

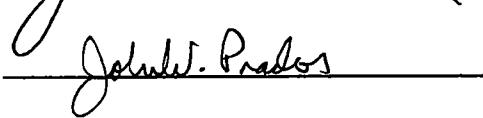
To the Graduate Council

I am submitting herewith a thesis written by Parag Dilip Patil entitled "Kinetic Modeling and In-Line Monitoring using Fiber Optic Raman Spectroscopy of Emulsion Copolymerization Reactions." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemical Engineering.



Marion G Hansen, Major Professor

We have read this thesis
and recommend its acceptance.

Accepted for the Council



Associate Vice Chancellor and
Dean of The Graduate School

**KINETIC MODELING AND IN-LINE MONITORING USING FIBER
OPTIC RAMAN SPECTROSCOPY OF EMULSION
COPOLYMERIZATION REACTIONS**

A Thesis
Presented For The
Master of Science
Degree

The University of Tennessee, Knoxville

Parag Patil

August 2000

DEDICATION

This thesis is dedicated to my parents

Mr. Dilip Patil and Mrs Nisha Patil

who have inspired and loved me at all times in my life.

आदरणीय आई आणि बाबा

यांना सप्रेम अर्पण

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ABSTRACT

In this research, kinetic modeling and in-line monitoring using fiber optic Raman spectroscopy of emulsion copolymerization reactions was studied. A model was developed for describing the kinetics of emulsion copolymerization of 2-ethylhexyl acrylate and acrylic acid. Experimental data of total conversion was obtained separately by gravimetric analysis and the analysis of Raman spectra taken continuously during the course of a reaction. Both the data sets were best fitted and the values of unknown parameters in the kinetic model were independently determined using these two techniques.

Use of in-line Raman spectroscopy was found to give slightly better results in estimation of best-fit parameters as compared to the off-line gravimetric analysis. The predictions of the kinetic model for a different set of reactions matched very well with the experimental results of both gravimetry and Raman spectroscopy. The kinetic model also predicted the individual conversions of 2-ethylhexyl acrylate and acrylic acid, which could not be determined from gravimetric and Raman spectra analysis.

A new method of normalization of the intensity of (C=C) peak in Raman spectra of the emulsion was used in calculating the monomer conversions, which resulted in less scatter in the calculated conversion profiles and also improved the accuracy of the final conversion values. In-line Raman spectroscopy was found sensitive in observing changes in the reaction rates due to the changes in the initiator and surfactant concentrations. Use of this fact can be made in designing control systems for emulsion copolymerization reactors.

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NOMENCLATURE

Symbol	Description
AA	Acrylic acid
$[A]_p$	Concentration of monomer A in polymer particles
a_s	Area of adsorption per emulsifier molecule
$[B]_p$	Concentration of monomer B in polymer particles
CCD	Charged couple device
CMC	Critical micelle concentration
CSD	Copolymer sequence distribution
CSTR	Continuous stirred tank reactor
C_I	Ratio of rate coefficient for transfer to initiator to the propagation rate constant
C_M	Ratio of rate coefficient for transfer to monomer to the propagation rate constant
C_S	Ratio of rate coefficient for transfer to solvent to the propagation rate constant
C_{TA}	Ratio of rate coefficient for transfer to chain transfer agent to the propagation rate constant
c	Rate constant for homo-termination
c_{ij}	Rate constant for termination of an i radical with a j radical
D_p	Diffusivity of a radical in polymer particle
D_w	Diffusivity of a radical in aqueous phase

EHA	Ethylhexyl acrylate
E_d	Energy of activation for decomposition of initiator
E_p	Energy of activation for propagation of radicals
E_t	Energy of activation for termination of radicals
$E_{tr,i}$	Energy of activation for transfer of radicals to species i
F_m	Radical efficiency in the micelle phase
F_p	Radical efficiency in the particle phase
IR	Infra-red
I	Initiator
k	Rate coefficient for desorption of a free radical from the particle in emulsion homopolymerization
k_I	Rate coefficient for the reaction of initiator radical with monomer
k_i	Rate coefficient for desorption of a radical species i from the particle in emulsion copolymerization
k_i	Rate coefficient for generation of radicals from the initiator
k^p	Rate coefficient for propagation of radicals in emulsion homopolymerization
k^p_{ij}	Rate coefficient of propagation of radical activity from an i free radical to a j monomer
k_t	Rate coefficient for termination of radicals in emulsion homopolymerization
k_{tc}	Rate coefficient for termination by combination
k_{td}	Rate coefficient for termination by disproportionation

$k_{tr,i}$	Rate coefficient for transfer of radicals to species i in emulsion homopolymerization
k_{ij}^{tr}	Rate coefficient for transfer of radical activity from an i radical to a j radical
MMA	Methyl methacrylate
MWD	Molecular weight distribution
M	Monomer
$[M^*]$	Concentration of monomer radicals
M_{j_0}	Moles of monomer j initially charged per liter of water
$[M]_p$	Concentration of monomer in the polymer particle
M_d	Partition coefficient for the monomer radicals between the particle phase and the aqueous phase
NIR	Near Infra-red
NMR	Nuclear magnetic resonance
N_A	Avogadro number
N_T	Total number of polymer particles per liter of water
$N_i(t)$	Number of particles containing i number of free-radicals in an emulsion homopolymerization
$N_{ij}(t)$	Number of particles containing i free radicals of monomer A and j free radicals of monomer B
$\bar{n}$	Average number of radicals per particle
PBE	Population balance equation
PSA	Pressure sensitive adhesives

PSD	Particle size distribution
PTA	Phosphotungstic acid
P	Polymer
P_i^p	Probability of a growing chain in the particle having the growing radical on the i monomeric unit
q	Ratio of termination rate constant due to decomposition to the overall termination rate constant
R	Universal gas constant
R^*	Radical in the aqueous phase
R_0	Ratio of intensity of C=C peak to the intensity of CH ₂ ,CH ₃ deformations peak at time $t = 0$
R_i	Rate of generation of radicals from the initiator
R_p	Rate of a polymerization reaction
R_t	Ratio of intensity of C=C peak to the intensity of CH ₂ ,CH ₃ deformations peak at any time t
R_m	Radius of a micelle
R_p	Radius of a particle
SEM	Scanning electron microscope
S	Solvent or surfactant
TEM	Transmission electron microscope
T	Temperature
t	Time
UV	Ultra-violet

V_s	Volume of a monomer swollen particle
W_0	Initial amount of monomer
W_t	Amount of monomer present at time t
X_{Mt}	Total monomer conversion
x	Number of free radicals generated from one initiator molecule
x_n	Degree of polymerization
$(x_n)_0$	Number-averaged degree of polymerization in the absence of chain transfer

Greek Symbol	Description
α	Fate parameter
γ_{AB}	$=(k_{AB}^p+k_{AB}^{tr})[B]_p$
μ	Volume growth rate of polymer particles
ρ_A	Rate coefficient for entry of A free radical
ρ_B	Rate coefficient for entry of B free radical
ρ_p	Rate coefficient for radical absorption to polymer particles
ρ_m	Rate coefficient for radical absorption to micelle
τ	Lifetime of a radical entering the polymer particle

CHAPTER 1

INTRODUCTION

Polymers are macromolecules built up by the linkage of a large number of much smaller molecules. The small molecules that combine with each other to form polymer molecules are termed *monomers*, and the reactions by which they combine are termed *polymerizations*. Emulsion polymerization involves polymerization of monomers that are in the form of *emulsions*. The term “emulsion” describes a heterogeneous mixture of an organic material with water. In emulsion polymerization, water is the continuous phase with droplets of organic monomers dispersed in it.

The technique of emulsion polymerization was developed in industrial laboratories in Germany, USA and the former Soviet Union from 1927 onwards. Emulsion polymerization was first employed on a large-scale in the United States for the production of synthetic styrene-butadiene rubber during the 1940s (8) when the supplies of natural rubber were cut off during World War II. Emulsion polymerization is presently the predominant process for the commercial polymerizations of vinyl acetate, chloroprene (2-chlorobutadiene), various acrylates, and copolymerizations of butadiene with styrene and acrylonitrile. The final product of an emulsion polymerization, referred to as *latex*, is often used directly as an emulsion without prior separation of the polymer from water and the other components.

The emulsion polymerization process has several distinct advantages. The colloidal nature of the emulsion systems makes it easy to control the process and the

final properties of the polymer Thermal and viscosity problems are much less significant than in bulk polymerization, in which monomers polymerize in the absence of a solvent The products of emulsion polymerizations can in some instances be employed directly without further separations but with appropriate blending operations. Such applications involve coatings, finishes, floor finishes, and paints. Emulsion polymerization is a unique process that provides a means of increasing the polymer molecular weight without decreasing the polymerization rate. In recent years, environmental pressures on the use of solvent-borne coatings and adhesives have led to a growing interest in the water-borne polymer latexes produced by emulsion polymerization.

Emulsion polymerization is a type of free-radical chain polymerization Chain polymerizations are those reactions in which the polymer chains grow exclusively by reactions of monomer with a reactive end-group on the growing chain. Free radical polymerization is the most widely practiced method of chain polymerization and is used almost exclusively for the preparation of polymers from olefinic monomers of the general structure $\text{CH}_2=\text{CR}^1\text{R}^2$, where R^1 and R^2 are two substituent groups which may be identical, but are more often different. A free-radical chain polymerization can be divided into three distinct stages. initiation, propagation and termination. In the first stage an initiator is used to produce free-radicals which react with the olefinic monomer to *initiate* the polymerization. Each polymer chain propagates by rapid sequential addition of molecules of monomer to the terminal free-radical reactive site, which is known as the *active center* for polymerization As the monomer is

continuously added, the active center is transferred to the newly created chain end. Termination of the growth of polymer chains results from reactions between actively growing polymer chains.

Both the kinetic modeling and in-line monitoring of emulsion polymerization reactions are areas of vast research interest. A kinetic model takes into account the various microscopic processes involved in an emulsion polymerization reaction and predicts *a-priori* the kinetic behavior of the reaction. The term “kinetic behavior” implies the progress of conversion and the reaction rate, the latex particle size evolution, and the copolymer composition variation with time. Kinetic modeling of emulsion polymerization processes is important in design, control and efficient operation of these processes.

Methods of in-line monitoring of emulsion polymerization reactions are complementary to the kinetic models. Kinetic models enable one to have an *a-priori* idea about the behavior of the system when subjected to specific reaction conditions, based on which, control strategies can be decided. In-line monitoring methods follow the behavior of the reaction as it progresses, and appropriate control actions can be taken instantaneously, provided a sensitive control system exists.

In this research work, in-line monitoring of emulsion polymerization reactions using Raman spectroscopy is studied. Emulsion copolymerization of 2-ethylhexyl acrylate (2-EHA) and acrylic acid (AA) is considered. The polymer formed in this copolymerization reaction is sticky in nature, and finds applications in pressure sensitive adhesives. Homopolymer of 2-EHA has a very low glass transition

temperature ($T_g = -60^\circ\text{C}$), which is the requirement for formation of a sticky polymer. Hence, in the copolymerization recipe, 2-EHA is used in excess (about 80-90 percent). The carboxylic monomer (AA) is used in small quantities (10-20 percent) in the comonomer mixture. It acts as a reinforcing or binding agent, and improves the mechanical properties of the adhesive film formed from the polymer latex. Understanding of the individual conversions of 2-EHA and AA, and incorporation of AA in the copolymer with time is critical in predicting the final properties of the polymer. An insight to this area is sought in this research work, by combining the kinetic modeling of emulsion copolymerization of 2-EHA and AA with its in-line monitoring using Raman spectroscopy.

CHAPTER 2

FEATURES OF EMULSION POLYMERIZATION REACTIONS

Emulsion polymerization has developed into a widely used process for the production of synthetic latexes since its first introduction on an industrial scale in the mid-1930s. Today, millions of tons of synthetic polymer latexes are prepared by the emulsion polymerization process for use as commodity polymers in a wide variety of applications, such as synthetic rubber, high-impact polymers, latex foam, latex paints, paper coatings, carpet backing, adhesives, binders for non-woven fabrics and barrier coatings additives for construction materials. Latexes are also manufactured for a growing number of specialty applications such as diagnostic tests, immunoassays, biological cell-labeling, drug delivery systems, chromatographic separations, and as size calibration standards for many instruments such as blood counters and electron microscopes

2.1 Basic Ingredients of A Classical Emulsion Polymerization

Emulsion polymerization is a free-radical initiated chain polymerization reaction in which a monomer or a mixture of monomers is polymerized in the presence of an aqueous solution of a surfactant to form a product, well known as latex. The latex is a colloidal suspension of polymer particles in aqueous medium. The main ingredients for conducting these polymerizations include, in addition to monomer and

water, surfactants, initiators and chain transfer agents. A typical recipe for an emulsion polymerization is shown in table 2 1.

Water is a chief ingredient in both suspension and emulsion polymerization. It acts as an inert continuous phase maintaining low viscosity and providing good heat transfer. In addition, it serves to isolate the polymerization loci from each other. Termed compartmentalization, this is a particular advantage in emulsion polymerization, as the reaction rates are very high. Water also serves as the medium of transfer of monomer from monomer droplets to polymer particles and the medium of dynamic exchange of surfactants between the phases. It also is the locus of initiator decomposition and oligomer formation.

The surfactants (also referred to as emulsifiers) perform the dual function of providing sites for particle nucleation (i.e. monomer swollen micelles), as well as providing colloidal stability to the growing particles as a result of their adsorption at the particle-water interface. In most cases water-soluble initiators are used to initiate the free radical reaction. The most commonly used water-soluble initiators are the inorganic salts of persulfuric acid, such as potassium persulfate ($K_2S_2O_8$), which dissociates into two sulfate radical anions which can initiate the polymerization. Redox initiators, typically a mixture of an oxidizing agent and a reducing agent whose reactions generate radicals (such as persulfate-bisulfate), are typically useful for polymerization at low temperatures. Oil-soluble initiators, such as azo compounds, are also used in emulsion polymerizations in order to control particle morphology and grafting reactions within the particles, and to reduce the residual monomer at the end

Table 2 1. Typical recipe of an emulsion polymerization reaction

Ingredients	Parts by weight
Water	80 - 90
Monomer(s)	10 - 20
Initiator	0.05-0.5
Surfactant	0.1-0.5
Chain transfer agent	0.02
Total	~100

of the polymerization. A variety of chain transfer agents, such as mercaptans, are used to primarily control the molar mass of polymer

2.2 Physical Picture of Emulsion Polymerization Process

Perhaps the most important feature of emulsion polymerization is its heterogeneity from the beginning to end. Figure 2.1 gives a pictorial representation of a typical emulsion polymerization system. Upon mixing the monomers, water and surfactant(s), the latter molecules cluster into micelles with their hydrophobic cores being swollen with the monomer, their diameters are typically in the order of 50 – 150 Å, and their number density is in the order of $10^{17} - 10^{18} \text{ dm}^{-3}$. The bulk of the monomer, however, exists in the form of large-size droplets with surfactant molecules adsorbed on their surfaces; their diameters are typically in the range of 1-10 μm , and their number density is in the order of $10^9 - 10^{11} \text{ dm}^{-3}$. Upon addition of the initiators, radicals are formed in the aqueous phase typically at the rate of $10^{16} - 10^{18} \text{ radicals dm}^{-3} \text{ s}^{-1}$; these radicals may propagate in the aqueous phase to form oligoradicals by adding monomer molecules (present as a small fraction of the total monomer) dissolved in the aqueous phase. Particle nucleation begins at this point via one or more mechanisms (i.e. micellar, homogeneous or droplet), forming polymer particles which swell with monomer by diffusion of monomer from the monomer droplets. These monomer-swollen polymer particles become the main sites for further propagation reactions which results in polymer particle growth. The monomer required for this propagation reaction is supplied from the monomer droplets by diffusion through the

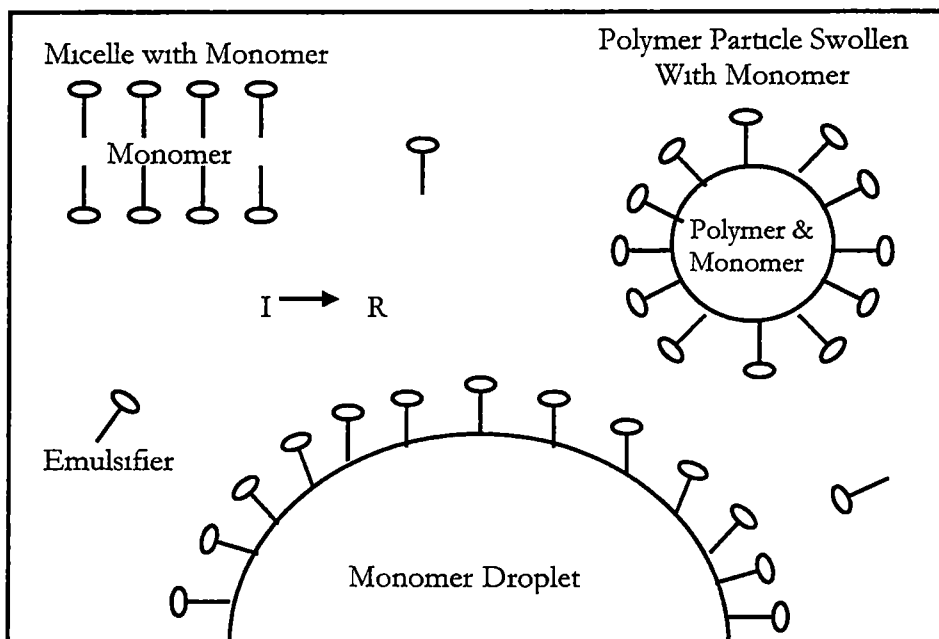


Figure 2.1 A Pictorial Representation of an Emulsion Polymerization Reaction System

[Source Odian, G , "Principles of Polymerization", pg 322, (John Wiley and Sons, Inc , New York, 1981)]

water phase Redistribution of surfactant molecules from micelles, which have not been initiated, and/or the surfaces of the disappearing droplets, and their adsorption on the surface of the growing polymer particles maintains the colloidal stability of the particles The polymerization is completed when all the monomer is converted to polymer. The final product comprises submicron polymer particles dispersed in the aqueous phase and stabilized chiefly by the adsorbed surfactant layer.

Harkins' (1) original qualitative description of emulsion polymerization has constituted the general framework for the various qualitative treatments that followed, starting with Smith and Ewart (2) with further modifications by a number of other authors (3-7). According to Harkins' original picture, emulsion polymerization is divided into three intervals encompassing the particle formation stage, termed interval I, and the particle growth stages, intervals II and III. During interval I, both the particle number and polymerization rate increase with time, and its end is signified by the disappearance of micelles, which are the main source of particle nucleation in Harkins' picture. During interval II, the particle number remains constant and monomer droplets provide the growing polymer particles with the required monomer to maintain saturation swelling and support the propagation reaction. The polymerization rate during the interval III is signified by the disappearance of the monomer droplets, at which point the polymerization rate should decrease as a result of the decreasing monomer concentration inside the polymer particles The particle number also remains constant during this period The polymerization rate during Interval III may also show a decrease-increase-decrease behavior depending on the

nature of the monomer/polymer and particle size. This second increase in the rate during Interval III is attributed to a decrease in the termination rate between radicals inside the particles due to the increased internal viscosity, a phenomenon known as the Tromsdorff gel effect.

2.3 Basic Issues in Emulsion Polymerization

The main issues dealing with the mechanisms and kinetics of emulsion polymerization involve the understanding of the processes by which latex particles form and grow, which includes the evolution of particle size (or particle number) and size distribution, the development of molar mass and molar mass distribution, the polymerization rate profile during the course of the reaction, and how these are influenced by the basic polymerization parameters such as monomer(s), surfactant(s) type and concentration, initiator type and concentration, temperature, and mode and rate of monomer addition. The complexity of particle nucleation in emulsion polymerization stems from the various physical processes and chemical reactions which follow the formation of ionic radicals by initiator decomposition. Figure 2.2 illustrates the possible fates of these aqueous-phase radicals and divides them into physical and chemical processes. They include:

- 1 Propagation in the aqueous phase by addition of dissolved monomer molecules to form oligomers;
- 2 If the oligoradical reaches its critical chain length for water solubility, the precipitation of the oligoradical to form a primary particle;

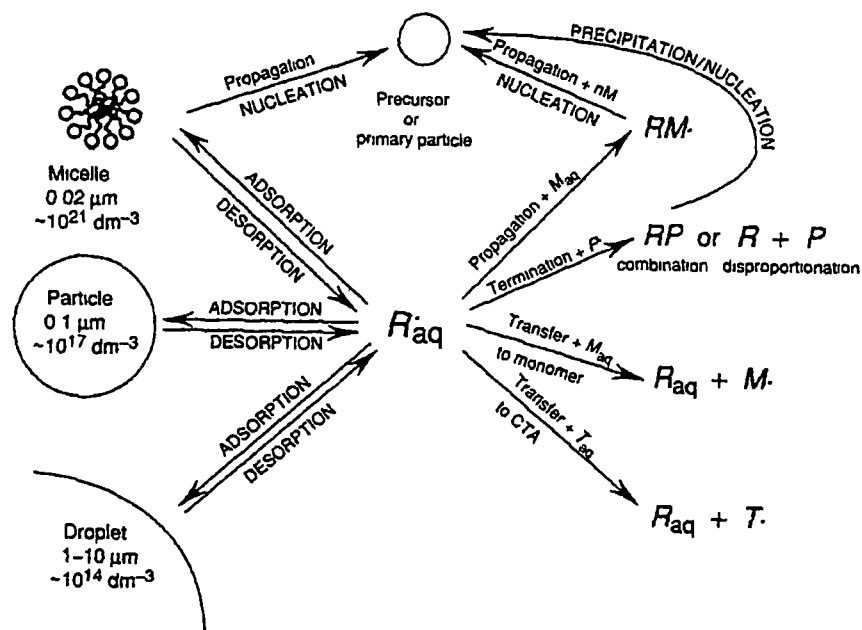


Figure 2.2 Schematic illustrating the possible fates of aqueous phase free radicals
 [Source P A Lovell and M S El-Aasser, "Emulsion Polymerization and Emulsion Polymers", pg 49, (John Wiley & Sons, Inc , New York, 1997)]

- 3 Absorption (entry) into and desorption from monomer-swollen micelles;
- 4 Absorption (entry) into monomer-swollen micelles, propagation within the micelles, and exit (either as is or after adding one more monomer unit),
- 5 Adsorption (entry) and desorption (exit) from the surface of monomer droplets,
6. Adsorption (entry) onto monomer droplets, propagation therein, transfer to monomer, exit as is or after transfer to monomer,
- 7 Adsorption (entry) and desorption (exit) from the surface of polymer particles;
- 8 Adsorption (entry) onto polymer particles, propagation therein, transfer to monomer, to a polymer chain or to an added chain transfer agent, termination and exit after transfer to monomer (this new radical differs from the original in that it does not carry a charge),
- 9 Re-entry of a desorbed radical to a particle, re-escape therefrom, propagation therein or termination
- 10 Termination in the aqueous phase with another radical

The contribution of each of these reactions and processes to particle nucleation depends upon the nature of many of the polymerization parameters such as the water solubility of the monomer(s), the ionic strength of the aqueous phase, the reaction temperature and pressure, and the type and degree of agitation. Research over the past 50 years has dealt with all of these issues resulting in tremendous advances in the basic knowledge of emulsion polymerization.

