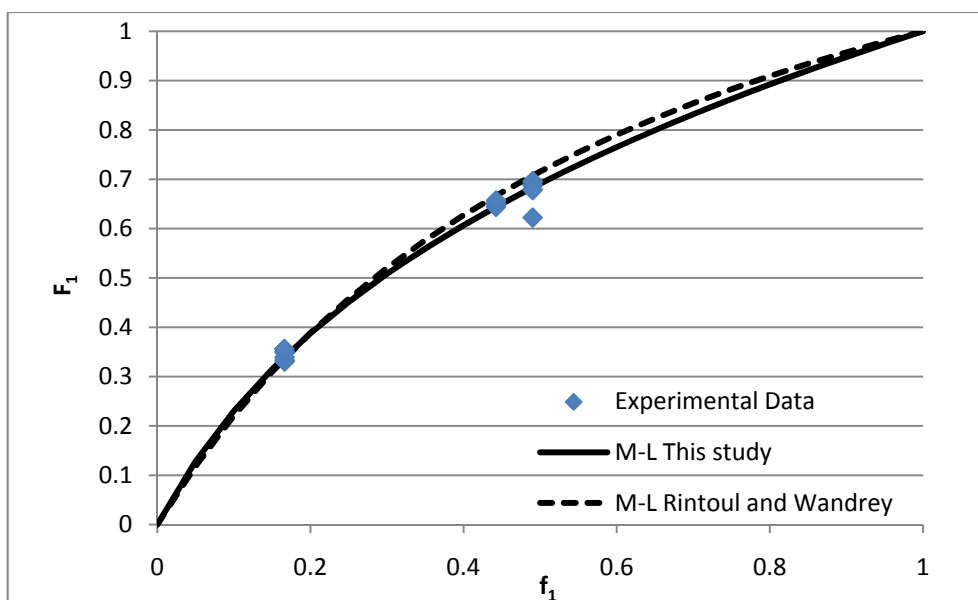


Figure 4-2 Mayo-Lewis Curves for Experimental and Literature Reactivity Ratios; Based on the Data from Table 4-2

It is worth noting that Rintoul and Wandrey used the Kelen-Tudos method to calculate r_1 and r_2 . So this could also lead to the differences seen in the reactivity ratio values. In addition, they did not include any estimates of error in their measurements and it is likely that, if this were done, overlapping confidence contours would be obtained for the sets of results from their experiments and those obtained in the current study.

It should be noted that Rintoul and Wandrey have shown that for AAm/AA copolymerization, at a pH =12, r_1 drops with increasing total monomer concentration; see

Figure 2-14. The concentrations of monomer used in our study were higher than those used by Rintoul and Wandrey. Therefore, their reported trend in r_1 values is followed with the differences noted in r_1 values for their study and this current investigation. However, they also showed that r_2 increases slightly with increasing monomer concentrations, which was not the case in going from their study to this one.

Looking at this in more detail, it might be expected that the values of r_1 and r_2 would be significantly different from the two studies. Firstly, it should be considered that the total concentration of monomer used in the earlier study was less, which could explain the differences. Moreover, the studies by Seabrook and Gilbert have shown that k_p for AAm (k_{11} for the AAm/AA copolymerization) is affected by monomer concentration. It was shown in their study that the value of k_p decreases with increasing monomer concentration (e.g., for AAm polymerization at 30°C with an azo-initiator, k_p drops by 20% when the [AAm] increases from 0.3 mol/L to 0.7 mol/L). Similarly, for fully ionized AA monomer, Lacik et al. showed that k_p increases with an increase in AA concentration. In contrast, for non-ionized AA, k_p decreases with an increase in concentration. In our study the AA should be essentially fully ionized at pH = 6.3 so it might be expected that $k_{p(AA)}$ would increase, which would lead to an increase in the determined r_2 , which is not what was noted.

There are no studies of how the two cross propagation rate constants (k_{12} and k_{21}) vary with conditions and so we cannot make definitive statements as to how the reactivity ratios would be affected under these changing conditions, since presumably both k_{12} and k_{21} would be affected as well as the two homopropagation constants. The indications are from all previous studies that for polymerizations involving AAm and AA the k_p 's are

very sensitive to all possible reaction variables. This then should lead to some changes in reactivity ratios with changing conditions. Further work is needed to confirm or discount the ideas put forward above.

4.3 Estimation of Reactivity Ratios for AA/AM Copolymerization at pH 6.2 with 4,4'-Azo-bis-(4-cyano valeric acid) Initiator

It has been known that AAm leads to enhanced initiator decomposition. This promoted decomposition leads to polymerization being quite fast, which in turn leads to difficulties in reproducibility of conversion levels in the kinetic runs. So a study was done to look at the copolymerization of AAm with AA using an alternate initiator to KPS, with the thought that extent of polymerization would then be easier to control. The initiator chosen was 4,4'-azo-bis-(4-cyano valeric acid) (ACVA). This is an azo-initiator that had been used in an earlier study by Paril et al¹⁸.

The experiments initially carried out used the same feed levels as those described in Table 4-1. Assuming that initiator should not change reactivity ratio values, the optimal feeds by the Tidwell-Mortimer criterion should have been the same for this study as they were for the reactions using KPS initiator. The actual feeds used are shown in Table 4-3. The extra feeds at $(f_1)_0 \approx 0.13$ were done to obtain more data for confirmation of trends. It can be seen that there was more scatter in the conversion levels for this set of runs. This highlights the difficulties in getting reproducible low conversions with this system when the underlying reaction rates are inherently fast. However, it was decided that they would be acceptable for the reactivity ratio analysis in conjunction with higher levels of uncertainty than is recommended for best accuracy. Copolymer compositions were again obtained from elemental (C, H, and N) analysis of the samples. The molar proportion of

AAm was calculated directly from the percentage of N in the samples, whereas the molar equivalent of AA was calculated from the amounts of C, after the calculated carbon content from AAm was deducted from the total C content in the samples.

Table 4-3 Results of Low Conversion AAm/AA Copolymerization with ACVA as Initiator

$(f_1)_0$	F_1	Conversion (%)
0.4988	0.643	7.6
0.4988	0.617	6.1
0.4988	0.624	9.1
0.1747	0.356	4.9
0.1747	0.355	5.8
0.1747	0.369	3.6
0.4426	0.604	5.9
0.4426	0.627	6.9
0.4426	0.648	6.3
0.1375	0.304	3.4
0.1375	0.305	4.9
0.1352	0.314	15.5
0.1352	0.307	16.8
0.1352	0.315	15.4

These data were used in the calculation of r_1 and r_2 by EVM. The point estimates obtained in this case were $r_1 = 1.3465$ and $r_2 = 0.2592$. The confidence contours for the estimates assuming 5 and 10% error in copolymer composition were also obtained. These results are illustrated in Figure 4-3 along with the point estimates for the

experiments using KPS as the initiator and those from the Rintoul and Wandrey study. As with previously shown 95% joint confidence regions (posterior probability contours), the calculated confidence regions are elliptical, approximate shape and approximate probability content, contours.

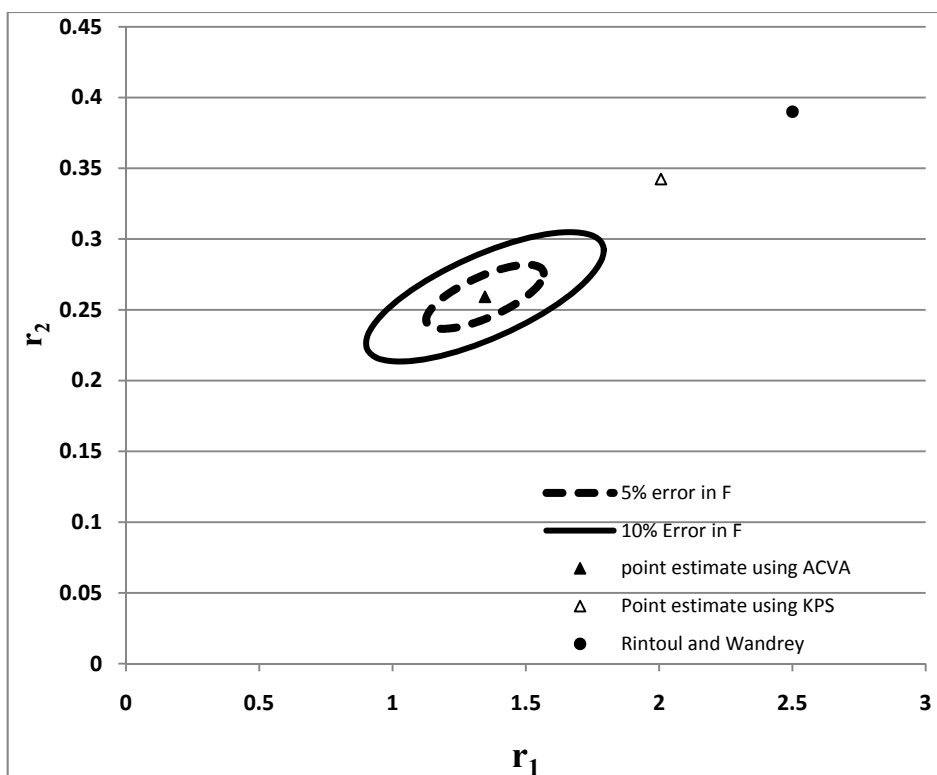


Figure 4-3 Reactivity Ratios for AAm/AA Copolymerization with ACVA as Initiator and Comparison with Other Results

The results of Figure 4-3 suggested that there was a definite difference between the results from the ACVA study and the earlier works, even if the highest level of error in the composition was used. If the confidence contours (using 10% error in F_1) are considered for the results from the experiment using KPS, then there is some overlap but only to a small degree (see Figure 4-4).

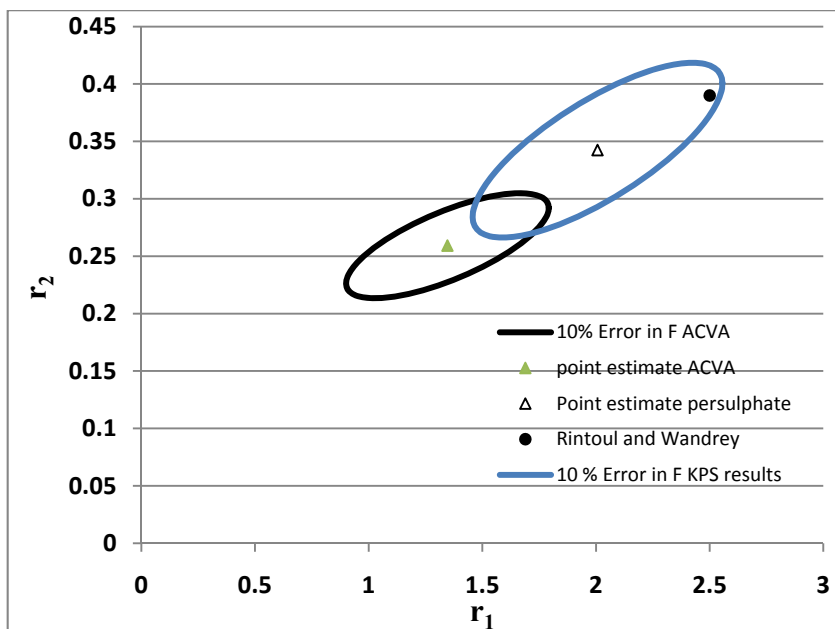


Figure 4-4 Comparison of Reactivity Ratios for AAm/AA Copolymerization.

This apparent difference in reactivity ratios for the copolymerizations using the different initiators was surprising and so it caused questions about whether the data analysis was consistent or whether there were some problems in the experimentation in relation to copolymer composition values for specific feed compositions. Checking the data shown in Tables 4-2 and 4-3, it is clear that the main deviation was for the feeds where $(f_1)_0$ values were close to 0.4 and 0.5. With these feeds the compositions for polymers from the reactions using ACVA as the initiator were generally lower in AAm than the ones when using KPS as initiator. After initiation of a chain the initiator fragment is not expected to have much influence on the reactivity of the chain end radical as the chain grows (it is normally expected in radical copolymerization that copolymer composition should not depend on the initiator used). Given this, these points were a

possible experimental discrepancy. Therefore it was decided to conduct experiments at an extra feed level in order to check again the trends seen for the runs using ACVA. The level chosen was higher in AAm ($(f_1)_0 \approx 0.6$), since it was at higher AAm levels that the largest deviation happened in the initial work. The expectation was that if the composition followed the trends seen for the experiments with KPS, then the copolymer composition would be about 0.77. If the composition followed the trend for the experiments using ACVA, then the composition would be about 0.7. The actual feed and resulting copolymer composition results are shown in Table 4-4.

Table 4-4 Extra Feed for AAm/AA Reactivity Ratio Study with ACVA

$(f_1)_0$	F_1	Conversion (%)
0.5866	0.688	6.8
0.5866	0.715	15.0
0.5866	0.721	6.0

These data once more confirmed the difficulty in getting good consistency in conversion levels; nevertheless, the composition data were used, along with the data shown in Table 4-3, to recalculate r_1 and r_2 . The results for composition were clearly in the region expected for the earlier experiments using the ACVA initiator. The data were included in another evaluation of reactivity ratios by EVM (and the computer program RREVM). The results were $r_1 = 1.3359$ and $r_2 = 0.2585$. This largely confirmed the earlier ACVA results since the value of the point estimate changed very little. Figure 4-5 shows comparisons between the confidence contours with the new results, along with point estimates for the two stages of reactivity ratio estimation.