Since emulsion polymerization is a free-radical addition polymerization, all the kinetic events, namely, initiation, propagation, termination and chain transfer

reactions, are applicable to describe the overall rate of the polymerization and molar mass development of the latex polymer. However, the heterogeneous nature of the polymerization adds some complications due to partitioning of the various ingredients between the phases, namely, the micellar phase, the aqueous phase, the monomer droplet phase and the particle phase. Overall, the polymerization in the polymer particles is generally predominant in emulsion polymerization.

2.4 Particle Formation Mechanisms in Emulsion Polymerization

Three major mechanisms (8) have been proposed for particle formation in emulsion polymerization, namely, micellar, homogeneous, and droplet nucleation. These are described in the following sections.

2.4.1 Micellar Nucleation

Initiator radicals generated in the aqueous phase enter the monomer-swollen surfactant micelles, as single radicals or oligoradicals, and initiate polymerization to form monomer-swollen polymer particles, which grow by propagation reactions. Usually, only one out of every 100-1000 micelles capture a radical and becomes a polymer particle. Unentered micelles give up their surfactant and monomer molecules to the growing particles. Particle nucleation ends with the disappearance of the micelles, after which the number of particles generally remains constant. In some cases, however, it may decrease because there is insufficient surfactant to maintain colloidal stability, or it may increase slightly in the latter stages of the polymerizations.

due to desorption of surfactant molecules from the surface of the particles causing new particle generation. The monomer droplets, which are relatively large in size (1-10 μm in diameter), serve as reservoirs, feeding monomer to the growing particles by diffusion through the aqueous phase, until they disappear at approximately 30-40% conversion

2.4.2 Homogeneous Nucleation

Radicals generated in the aqueous phase propagate by adding monomer units to form water-soluble oligomers until they reach the limit of their solubility in the aqueous phase and precipitate out of solution. The precipitated oligomeric radicals form primary particles which adsorb surfactant molecules, bringing about their stabilization, and absorb monomer, allowing further propagation and growth. These primary particles can persist or coagulate with themselves or with growing stable particles. Thus, the profile of particle size (and number) development during the course of the polymerization and the final particle size (and number) are determined by the amount of surfactant and its effectiveness in stabilizing the primary and the growing particles

Particle formation by coagulative nucleation has also been proposed (9). This, however, may be considered as a subset of homogeneous nucleation. In coagulative nucleation, small size “precursor” particles initially form by homogeneous nucleation, followed by their aggregation to form stable, mature particles. The distinctive feature in this mechanism is that the precursor particles are extremely small in size which only

allows a relatively low concentration of monomer to be present within them, they grow in volume much faster by coagulation rather than by propagation reactions. When these particles are sufficiently large to absorb appreciable amounts of monomer, they are considered to be mature latex particles.

2.4.3 Droplet Nucleation

Radicals generated in the aqueous phase enter monomer emulsion droplets as single radicals or oligoradicals and propagate to form particles. The colloidal stability is due to the adsorption of surfactant molecules on the surfaces of the monomer droplets and growing polymer particles. This mechanism is considered predominant in both miniemulsion polymerizations and microemulsion polymerizations, where the small size droplets compete effectively for radicals. These systems require the use of a "cosurfactant" in addition to the main surfactant. In miniemulsion systems, the cosurfactant (e.g. hexadecane or cetyl alcohol) must have a low molar mass and simultaneously a low water solubility. For microemulsion systems, the cosurfactant usually is a low molar mass alcohol such as pentanol or hexanol.

In conventional emulsion polymerizations, all three particle formation mechanisms described above may, in principle, be operating simultaneously. However, their relative contributions to particle formation can vary considerably. Typically, one mechanism dominates particle formation depending on the surfactant concentration, the monomer solubility in the aqueous phase, and the level of subdivision of monomer droplets. For example, micellar nucleation is considered to be

the primary nucleation mechanism for monomers with lower water solubilities. Homogeneous nucleation, on the other hand, is considered to be the primary mechanism for particle formation for monomers with high water solubilities. Homogeneous nucleation is also proposed as the primary nucleation mechanism in systems where the surfactant concentration is below its critical micelle concentration (CMC) and in surfactant-free emulsion polymerization systems. In the latter, the stabilization of primary particles and growing particles is attributed to the presence of ionic groups (such as sulfate) from the initiator fragments on the surface of the particles which leads to electrostatic stabilization of these particles. Particle formation by droplet nucleation mechanism is considered to be insignificant in conventional emulsion polymerizations. However, when the droplets are in the submicron range, such as, in miniemulsion polymerizations or microemulsion polymerizations, they become the primary source of particle formation.

2.5 Emulsion Polymerization Processes

Three types of processes are commonly used in emulsion polymerization: batch, semi-batch, and continuous. In a batch polymerization, all ingredients are added at the beginning of the polymerization. Polymerization begins as soon as the initiator is added and the temperature is increased, with the simultaneous formation and growth of latex particles. Thus, little further control can be exerted over the course of the polymerization other than the rate of removal of the heat generated by the polymerization. In order to exercise some control over the reproducibility of the

particle number, pre-made seed latex is often used at the start of the polymerization. In the semi-batch process, one or more of the ingredients are added continuously or in increments. The monomers may be added neat, or as emulsions. The various modes of addition of the ingredients usually lead to different profiles of particle nucleation and growth throughout the polymerization process. The advantage of this process is the ability to exercise rigorous control over the various aspects of emulsion polymerization, which include the rate of polymerization and thus the rate of generation and removal of the heat of polymerization, the particle number, colloidal stability and coagulum formation, and copolymer composition and particle morphology. In the continuous process, the polymerization ingredients are fed continuously into a stirred tank, or more than one stirred tank reactors in series, while the latex product is simultaneously removed at the same rate. Continuous processes can offer the advantage of high production rate, steady state heat removal, and uniform quality of latexes.

2.6 Characteristics of Emulsion Copolymerization of 2-Ethylhexyl Acrylate and Acrylic Acid

Emulsion polymers derived from acrylic monomers are easily the most compositionally diverse and versatile family of the commercially important broad classes of emulsion polymers. The term “acrylic” represents polymers of monomeric alkyl esters of acrylic and methacrylic acid. The free acids themselves and their derivatives such as amides, nitriles, and aldehydes are generally present as minor

components in these polymers. Acrylic emulsion polymers find use in the industry for various applications under the broad category of non-woven fabric binders. High volume commercial production of these acrylic emulsion polymers provides economic accesses to a continuous range of copolymers of glass transition temperatures (T_g) ranging from $-80\text{ }^{\circ}\text{C}$ to over $100\text{ }^{\circ}\text{C}$, and with solubility characteristics ranging from highly oil-soluble to highly polar and solvent resistant emulsions. This property range has permitted application of acrylic latexes in markets ranging from the very soft pressure sensitive adhesives, to film forming yet tough binders for latex paints, to quite hard compositions for floor polishes and organic pigments. Various applications of acrylic emulsions classified according to T_g are shown in figure 2.3.

A salient feature of the chemistry of these polymers is the ability to incorporate a broad range of functional groups into the polymer chain via ester, amide, etc derivatives of acrylic or methacrylic acid. These functional groups can provide sites for crosslinking, adhesion, compatibility with other polymers, and post-polymerization reactions. The versatility of acrylic emulsion copolymers extends beyond the parameters of glass transition temperatures and solubility, to that of versatility in manufacturing. Pressure equipment is not required for their manufacture and a large variety of monomer additions and polymerization initiation schemes can be used.

Higher acrylates, such as 2-EHA find application as pressure sensitive adhesives (PSA). These acrylic adhesives are generally composed of two monomers that are copolymerized. One of the monomers that is present in excess (about 80-90 % of the total weight of the two monomers), is hydrophobic and its carbon number

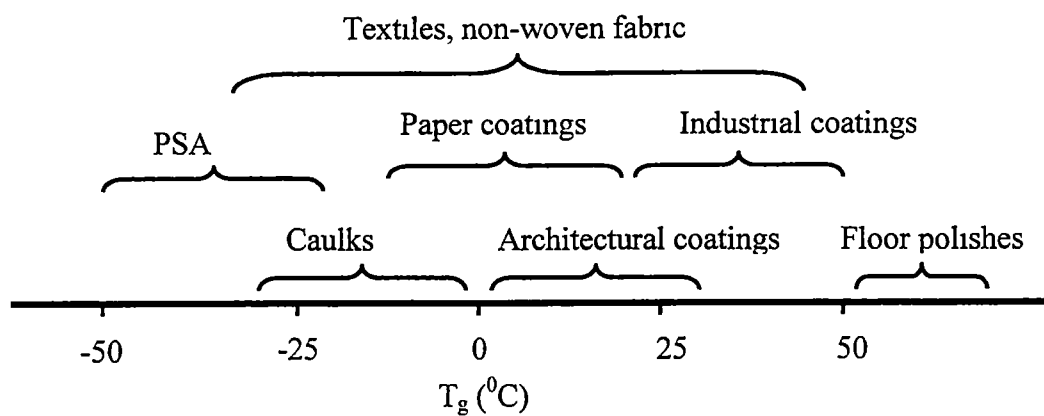


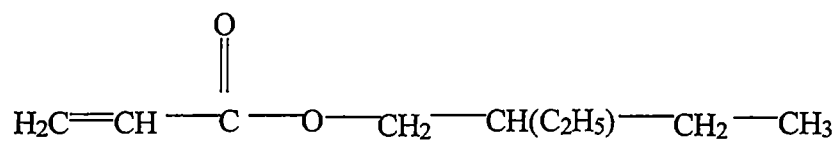
Figure 2.3 Polymer glass transition temperature (T_g) ranges for various product applications

[Source Lowell, P A , El-Aasser, M S in "Emulsion Polymerization and Emulsion Polymers", pg 640 (John Wiley and Sons Inc , New York, 1997)]

ranges from 4-10 carbon atoms (10). The second monomer incorporated during copolymerization is a reinforcing monomer, present in 2-20 % of the total weight of monomers. It usually contains 1-3 carbon atoms in the alkyl group. In the copolymerization system under study, 2-EHA is the excess hydrophobic monomer (about 90 % of the monomer mixture) and acrylic acid is the reinforcing monomer forming 10 % of the monomer mixture. The chemical structures of the two monomers are shown in figure 2.4

With regards to the water solubilities of the monomers, the system 2-EHA/AA is similar to that of styrene/methyl methacrylate emulsion copolymerization, which is widely studied in the literature. Like styrene, 2-EHA has a negligible solubility in water, whereas, acrylic acid is highly soluble in water like methyl methacrylate. The rates of polymerization of acrylic monomers are generally very high, which makes the kinetic analysis of these systems difficult especially during the start of the reaction. The final latex particle sizes range from 5 nm to 500 nm depending upon the specific recipe used.

(A) 2-Ethylhexyl acrylate



(B) Acrylic acid

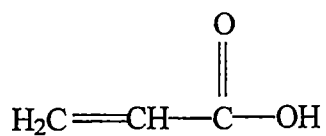


Figure 2 4 Chemical structures of 2-ethylhexyl acrylate and acrylic acid

CHAPTER 3

KINETICS OF EMULSION POLYMERIZATION

Investigation of the kinetics of emulsion polymerization typically involves the determination of the polymerization rate and its dependence on the polymerization parameters such as the monomer, emulsifier and initiator concentrations, and the temperature. The experimental approach typically starts with determination of conversion-time curves by varying the above parameters one at a time, followed by calculation of the polymerization rate by taking the first derivative of the conversion-time profiles over certain time intervals. The rate profiles are usually plotted versus time or conversion. In order to complete the kinetic analysis, one needs to know the number of particles and the monomer concentration in the particles as a function of conversion, which allows for the calculation of the average number of radicals per particle, $\bar{n}$. The number of particles is usually calculated from the knowledge of percentage conversion and the particle size, as measured by electron microscopy or a light scattering technique. The monomer concentration in the particles can be estimated using molecular thermodynamics and the knowledge of unreacted amount of monomer, the particle number and the particle size.

Determination of the percentage conversion is typically accomplished by gravimetry, gas chromatography, or dilatometry. Assuming that all experimental approaches are accurate, one must take the derivative of conversion-time curve in order to determine the polymerization rate as a function of conversion or time.

However, due to the fact that derivative must be taken, details of the polymerization rate are often missed (due to noise inherent in the data or the need to “smooth” it by curve-fitting techniques), particularly in the initial stages of the polymerization, where changes take place quickly and usually insufficient data are obtained.

3.1 Special Features of Emulsion Polymerization Kinetics

Because emulsion polymerization takes place in isolated loci, the kinetics are completely different from those of radical addition polymerizations taking place in bulk monomer, solutions, or suspensions of large monomer droplets in an immiscible continuous phase without micellar surfactant. General free-radical kinetics shows that increasing the rate of polymerization by increasing the initiator concentration or the temperature reduces the molar mass of the polymer formed. Emulsion polymerizations are faster, but also yield polymer with much larger molar mass than would be obtained in bulk, solution or suspension. Haward (11) showed that continued subdivision of a polymerizing system must ultimately result in the isolation of growing radicals in separate particles so that termination is practically instantaneous when a second radical enters a polymerizing particle.

The rate coefficient for the mutual termination of polymer radicals is large, but the reaction is second order in polymer radical concentration which is small ($\sim 10^{-8} \text{ mol dm}^{-3}$). Thus, in a typical bulk system where the rate of termination $R_t = 2k_t[M^*]^2$, is much lower than the rate of propagation, permits the formation of high polymer. However, when the volume in which two radicals are contained is reduced

sufficiently, the polymer radical concentration becomes large which reduces the lifetime, τ , of the second radical entering the particle to such an extent that termination can be considered to be instantaneous. Therefore, small particles can have only one growing radical or no radicals. The system is said to follow “zero-one” type of kinetics. The average number of radicals per particle ($\bar{n}$) equals $\frac{1}{2}$ (provided ρ , the entry rate of radicals into particles, is sufficiently high) This is generally approximately correct for monomers such as styrene, which have low transfer constants to monomer, which makes the rate of escape of radicals from particles almost negligible, but is only precisely fulfilled at high initiator concentrations.

The growth of a radical within an isolated particle is

$$r_p = k_p [M]_p \quad \dots(3.1)$$

Where k_p is the propagation rate coefficient of the monomer at the appropriate temperature and $[M]_p$ is the equilibrium concentration of the monomer swelling the latex particle. If N_T is the number of latex particles per unit volume of the aqueous phase (of which the volume is invariant during the reaction) the rate of polymerization per unit volume of water is (2)

$$R_p = \bar{n} N_T k_p [M]_p / N_A \quad \dots (3.2)$$

Division by the Avogadro number N_A , is necessary to convert the molecular rate of polymerization to molar rate.

Here R_p , N_T , and $[M]_p$ can be determined experimentally. Provided $\bar{n} = \frac{1}{2}$, equation (3.2) can be used to determine k_p independently of non-stationary state

methods The principal difficulty is in determining N_T with sufficient accuracy. Although, several methods exist for determining N_T directly, it is generally calculated from the measurements of average particle size and knowledge of molar mass of polymer.

Monomers which are more soluble in water than styrene and which produce highly active radicals and have high transfer constants (e.g vinyl chloride, vinyl acetate) have $\bar{n} \ll \frac{1}{2}$ because of relatively facile transfer of radicals out of particles into the water phase.

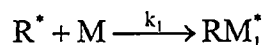
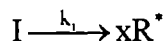
When $\bar{n} \sim \frac{1}{2}$, N_T is the principal factor determining the rate of polymerization. When $\bar{n} < \frac{1}{2}$ the rate of polymerization is much sensitive to N_T . When the latex particles are large, an increase in $\bar{n}$ is reflected in an increased rate of polymerization although N_T is constant

Although good reproducibility can be achieved under laboratory conditions, reproducibility of N_T under plant conditions can be poor. This problem can be overcome by the use of seeded polymerization in which N_T is predetermined by dilution of a completely polymerized seed latex with a small particle size, provided the dilution is not excessive, renucleation can be avoided and reproducibility ensured.

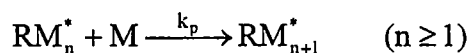
3.2 General Kinetic Scheme for Free Radical Polymerization

In common with other types of chain polymerization, free radical emulsion polymerization can be divided into three distinct stages initiation, propagation, and termination as shown in the kinetic scheme shown below:

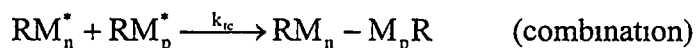
Initiation



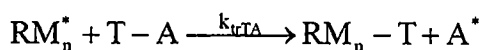
Propagation



Termination



Chain transfer



In the scheme shown above, x is the number of primary free radicals R^* formed from one molecule of the initiator I (usually $x = 1$ or 2). M represents either a molecule of monomer or monomer unit in a polymer chain; RM_n^* and RM_p^* are propagating chain radicals with degrees of polymerization equal to n and p respectively; RM_n , RM_p , and $RM_n - M_pR$ are terminated ("dead") polymer chains with degrees of polymerization equal to n , p , and $n+p$ respectively; $T - A$ represents species which undergo chain transfer; the symbols for the individual rate coefficients are given above the reaction arrows for each process

Since the individual reactions in the scheme given above are primary chemical processes, they can be analyzed directly to obtain equations that describe the kinetics

of free-radical polymerization. In the following sections, equations for the rate of polymerization and number-average degree of polymerization are derived.

3.2.1 Rate of Polymerization

On the basis of scheme presented above, the following expression for the rate of polymerization R_p can be written.

$$R_p = -\frac{d[M]}{dt} = k_i[R^*][M] + k_p[M^*][M] \quad \dots (3.3)$$

Where k_i is the rate coefficient for reaction of primary free radicals with monomer, $[R^*]$ the concentration of primary free radicals and $[M^*]$ the total concentration of chain radicals, i.e.

$$[M^*] = \sum_{i=1}^{\infty} [M_i^*] \quad \dots (3.4)$$

in which i is the number of monomer units in the chain radical. Since the amount of monomer consumed in the initiation stage is negligible compared to that consumed by the growing chains in propagation, the equation for R_p can be simplified, without loss of accuracy, to the form

$$R_p = k_p[M^*][M] \quad \dots (3.5)$$

This is a very important equation, which is applicable under all reaction conditions. However, in order to use the equation predictively, it is necessary to define $[M^*]$ in terms of easily accessible quantities. In order to obtain an expression for $[M^*]$, the balance between creation and loss of chain radicals must be considered. Assuming that

chain transfer reactions are followed by rapid reinitiation, the chain transfer has no effect upon $[M^*]$ and the rate of change of $[M^*]$ with time is given by

$$\frac{d[M^*]}{dt} = R_i - 2k_{tc}[M^*][M^*] - 2k_{td}[M^*][M^*] \quad (3.6)$$

Where R_i is the rate of formation of chain radicals, k_{tc} is the rate coefficient for termination by combination and k_{td} is the rate coefficient for termination by disproportionation. The factors of 2 and use of the total concentration of radical species in the terms arising from the termination reactions arise because two growing chains of any length are lost in each termination reaction. The equation can be simplified to

$$\frac{d[M^*]}{dt} = R_i - 2k_t[M^*]^2 \quad \dots(3.7)$$

Where k_t is the overall termination coefficient and is given by

$$k_t = k_{tc} + k_{td} \quad \dots (3.8)$$

The precise form of the equation for R_i depends upon the initiation system used and will not be discussed here

At the start of the polymerization, the rate of formation of radicals greatly exceeds the rate at which they are lost by termination. However, $[M^*]$ increases rapidly and so the rate of loss of radicals by termination increases. A value of $[M^*]$ is quickly attained at which the latter rate exactly equals the rate of radical formation. The net rate of change in $[M^*]$ is then zero and the reaction is said to be under steady-state conditions. In practice, most free-radical polymerizations operate under steady-state

conditions for all but the first few seconds. It is, therefore, quite satisfactory to assume steady-state conditions and to set $d[M^*]/dt = 0$ in equation (3.7). This yields the following equation for the steady-state concentration of chain radicals:

$$[M^*] = \left(\frac{R_i}{2k_t} \right)^{1/2} \quad \dots(3.9)$$

This equation can be substituted into equation (3.5) to give a general expression for the rate of polymerization

$$R_p = k_p \left(\frac{R_i}{2k_t} \right)^{1/2} [M] \quad \dots(3.10)$$

It must be emphasized that equation (3.10) and any other equation derived from it, applies only under steady-state conditions

3.2.2 Degree of Polymerization

The number-average degree of polymerization, x_n , of the polymer produced in a chain polymerization is given by

$$x_n = \frac{\text{moles of monomer consumed in unit time}}{\text{moles of polymer formed in unit time}} \quad \dots(3.11)$$

On the basis of the kinetics scheme for free-radical polymerization, the numerator is defined by equation (3.5). In deriving an expression for the rate of polymer formation, $d[P]/dt$, a series of terms are required in order to take account of the polymer molecules formed by chain transfer to molecules of monomer, initiator and solvent, as well as those formed by combination and disproportionation. In obtaining the individual terms it is necessary to take into account the fact that a single molecule of

polymer is produced by each combination of chain transfer event, whereas two are formed by each disproportionation event. Thus

$$\frac{d[P]}{dt} = k_{ic}[M^*]^2 + 2k_{id}[M^*]^2 + k_{trM}[M^*][M] + k_{trI}[M^*][I] + k_{trS}[M^*][S]$$

i.e.