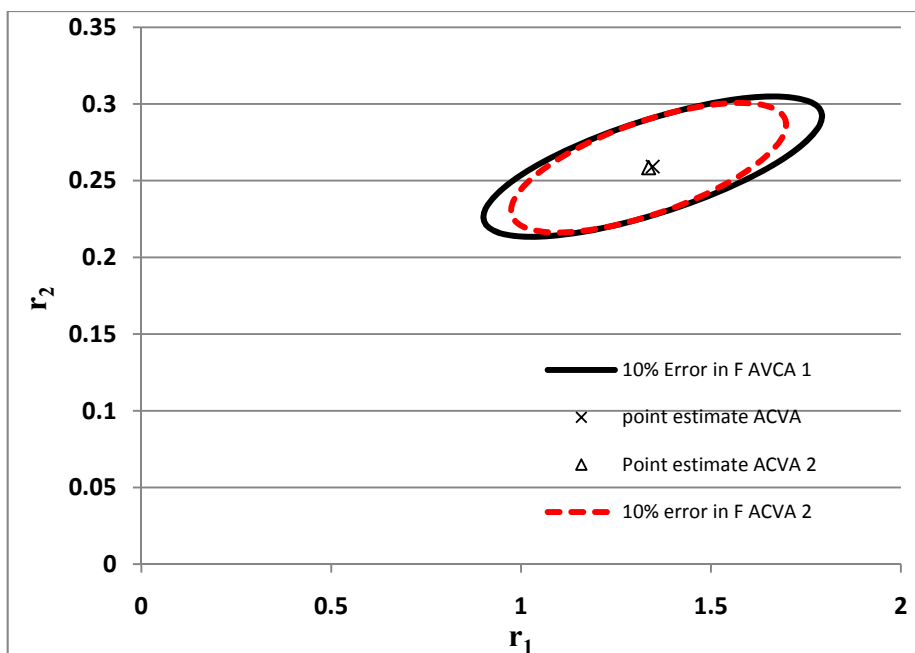


Figure 4-5 Estimated Reactivity Ratios and 95% Joint Confidence Regions for AAm/AA Copolymerizations with ACVA initiator

It can be seen that the addition of the extra feed shrinks the elliptical confidence regions but leads to little change in the point estimates. This gives support to the fact that the values of r_1 and r_2 for the studies using ACVA are different from those obtained when KPS is the initiator. The differences in the data sets and the resulting composition trends from the Mayo-Lewis equation are shown in Figure 4-6.

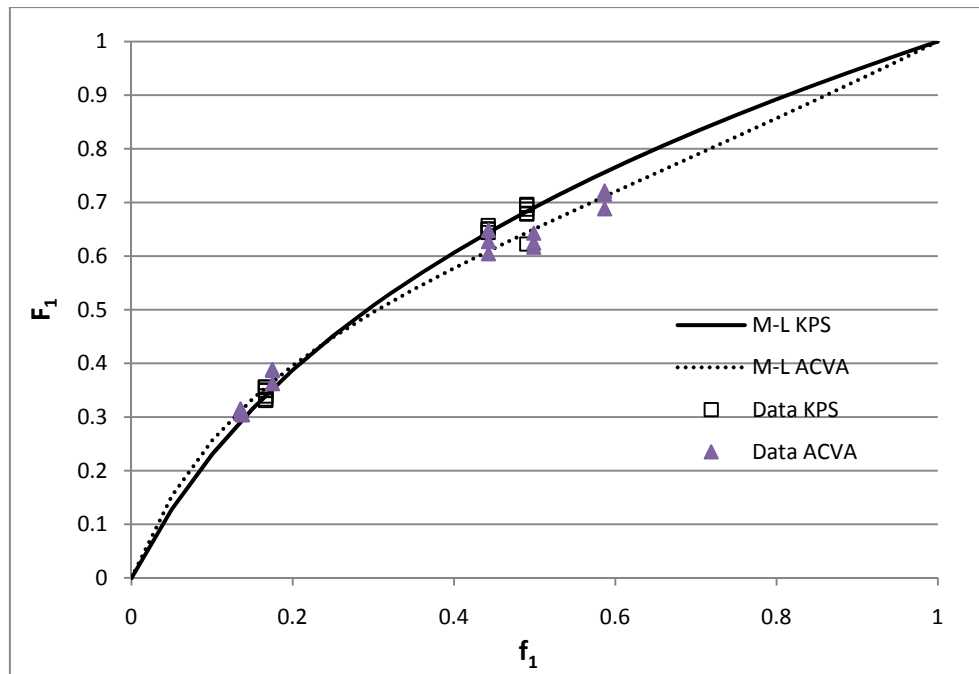


Figure 4-6 Copolymer Composition Trends for the Two Initiators

It can be seen from the information in Figure 4-6 that the main differences between the two sets of data (and therefore the expected Mayo-Lewis equation curves, designated on the figure as M-L) are clearly at the higher AAm feed levels. The reasons for the differences are not clear as the only major difference between the two sets of experiments were the initiators. The implication in the decrease of both r_1 and r_2 is that the two possible cross-propagation reactions are more favoured when ACVA is used as initiator, compared to what happens with KPS as initiator. This could be from decreases in the homo-propagation constants (k_{11} and k_{22}) or increases in the cross-propagation constants (k_{12} and k_{21}) or both. The one obvious difference between the two systems is that the persulphate was used as the potassium salt and the ACVA was added as the sodium salt form. In addition, if it is assumed that persulphate complexes with AAm (as per

Hunkeler³⁵), then perhaps it leads to localized inhomogeneities where initiation (and presumably some homopropagation of AAm) is favoured among the AAm monomer units. Given the lack of precedent for such results any interpretation would largely be speculative and further work is needed to check whether the differences between the two systems are real before further analysis of the results is considered.

4.4 Full Conversion Copolymerization of AA/AM

An initial check of the reactivity ratios results was made by running full conversion range copolymerizations using the two different initiators. Again the expectation here was that the initial copolymer composition for the experiments would be different for the two experiments but that the compositions would tend to the same final composition (equal to the initial monomer feed composition). For both experiments the feed composition was chosen to be about 0.5 (KPS experiment $(f_I)_0 = 0.5028$, ACVA experiment $(f_I)_0 = 0.5003$). At this level the low conversion runs showed a noticeable difference in terms of copolymer composition obtained. The initiator concentrations were chosen to be 4×10^{-3} mol/L and the temperature was 40°C.

The results obtained for monomer conversion with respect to time are shown in Figure 4-7.