$$\frac{d[P]}{dt} = [M^*]\{(k_{ic} + k_{id})[M^*] + k_{trM}[M] + k_{trI}[I] + k_{trS}[S]\} \quad \dots (3.12)$$

Where k_{trM} , k_{trI} , and k_{trS} are respectively the rate coefficients for chain transfer to monomer, initiator, and solvent. Substituting equations (3.5) and (3.12) into equation (3.11) gives

$$x_n = \frac{k_p[M]}{(k_t + k_{id})[M^*] + k_{trM}[M] + k_{trI}[I] + k_{trS}[S]} \quad \dots (3.13)$$

Under steady-state conditions $[M^*]$ can be substituted using equation (3.9) to give the following expression, known as the Mayo or Mayo-Walling equation, for the reciprocal of x_n .

$$\frac{1}{x_n} = \frac{1}{(x_n)_0} + C_M + C_I \frac{[I]}{[M]} + C_S \frac{[S]}{[M]} \quad \dots (3.14)$$

In which

$$(x_n)_0 = \frac{2^{1/2} k_p [M]}{(1 + q)(R_i k_t)^{1/2}} \quad \dots (3.15)$$

$$C_M = \frac{k_{trM}}{k_p}; \quad C_I = \frac{k_{trI}}{k_p}, \quad C_S = \frac{k_{trS}}{k_p} \quad \dots (3.16)$$

Where $(x_n)_0$ is the number-averaged degree of polymerization in the absence of chain transfer; q ($=k_{td}/k_t$), the fraction of termination reaction that proceeds by disproportionation ($0 \leq q \leq 1$), and the quantities C_M , C_I , and C_S are known as the transfer constants for chain transfer to monomer, initiator, and solvent, respectively. Note that when termination occurs only by combination $q = 0$, whereas when it occurs by disproportionation $q = 1$

3.2.3 Effects of Temperature

The effects of temperature upon the rate of polymerization and the degree of polymerization must be considered in terms of the contributions arising from the individual rate coefficients, which constitute the overall rate coefficients in the kinetic expressions. Applications of the Arrhenius equation to each of the rate coefficients and assuming that the pre-exponential factors are independent of temperature, leads to the following equations for initiation by thermolysis.

$$\frac{d \ln R_p}{dT} = \frac{(2E_p + E_d) - E_t}{2RT^2} \quad \dots (3.17)$$

$$\frac{d \ln (x_n)_0}{dT} = \frac{2E_p - (E_d + E_t)}{2RT^2} \quad \dots (3.18)$$

$$\frac{d \ln C_{IA}}{dT} = \frac{E_{irIA} - E_p}{RT^2} \quad \dots (3.19)$$

In which R_p and $(x_n)_0$ have their usual meanings, C_{TA} is the transfer constant for chain transfer to the species TA and E_d , E_p , E_t , and E_{irTA} are the respective activation

energies for initiator dissociation, propagation, termination and chain transfer to species TA. Some typical ranges for the values of these activation energies are given in table 3.1 Taking these values into account following conclusions can be drawn:

- 1 equation (3.17) suggests that R_p will continuously increase as the reaction temperature increases.
2. Equation (3.18) indicates that $(x_n)_0$ will decrease continuously as the reaction temperature increases Since equation (3 19) shows that C_{TA} will increase with temperature, then terms which take account of chain transfer in equation (3 14) will make an increasing contribution as the reaction temperature increases, leading to greater reductions in the value of x_n Thus, irrespective of whether or not chain transfer is significant, x_n is predicted to decrease continuously as the reaction temperature rises

Tables 3.1 Typical ranges of values for the activation energies of the processes which occur in free-radical polymerization

[Source P A Lovell and M S El-Aasser, "Emulsion Polymerization and Emulsion Polymers", pg 20, (John Wiley & Sons, Inc , New York, 1997)]

Process	Activation energy (KJ/mol)
Thermal dissociation of initiator	$110 < E_d < 160$
Propagation	$15 < E_p < 40$
Termination	$2 < E_t < 20$
Chain transfer	$40 < E_{tr} < 80$

CHAPTER 4

RAMAN SPECTROSCOPY - THEORY AND APPLICATIONS

The Raman effect was discovered in India by Sir C. V. Raman in 1928. In the first two decades after its discovery, Raman spectroscopy played a major role in many chemical and structural studies. The next two decades, however, saw the rapid development of commercial infrared (IR) instrumentation, with almost no major advances in Raman instruments. The introduction of laser sources, beginning with the routine availability of 50 to 100 mW continuous wave (CW) He-Ne lasers in the mid-1960s, greatly increased the interest in Raman spectroscopy. Other advances in monochromators, detectors, and amplifiers contributed to the renewed interest, as did the routine availability of minicomputers. While IR spectrometers are much cheaper and more widely used, Raman spectroscopy fills a sizable role in vibrational spectroscopic work. The following sections describe the origin, theory and advantages of Raman spectroscopy. Applications to in-line monitoring of emulsion polymerization processes are discussed. The instrumentation required for Raman spectroscopy is not discussed here, which can be found in the literature (12-14).

4.1 Theory of Raman Spectroscopy

When electromagnetic radiation of energy $h\nu$ irradiates a molecule, the energy may be transmitted, absorbed, or scattered. Here, h is Planck's constant, ν is

the wavenumber, and c is the velocity of radiation. In the Tyndall effect the radiation is scattered by particles (smoke or fog for example) In Rayleigh scattering the molecules scatter the light. No change in wavelength of individual photons occurs in either Tyndall or Rayleigh scattering. In the Raman effect, photons of the exciting radiation interact with molecules of the sample being irradiated. The energy of the scattered photon is either increased or decreased relative to the energy difference in the vibrational and rotational energy levels of the molecule. Thus, wavelength changes occur in Raman effect.

Figure 4.1 shows the energy level diagram for the Raman effect. In figure 4.1, the lines designated $v = 0$ and $v = 1$ represent the vibrational energy levels of the molecule. Three types of lines are observed in a Raman spectra viz Rayleigh, Stokes lines, and anti-Stokes, depending upon the interaction of the molecule with the incident photons. When a photon interacts with a molecule in the ground state ($v = 0$), the molecule is raised momentarily to a higher energy level (indicated by a dashed line) which is not a stable energy level at room temperature for the molecule. Since the molecule cannot remain in this unstable level, it may scatter a photon and return to the ground state as illustrated in figure 4.1. The scattered photon has therefore the same energy content and frequency as the individual exciting photon, and gives rise to Rayleigh scattering. However, the molecule may not return to the ground state but may only drop in energy to an excited vibrational state such as $v = 1$. The energy of

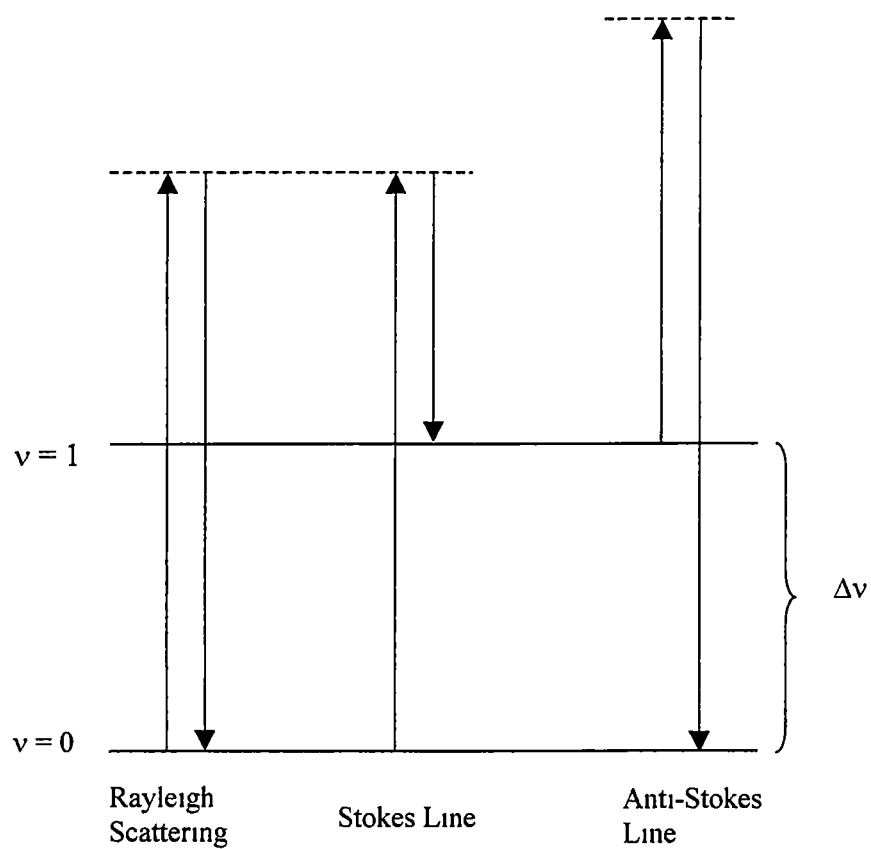


Figure 4.1 Energy level diagram for the Raman effect.

[Source N B Colthup, L H Daly, and S E Wiberly, "Introduction to infrared and Raman spectroscopy", pg 30, (Academic Press Inc , New York, 1964)]

the scattered photon is equal to the energy of the exciting photon minus the energy difference between the $\nu = 1$ and $\nu = 0$ levels. Therefore, the wavelength of the scattered photon is longer than that of the incident light. The Raman lines at longer wavelengths (or lower frequencies) than the incident excitation radiations are called Stokes lines. This terminology arose from Stokes' rule of fluorescence, which states that fluorescent radiation always occurs at longer wavelengths than that of the exciting radiation.

Another possibility is that the molecule in an excited level (such as $\nu = 1$) is raised to a higher unstable level by interaction with the exciting photon. The molecule may then scatter a photon and return to the ground state ($\nu = 0$). The energy of the scattered photons is equal to the energy of the exciting photon plus the energy difference between the $\nu = 1$ and $\nu = 0$ levels. The spectral line observed in this case is called as an anti-Stokes line. At room temperature most of the molecules are in the ground state rather than in the excited state. Consequently, the anti-Stokes lines are of lower intensity than the Stokes lines, particularly those anti-Stokes lines originating from the highest energy levels since these have lower molecular population than levels of low energy. Figure 4.2 shows the Stokes, anti-Stokes, and Rayleigh lines for CCl_4 .

4.2 Selection Rules for Raman Spectra

Raman spectra of molecules are observed due to the various vibrations occurring in molecules. In diatomic molecules, the vibration occurs only along the

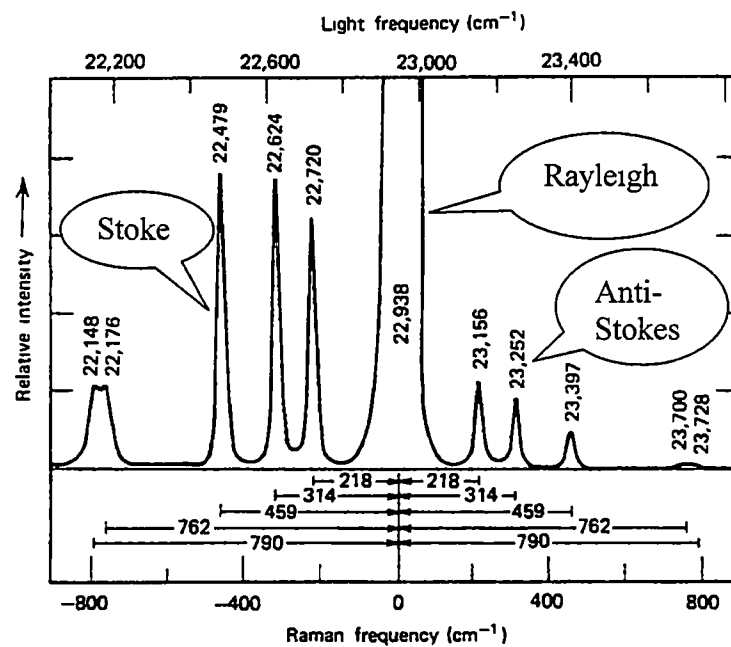


Figure 4.2 Stokes, anti-Stokes, and Rayleigh lines in the Raman spectrum of CCl_4 observed by mercury arc excitation, 435.8 nm ($22,938 \text{ cm}^{-1}$)
 [Source J G Grasselli, M K Snavely, and B J Bulkin, "Chemical Applications of Raman Spectroscopy", pg 6, John Wiley & Sons Inc, New York, 1981]

chemical bond connecting the nuclei. In polyatomic molecules, the vibrations of all the nuclei have to be considered. Most of the complicated vibrations can be expressed as a superposition of a number of normal vibrations that are completely independent of each other. Not all of these vibrations are IR or Raman active. Group theory calculations allow one to derive selection rules for Raman scattering by molecules and crystals. The detailed procedure of these calculations has been described in the literature (15,16) and is very time consuming. Some common observations about the Raman spectral intensities are given below, which should be used as a general guideline only.

A vibration mode is IR-active if there is a change in the magnitude and the direction of the net dipole moment during the vibration, and Raman-active if there is a change in the polarizability of the molecule. Thus, molecules having a center of symmetry show a strong Raman activity due to stretching vibrations that do not distort the molecule e.g., C=C, P=S, S-S etc. It has generally been observed that stretching vibrations associated with chemical bonds are more intense than deformation vibrations. Multiple stretching bands give rise to intense stretching modes, e.g., a Raman band due to C=C vibration should be more intense than that due to C-C vibration.

Vibrations are strong in Raman if the bond is covalent, and strong in IR if the bond is ionic. In an emulsion polymerization reaction, 80-90 percent of the reaction mixture is water. Water being a polar molecule, shows changes in the dipole moment during its vibrations, and hence is strongly IR-active. Thus, very high fraction of water

in an emulsion polymerization reaction does not make IR a good choice for in-line monitoring of these reactions. Conversely, vibrations of water are very weakly Raman active. Hence interference of water is not observed in Raman spectra of emulsion polymerization reactions. Also, the stretching vibrations of the symmetric and covalent C=C bond are highly Raman active. This makes Raman spectroscopy an ideal choice for monitoring emulsion polymerization reactions.

4.3 Applications of Raman Spectroscopy to Emulsion Polymerization Monitoring

Raman spectroscopy finds a lot of applications and uses in the field of chemical and structural analysis (17). Applications of Raman spectroscopy to the study of polymers and polymerization reactions is an area of vast research interest. Edwards *et al* (18) has reviewed the applications of Raman spectroscopy to the study of polymers and polymerization processes. A comparison between the IR and Raman spectroscopy technique reveals that IR is advantageous for identifying the polar substituents on the macromolecular chain, whereas Raman spectroscopy is helpful in characterizing the homonuclear polymer backbone. This underlines the usefulness of Raman spectroscopy in analysis of polymers with a carbon-carbon linkage.

In a typical free-radical emulsion polymerization, the attack of free radicals opens up the carbon-carbon double bond (C=C) into a carbon-carbon single bond (C-C). Thus, any technique that can follow the continuous change in the concentration of C=C is a good technique to follow the progress of emulsion polymerization reactions. A very strong intensity peak for C=C in Raman spectroscopy makes it an

ideal tool for this purpose. Very weak Raman scattering from water is an additional advantage, as in emulsion polymerizations about 90 percent of the reaction mixture is generally water. Another attractive feature of this technique is that it can provide an accurate and non-invasive method to follow the monomer concentration during polymerization when reaction is carried out under high vacuum conditions in glass apparatus. The following discussion reviews the work done in the past regarding in-line monitoring of emulsion copolymerization processes using Raman spectroscopy followed by the discussion of the present research work

Since intensity of C=C peak in Raman spectra is proportional to the concentration of C=C species present, comparison of the intensity of the C=C peak at any time to that of the initial intensity (at the start of the reaction) gives an idea about the conversion of monomer to polymer in a polymerization reaction (17,18) Damoun *et al* (19) studied and monitored the radical polymerization of methyl methacrylate in solution using Raman spectroscopy. The reaction was carried out at 70 °C using toluene as a solvent. The decrease in the intensity of the 1636 cm^{-1} C=C stretching band normalized with the band of toluene in the region 1550 to 1620 cm^{-1} as an internal standard allowed an accurate determination of the rate of conversion of monomers to polymeric chains. Normalization means taking the ratio of intensity of one peak to that of another peak. Wang *et al* (20) have studied monitoring of emulsion polymerization of styrene at 70°C using fiber-optic Raman spectroscopy. Wang *et al* monitored the disappearance of styrene band at 1631 cm^{-1} using another band at 1601 cm^{-1} that was common to styrene monomer and polymer, as an internal standard. The

results obtained from Raman measurements were compared with those obtained by UV absorption measurements on extracted samples and found to give essentially the same results. The reaction was monitored using argon laser with 514.5 nm excitation. The laser power at the sample was 140 mW

Claybourn *et al* (21) used Fourier transform (FT) Raman spectroscopy with NIR laser excitation to follow an emulsion copolymerization reaction involving methyl methacrylate, butyl acrylate and allyl methacrylate monomers in water as a continuous phase. Claybourn *et al* used a Nd/YAG laser operating in the NIR region at 1064 cm^{-1} . The authors also used a seeded emulsion to reduce any probability of re-initiation of new crops of particles during emulsion polymerization process and this allowed control of the final particle size and distribution. The ratio of C=O to C-H bending band (which itself is invariant during polymerization) remained constant when plotted over the progress of reaction. This result showed that C=O stretching band can be used as an internal standard for normalizing the intensity of C=C peak, and thus for real-time monitoring of emulsion polymerization reactions. Clarkson *et al* (22) monitored polymerization processes for styrene and methyl methacrylate at a range of temperatures using the symmetric stretching band of the vinyl moiety at 1640 cm^{-1} . The authors also studied the effect of oxygen on reaction progress.

A. Al-Khanbashi studied the in-line monitoring of emulsion copolymerization of Styrene and butyl acrylate. Al-Khanbashi *et al* (23) developed an improved method for monitoring emulsion composition using Raman scattering. In this work, Al-Khanbashi *et al* examined the effects of different optical configurations on collection

of Raman spectra from opaque mixtures such as emulsions and suggested methods to reduce interference from the optical fiber while simultaneously improving efficiency in the collection of the Raman scattering light. In another paper, Al-Khanbashi *et al* (24) reported the in-line monitoring of styrene-butylacrylate emulsion copolymerization and MMA polymerization using Raman scattering. The total conversion was followed by normalizing the intensity of C=C peak at 1631 cm^{-1} to the intensity of ring-breathing mode of styrene at 1000 cm^{-1} . The individual conversion of styrene was followed by using the peak at 1412 cm^{-1} , associated with C-H bending mode of vinyl group in styrene.

M. Dhamdhere (25) studied the in-line monitoring of homopolymerizations of vinyl acetate, methyl methacrylate and copolymerization of 2-ethylhexyl acrylate and acrylic acid. Both univariate and multivariate partial least square models were developed using chemometric techniques to correlate the Raman spectra taken during the course of reaction to conversion. A. Al-Khanbashi used a Kaiser Optical Inc Holoprobe[®], which focused the reaction contents from outside the reactor through the glass. A large amount of fluorescence was observed in the Raman spectra due to the glass. M. Dhamdhere used a Visionex[®] Inc. immersion probe, which could be immersed into the reaction contents. The use of this probe reduced the fluorescence in the spectra, however, sticky nature of polymer (poly 2-EHA/AA) sometimes caused the fouling of the probe window. This problem can be solved by using a higher surfactant concentration in the recipe to reduce the coagulation of particles. Though total conversions of monomers were monitored very well, individual conversions of

monomers could not be obtained from Raman spectra for 2-EHA/AA system because a separate peak for C=C in AA is not observed due to its very low concentration (1%) in the reaction mixture.

In the present work, CH₂ and CH₃ deformation band at 1450 cm⁻¹ is used to normalize the C=C peak intensity at 1638 cm⁻¹, as compared to the previous (25) use of C=O stretching band at 1730 cm⁻¹ for normalization. This resulted in reduced scatter in the conversion predictions from Raman spectroscopy data. In this research work, modeling of kinetics of emulsion copolymerization of 2-EHA and AA is done. Separate kinetic models are built using conversion profiles obtained from both gravimetry and Raman spectroscopy as the primary data. Individual model predictions are then compared with the experimental results of corresponding techniques.

CHAPTER 5

LITERATURE REVIEW OF KINETIC MODELING OF EMULSION

COPOLYMERIZATION REACTIONS

The design and efficient operation of emulsion polymerization processes requires tools in which the knowledge and vast experience about these systems, accumulated over the years, can be put in a quantitative form that can be readily used. Mathematical models of a comprehensive nature seem to be a powerful tool to achieve the aforementioned goals.

Various models of different degrees of detail and usefulness have been presented in the literature for different aspects of emulsion homopolymerization and copolymerization. The more detailed models generally describe the kinetic variables, conversion and copolymer composition, as well as the particle size distribution (PSD) and molecular weight distribution (MWD). These are usually based on the population balance equations, first given by Smith-Ewart (2). On the other hand, the models aim to describe only the kinetic variables, conversion and copolymer composition, without considering the PSD or describing only an average particle size. The amount of experimental data required to build these models (or get the best-fit parameters) is much lesser than that required for comprehensive models. Still, these simple models provide valuable information regarding the kinetic behavior of the emulsion polymerization system at hand. Often these models explain the behavior of a system

over a certain range of reaction conditions, which is large enough to include those typically occurring in industries.

5.1 Review of Models for kinetics of Emulsion Homopolymerization

Reviews on general modeling of emulsion homopolymerization are provided by Min and Ray (26) and Penlidis *et al* (27). The emulsion homopolymerization model published by Min and Ray is the first comprehensive model that includes detailed population balance equations (PBEs) for the evolution of conversion, PSD, and MWD. The most important assumptions underlying the Smith-Ewart theory are:

- The locus of chain propagation is the monomer-swollen latex particle
- Polymeric chains are initiated by radicals entering from the water phase into the particles.
- Chain termination is an instantaneous reaction between two radicals within one particle.
- Particles are nucleated by radicals absorbed into monomer-swollen micelles

One possible limitation of Smith-Ewart theory is that the basic assumptions are not applicable to all monomers and to all experimental conditions. J. L. Gardon (4) has attempted to establish the limits of validity of the Smith-Ewart model and derived new, experimentally viable formulae, for describing the kinetics of emulsion homopolymerization. In another paper, J. L. Gardon (5) described the radical termination constants as a function of latex particle size to explain the behavior of the system not following “zero-one” kinetics as mentioned by Smith-Ewart.