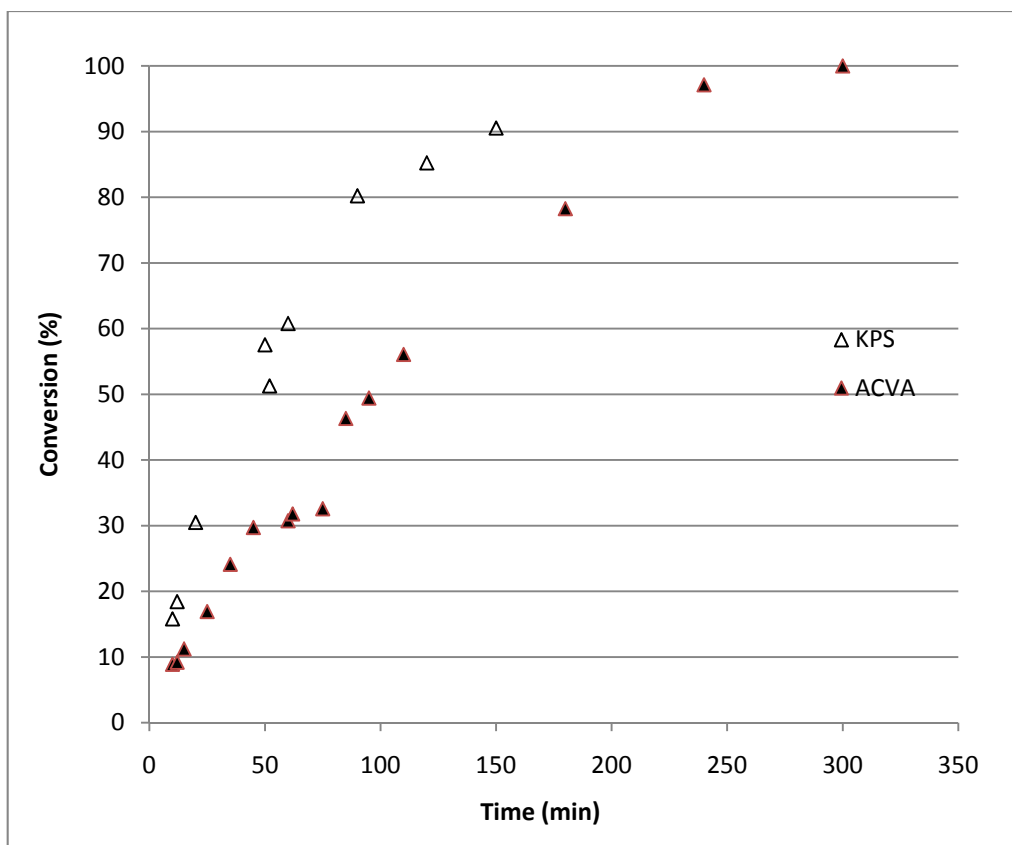


Figure 4-7 Conversion versus Time for AAm/AA Copolymerization at 40°C for two Different Initiators ($[I] = 4 \times 10^{-3} \text{ mol/L}$)

It can be seen from the results that the reaction using KPS as the initiator is significantly faster (in the initial stages R_p is about twice as large) than that when using ACVA as the initiator. The differences in rates can probably be explained by differences in the k_d values for the two initiators and the respective efficiencies of the initiators. However, we cannot neglect the possibility of promoted dissociating of KPS by AAm leading to higher rates of initiator decomposition in the experiment using KPS³⁵.

Of more importance for this study in regard to the differences in reactivity ratios was the comparison of copolymer composition with respect to conversion for the two

reactions. The results obtained for this are shown in Figure 4-8; once again the compositions were obtained using elemental analysis.

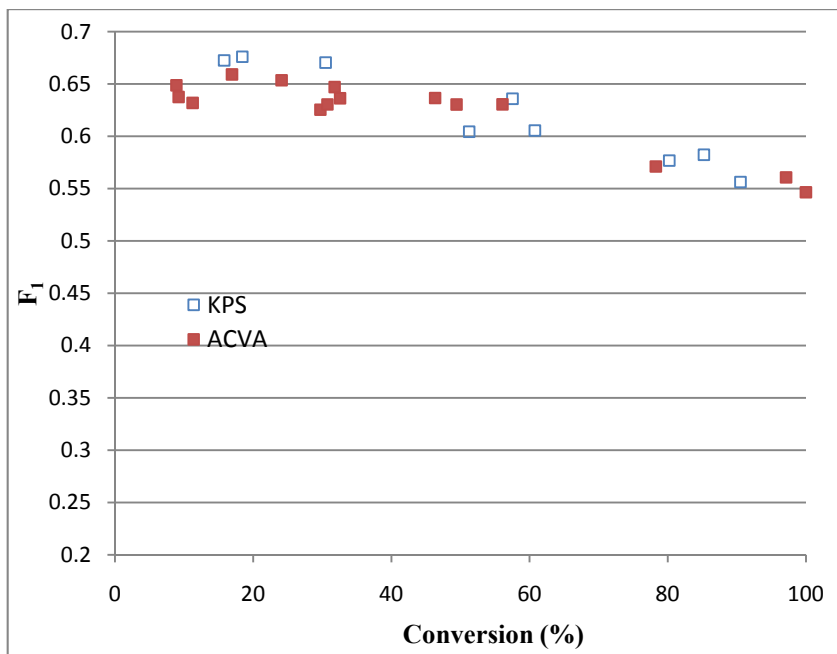


Figure 4-8 Copolymer Composition in Relation to Conversion for AAm/AA Copolymerization; Initiator Effect

It can be seen in Figure 4-8 that the trends verify what was observed in the low conversion studies, in that the copolymer compositions for the samples obtained using KPS as initiator seem to be slightly higher than those for ACVA at the early stages of reaction. The values are close to those expected from the trends seen in the low conversion experiments (KPS F_1 expected = 0.69, ACVA F_1 expected = 0.65). As reaction proceeds, the copolymer composition should drift towards the same final

composition (this should equal the starting feed composition). This is essentially what was observed.

The data were further analyzed using the Meyer-Lowry expression (see equation (7)) to estimate the reactivity ratios (but now using a different computer program that handles reactivity ratio estimation based on the integrated copolymer composition model, thus capable of including data from low/moderate and high conversion levels). The reactivity ratios obtained for the reaction using KPS as initiator were $r_1 = 1.93$ and $r_2 = 0.37$, whereas the reactivity ratios using ACVA were $r_1 = 2.31$ and $r_2 = 0.656$. The reactivity ratios and their 95% joint confidence regions are shown in Figure 4-9.

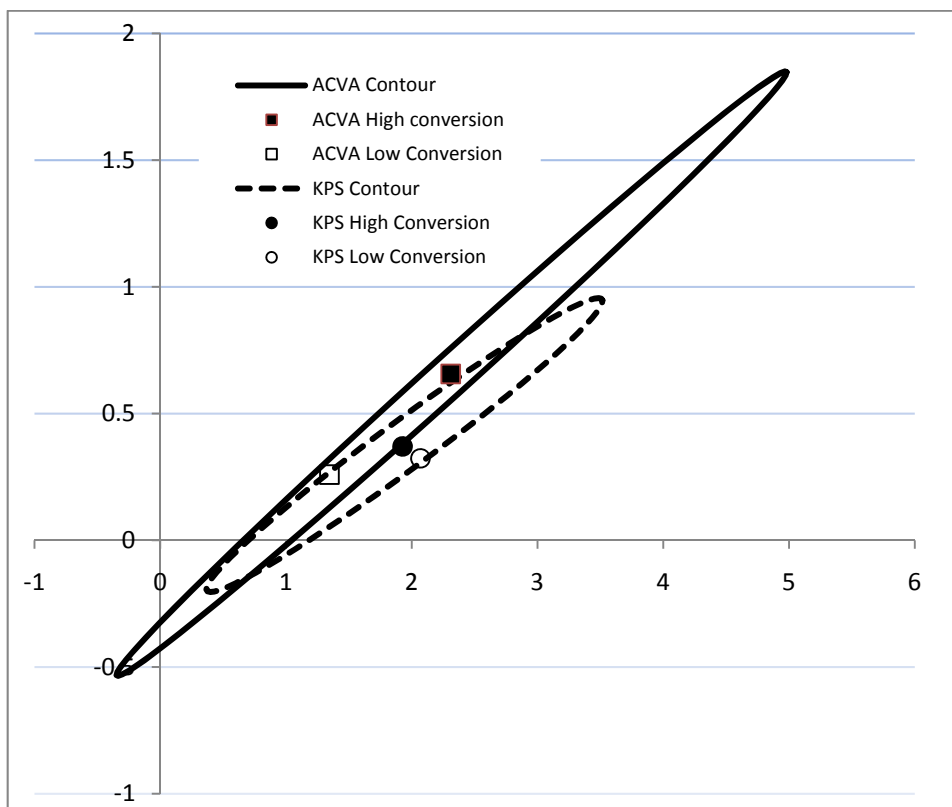


Figure 4-9 Full Conversion Range AAm/AA Copolymerization Reactivity Ratio Estimation Results

First it can be seen, from the results shown in Figure 4-9, that the joint confidence regions (elliptical contours) obtained for both reactions are rather elongated (thus indicating highly correlated parameter estimates) and include (infeasible) areas of negative values. This means that the results obtained have a very high degree of uncertainty and since there are negative values included in the confidence regions, the results do not seem awfully reliable. However, it can also be seen that the point estimates for the low conversion studies are within the boundaries of the elliptical confidence regions, giving some support to the fact that the reactivity ratio estimates are reasonable for producing the trends in composition seen in the full conversion range polymerizations.