The kinetics of species in the aqueous phase control many events in emulsion polymerization: the rate of entry of free radicals into the particles, the rate of exit of free radicals from the particles, the fate of desorbed radicals and of free-radicals species derived directly from the aqueous phase initiator. Casey *et al* (28) studied the role of aqueous phase kinetic events on the rate of emulsion polymerization in detail and showed how general methods could be constructed to deduce the rate-determining events for each of these. The role of surfactant micelles in particle nucleation has been studied by F~~U~~K. Hansen (29).

One of the main parameters in the kinetic modeling of emulsion polymerization is the average number of radicals in latex particle, $\bar{n}$. The recursion differential equations, which describe the time-dependent population distribution of particles containing i radicals, were proposed by Smith and Ewart (2). However, the explicit and analytical solutions of these equations, which can be used to predict directly the time-dependent values for $\bar{n}$, have so far been obtained only for certain special cases. W. H. Stockmayer (30) and J. T. O'Toole (31) came up with solutions for these equations assuming a steady state approach. Their solutions involved a modified Bessel function. Li and Brooks (32) obtained general analytical solutions to these equations by an approximation procedure to give explicit expressions for predicting both time-dependent and steady state values of $\bar{n}$ for the general case.

Modeling of the kinetics of Styrene and Methyl methacrylate (MMA) homopolymerization, as well as their copolymerization, has been most extensively studied in the literature. Nomura *et al* (33-35) developed kinetic models for unseeded

homopolymerization of styrene using both oil-soluble and water-soluble initiators. Nomura *et al* studied the effect of initiator, emulsifier, and initial monomer concentrations on both the number of particles produced and the monomer conversion versus time histories. The authors found that the kinetic behavior of an oil-soluble initiator system is the same as that of the water-soluble initiator system. Modeling of free radical homopolymerization of styrene and MMA by a semibatch process has been done by Li and Brooks (36) and Tefera *et al* (37). In these papers the “gel effect”, i.e., effect of diffusional factors on the values of various rate parameters (and eventually on the conversion profiles) was studied. The models were developed to predict the average number of radicals in the particles, the monomer conversion and the average degree of polymerization. Modeling of kinetics of emulsion homopolymerization of vinyl chloride by Tauer *et al* (38) is noteworthy as it takes into account the effect of particle coalescence in modeling the particle size distribution in emulsion polymerization.

5.2 Review of Models for Kinetics of Emulsion Copolymerization

The model of Haskell and Settlage (39) is one of the earliest attempts to generalize the ideas of Smith-Ewart for homopolymerization to the copolymerization case. The model describes a monodisperse population of particles and does not account for desorption of radicals. It is applied to simulate cases of batch and semibatch copolymerization of vinylidene chloride with other unspecified monomers,

and the authors mentioned that qualitative agreement of the model predictions with experimental data was obtained

Ballard, Napper and Gilbert (40) provided the first successful attempt to generalize the Smith-Ewart recurrence equation of emulsion homopolymerization to the copolymerization case. They used a monodispersed population balance equation to describe the kinetics in the interval II and III of a batch emulsion copolymerization and gave an analytical solution for a “zero-one” system.

A major contribution in the field of kinetic modeling of emulsion copolymerization reactions comes from the research work of Nomura and coworkers in 1980s. Nomura *et al* (41) clarified the use of average or apparent rate constants to extend previous emulsion homopolymerization results to the copolymerization case. The authors have proposed a simple monodispersed kinetic model, which is applied to the case of styrene-methyl methacrylate batch copolymerization at 50 °C. Very good agreement of model predictions with the experimental data for the evolution of conversion and the total number of particles was obtained. An important contribution of these authors is the development of a desorption rate coefficient for the case of emulsion copolymerization. The authors also mention that desorption of radical from the particle does not affect the copolymer composition but affects the rate of emulsion copolymerization. Nomura *et al* developed several models (42,43) describing the kinetics of “seeded” emulsion copolymerization of styrene and methyl methacrylate. In these papers, the authors considered the effect of various variables like initial concentrations of initiator, emulsifier, and monomers on the rate of copolymerization.

and copolymer composition. Later, Lin *et al* (44) and Storti *et al* proved that this kinetic model and the approach were very useful in simplifying the mathematical treatment of emulsion copolymerization equations. In 1989, Nomura *et al* (45) came up with the first kinetic model for the “unseeded” emulsion copolymerization of styrene and methyl methacrylate based on micellar nucleation theory. The authors discriminated the radicals with and without electrical charge from each other in view of the role in the particle nucleation process and found that almost all the particles were generated by the charged radicals stemming from the initiator.

Forcada and Asua (46) also proposed a model for kinetics of unseeded emulsion copolymerization of styrene and methyl methacrylate in which they included a new rate coefficient for radical desorption based on the one proposed by Asua *et al* (47) for emulsion homopolymerization. Asua *et al* analyzed the effect of the styrene/methyl methacrylate molar ratio in the initial charge on the number of particles produced, overall conversion and copolymer composition. The authors found that number of particles increased with the methyl methacrylate content and that a drift of the copolymer composition resulted during the polymerization of styrene/methyl methacrylate molar ratios other than 50/50.

Mead and Poehlein (48) developed a steady-state model for seeded emulsion copolymerization of styrene-methyl acrylate and styrene-acrylonitrile in a continuous stirred tank reactor (CSTR). The model predictions include the latex particle size distribution, average number of radicals per particle, rate of copolymerization, and copolymer composition. The rate coefficients for radical desorption were determined

by the best-fit simulation of the experimental particle size distribution. Later, these authors (49) included the particle growth by aqueous-phase polymerization and proposed a new model for the same system. Expressions were derived for the concentrations and average chain length of oligomeric radicals in the aqueous phase. Dube *et al* (50) published a model for emulsion copolymerization of acrylonitrile/butadiene for application to the testing of non-linear model based control schemes for an industrial reactor facility. The authors performed an extensive sensitivity analysis to identify the parameters that have a major effect on the copolymerization reaction progress and the copolymer properties.

One of the important factors that affect the properties of a copolymer is the copolymer sequence distribution (CSD) namely, the microstructure of copolymer. It gives the number fraction of chains of both A and B (comonomers) of various lengths in the copolymer. Pichot *et al* (51) first studied the influence of emulsion polymerization process on the microstructure of a copolymer (vinyl acetate-butyl acrylate) by ^{13}C -NMR spectroscopy. In the paper by Ballard *et al* (40) a method to predict the time evolution of the CSD was first proposed. Forcada and Asua (52) later showed that for given monomer concentrations in the particle, the microstructure of the copolymer was independent of the number of radicals per particle, as well as the termination and transfer reactions. The authors calculated the CSD for styrene-methyl methacrylate copolymer by means of a simple Markovian distribution function. This simpler approach allowed the prediction of the CSD as accurately as the previous complex method of Ballard *et al*.

Shoaf and Poehlein (53) specifically studied the copolymerization of acrylic acid and its derivatives with other monomers. Their work on acrylic acid-styrene and methacrylic acid-styrene revealed that significant polymerization occurs in both the aqueous and particle phases. The authors report that the primary reaction locus in the acrylic acid-styrene system shifts from the particle phase to the aqueous phase after the hydrophobic monomer, styrene, has been consumed. The most recent work in the field of kinetics of emulsion copolymerization of acrylic monomers includes studying the effect of mercaptan chain transfer agents on copolymerization behavior (54), effect of acrylic acid on radical penetration length and conversion in an "emulsifier-free" copolymerization (55), effect of various emulsifiers in a mixed emulsifier copolymerization (56) and effect of seed diameter and number of seeds on seeded emulsion copolymerization behavior (57).

Till date, no work has been published in the open literature specifically studying the kinetics of emulsion copolymerization of 2-ethylhexyl acrylate and acrylic acid except for that of F. Loncar (58). Loncar developed a mechanism for emulsion copolymerization behavior of an oil-based monomer (2-ethylhexyl acrylate) with two types of carboxyl monomers (acrylic acid and methacrylic acid). The primary outcome of the study of the mechanism was that the time of incorporation of the carboxyl monomer during the reaction determines the final latex properties. This work was very helpful in gaining an insight to the particle growth mechanism for the specified polymerization reactions, although no mathematical model describing the kinetics was developed. The model proposed in this work is the first attempt to

mathematically predict the kinetic behavior of emulsion copolymerization of 2-ethylhexyl acrylate with acrylic acid.

CHAPTER 6

KINETIC MODELING OF 2-EHA/AA COPOLYMERIZATION

The Smith-Ewart theory has gained wide acceptance for providing an adequate description of the emulsion polymerization of a wide range of monomers. The theory, with appropriate extensions where necessary, makes possible both a quantitative understanding and a prediction of dynamic and steady state properties. These properties include the overall kinetics, the particle size distributions, and the molecular weight distributions. Ballard *et al* (40) have presented a theoretical description of an emulsion copolymerization system, based on Smith-Ewart mechanism, which enables the time evolution of the copolymer composition and copolymer sequence distribution to be computed from the knowledge of the rate coefficients for the various microscopic processes involved. The evolution equations given in the paper by Ballard *et al* are applicable only to the intervals II and III, the intervals where no particle nucleation takes place. In a typical emulsion copolymerization, bulk of the polymer is formed in these intervals. The mechanisms operating in interval I, when the latex particles are formed, are still uncertain for the copolymerization system, 2-EHA and AA. In the proposed kinetic model, the equations given by Ballard *et al* (40) for generalization of Smith-Ewart theory to emulsion copolymerization are used. These equations are applied for the copolymerization of 2-EHA and AA, and a kinetic model is developed using the values of parameters estimated by best fitting the experimental data.

6.1 Generalization of Emulsion Homopolymerization Theory to Emulsion Copolymerization

The extension of Smith-Ewart homopolymerization theory to the copolymerization case is not trivial. For example, the overall kinetics of an emulsion homopolymerization are determined by the distribution functions $N_i(t)$: the relative number of latex particles containing i free radicals at time t , the evolution equations for these quantities involve the rate coefficients for free radical entry, exit, and bimolecular termination. While only the total number of free radicals in a given latex particle is necessary to specify emulsion homopolymerization, the nature of these free radicals must also be known to specify emulsion copolymerization. This information is encapsulated in a distribution function which, for the copolymerization of monomers A and B is denoted as $N_{ij}(t)$, and is defined as follows. An A-type free radical is defined as a growing polymer chain of any length with a growing A-type radical as end group (and a B-type radical similarly). $N_{ij}(t)$ is then defined as the relative number of latex particles containing $(i+j)$ free radicals at time t , i of which are of type A, and j of which are of type B. The evolution equations for these distribution functions not only involve the rate coefficients of entry, exit, and termination of each monomeric species, but also cross propagation and cross transfer, since the latter events change the relative number of free radicals of each species without changing the total number of free radicals. The rate coefficients for self-propagation and self-transfer affect neither the total number of free radicals in the particle nor the number of free radicals of each monomeric species.

Before discussing the modeling of emulsion copolymerization, it is essential to summarize the generalized Smith-Ewart theory for emulsion homopolymerization in intervals II and III. In this theory, the following rate coefficients are needed to specify the overall kinetics:

- ρ , the first order rate coefficient for entry of free radicals into the latex particle.
- k , the first order rate coefficient for exit of free radicals out of latex particle
- c , the pseudo-first order rate coefficient for bimolecular termination of growing chains within a latex particle
- k^p , the second order rate coefficient for propagation of free radicals within the particle

In addition, knowledge of $[M]_p$, the monomer concentration within the particles is needed. $N_i(t)$, the relative number of particles containing i free radicals at time t , is then specified by

$$\frac{dN_i}{dt} = \rho [N_{i-1} - N_i] + k [(i+1)N_{i+1} - iN_i] + c [(i+2)(i+1)N_{i+2} - i(i-1)N_i] \dots (6.1)$$

where, $i = 0, 1, \dots, \infty$

The negative subscripts and the coefficients are ignored for $i = 0, 1$. The molar conversion of monomer to polymer in an emulsion homopolymerization x is then given by

$$\frac{dx}{dt} = N_T N_A^{-1} [M]_p k^p \sum_{i>0} i N_i(t) \dots (6.2)$$

Here the particle numbers N_i are normalized with respect to the total number of particles such that $\sum N_i = 1$, N_T is the total number of particles present per unit volume of emulsion and N_A = Avogadro's constant

In interval II of emulsion polymerization, the rate of diffusion of monomer from monomer droplets into the polymer particle is generally equal to their rate of consumption in polymer particle. This dynamic equilibrium keeps $[M]_p$ essentially constant during interval II. During interval III, these droplets have disappeared which means the monomer concentration in polymer particles is no longer constant. Thus, above differential equations must be supplemented by an equation for change in $[M]_p$, viz.

$$\frac{d[M]_p}{dt} = -[M]_p (N_A V_s)^{-1} k_p \sum_{i>0} i N_i \quad \dots(6.3)$$

where V_s = volume of the monomer-swollen latex particle

The generalizations of equation (6.1) through equation (6.3) to an emulsion copolymerization requires the knowledge of $N_{ij}(t)$, which is the relative number of particles containing i chains with free radical species A and j chains with free radical species B. In this work, A represents the 2-ethylhexyl acrylate monomer and B represents the acrylic acid.

Consider firstly the events that can change these populations. All the rate coefficients for population gain or loss must be distinguished according to the species involved.

Let,

ρ_A, ρ_B = the rate coefficients for entry of any A and B free radical species, respectively.

k_A, k_B = the rate coefficients for exit of any A and B free radical species, respectively

For bimolecular events (i.e. propagation, termination, and transfer) the situation is more complex. The rate coefficients for such processes will firstly depend on the nature of both species involved (e.g., for transfer rate coefficients, on the species of the growing chain and on the species to which the free radical activity is transferred). If the kinetics are first-order Markov processes, then only the end group unit of a growing free-radical affects the kinetics of the process. Thus, no further specification is necessary. However, if second-order Markov processes also influence the kinetics, then specification of the penultimate monomeric unit, (i.e., the nature of the monomeric unit adjacent to the growing one) is also required and so on for higher-order Markov processes. In the proposed model the attention has been confined only to first-order Markov processes. It is then sufficient to specify the rate coefficients of the two monomeric species for each rate coefficient for bimolecular events. Thus the rate coefficients for various bimolecular events are defined as follows:

k_{AB}^p = the rate coefficient for addition of a B monomer unit to a chain with an active A terminal unit.

k_{AB}^r = the rate coefficient for transfer of radical activity from a chain with an active A terminal unit to a B monomer

c_{AB} = the (pseudo-first-order) rate coefficient for bimolecular termination of two growing chains, one with an active A and the other an active B terminal unit.

Similar definitions hold true for k_{AA}^p , k_{BA}^p , k_{BB}^p , k_{AA}^{tr} , k_{BA}^{tr} , k_{BB}^{tr} , c_{AA} , c_{BA} , and c_{BB}

The concentrations of monomer A and B within the latex particles are denoted as $[A]_p$, and $[B]_p$, respectively.

Consider now the population balance equations for $N_{ij}(t)$ The events affecting the “status” of number of particles containing i of A free radicals and j of B free radicals are shown in table 6.1 and table 6.2 Table 6.1 shows the events causing increase in $N_{ij}(t)$, and table 6.2 shows the events causing decrease in $N_{ij}(t)$

Following Smith and Ewart one notes that, since $k_A N_{ij}$ is the rate of exit of a particular A free radical, the total rate of exit of A free radicals is i times $k_A N_{ij}$, and so on, for the other events Taking all population changing events into account, one obtains the following equation for N_{ij}

$$\begin{aligned} \frac{dN_{ij}}{dt} = & -[\rho_A + \rho_B + ik_A + jk_B + i(i-1)c_{AA} + 2ijc_{AB} + j(j-1)c_{BB} + i\gamma_{AB} + j\gamma_{BA}]N_{ij} \\ & + \rho_A N_{(i-1)j} + \rho_B N_{i(j-1)} + (i+1)k_A N_{(i+1)j} + (j+1)k_B N_{i(j+1)} \\ & + (i+2)(i+1)c_{AA} N_{(i+2)j} + 2(i+1)(j+1)c_{AB} N_{(i+1)(j+1)} \\ & + (j+2)(j+1)c_{BB} N_{i(j+2)} + (i+1)\gamma_{AB} N_{(i+1)(j-1)} + (j+1)\gamma_{BA} N_{(i-1)(j+1)} \end{aligned} \quad (6.4)$$

where, $\gamma_{AB} = (k_{AB}^{tr} + k_{AB}^p)[B]_p$ and same for γ_{BA} .

Equation (6.4) is the desired evolution equation, the copolymerization equivalent of equation (6.1).

Table 6.1 Events leading to formation of particles containing i of A free radicals and j of B free radicals

Event	Initial "status" of particle		Final "status" of particle	
	No. of A radicals	No. of B radicals	No. of A radicals	No. of B radicals
Entry of an A free radical	$i-1$	j	i	j
Entry of a B free radical	i	$j-1$	i	j
Exit of an A free radical	$i+1$	j	i	j
Exit of a B free radical	i	$j+1$	i	j
Termination by combination of two A free radicals	$i+2$	j	i	j
Termination by combination of two B free radicals	i	$j+2$	i	j
Termination by combination of an A free radical with a B free radical	$i+1$	$j+1$	i	j
Propagation of an A free radical by reaction with B monomer	$i+1$	$j-1$	i	j
Propagation of an B free radical by reaction with an A monomer	$i-1$	$j+1$	i	j
Transfer of radical activity from an A free radical to a B monomer	$i+1$	$j-1$	i	j
Transfer of radical activity from a B free radical to an A monomer	$i-1$	$j+1$	i	j

Table 6.2 Events leading to depletion of particles containing i of A free radicals and j of B free radicals

Event	Initial "status" of particle		Final "status" of particle	
	No. of A radicals	No. of B radicals	No. of A radicals	No. of B radicals
Entry of an A free radical	i	j	$i+1$	j
Entry of a B free radical	i	j	i	$j+1$
Exit of an A free radical	i	j	$i-1$	j
Exit of a B free radical	i	j	i	$j-1$
Termination by combination of two A free radicals	i	j	$i-2$	j
Termination by combination of two B free radicals	i	j	i	$j-2$
Termination by combination of an A free radical with a B free radical	i	j	$i-1$	$j-1$
Propagation of an A free radical by reaction with B monomer	i	j	$i-1$	$j+1$
Propagation of an B free radical by reaction with an A monomer	i	j	$i+1$	$j-1$
Transfer of radical activity from an A free radical to a B monomer	i	j	$i-1$	$j+1$
Transfer of radical activity from a B free radical to an A monomer	i	j	$i+1$	$j-1$

It is to be noted that, in general, the ratio of the quantities $[A]_p$, and $[B]_p$ may well be significantly different from that specified by the relative composition of the two monomers in the emulsion droplets. Moreover, this ratio would be expected to vary as polymerization proceeds and the composition of polymer in the latex particles, as well as the composition of the emulsion droplets changes. One can comprehend such changes, if $[A]_p$, and $[B]_p$ are known, either through experimental measurement or through some predictive calculation method. It is also to be noted that quantities of the type c_{AA} may also vary as polymerization proceeds due to the changing composition of the polymer or due to non-ideal mixing effects, and so be dependent upon all of the N_{ij} 's. The resulting equations for the evolution of the N_{ij} are then nonlinear, which may be solved easily using standard numerical methods. Moreover, an approximate linearity holds when both monomers are in interval II (i.e. when the variation of $[A]_p$ and $[B]_p$ with the amount of polymer present is slight) and if the variation of the other rate coefficients with the amount of polymer is also negligible. Under these circumstances, equation (6.4) is linear, and a solution may be found employing an eigenvalue method.

The generalization of equation (6.2) to a copolymer system can be written down directly as

$$\frac{dx_A}{dt} = N_i N_A^{-1} [A]_p \sum_{i>0} \left[k_{AA}^p \sum_{j=1}^i j N_{i(i-1)} + k_{BA}^p \sum_{j=1}^i j N_{(i-1)i} \right] \quad \dots (6.5)$$

During interval II, if monomer mixing in the droplets and in the latex particles is ideal, $[A]_p$, and $[B]_p$ are essentially constant. This no longer holds in interval III, since they

will be consumed at different rates. When A is interval III, the time evolution of $[A]_p$ is given by a straightforward generalization of equation (6.3)

$$\frac{d[A]_p}{dt} = -[A]_p (N_A V_s)^{-1} \sum_{i>0} \left[k_{AA}^p \sum_{j=1}^i j N_{(i-j)} + k_{BA}^p \sum_{j=1}^i j N_{(i-j)} \right] \quad \text{..(6.6)}$$

and similarly for $d[B]_p/dt$ when B is in interval III. With either or both A and B in interval III, equation (6.6) is coupled with equation (6.4), and with equation (6.5) as well. Thus in general the whole set of coupled ordinary differential equations must be solved numerically.