It can be noticed for the reaction using ACVA as the initiator that there is a discrepancy in terms of either the copolymer composition data or the monomer conversion data. It seems for this reaction that 100% conversion of monomer was obtained for the final sample. If that were absolutely correct then the copolymer composition for the final sample should be close to the original feed composition. The data for copolymer composition for that last point is actually at 0.55. This implies that either the composition value, or the monomer conversion level, is over-estimated. The reasons for this cannot be confirmed without further experimental probing of the system. This point is discussed further below in the suggestions for further work.

4.5 Reactivity Ratios for AAm/AA Copolymerization in Methanol

As another comparison of how this copolymer system is affected by the conditions of reaction, it was decided to conduct a study with methanol as the solvent. Even though it was likely that the reactivity ratios would be different, the feeds used for the study were the same as those used for the reactions in water, given earlier findings by Chapiro et al⁴⁵. ACVA was used as the initiator and the temperature was again 40°C. The results for the examples run are shown in Table 4-5.

Table 4-5 Results of Low Conversion AAm/AA Copolymerization with ACVA as Initiator in Methanol

$(f_1)_0$	F_1	Conversion (%)
0.4769	0.532	3.4
0.4769	0.497	3.4
0.4769	0.530	2.9
0.4364	0.502	4.4
0.4364	0.491	4.0
0.4364	0.501	3.4
0.1749	0.160	18.3
0.1749	0.162	17.2
0.1749	0.158	16.8

The conversion values for the feed with the $(f_1)_0 = 0.1749$ were higher than recommended but the copolymer composition was close to that of the feed and so composition drift would be slight. Therefore the data points were used to estimate the reactivity ratios using EVM, and the values obtained were $r_1 = 2.096$ and $r_2 = 1.393$. The obtained 95% joint confidence regions are shown in Figure 4-10 along with those

obtained for the studies in water with the KPS and ACVA initiators. It can be seen that the values in methanol are completely different from those seen for the reactions in water. This gives further support to the effect of the reaction medium on reactivity ratios for the AAm / AA copolymerization system. It was also noticeable that the joint confidence contours for this evaluation were far larger than the ones obtained for the studies using water as solvent.

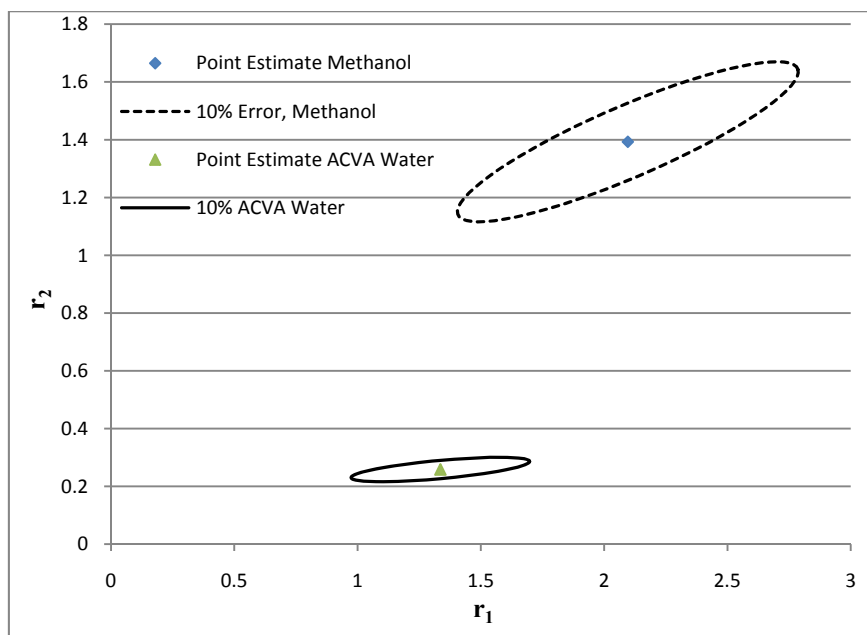


Figure 4-10 Reactivity Ratios and 95% Joint Confidence Contours for AAm/AA Copolymerization in Methanol

It is interesting to plot the composition data for this set of results. This is shown along with a 45° line in Figure 4-11. It can be seen that the copolymer composition is similar to the feed composition for all the feeds studied. It can also be seen, by looking at the trend line for the Mayo-Lewis composition plot for the reaction in water with ACVA initiator (pH = 6.3), that there is a large difference in the compositions observed for the

reactions in the different solvents. This again indicates how sensitive this system is to the nature of the reaction medium. It can be seen that the data points obtained for our study are located close to the predicted line for the reactivity ratios found by Chapiro et al. (see Table 2-4). The main differences in the trend lines are when the AAm levels in the feed are higher than those used in our study. A point to note about our results in this section of work is that since the reactivity ratios obtained in the EVM analysis are quite different from those of the earlier studies in water, it means that the feeds used would not necessarily be optimal (based on the Tidwell-Mortimer criterion) for this analysis. If the appropriate calculations were made, then $(f_1)_{0'} = 0.512$ and $(f_1)_{0''} = 0.589$. Therefore, if time allowed, further feeds would be run at the new $(f_1)_{0''}$ value in order to obtain data in that composition region.