6.2 Estimation of Parameters Required in the Kinetic Modeling

As seen in the previous section a number of parameters are needed to perform the simulations of the kinetic model for emulsion copolymerization. The most ideal approach would be to estimate the parameters from specific experiments performed on the chosen system. However, the large number of parameters required for modeling makes this an impractical approach. Thus, the very next idea would be to obtain the accurate values of these parameters from the reported literature. Of all the rate coefficients required, those for propagation, transfer and termination are approximated as those estimated in bulk and homopolymerization. The values of these parameters are generally available in the literature (59). Values of the other parameters like rate coefficients for entry and exit of free radicals are not readily available in the literature (especially for the system 2-EHA/AA copolymerization). Numerous papers have been published on the estimation of these rate coefficients as well as on the estimation of

monomer concentrations in the polymer particle and the number of particles formed during polymerization. A detailed review of work in this direction is given below

6.2.1 Estimation of Number of Particles Initially Formed

In the Smith-Ewart theory, where the main loci of particle nucleation is micelles, the number of polymer particles formed is given by equation (6.7)

$$N = k(\rho / \mu)^{0.4} (a_s S)^{0.6} \quad \text{..(6.7)}$$

where ρ is the rate of radical generation, μ is the rate of particle volume growth, a_s is the area occupied by a surfactant molecule, and S is the total amount of surfactant in the micelles (the amount of dissolved surfactant is neglected)

Nomura *et al* (60) and Hansen and Ugelstad (61) recognized the importance of chain transfer of radicals to monomer and the radical absorption, desorption and reabsorption during interval I, and generated the following general expression.

$$N = k(\rho / \mu)^{(1-z)} (a_s S)^z \quad \text{..(6.8)}$$

where $0.6 < z < 1.0$ and depends on the chain transfer constant and water solubility of the monomer. The sum of the exponents for the dependence of the number particles with respect to the emulsifier (S) and the rate of initiator decomposition (ρ) is always equal to unity. An increase in the order with respect to S will be accompanied by a decrease in order with respect to ρ . This is usually true for monomers with water solubilities higher than styrene, such as vinyl acetate, methyl methacrylate and vinyl chloride

6.2.2 Estimation of Entry and Exit Rate Coefficients

Various researchers have published papers on estimating the rate coefficients for entry and exit of free radical into and out of a polymer particle. Unzueta and Forcada (56) have reported the equations for radical absorption rate constants to particles ρ_p , and micelles ρ_m , assuming diffusional mechanism:

$$\rho_p = 4\pi D_w r_p N_A F_p \quad . \quad (6.9)$$

$$\rho_m = 4\pi D_w r_m N_A F_m \quad \dots(6.10)$$

where r_p and r_m are the particle and micelle radii, respectively, D_w , the radical diffusion constant in the aqueous phase; and F_p and F_m , the radical efficiencies in the particle and in the micelle. Unzueta and Forcada also assumed that only monomer radicals could desorb out of a particle (47), i.e. a previous chain transfer to a monomer must take place before radical desorption. Based on this assumption, the authors proposed the following equation for radical desorption of monomer i :

$$k_i = \frac{(k_{ii}'' P_i^p + k_{ii}'' P_i^p) [i]_p}{\frac{r_p^2}{2D_p} (k_{ii}'' [i]_p + k_{ij}'' [j]_p) + 1} \quad .(6.11)$$

where k_{ii}'' and k_{ij}'' are the transfer and propagation rate constants, respectively; between the i radical and the j monomer; P_i^p and P_j^p are the probabilities of a growing chain in polymer particle having the growing radical on the i and j monomeric unit; r_p , the radius of the particle, D_p , the diffusion rate constant for radicals in the particle, and $[i]_p$, the concentration of monomer i in the particle. The transfer rate constants between

i and j radicals were obtained as the geometric average of the rate constants for homopolymerization. Li and Brooks (36) reported the following equation for radical desorption rate coefficient in emulsion homopolymerization as

$$k = k_m' [M]_p \frac{K_0}{K_0 \bar{n} + k_p [M]_p} \quad \dots (6.12)$$

where, k_m' = the rate coefficient for the chain transfer to the monomer.

$\bar{n}$ = the average number of radicals per particle.

k_p = the propagation rate coefficient

$[M]_p$ = the concentration of monomer in polymer particles, and

K_0 is given as

$$K_0 = \frac{12 D_w / m_d d_p^2}{1 + (2 D_w / m_d D_p)} \quad \dots (6.13)$$

where, D_p = the diffusion coefficient for the monomer radicals in the particle phase

m_d = the partition coefficient for the monomer radicals between particles and the aqueous phase

A number of papers have been published giving equations and procedures for calculating the rate coefficient for entry and exit of free radicals (33,38,41,45,46,48,53,62). All these methods describe the entry and exit rate coefficients of radicals as a function of particle size, diffusivity of radicals into particle and aqueous phase, and the partition coefficient of monomers between aqueous and organic phase. Barandiaran *et al* (63) and Arbina *et al* (57) separately investigated the usefulness of calorimetric measurements for estimation of parameters required in the

kinetic modeling of emulsion copolymerization Barandiaran *et al* attempted to estimate three rate coefficients, viz, the rate coefficient for radical generation from initiator, k_i ; the radical entry rate coefficient, ρ , and the exit rate coefficient, k . They found that the estimation of these parameters depends on the value of average number of radicals per particle, $\bar{n}$. If $\bar{n}$ exceeds 0.5, only two of the three rate coefficients could be determined together provided that an accurate value for the third parameter is available. For $\bar{n} < 0.5$, it was found that all the three parameters could be estimated accurately.

Hawket *et al* (64) studied the time evolution of the conversion in chemically initiated seeded emulsion polymerizations to determine the rate coefficients for entry and exit of radicals. They considered the straight-line portion of the curve of monomer conversion vs. time for an emulsion homopolymerization (65)

$$x = at + b \quad . \quad (6.14)$$

Where a and b , the slope and the intercept of the straight line, are functions of the parameters ρ , α , and k , where α is the fate parameter whose value lies between -1 and +1. It is -1 if all desorbed radical terminate in the aqueous phase and +1 if all desorbed radicals re-enter the polymer particles. For an individual experiment ρ and k can be obtained provided α is known. This group used two criteria to estimate a single value of α that would describe a seeded styrene emulsion polymerization system in the presence of any concentration of aqueous phase soluble initiator. (1) the exit rate coefficient obtained from the slope and the intercept analysis should be independent of

initiator concentration and particle number and (2) the value of k should agree with the value deduced from relaxation studies where α was assumed to be equal to +1. The value of α that resulted from their analysis could be used for describing the kinetics of experiments that had an initiator concentration range over 3 orders of magnitude and a particle number that ranged by a factor of 4. No approach for estimating ρ and k without assuming a constant value of α for the system has been proposed, and it does not appear to be a simple task.

Lichti *et al* (66) used the time evolution of the particle size distribution (PSD) to estimate the rate coefficients for entry, exit, and propagation of free radicals in seeded and *ab initio* styrene polymerizations. The method is laborious, as it requires the measurement of at least 3000 particles of each sample to ensure reproducible results. In addition, the authors found the PSD to be insensitive to the value of the radical desorption coefficient in two out of the three cases studied. The model proposed by Lichti *et al* (67) was used by Chen and Wu (68) to determine the kinetic parameters from PSD. These authors (68) proposed the use of first three moments of the PSD to estimate the kinetic parameters and applied their method to the experimental data obtained by Lichti *et al*. In order to obtain the basic equations in their approach, Chen and Wu considered both ρ and k to be independent of the volume of the particle but then used the resulting equations to determine the dependency of ρ and k on the particle size.

A novel approach for parameter estimation is presented by Asua *et al* (69). The approach is also based on the study of the time evolution of the conversion in chemically initiated seeded emulsion polymerizations as first proposed by Hawket *et al* (64). The advantage of this method is that the time dependence of the conversion during the approach to steady-state values of $\bar{n}$ is more sensitive to the values of the parameters than both steady-state measurements and PSD analysis. Secondly, the experiments can be carried out more easily with standard laboratory equipment and neither laborious postexperiment manipulations (as measuring thousands of particles in the case of using the PSD) nor sophisticated equipment other than electron microscope is required. The authors have developed an algorithm for parameter estimation in stiff differential equations, which allows for the estimation of all the kinetic parameters including the propagation rate coefficients. In order to check the usefulness of the present approach, a classic methodology is used. Data are generated by simulation using arbitrary but reasonable values of the rate coefficients and then the proposed method is applied to the generated data in an attempt to estimate these rate coefficients. The fit of the data and a comparison of the values of the rate coefficients used in the data generation and the estimated ones give a measure of the usefulness of this method.

6.2.3 Monomer Concentration in the Polymer Particles

A method to experimentally measure the concentration of monomers in polymer particles has been reported by Nomura *et al* for both homopolymerization

(33,34) and copolymerization (41). The method requires the use of a centrifuge and a gas chromatograph and is described here. A sample of reaction mixture withdrawn from the sampling cock, attached at the bottom of the reactor was immediately subjected to centrifugation for separating monomer droplets in the sample as a monomer layer when they existed. A fraction of the aqueous layer thus separated, which contained only the monomer swollen polymer particles and water, was then taken out with a syringe and was poured into excess methanol to precipitate the polymer after weighing the sample. The precipitated polymer was filtered off with a glass crucible and was weighed after complete dryness in an oven. The monomer concentration in the filtrate was measured by gas chromatography to determine the total amount of monomer in the filtrate that was contained in the monomer-swollen polymer particles in the sample. In calculating the monomer concentration in the polymer particles using the weights of polymer and monomer thus determined, the volumes of polymer and monomer were assumed to be additive. By measuring the monomer concentration in the separated monomer layer by gas chromatography, the monomer concentration in the monomer droplets can be determined directly.

The method described above is laborious, and is prone to a lot of experimental errors due to the fast kinetics of these reactions. Furthermore, the method is unsuitable for emulsion copolymerization of 2-EHA and AA, as it is very difficult to measure the small amounts of AA present (AA fraction is typically about 1 percent by weight, in the reaction recipes used) with high accuracy in the monomer mixture. Therefore, it would be useful to predict the monomer concentration *in situ*, from the reaction

conditions used. Both empirical and thermodynamic approaches have been proposed in the literature for this purpose (40,42,45,46,70-73). In the first approach, empirical relationships describing monomer partitioning were developed often based on questionable assumptions, e.g., neglecting the monomer in the aqueous phase (42,45). Another empirical approach (70-72) is the experimental determination of monomer partition coefficients fitted with empirical relationships. The thermodynamic approach for prediction of monomer concentration was first developed by Morton for emulsion homopolymerization (74), which was later extended to emulsion copolymerizations (46,73,75-78). The thermodynamic approach is very fundamental and promising. However, it requires values of many parameters, which are not easily known. In this approach, chemical potential of monomer in a given phase in the form of a sphere is given as a function of volume fraction of the polymer in the given phase, the Flory-Huggins interaction parameter, the partial molar volume of monomer, the interfacial tension, temperature and the diameter of the sphere. When the monomer concentrations in the monomer droplets and polymer particles are in thermodynamic equilibrium, the chemical potential in each phase is equal. This results in a system of algebraic equations, which can be solved to obtain the concentration of monomer in both droplets and the polymer particles.

6.3 Methodology Proposed for Model Simulations

This section describes how the evolution equation (6.4) coupled with equation (6.5) for individual conversion, and equation (6.6) for monomer concentration in the

polymer particles are solved to get the profiles of number of particles, average number of radicals per particle, individual conversion, and copolymer composition. In equation (6.4), ' i ' can theoretically take any non-negative value. One should note however, that the termination and propagation rate coefficients of monomers have much higher values than the entry rate coefficients, which does not allow for a very high concentration of radicals in the polymer particles. For example, for the system of styrene homopolymerization, it is well known that the average number of radicals per particle is 0.5. This is called as "zero-one" kinetics, one in which due to very high value of termination rate coefficient, a radical entering a particle containing one free radical is immediately subjected to termination thus destroying both the radicals. Therefore, the polymer particles contain either one or no free radicals at any instant of time.

In the proposed modeling of copolymerization of 2-EHA and AA it is assumed that the polymer particles contain no more than 2 radicals, every single one of which can be either A type or B type. For this case, equation (6.4) becomes a system of six ordinary differential equations, one each for N_{00} , N_{01} , N_{02} , N_{10} , N_{11} , and N_{20} . In addition there would be four differential equations, one each for x_A , x_B , $[A]_p$, and $[B]_p$, respectively.

To be able to solve this system of ten simultaneous differential equations we must know the values of all the rate coefficients discussed above, the volume of monomer swollen particle, the total number of particles per unit volume, and the individual monomer concentrations in the latex particles. The previous section

described the methods for estimating these parameters using both experimental techniques and predictive calculation methods. Table 6 3 shows the known and unknown parameters for the copolymerization system of 2-EHA/AA. The values of the rate coefficients for propagation and termination are reported in the literature (59) for the monomers 2-EHA and AA. The values of the rate coefficients for entry and exit of free radical species and of transfer to monomers (for 2-EHA/AA system) are not reported in the literature. In the absence of values for diffusivities of both the monomers in aqueous phase and in polymer particles, estimation of these rate coefficients by the methods described in the previous section is not possible. Therefore, the values of these rate coefficients are taken as those that give the best fit of the experimental data. The complexities involved in obtaining the individual 2-EHA and AA concentration in the latex particle by both experimental techniques and predictive methods are also discussed in the previous section. Therefore, the initial concentrations of monomers in polymer particles is assumed to be constant during interval II. This constant value is obtained as the best fit of the experimental data. In the interval III equation (6 6) applies till the monomer concentration in polymer particle becomes zero. The system of equations can now be solved to give profiles of N_{00} , N_{01} , N_{02} , N_{10} , N_{11} , N_{20} , x_A , x_B , $[A]_p$, and $[B]_p$ with time. The total molar conversion, X_{Mt} , is then calculated as

$$X_{Mt} = \frac{M_{A_0} \cdot x_A + M_{B_0} \cdot x_B}{(M_{A_0} + M_{B_0})} \quad (6\ 15)$$

Table 6.3 Parameters required for modeling the kinetics of 2-EHA/AA emulsion copolymerization

Known parameters (From literature)	Unknown parameters
➤ Rate coefficients for - ▪ Propagation: $k_{AA}^p, k_{AB}^p, k_{BA}^p, k_{BB}^p$ ▪ Termination : c_{AA}, c_{BB}, c_{AB}	➤ Rate coefficients for- ▪ Entry of radicals. ρ_A, ρ_B ▪ Exit of radicals. k_A, k_B ▪ Transfer: k_{AB}^{tr}, k_{BA}^{tr} ➤ Initial number of particles N_0 ➤ Initial monomer concentrations in particle. $[A]_p$ & $[B]_p$

where, M_{A_0} and M_{B_0} are the moles of A and B per liter that are charged at the start of the reaction. The total number of particles, N_t , at any instant of time is

$$N_t = N_{00} + N_{01} + N_{02} + N_{10} + N_{11} + N_{20} \quad \text{..(6.16)}$$

The average number of radicals per particle is

$$\bar{n} = \frac{N_{01} + N_{10} + 2(N_{02} + N_{20} + N_{11})}{N_t} \quad \text{.. (6.17)}$$

The particle radius at any instant of time is calculated from the knowledge of total number of particles and overall conversion assuming uniform particle size as follows:

$$d_p = \left(\frac{6M_0 X_{Mt}}{\pi N_t \rho_p} \right)^{1/3} \quad \text{..(6.18)}$$

where, d_p = the diameter of the particle.

M_0 = the total amount in gms of monomer initially charged per liter.

X_{Mt} = the total molar conversion.

ρ_p = the density of the polymer formed.

The model is simulated with different guess values of unknown parameters till the conversion obtained from the gravimetric and the Raman spectroscopy data and the particle size obtained from the Scanning Electron Microscope matches with the simulation results. Figure 6.1 shows the flow-chart for obtaining the best fit parameters from the experimental data.

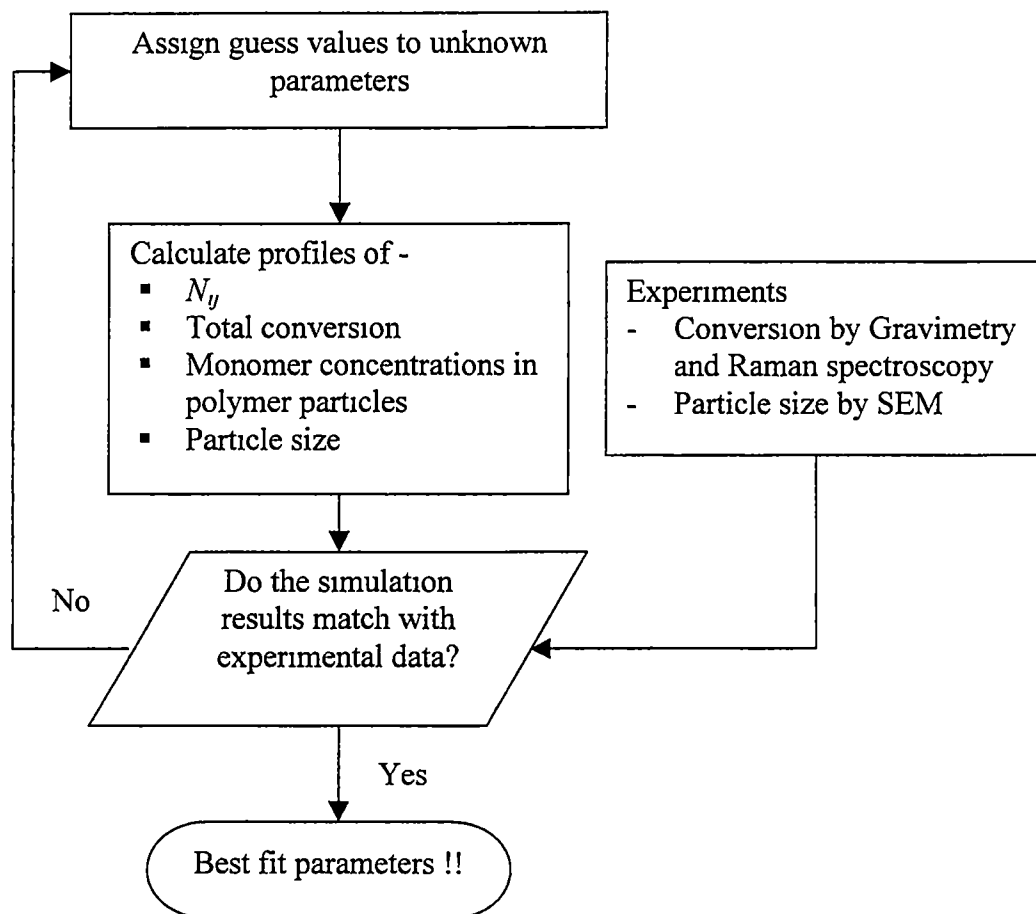


Figure 6 1 Modeling methodology to obtain the best-fit parameters from the experimental data

CHAPTER 7

EXPERIMENTAL SETUP

The experimental setup developed and used earlier by A. Al-khanbashi (79) and Mrunalini Dhamdhare (25) was used for the purpose of this work. It consists of a batch reactor, a Raman spectrometer, and a personal computer. A schematic of the experimental setup is shown in figure 7.1.

7.1 The Batch Reactor

The polymerization reactions are conducted in a one-liter capacity batch reactor. The reactor is provided with inlets to insert a stirrer, a thermometer, and to take samples using glass pipettes. The reactor is equipped with a jacket through which water is circulated to maintain constant reaction temperature. An automated water bath obtained from NESLAB Instruments Inc. is used for this purpose. The bath controls the temperature within $\pm 0.01^\circ\text{C}$. It should be noted that the automated bath measures and controls the temperature of the bath itself and not the temperature of the reaction mixture. The reaction setup is maintained under inert atmosphere by bubbling nitrogen through the reaction contents. This is necessary for any free radical polymerization reaction as contact of the reaction contents with oxygen kills the free radicals in the system, which can affect the rate of polymerization.

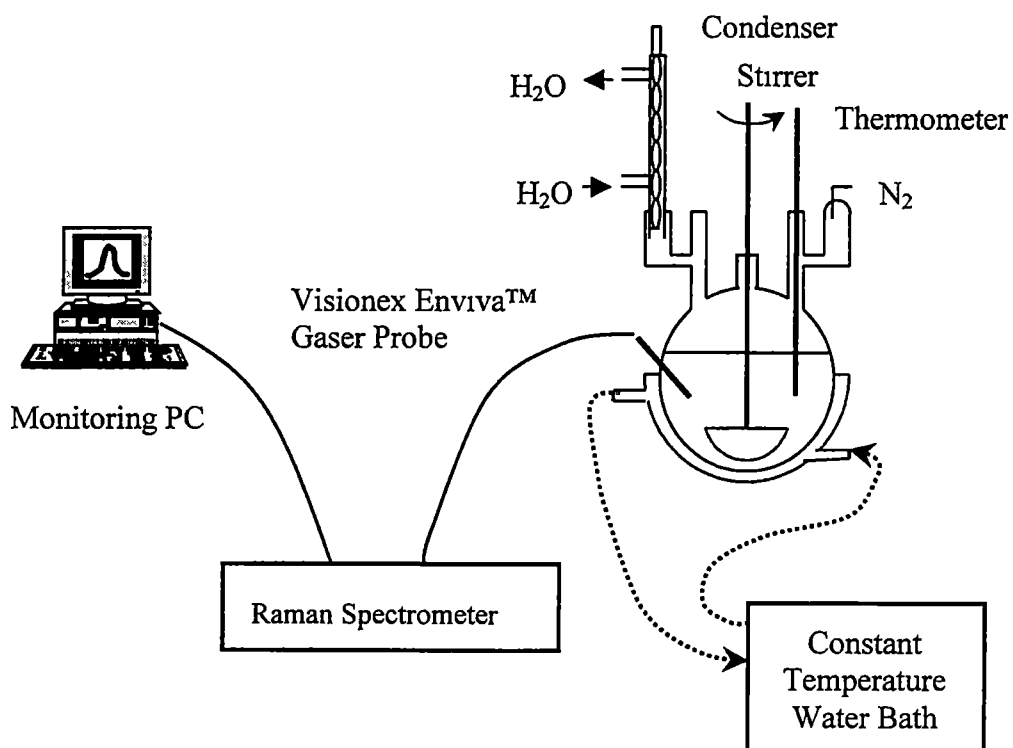


Figure 7.1 Schematic of Raman Spectrometer and Emulsion polymerization reaction setup

[Source Mrunalini Dhamdhare, "Applications of In-Line Fiber Optic Raman Spectroscopy to Polymer Processes", University of Tennessee, Knoxville]

7.2 The Raman Spectrometer

The reaction is monitored in-line using a Kaiser Optical Systems Inc Holoprobe[®] Raman Spectrometer (80). This spectrometer unit consists of the base unit and monitoring probes. The Holoprobe[®] consists of a base unit that connects to a fiber optic probe and a computer system. The base unit contains a laser excitation source, a spectrograph, and a two-dimensional array detector.

7.2.1 Description of the Light Path

The light from the laser source is coupled into an optical fiber with 50 μm core diameter. These optical fibers can be used over a distance of hundreds of meters to carry the light without significant loss of light. Silica Raman generated in the fiber is filtered out at the probehead and the laser light is focussed onto the sample. Backscattered light from the sample is filtered to remove the light at the laser wavelength and then sent to the spectrograph in the base unit through a 100 μm core diameter fiber optic cable. The spectrograph removes any residual laser light and disperses the Raman light into two tracks that are imaged onto a charged coupled device (CCD) detector. The CCD detector measures the intensity of the Raman scattered light. It is a rectangular two-dimensional array of independent, integrating detectors on a silicon chip. The individual detectors, called pixels, collect light and store it in a potential well under the photo-active surface of the pixel. The spatial and axial resolution of the spectrograph is determined by the detector pixel size. The Holoplex[®] transmission grating disperses and divides the undispersed Raman light

into a low wavenumber shift stripe and a high wavenumber shift stripe on the CCD detector. Thus, the grating nearly doubles the spectral coverage without reducing its spectral resolution.