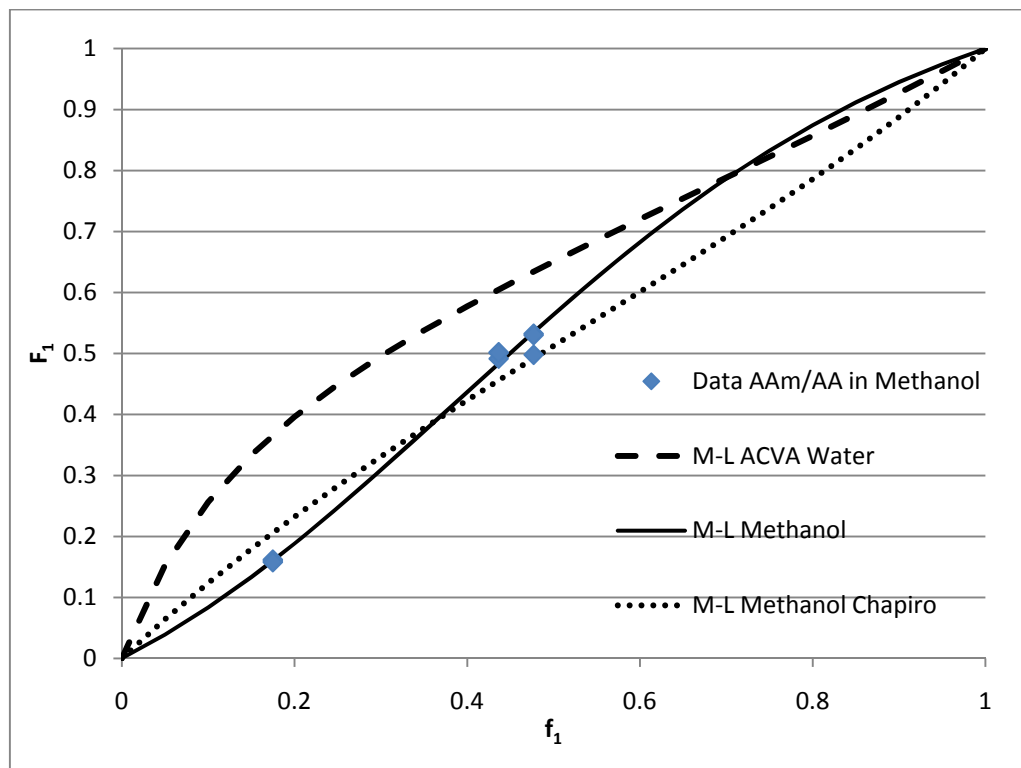


Figure 4-11 Mayo-Lewis Trends for Different Sets of Reactivity Ratios

The experiments run for the reactivity ratio studies are limited but they do go some way to show that if appropriate conditions are not chosen, then great variability in the reactivity of these monomers is possible. This means that the copolymerization reaction can be tailored, since any change in reactivity ratios means that the copolymer microstructure would change. A benefit in running copolymerizations in an alcohol medium as opposed to water is that the alcohol has significant chain transfer activity, which would give lower molecular weight polymers. A disadvantage is that for some feeds the copolymers formed are not soluble in the methanol and so heterogeneous systems are obtained (polymer-rich phase that precipitates). It had been planned to obtain comparative molecular weights for the different polymers but difficulties with solubility of samples and GPC equipment have held back that portion of the study. More detailed GPC analysis using the aqueous GPC set-up will be left as a future step.

Chapter 5 Conclusions and Suggestions for Further Work

5.1 Conclusions

Reactivity ratios are important parameters in understanding reaction kinetics and composition trends in copolymerization of monomers. This experimental investigation provides an understanding of some of the variables affecting free radical copolymerization of AAm and AA in terms of their reactivity ratios at a chosen pH, and other conditions, with two different initiators, KPS and ACVA. The study reveals that in addition to other factors like nature of solvent, monomer concentration, ionic strength and pH of the reaction media, the actual initiator also seems to play a significant role in altering the kinetics and, finally, the reactivity ratios of AAm and AA. Comparison of estimated values of reactivity ratios with those of most relevant literature values, which were recently published, has also been made in order to verify the consistency of our experimental data and analytical testing results.

The studies to examine the reactivity ratios of AAm and AA, using a pH of about 6.3, with KPS as initiator gave results that were close to the literature values of Rintoul and Wandrey¹¹. Any differences could be explained probably by the differences in experimental conditions for our study and those used in the Rintoul and Wandrey study (mainly higher overall monomer concentration). In addition, the Rintoul and Wandrey work used the Kelen-Tudos method to determine the reactivity ratio values. They also used different methods to assess the compositions of copolymer formed, i.e., measurement of monomer consumed during a fixed reaction period. Compounding all these factors could easily lead to the differences that were seen.

In contrast, the estimated reactivity ratio values obtained when using ACVA as initiator at the same conditions did not match with literature values, or our own values when using KPS as initiator. This is unexpected according to principles associated with conventional free radical polymerization, as changing the type of initiator should not have a significant effect on the overall copolymerization kinetics that lead to the final composition of the copolymer.

The reasons for this difference are not immediately clear but looking at the results from the experiments it does seem that, when using feed compositions (with respect to AAm, designated as monomer 1) where $(f_1)_0 \geq 0.5$, the results using the ACVA as initiator produced copolymer with relatively lower levels of AAm. Considering the method of copolymer analysis, the only major source of nitrogen is AAm either as free monomer or as monomer incorporated in the copolymer (there is some in ACVA but that is a relatively small amount and moreover higher N values are seen using KPS). In obtaining the relative amount of each monomer in the polymer, the key ratio is the N to carbon ratio. So a lower fraction of AAm results from lower N to C ratios. This may be because the copolymer is either truly lower in AAm or there is some other component in the final product that contains C but not N. Checking the materials used in our study this means either acrylic acid (salt) or methanol. Acrylic acid salt could co-precipitate and be trapped in the polymer if the washing procedures during filtration were inadequate. Similarly, methanol will associate with the polymer by polar interactions.

Alternatively, the results using KPS reflect a higher AAm content in the analysis of copolymer from reactions using KPS compared to similar reactions using ACVA. This stems from a higher N to C ratio which can be explained by either AAm being entirely in

the copolymer or coming from AAm monomer being co-precipitated with polymer and not being removed. A disadvantage of the elemental analyses is that it only gives a measure of N content and does not distinguish between N in monomer or in copolymer.

These possible scenarios may account for some sources of uncertainty at different stages of the experimentation and the analytical testing methods used for calculation of copolymer composition, which need to be considered. However, it would seem odd that apparently systematic differences in the reactions with the two initiators would occur in the types of experiments carried out, because in the course of the reaction studies care was taken to try and ensure consistency in procedures in all polymerization stages considered.

It was also mentioned in the introduction that ionic strength can have an effect on the rate constants for polymerization of the two monomers. In the make-up of the solutions the pH was maintained constant but the Na^+ ion content was not exactly the same for the two different initiators. In making up solutions to give fixed pH values the amount of NaOH added to a given solution to achieve the desired pH would vary depending on the amounts of AAm and AA in the system. This means that the degree of ion pairing could be varying. In addition, ACVA was not completely soluble in acidic form in monomer solution and so it was necessary to use initiator in salt form (by adding NaOH) in order to obtain a homogeneous solution. This would lead to slightly higher Na^+ contents in comonomer mixtures after pH adjustment, than was the case when KPS was used as the initiator for the polymerization reaction. Of course, by considering this it also should be noted that this may be balanced somewhat by the presence of potassium ion in the persulphate initiator. These differences are slight but the kinetics for these monomers

have been shown to be sensitive to many factors in the system and so it may be enough to have an effect on the magnitudes of all four k_p values for the system, causing a shift in the r_1 and r_2 values.

As mentioned in the introduction, the pH of reaction media plays a significant role to affect the reaction kinetics of AAm and AA polymerizations. Therefore, a pH variation at different stages of the reaction may be another reason for different results seen for the polymerization system using KPS or ACVA initiators. In the experiments using the two initiators, the starting pH was kept at about 6.3 for all experiments; however the pH of the solutions was not checked as reaction progressed. It is known from studies of AA polymerization initiated by KPS that pH changes as reaction proceeds³³. This is largely because the pK_a of AA is higher for free monomer relative to monomer in a polymer. In addition, the breakdown of persulphate can acidify the medium because of formation of sulphate. It is possible that the nature of pH change in reactions using ACVA is different to that using KPS. It has been shown by the study of Rintoul and Wandrey¹¹ and that of Cabaness¹⁹, that reactivity ratios for this system are very sensitive to pH change and so slight differences during reaction with the two initiators may change the results enough to lead to changes in the apparent values of r_1 and r_2 .

Another potential source of error is the degassing procedure. It is possible that loss of monomer may occur during nitrogen purging, which would lead to differences in the true values of f_1 and in the total monomer content in a vial. If the initial mole fraction value of feed (f_1) is incorrect, then this will skew results with respect to F_1 but again it is unlikely that there would be much change since AAm is a solid and in solution the AA is in salt form and therefore neither would be significantly volatile. Moreover, if this was

happening, then it would be expected that the changes would be random and not systematically tied to one initiator or the other.

The full conversion range experiments were useful in confirming differences in copolymer composition from two similar feed compositions when using the different initiators. They were also useful for pointing out that the experimental methods for determining conversion and composition were not perfect. A high value for copolymer composition was apparent for the final sample in the full conversion run using ACVA as initiator and this clearly indicates some inconsistencies in the measurements, since for that level of conversion the measured composition of copolymer should be the same as the initial monomer concentration. The apparent high content of AAm present in the product may be due either to errors in the monomer conversion value, perhaps because of incomplete drying of the samples. This is possible because the polymer tends to ‘lump’ on precipitation from methanol, thus likely trapping some solvent or other small molecules inside the polymer lump. These materials may stay trapped even with extended drying in a vacuum oven, especially if the temperature is too low to soften the polymer. Insufficient drying then leads to an overestimate of the polymer mass. Alternatively, the elemental analysis methods conducted by Guelph Chemical Laboratories may have inherent error (bias) and so the high values of copolymer composition may stem from this.

The effect of changing solvent, using ACVA initiator, on the copolymerization was also verified by changing solvent from water to methanol in this investigation. This allowed assessment of changes in reaction kinetics without considering pH as a factor at the same reaction conditions. This study showed that there is a big effect from solvent on

the copolymer composition of products. This part of the study may be extended in the immediate future steps.

5.2 Suggestions for Future Work

- 1) The differences observed in the reactivity ratios obtained for reactions initiated by KPS and ACVA are difficult to explain and further work should be done to either confirm or refute that the differences are real. Therefore, some of the reaction feeds already examined, for both initiators, should be revisited and independent replicate experiments (possibly with additional tests for the final analysis of samples, see below) should be run to confirm the data already obtained.
- 2) As discussed earlier, it is possible that some of the differences in copolymer compositions arise from the fact that unreacted monomer (and/or solvents) may be trapped in the polymer, thus giving misleading results for elemental composition of copolymer. Therefore further steps should be taken to ensure that the isolated polymer does not contain monomer or other impurities. This may be done by extending the polymer purification procedures used, for instance by redissolving (or swelling) the polymer produced in water and then reprecipitating with non-solvent (methanol or acetone). Such repeated practice will greatly help in removing unreacted monomer before final isolation of polymer as AAm and AA salt are readily soluble in water and methanol. This procedure should probably be repeated 3 times to give more assurance that monomer would not be in the mass after drying.
- 3) The polar-polar interaction of polymer and methanol as well as the bulky structure of the polymer provides a barrier against the complete removal of solvent molecules (H₂O or methanol) after drying in vacuum oven, which may lead to error in

conversion and final copolymer composition values. This aspect of insufficient drying time or too low a drying temperature should be investigated further. It is possible that using a higher temperature for drying is advisable as softening the polymer should lead to better drying behavior. However, the T_g for polyacrylic acid is 126°C (Encyclopedia of Chemical Technology) and heating at such a high temperature may lead to degradation of the polymer. In addition, it is known that extended drying of such polymer leads to anhydride formation, thus changing the nature of the copolymer so any study of this type would have to consider these aspects as well.

- 4) Other groups have found difficulties in handling AAm and AA in kinetic studies because of the extremely fast reaction rates and tendency to side reactions.^{32,27} Copolymer composition may be better obtained by another experimental technique that could distinguish between unreacted and reacted monomer and so avoiding any problems where unreacted monomer can affect the composition analysis. Most commonly, for other polymers, this may be done by using NMR techniques. ^1H NMR is the most sensitive NMR type but it is not particularly useful for these polymers as there are no protons that give good unique diagnostic signals. ^{13}C NMR does give distinct signals for the two monomers but has less sensitivity than ^1H NMR. However, it was found in the screening work done for this study that the NMR solutions made from the copolymers produced were not sufficiently concentrated to obtain good NMR signals for ^{13}C NMR. In addition, the polymer solutions must be homogeneous in solvent to avoid signal broadening and again when samples were screened this was not observed. This was probably because the polymers made have

very high molecular weights (AAm and AA have very high k_p^2/k_t values, which leads to long chains and hence high molecular weights) and so solution viscosity is very high for low concentrations of polymer, making it difficult to get high concentration levels in an NMR tube. So NMR may only be an option if lower molecular weight polymer is made, as higher NMR solution concentrations should be possible. This can be done by doing the polymerizations in the presence of a chain transfer agent. Chain transfer agents lower molecular weights for polymers produced by free radical polymerization¹² but they should have little influence on copolymer composition.

- 5) The conversion of monomer to polymer and their corresponding copolymer composition should be cross-checked by using an alternate method such as the measurement of residual monomer concentration¹¹ in addition to the gravimetric method used in this study.
- 6) Another possible method for analysis with such copolymers is potentiometric titration. This method was used by Shawki and Hamielec²⁶ and is very applicable to analyzing systems that have monomers that respond to changes in acid and base content such as polymers based on AA and MAA. The system consists of standard reference- and neutral-electrodes and the voltage variation of the polymer solution (electrolyte) is monitored as a titrant (NaOH, if starting from acid form or acid, if starting from salt form) is added to it. The end point of neutralization is determined by plotting voltage values (y axis) against volume of titrant added. The neutralization point can then be tied to the moles of acrylate from the moles of added titrant.