A simplified schematic of the Holoprobe[®] spectrometer is given in figure 7.2. The laser light is carried through a fiber optic coupler via the optical fiber cables to the probe head (FPH). As the laser light travels towards the sample, a large amount of Raman signal and sometimes fluorescence is generated and efficiently collected by the fiber. It is thus necessary to separate the laser light from the background so that fiber background does not overwhelm the Raman signal. Light backscattered by the sample is collimated by PL4 and passed through a pair of notch filters in the probe head. The light enters the spectrograph from the fiber optic cable. The light is collimated by camera lens L2 and is then sent through a holographic notch filter (NF) and an electronic shutter (SH). Transmitted light is focussed onto a 50 μm wide spectrograph entrance slit (SL) by a camera lens L3. Light from the slit is collimated by lens L4 and then sent to the Holoplex transmission grating (HG). Diffracted light from the grating is imaged onto the detector by camera lens L5.

7.3 Sampling Systems

Optical fiber probes are widely used as sampling systems. They are compact, usable in the laboratory environment or for remote sampling. They provide stable, reproducible signals from solids, liquids and gases. There are two types of probe designs widely used in monitoring applications. The concentric “n around one” fiber

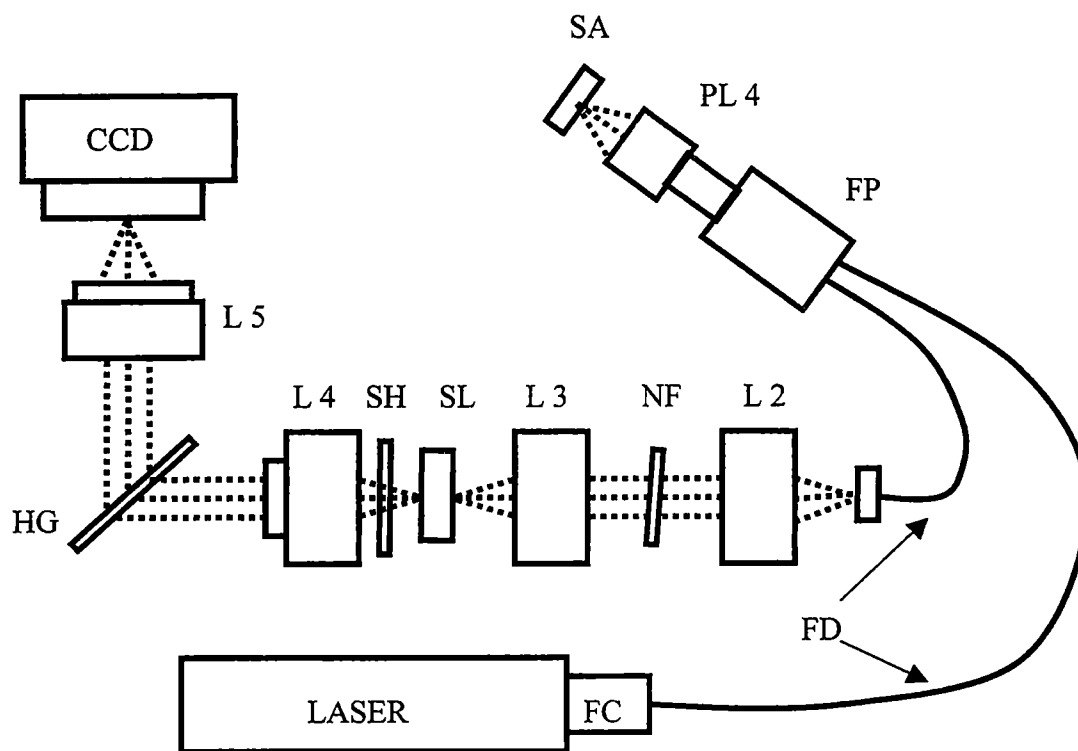


Figure 7.2 Schematic of the HoloProbe Raman Spectrometer Light Path

[FC: Fiber optic coupler, FO: Fiber optic cable, FPH: fiber optic probe head, PL4: Probe head focus and collection lens, SA: sample, L2: Pre-filter collimating lens, NF: Holographic Notch-filter, SH: Shutter, L3: Pre-filter focusing lens, SL: Spectrograph entrance slit, L4: Spectrograph collimating lens, HG: HoloPlex Grating, L5: Spectrograph focusing]

[Source: Mrunalini Dhamdhare, "Applications of In-Line Fiber Optic Raman Spectroscopy to Polymer Processes", University of Tennessee, Knoxville]

bundle type probe and the filtered probe (81,82) Figure 7.3 shows the concentric fiber bundle probe (80). An immersion probe obtained from Visionex[®] Inc. (83) that has such “7 around 1” design was used for monitoring The central fiber delivers the light to the sample and the surrounding fibers collect the Raman scatter The laser beam is focused into the delivery fiber with a microscopic objective or other short focal length lens. For better coupling to the spectrograph entrance slit, the output ends of the collection fibers are arranged in a linear array, as shown in figure 7 3.

7.4 The Personal Computer

The spectrometer is connected to a personal computer, which can store and analyze the Raman spectra. The spectra are collected using the Holograms[®] software and are analyzed using softwares like Grams/32[®] and MATLAB[®]

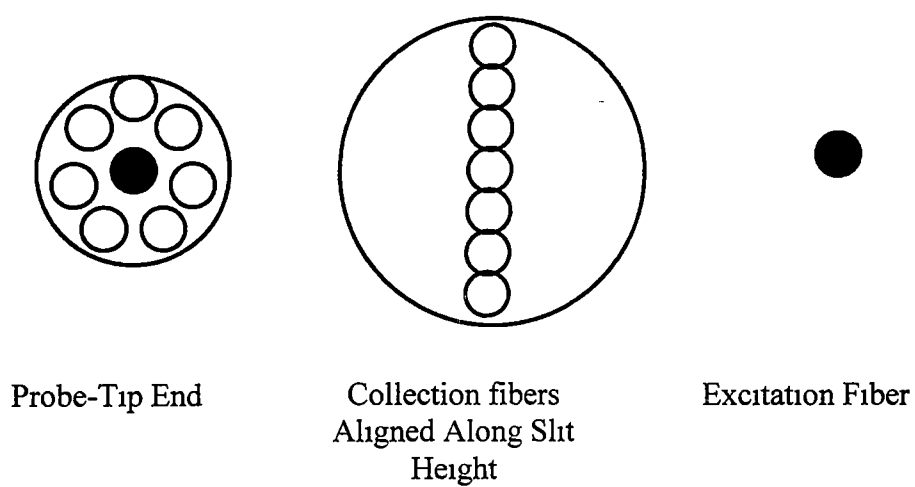


Figure 7 3 Schematic of 7 around 1 probe, showing excitation and collection end of the fiber

[Source Mrunalini Dhamdhare, "Applications of In-Line Fiber Optic Raman Spectroscopy to Polymer Processes", University of Tennessee, Knoxville]

CHAPTER 8

RESULTS AND DISCUSSIONS

In chapter 6, the theory behind the kinetic modeling of emulsion copolymerization was discussed with specific attention to 2-EHA/AA copolymerization system. In chapter 4, the use of Raman spectroscopy for in-line monitoring of emulsion polymerization reactions was reviewed. In this chapter, the discussion about the experimental results and the data analysis is given. Separate kinetic models are built using the primary experimental data obtained from both gravimetry and Raman spectroscopy. However, a general parameter sensitivity study of the model simulations is done prior to the actual modeling to decide the parameters to be varied in best fitting the experimental data.

8.1 Parameter Sensitivity Study

Table 5.3 gives the list of various parameters that are required for modeling the kinetics of 2-EHA/AA emulsion copolymerization. Of these parameters, values of the self-propagation rate constants and self-termination rate constants are taken from the literature (59). The values of the cross propagation rate constants are calculated using the reactivity ratio values estimated by F. Loncar (58) for 2-EHA and AA copolymerization. The value of cross termination rate constant is approximated as the geometric mean of the self-termination rate constants.

Therefore, This leaves the following unknown parameters: the transfer rate constants, k_{AA}^{tr} , k_{AB}^{tr} , k_{BA}^{tr} , k_{BB}^{tr} ; the entry and exit rate constants, ρ_A , ρ_B and k_A , k_B respectively, the number of particles initially formed, N_0 ; and the initial concentration of monomers in the polymer particles, $[A]_p$ and $[B]_p$. Before one tries to fit the experimental conversion data using the proposed model, it is required to see the effect of each of these parameters on the model predictions. This will enable us to distinguish the parameters that are insensitive to model predictions from those that strongly affect them. To start with, values of all the parameters are set to those given in the paper by Ballard *et al* (40) for the system of styrene-methyl methacrylate. Table 8.1 shows the base case values of the parameters used in the model simulations. In the symbols given in table 8.1, A represents 2-EHA and B represents AA. The value of each of the parameters is then varied one at a time keeping all other values constant. The effect of each of the parameters on model predictions is shown in figures 8.1 through 8.11.

From figures 8.1 through 8.4 we can infer that ρ_A has very little effect on the model predictions of conversion profiles (or the rate of reactions) whereas changes in ρ_B are more influential on the model predictions. The effect of both exit (desorption) rate coefficients (k_A and k_B) is much stronger than the corresponding entry rate coefficients. Figures 8.5 through 8.8 show that the model is insensitive to the changes in the values of transfer and termination rate constants. The insensitivity of transfer constants can be attributed to the comparable propagation rate constant values and

Table 8.1 Base case values of the parameters used in the model simulations for parameter sensitivity study

Parameter	Value
k_{AA}^p (L mol ⁻¹ s ⁻¹)	252
k_{BB}^p (L mol ⁻¹ s ⁻¹)	1500
k_{AB}^p (L mol ⁻¹ s ⁻¹)	$k_{AA}^p/0.93$
k_{BA}^p (L mol ⁻¹ s ⁻¹)	$k_{BB}^p/1.08$
k_{AA}^{tr} (L mol ⁻¹ s ⁻¹)	0.06
k_{BB}^{tr} (L mol ⁻¹ s ⁻¹)	0.04
k_{AB}^{tr} (L mol ⁻¹ s ⁻¹)	0.12
k_{BA}^{tr} (L mol ⁻¹ s ⁻¹)	0.08
c_{AA} (L mol ⁻¹ s ⁻¹)	2.75×10^5
c_{BB} (L mol ⁻¹ s ⁻¹)	2.7×10^6
c_{AB} (L mol ⁻¹ s ⁻¹)	$(c_{AA} \times c_{BB})^{1/2}$
ρ_A (s ⁻¹)	1×10^{-4}
ρ_B (s ⁻¹)	4×10^{-3}
k_A (s ⁻¹)	1.5×10^{-3}
k_B (s ⁻¹)	1×10^{-3}
N_0 (L ⁻¹)	1×10^{18}
$[A]_p$ (mol L ⁻¹)	0.95
$[B]_p$ (mol L ⁻¹)	0.1

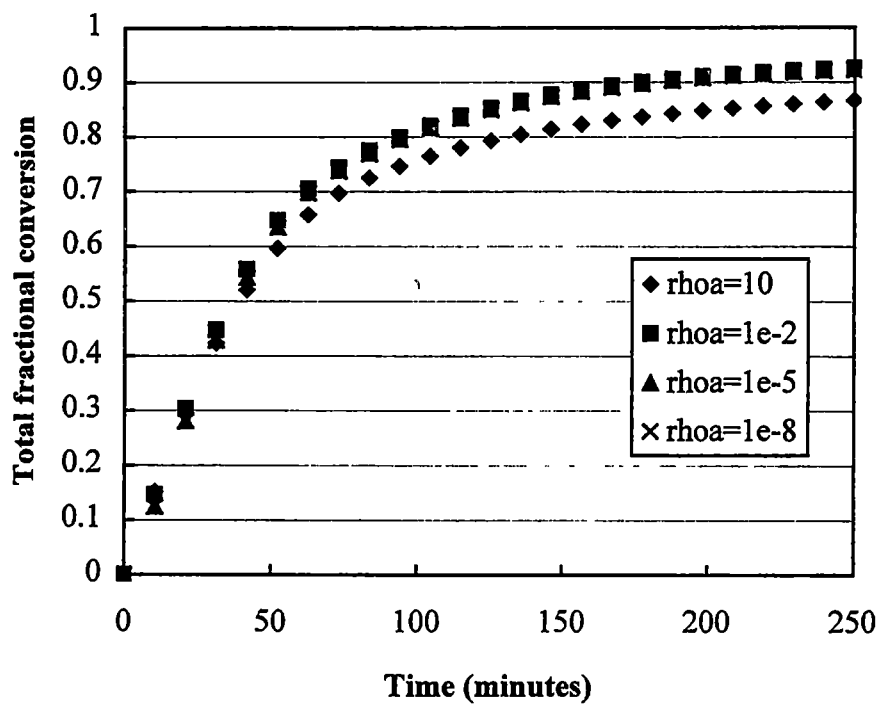


Figure 8.1 Effect of entry rate coefficient of A radical into particle on overall conversion

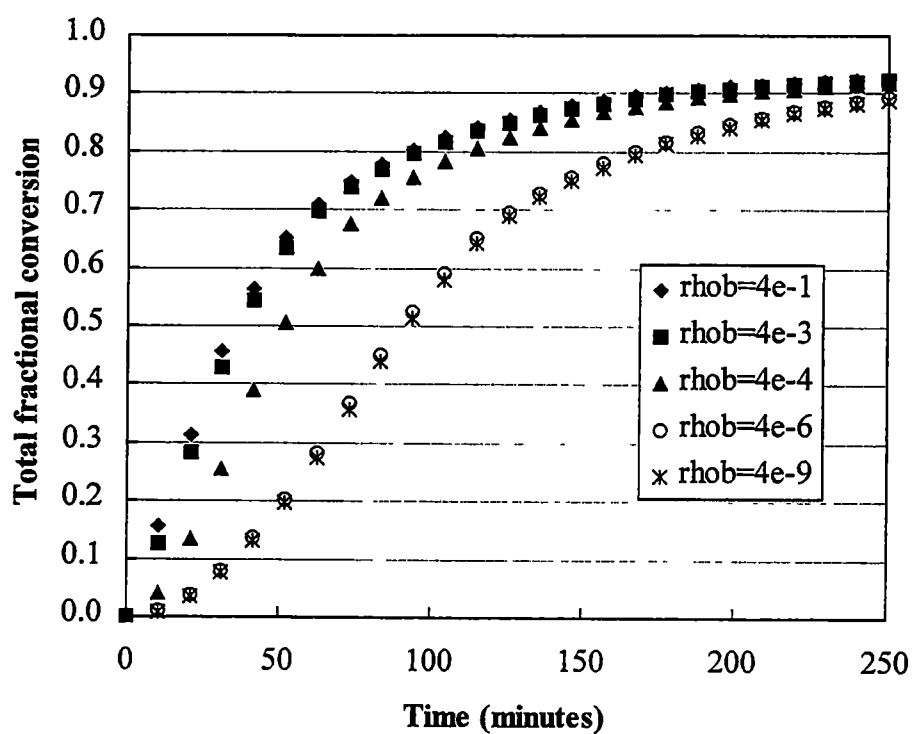


Figure 8.2. Effect of entry rate coefficient of B radical into particle on overall conversion

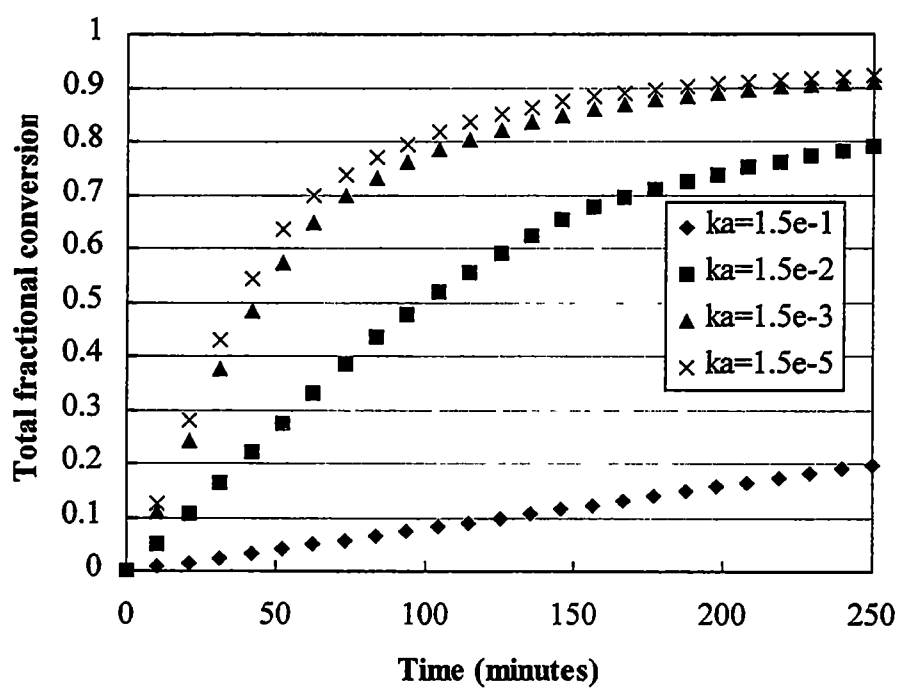


Figure 8.3 Effect of exit rate coefficient of A radical on overall conversion

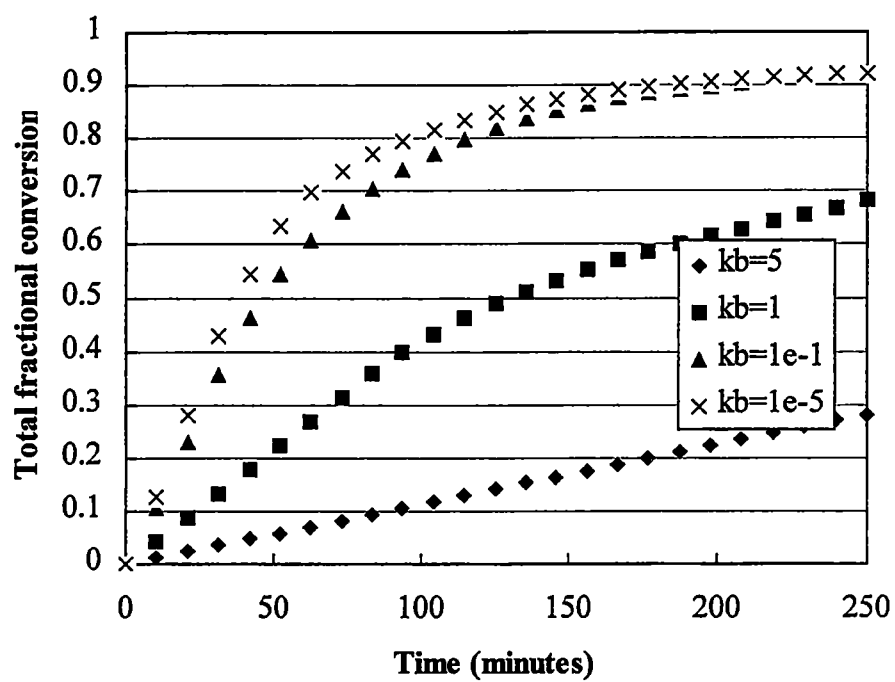


Figure 8.4 Effect of exit rate coefficient of B radical on overall conversion

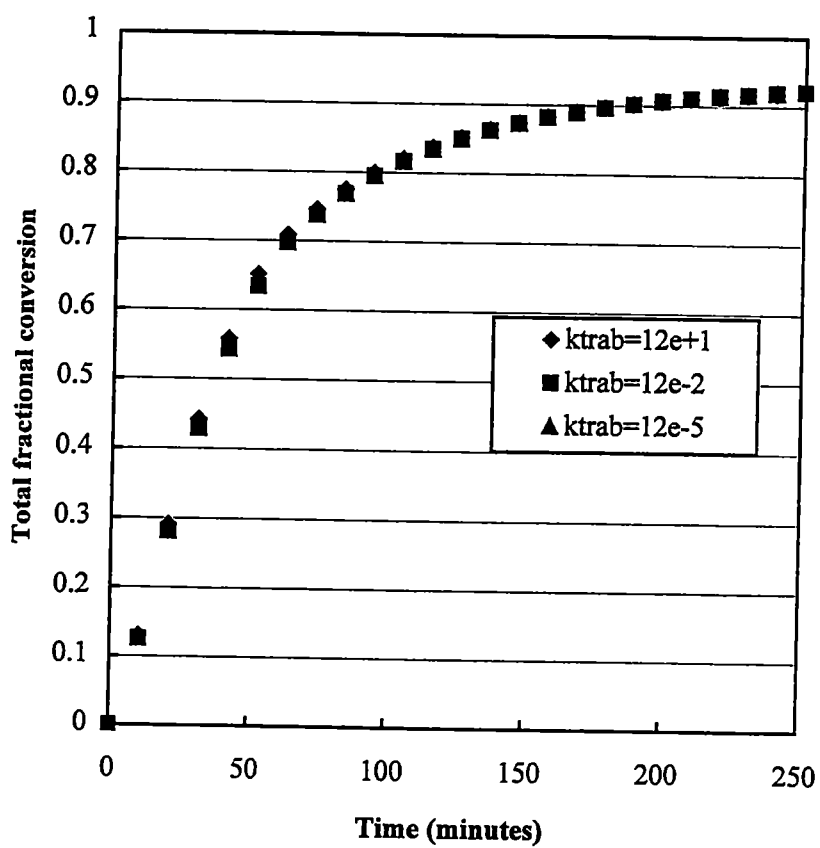


Figure 8.5 Effect of transfer rate coefficient, k^r_{ab} , on overall conversion

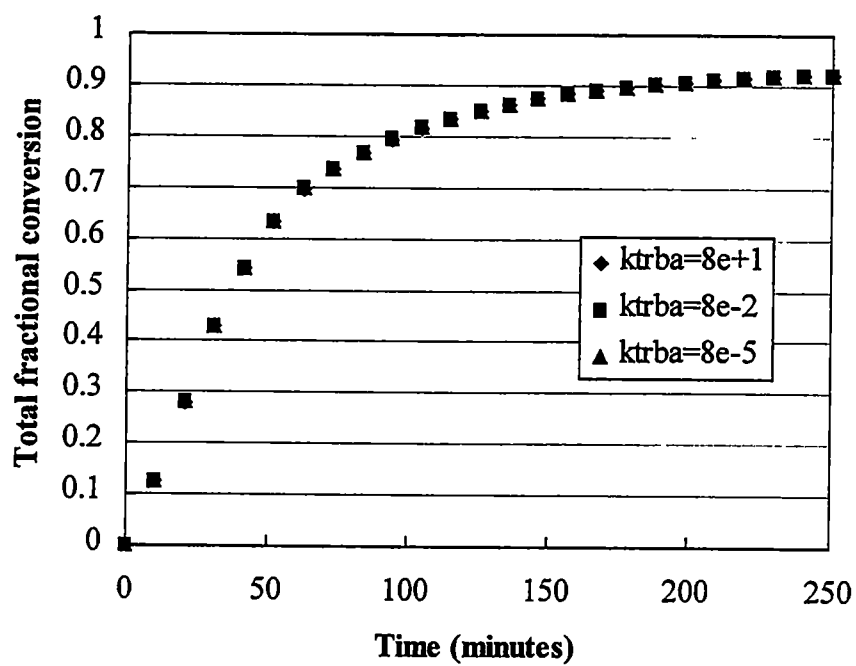


Figure 8.6 Effect of transfer rate coefficient, k_{ba}^{tr} , on overall conversion