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Appendices

APPENDIX A- Relevant Experimental Information

1. Reactivity Ratio Estimation with KPS

Total Vol (ml)	Mass of AAm (gms)	Mass of AA (gms)	NaOH (ml 3M)	f_1	F_1	Conversion (%)
100	3.5488	3.7416	16.8	0.4902	0.696	5.3551
100	3.5488	3.7416	16.8	0.4902	0.688	6.2699
100	3.5488	3.7416	16.8	0.4902	0.678	7.0923
100	3.5488	3.7416	16.8	0.4902	0.694	5.8713
100	3.5488	3.7416	16.8	0.4902	0.622	6.134
100	3.5488	3.7416	16.8	0.4902	0.680	9.7805
100	1.174	5.9623	27.5	0.1664	0.349	7.4351
100	1.174	5.9623	27.5	0.1664	0.333	4.9381
100	1.174	5.9623	27.5	0.1664	0.331	5.3286*
100	1.174	5.9623	27.5	0.1664	0.339	5.3286*
100	1.174	5.9623	27.5	0.1664	0.350	5.3286*
100	3.1832	4.0691	18.8	0.4423	0.644	5.7442
100	3.1832	4.0691	18.8	0.4423	0.651	8.9016
100	3.1832	4.0691	18.8	0.4423	0.649	5.0824
100	3.1832	4.0691	18.8	0.4423	0.657	5.2563

* Replicate analyses of the same sample

2. Reactivity Ratio Estimation with ACVA

Total Vol (ml)	Mass of AAm (gms)	Mass of AA (gms)	NaOH (ml 3M)	f_1	F_1	Conversion (%)
50	0.6007	3.0219	13.9	0.1677	0.356	4.9371
50	0.6007	3.0219	13.9	0.1677	0.355	5.7519
50	0.6007	3.0219	13.9	0.1677	0.369	3.6378
50	1.6376	2.0905	12.8	0.4426	0.604	5.8828
50	1.6376	2.0905	12.8	0.4426	0.627	6.8585
50	1.6376	2.0905	12.8	0.4426	0.648	6.2939
50	1.7837	1.8171	8.8	0.4988	0.643	7.6607
50	1.7837	1.8171	8.8	0.4988	0.617	6.108
50	1.7837	1.8171	8.8	0.4988	0.624	9.0597

3.Reactivity Ratio Estimation with ACVA in Methanol

Total Vol (ml)	Mass of AAm (g)	Mass of AA (g)	f_1	F_1	Conversion (%)
50	1.7696	1.9679	0.4769	0.532	3.4258
50	1.7696	1.9679	0.4769	0.498	3.4053
50	1.7696	1.9679	0.4769	0.530	2.8619
50	1.6191	2.1202	0.4364	0.502	4.3776
50	1.6191	2.1202	0.4364	0.491	3.99
50	1.6191	2.1202	0.4364	0.501	3.42
50	0.6194	2.9619	0.1749	0.160	18.3406
50	0.6194	2.9619	0.1749	0.162	17.2436
50	0.6194	2.9619	0.1749	0.158	16.8184

4. Full Conversion Range Copolymerization:

For each full conversion experiment 0.5mol/ L of each monomer was needed which was obtained from a stock solution of 2M concentration [AAm] = 1M and [AA] = 1M in a 100 ml flask (1.7839g AAm and 1.8065g AA). The reaction solution was prepared by taking 25 ml of stock solution along with the required amount of initiator ($4 \times 10^{-3}M$) for a 50 ml solution in a volumetric flask.

a. ACVA (as initiator)

Time	F ₁	Conversion (%)
10	0.649	8.8901
12	0.638	9.2101
15	0.632	11.2452
25	0.659	16.932
35	0.653	24.1225
45	0.625	29.7342
60	0.630	30.7493
62	0.647	31.7947
75	0.636	32.5826
85	0.636	46.3337
95	0.630	49.4411
110	0.6308	56.0757
180	0.571	78.2774
240	0.560	97.1324
300	0.546	100

b. KPS (as initiator)

Mass AAm in stock = 1.7858 g, mass AA in stock = 1.7903 g. Stock total volume = 100 mL.

Time (mins)	F₁	Conversion (%)
10	0.672	15.8024
12	0.676	18.4317
20	0.670	30.4863
50	0.636	57.5271
52	0.604	51.2649
60	0.605	60.7764
90	0.578	80.2179
120	0.582	85.2347
150	0.556	90.5304

APPENDIX B-Typical Example of F_I Calculation Using KPS

Element	%)	Moles	Mole ratio	C in AA	H in AA	Mole of AA	f_i	F_i
C	29.67	2.4702356	8.5875933	5.5875933	16.693179	1.8625311	0.166401	0.3493412
H	6.29	6.2400794	21.693179					
N	4.03	0.2876517	1					
C	25.15	2.0939139	8.9986914	5.9986914	17.724127	1.9995638	0.166401	0.3333818
H	5.33	5.2876984	22.724127					
N	3.26	0.2326909	1					
C	27.76	2.3112147	9.0700611	6.0700611	16.91885	2.0233333	0.166401	0.3307607
H	5.63	5.5853175	21.918851					
N	3.57	0.254818	1					
C	30.91	2.5734743	4.658188	1.658188	6.079542	0.5527293	0.442297	0.6440272
H	6.17	6.1210317	11.079542					
N	7.74	0.5524625	1					
C	31.8	2.6475731	4.6192402	1.6192402	5.921729	0.5397467	0.442297	0.6494575
H	6.31	6.2599206	10.92173					
N	8.03	0.573162	1					
C	32.25	2.6850387	4.5652175	1.5652175	5.677119	0.5217392	0.442297	0.6571428
H	6.33	6.2797619	10.677119					
N	8.24	0.5881513	1					
C	35.53	2.9581217	4.3080338	1.3080338	4.203265	0.4360113	0.490198	0.6963734
H	6.37	6.3194444	9.2032658					
N	9.62	0.6866524	1					
C	34.45	2.8682041	4.3630337	1.3630337	5.59388	0.4543446	0.490198	0.687595
H	7.02	6.9642857	10.593881					
N	9.21	0.6573876	1					
C	34.92	2.9073349	4.4225584	1.4225584	4.658238	0.4741861	0.490198	0.6783404
H	6.4	6.3492063	9.658239					
N	9.21	0.6573876	1					

APPENDIX C-Typical Example of F_I Calculation Using ACVA

Element	%(g)	Moles	Mole ratio	C in AA	H in AA	Mole of AA	f_i	F_i
C	65.05	5.4158688	8.2834412	5.2834412	14.7709	1.7611471	0.17472	0.3621683
H	13.03	12.926587	19.770905					
N	9.16	0.6538187	1					
C	39.68	3.3036383	7.7527593	4.7527593	11.32004	1.5842531	0.17472	0.386959
H	7.01	6.9543651	16.320043					
N	5.97	0.4261242	1					
C	33.48	2.7874448	7.7178068	4.7178068	10.134869	1.5726023	0.17472	0.3887115
H	5.51	5.4662698	15.13487					
N	5.06	0.3611706	1					
C	45.92	3.8231621	4.9640872	1.9640872	5.6141	0.6546957	0.44263	0.6043407
H	8.24	8.1746032	10.614105					
N	10.79	0.7701642	1					
C	43.97	3.6608109	4.7843247	1.7843247	4.87956	0.5947749	0.44263	0.6270477
H	7.62	7.5595238	9.8795642					
N	10.72	0.7651677	1					
C	39.59	3.2961452	4.6271537	1.6271537	5.61211	0.5423846	0.44263	0.6483467
H	7.62	7.5595238	10.612117					
N	9.98	0.7123483	1					
C	38.92	3.240363	4.6657231	1.6657231	5.38482	0.555241	0.49878	0.6429872
H	7.27	7.2123016	10.384825					
N	9.73	0.6945039	1					
C	42.79	3.5625676	4.8646757	1.8646757	9.19814	0.6215586	0.49878	0.6166906
H	6.79	6.7361111	9.19814					
N	10.26	0.732334	1					
C	37.73	3.1412872	4.8045233	1.8045233	5.515147	0.6015078	0.49878	0.6244116
H	6.93	6.875	10.515147					
N	9.16	0.6538187	1					