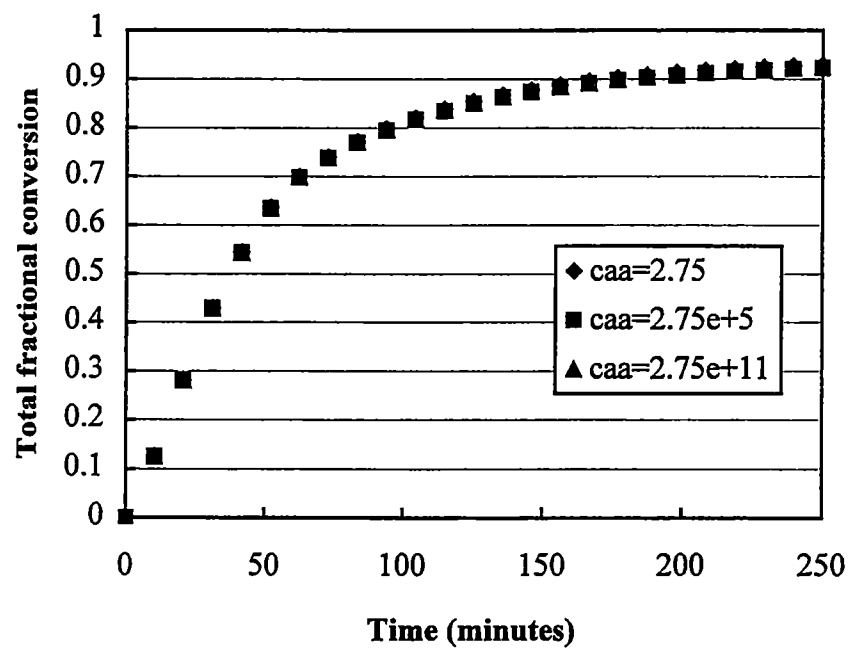


Figure 8.7 Effect of self-termination constant of 2-EHA on overall conversion

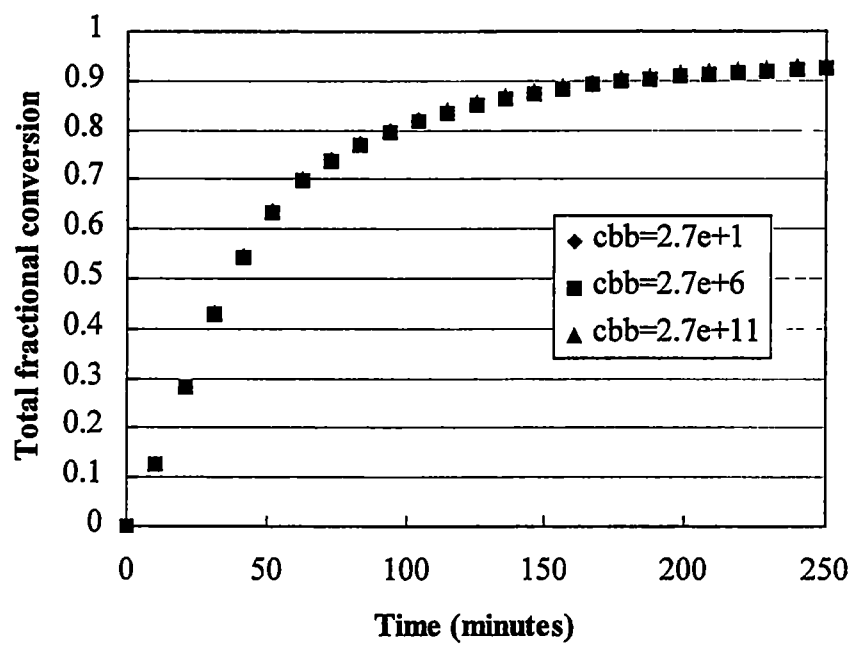


Figure 8.8. Effect of self-termination constant of AA on overall conversion

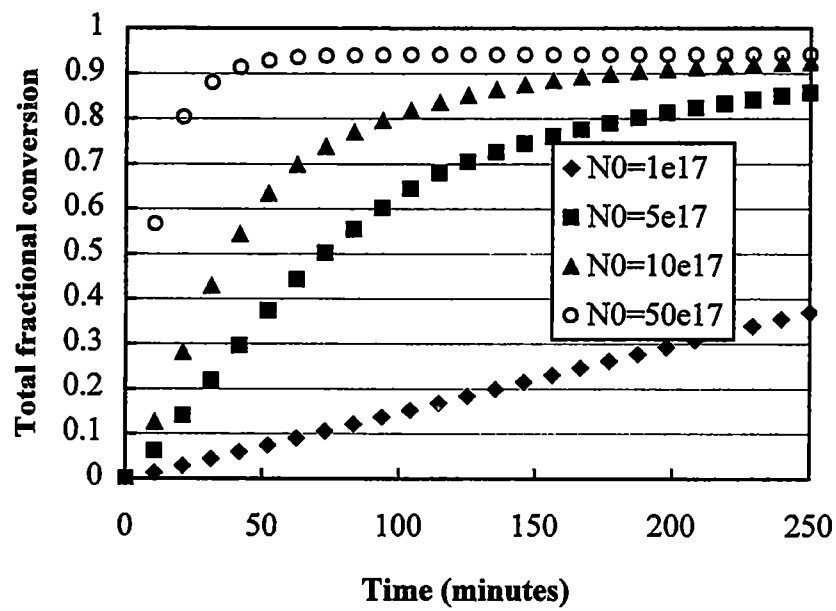


Figure 8.9 Effect of initial number of particles, N_0 , on overall conversion

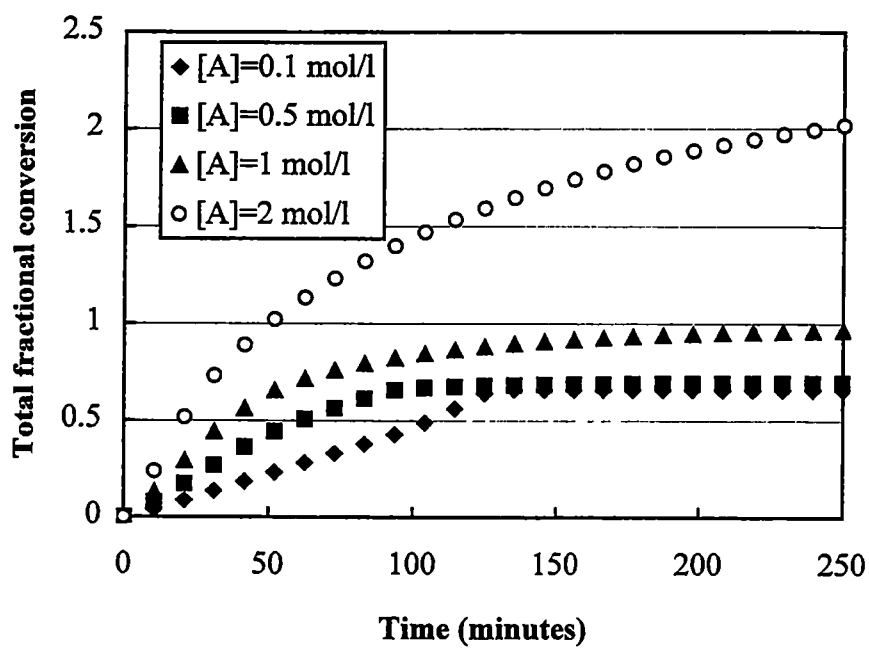


Figure 8.10. Effect of concentration of 2-EHA in the particles on overall conversion

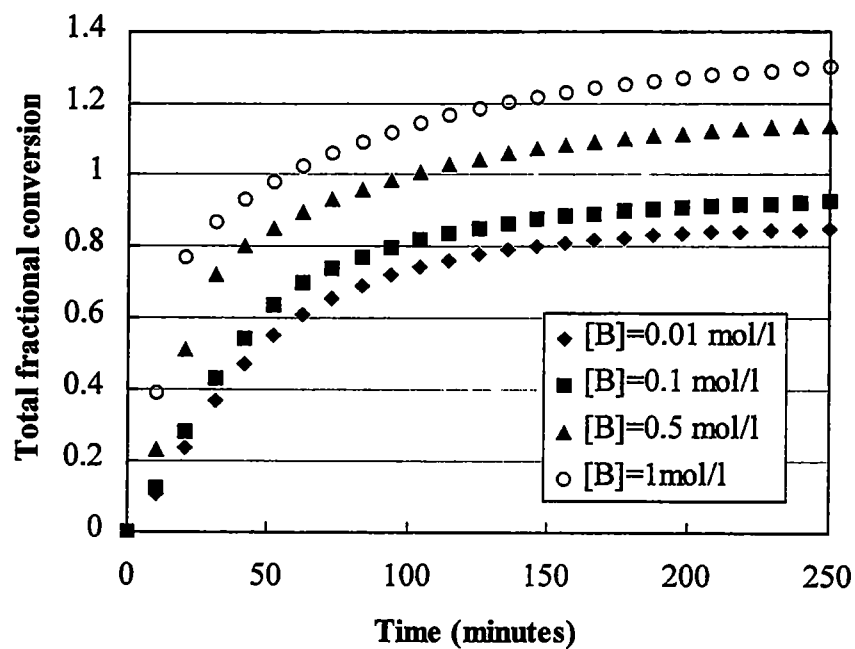


Figure 8.11 Effect of concentration of AA in the particles on overall conversion

reactivity ratios of the two monomers. The insensitivity of model predictions to large changes in termination constant values is due to the fact that they are already many magnitudes of order higher than the entry and exit rate coefficients of radicals. This always results in the instantaneous termination of a radical when it enters a particle already containing a free radical.

Figure 8.9 through 8.11 show the effect of N_0 , $[A]_p$, and $[B]_p$ on the model predictions. Changes in N_0 affect the rate of polymerization (or steepness of the conversion-time curve as shown in figure 8.9) keeping the final conversion value constant, whereas changes in $[A]_p$ and $[B]_p$ affect the final value of conversion itself (see figure 8.10 and 8.11).

8.2 Best Fitting the Experimental Data

One can conclude from the parameter sensitivity analysis done above that the major factors affecting the model predictions are the exit rate coefficients of radicals, k_A and k_B ; the number of particles initially formed, N_0 , and the concentrations of monomers in polymer particles $[A]_p$ and $[B]_p$. It is seen that model predictions do not change much if we decrease k_A and k_B beyond 1.5×10^{-5} and 1×10^{-5} respectively. For higher values of k_A and k_B , the model predictions of polymerization rate are too slow compared to the experimental kinetic data. Therefore, values of k_A and k_B are assigned as 1.5×10^{-5} and 1×10^{-5} respectively. The values of $[A]_p$ and $[B]_p$ should be fixed so that the final conversion value falls between 90 to 100 percent, which is the range of conversion values obtained in the set of experiments carried out for modeling. A value

of 0.95 mol/l for $[A]_p$ and 0.1 mol/l for $[B]_p$ is found to give the final conversion as 95%. Hence, these values are used for best fitting all the experimental data and are never changed. Thus, the changes in the rate of copolymerization are taken into account by varying only one parameter, N_0 , i.e. the number of particles initially formed. The variation in the number of particles is then related to the changes in initiator concentration and the changes in surfactant concentration using separate experimental data for each of the two. The two effects are then combined and a model is built that can calculate the number of particles formed and in turn predict the conversion profiles for reactions with any given initiator and surfactant concentration.

8.2.1. Importance of Latex Particle Size Measurement in the Proposed Kinetic

Model

In section 8.1, model simulations of total monomer conversions were studied. The proposed kinetic model can also calculate the evolution of latex particle size with time. The particle size is related to total conversion and the number of particles through equation 6.18, which is reproduced below

$$d_p = \left(\frac{6M_0 X_M}{\pi N_p \rho_p} \right)^{1/3} \quad \dots(8.1)$$

In the proposed model, the value of number of particles produced at the start of the reaction is assumed and conversion is calculated by solving a set of differential equations described in chapter 6. The particle size is then calculated for each conversion using equation 8.1. If the assumed value of number of particles is correct,

both the total conversion and the particle size should match with their experimental measurements. Thus, comparison of model predictions of both conversion and particle size with corresponding experimental measurements is necessary for complete verification of accuracy of model predictions.

In the present work, measurement of latex particle size using a Scanning Electron Microscope (SEM) was attempted. However, SEM micrographs of good quality could not be obtained despite trying several methods of sample preparation. Particles appeared both diffused and agglomerated in these micrographs. A specialized method reported by F. Loncar (58) is required to observe these soft acrylate particles. This method uses transmission electron microscope (TEM) to observe the particles with negative imaging by phosphotungstic acid (PTA). The technique involves mixing approximately 1 to 5 drops of 10% solid latex with a 1 wt.% PTA solution, and freezing a thin film of the latex in a cold stage holder with liquid nitrogen. Consequently, even soft particles hold their shape quite well and only become deformed by neighboring particles. Under the electron beam, the tungsten atoms of PTA in the aqueous phase scatter the electrons and thus the particles appear as holes against a dark matrix. In the present work, samples were prepared using this method, and were observed using SEM. However, this method of sample preparation did not work with SEM, as no particles could be observed. Only particles of PTA that remained on the slide after the evaporation of water were observed. Thus, in the absence of experimental data for particle size, the total conversion profiles obtained experimentally were compared to the model predictions.

8.2.2 Best Fitting the Gravimetric Data

A range of initiator concentrations and surfactant concentrations is used in the experiments to find out the best-fit parameter values. Table 8.2 shows the recipes of all the reactions that were carried out in order to get the experimental data for building up a kinetic model. The reactions were carried out at 60°C in a one-liter batch reactor. The reactor contents were stirred at a constant stirrer speed of 195 rpm. 650 gm of water was taken as the basis for all the reactions. In all the reactions, total monomer content was 10% by weight of the water and the individual monomers were charged in the ratio of 90 parts of 2-EHA to 10 parts of AA (by weight). In the first set of reactions, the initiator concentrations used were 5.0, 0.5, 0.08, and 0.02 gm per liter of water respectively, at a fixed surfactant concentration of 4.25 g/l. In another set of reactions the surfactant concentrations used were 10.0, 4.0, 2.0, and 0.8 g/l respectively, at a fixed initiator concentration of 0.08 g/l.

During the course of the reaction, samples were taken out using a glass pipette at fixed time intervals and were immediately transferred to vials containing known amounts of hydroquinone for inhibition of the reaction. The sample vials were then immediately immersed in ice for quenching the reaction. The samples were analyzed for total monomer conversion using gravimetric analysis based on the following method. A measured quantity of sample was taken in an aluminum pan and was dried in an oven at 80-90°C for about 24 hours so that both water and residual monomers were completely evaporated. Since water does not take part in the reaction, its weight fraction should remain constant throughout the reaction. Using this fact, the total

Table 8.2 Recipes for the reactions carried out to build a kinetic model

a) Reactions with varying initiator concentrations

Ingredients	Amounts in gm			
	I-1	I-2	I-3	I-4
Water	650	650	650	650
2-ethylhexyl acrylate	58.5	58.5	58.5	58.5
Acrylic acid	6.5	6.5	6.5	6.5
Potassium persulfate	3.2505	0.2996	0.0526	0.0130
Sodium lauryl sulfate	2.7625	2.7625	2.7625	2.7625
n-dodecyl mercaptan	0.175	0.175	0.175	0.175
Total	721.18	718.23	717.99	717.95

b) Reactions with varying surfactant concentrations

Ingredients	Amounts in gm			
	S-1	S-2	S-3	S-4
Water	650	650	650	650
2-ethylhexyl acrylate	58.5	58.5	58.5	58.5
Acrylic acid	6.5	6.5	6.5	6.5
Potassium persulfate	0.0525	0.0525	0.0525	0.0525
Sodium lauryl sulfate	6.500	2.7622	1.3005	0.5197
n-dodecyl mercaptan	0.175	0.175	0.175	0.175
Total	721.72	717.98	716.52	715.74

amount of monomers present in the evaporated liquid for the sample taken at time t was calculated and was denoted as W_t . The amount of monomers that would be present in the absence of reaction, W_0 , was calculated from the knowledge of initial fraction of monomers in the charge. Thus conversion at any given time is calculated as

$$\% \text{ conversion} = \frac{(W_0 - W_t)}{W_0} \times 100 \quad . . (8.2)$$

This is a total conversion based on the combined consumption of both the monomers. Individual conversions of monomers cannot be determined using gravimetric analysis.

The model simulations were carried out to best fit the conversion profiles obtained by gravimetry for reactions with different initiator concentrations (reactions I-1 to I-4). Figure 8.12 shows the results of the best fitting calculations for the above mentioned reactions. In figure 8.12 (and all figures to follow), the discrete solid points represent the experimental data points, whereas, the continuous solid lines represent the model predictions. The values of N_0 that were found to give these best fits are shown in table 8.3 along with the average absolute errors in data fitting. The average absolute error in the best-fitting is calculated as

$$\text{Average absolute error} = \frac{\sum_{i=1}^n (|X_{ei} - X_{mi}|)}{n} \quad . (8.3)$$

where, n = number of data points

X_{ei} = experimental conversion value of data point i

X_{mi} = conversion value of data point i as calculated from the model

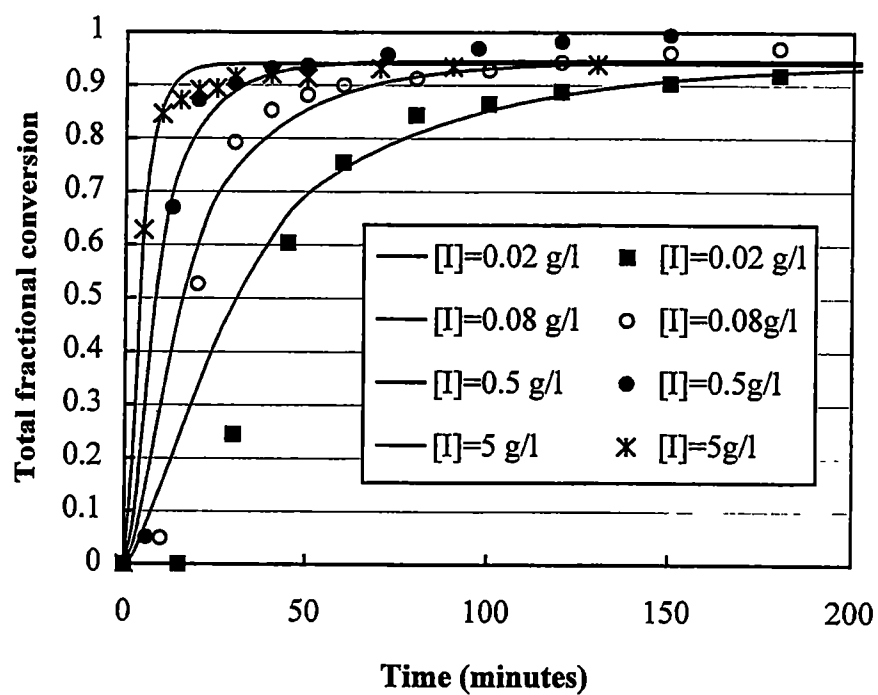


Figure 8.12 Best fitting the conversion profiles obtained from gravimetric analysis for reactions with varying initiator concentrations

Table 8.3 Values of N_0 that best fit the gravimetric conversion profiles for reactions with varying initiator concentrations

Initiator concentration (g/l)	Number of particles ($\times 10^{17}$)	Average absolute error
0.02	12.3	0.0373
0.08	25.3	0.0432
0.5	54.75	0.0496
5.0	155.0	0.019

The values of N_0 were plotted against the corresponding initiator concentrations. Figure 8.13 shows that power law fits the data well with 0.45 as the power of dependence of number of particles on the initiator concentration.

The same procedure is repeated for reactions S-1 to S-4 in which the surfactant concentration is varied at constant initiator concentration. Figure 8.14 shows the results of best fitting the data of this set of reactions. Table 8.4 gives the values of N_0 that best fit the data, and figure 8.15 shows the plot of N_0 against the surfactant concentration used. The dependence of N_0 on surfactant concentration was found to be linear as shown by figure 8.15.

8.2.3 Best Fitting the Raman Spectroscopy Data

The previous section described how the model simulations were carried out to best fit the conversion profiles obtained from the gravimetric analysis. In this section, description of exactly same analysis on the data obtained from Raman spectroscopy is given. Before discussing that, it is necessary to understand how a raw Raman spectrum was treated to obtain the total monomer conversions.

As discussed in chapter 4, the progress of a free-radical emulsion copolymerization reaction can be followed by looking at the decrease in the intensity of C=C peak. Figure 8.16 shows the Raman spectra taken at various time intervals during the reaction I-1 given in table 8.2. Figure 8.16 shows that the Rayleigh line is observed at 0 cm^{-1} , and its intensity increases as the reaction progresses. This line is observed due to inefficient filtering of the laser line from the scattered light collected

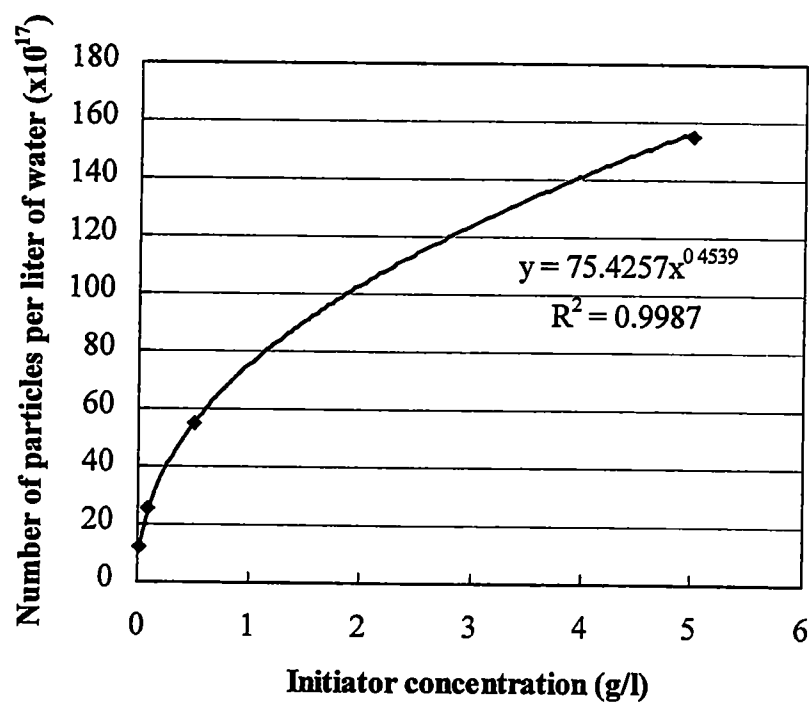


Figure 8.13 Correlation between number of particles initially formed and initiator concentration based on gravimetric data

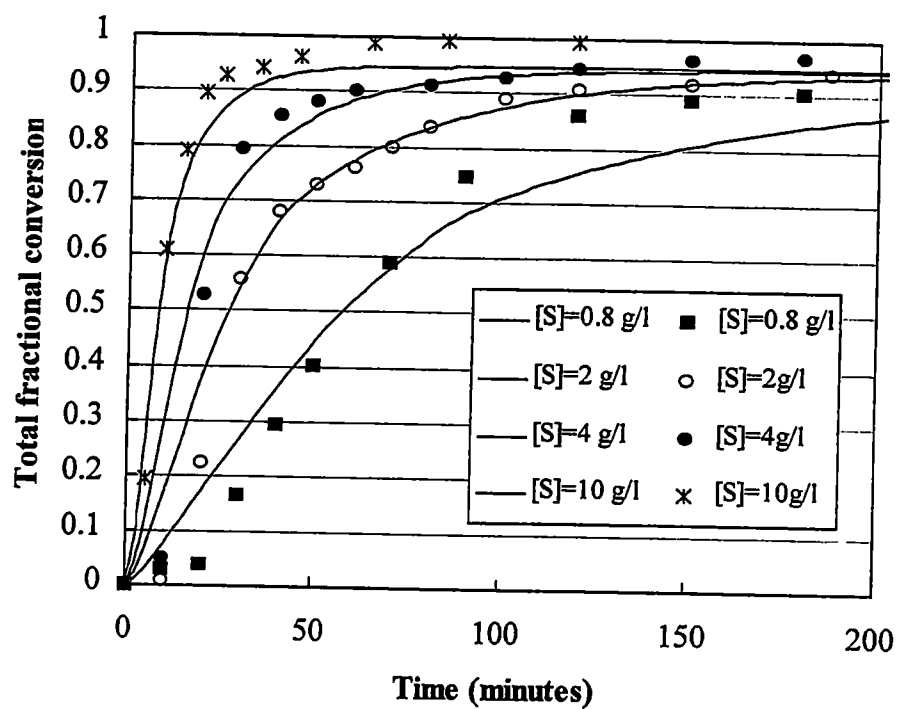


Figure 8.14 Best fitting the conversion profiles obtained from gravimetric analysis for reactions with varying surfactant concentrations

Table 8.4 Values of N_0 that best fit the gravimetric conversion profiles for reactions with varying surfactant concentrations

Surfactant concentration (g/l)	Number of particles ($\times 10^{17}$)	Average absolute error
0.8	6.35	0.064
2.0	14.1	0.0306
4.0	25.3	0.0432
10.0	56.75	0.0411

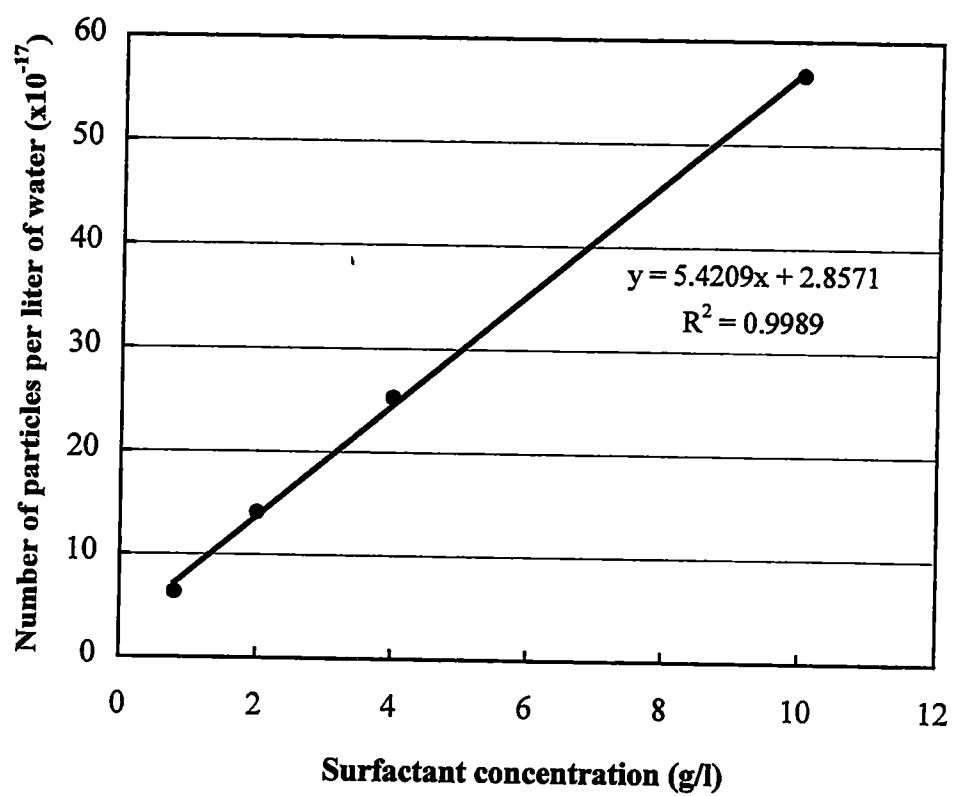


Figure 8.15 Correlation between number of particles initially formed and surfactant concentration

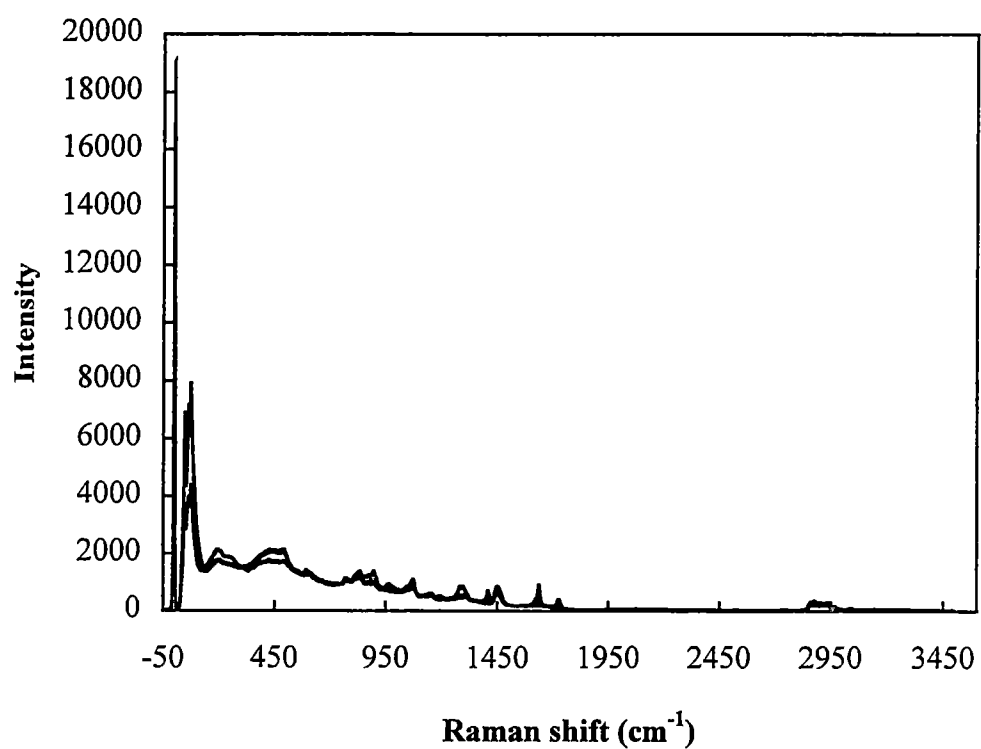


Figure 8 16 Raman spectra taken during the course of reaction I-1

by the Visionex[®] probe. This line can be removed by using appropriate filters in the optical probe. All the Raman spectra were collected using the average of 2 accumulations with 15 seconds exposure for each. In figure 8.17, the Raman spectra shown in figure 8.16 are reproduced neglecting the Rayleigh line for better visual representation of the spectra. Figure 8.17 shows more clearly the individual peaks observed in the Raman spectra of this reaction. Figure 8.18 shows the Raman spectra with neglecting the Rayleigh line for the reaction S-2 given in table 8.2. The part of the Raman spectra for reaction I-1 with Raman shift ranging from 1350 cm^{-1} to 1850 cm^{-1} are enlarged in figure 8.19. Figure 8.19 clearly shows the changes in the intensities of the peaks of interest along the progress of reaction. We can clearly see the decrease in the intensity of C=C peak at 1638 cm^{-1} along the reaction progress. The decrease in the intensity of this peak shows the total consumption of the monomers. The two other peaks of interest shown in figure 8.19 are C=O stretching vibrations at 1730 cm^{-1} and CH_2 , CH_3 deformations at about 1450 cm^{-1} . The peak at 1450 cm^{-1} is characteristic of n-alkanes. In figure 8.19, this peak is observed due to the alkyl chain (2-ethylhexyl moiety) in 2-ethylhexyl acrylate.

It has been reported previously (21,25) to use the C=O peak at 1730 cm^{-1} to normalize the intensities of C=C peaks for calculating the residual monomer concentration. The same method was tried initially, and the plot of intensity ratio $(\text{C}=\text{C})/(\text{C}=\text{O})$ along the reaction progress is shown in figure 8.20 for the reaction set in which initiator concentration was varied. The total conversion of monomers is then calculated as

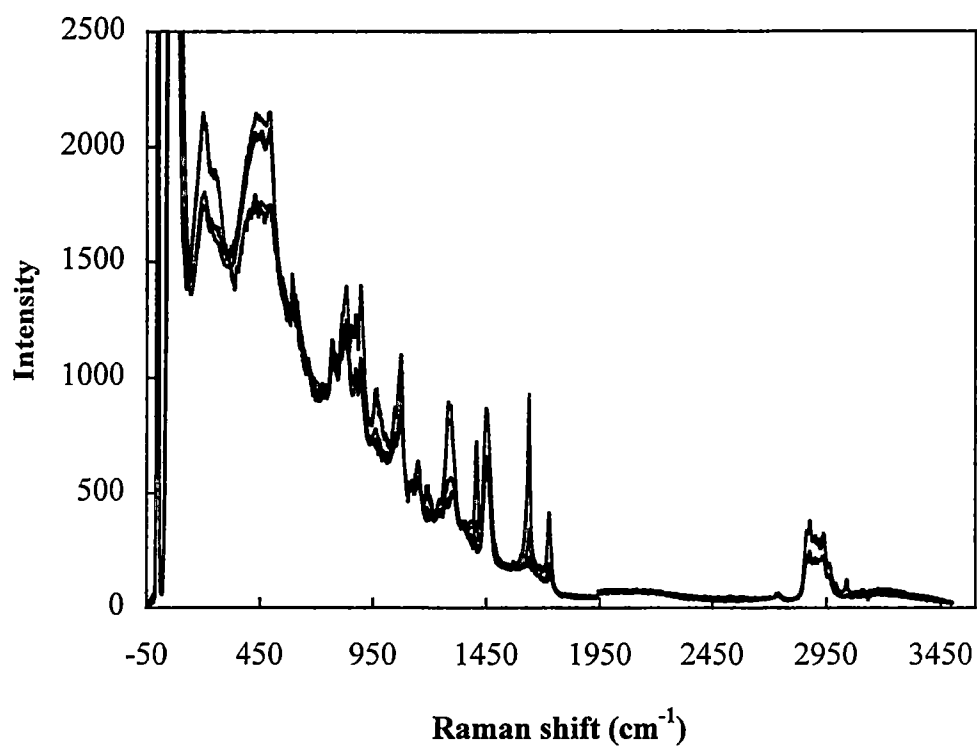


Figure 8 17 Raman spectra of reaction I-1 shown with neglecting the Rayleigh line

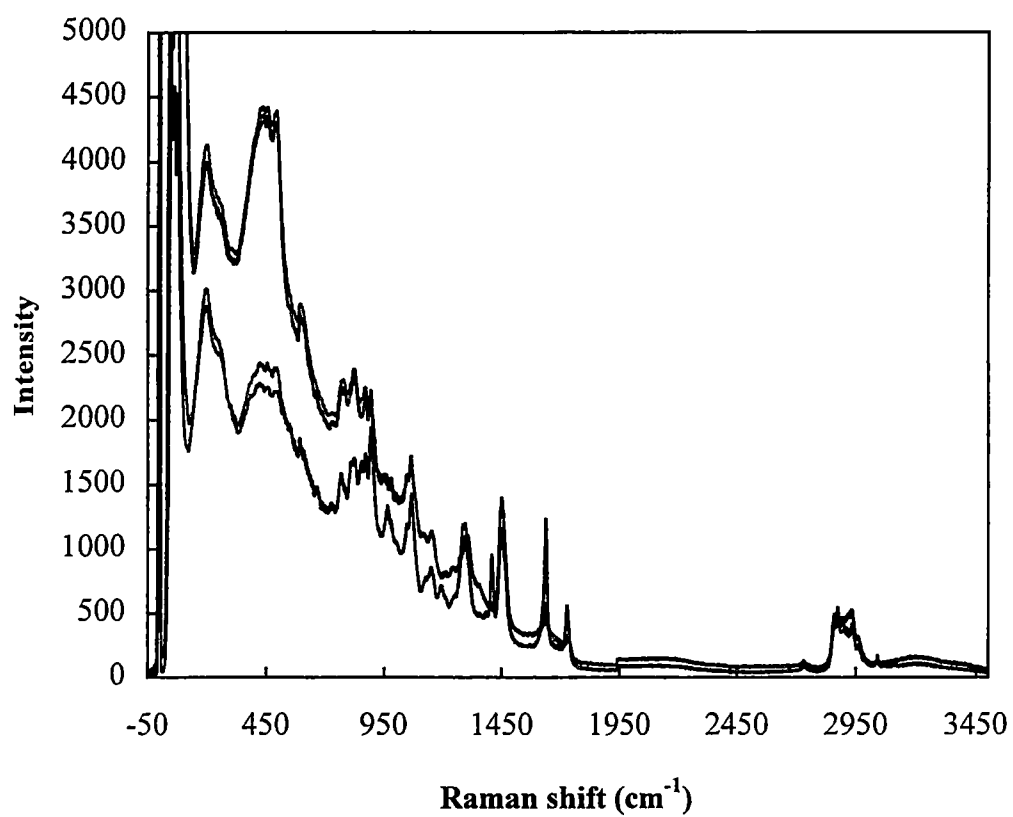


Figure 8.18 Raman spectra of reaction S-2 shown with neglecting the Rayleigh line

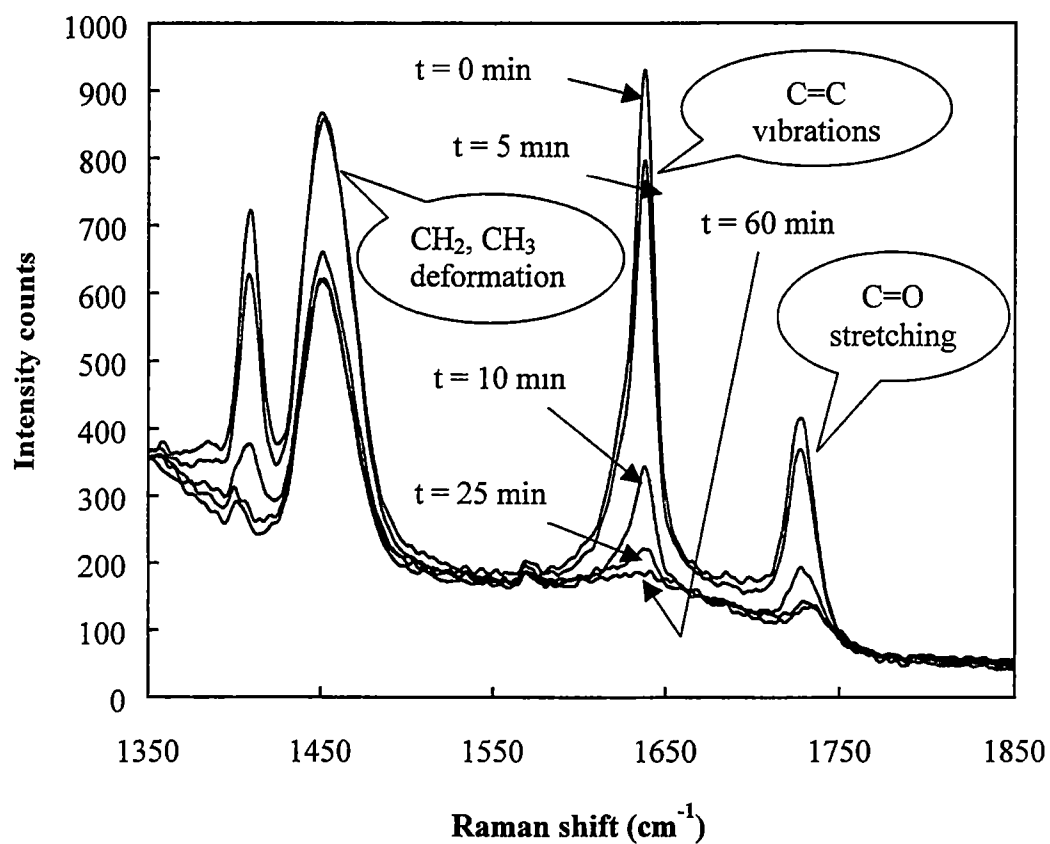


Figure 8.19 Part of the Raman spectra for reaction I-1 with Raman shifts ranging from 1350 cm⁻¹ to 1850 cm⁻¹

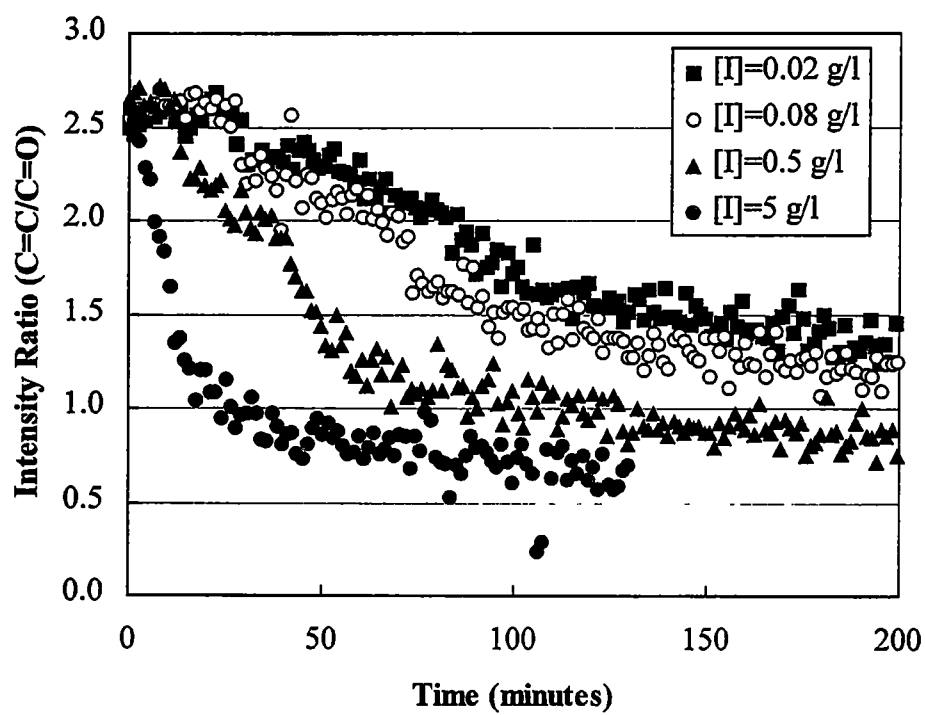


Figure 8.20 Plot of ratios of intensities of C=C peak to C=O peak in Raman spectra along the reaction progress

$$\% \text{ conversion} = \frac{(R_0 - R_t)}{R_0} \times 100 \quad \dots(8.4)$$

where, R_0 and R_t are the ratios of intensities of C=C peak to C=O peak at the beginning of the reaction ($t = 0$), and at any given time t , respectively. Figure 8.21 shows the plot of conversions thus calculated using the data in figure 8.20. As figure 8.21 shows, there is a large amount of scatter in the data. Also, the final values of conversion are much lower than given by gravimetric analysis, especially for the slower reactions. The reason for this behavior lies in figure 8.19, which shows a significant decrease in the C=O peak intensity along the reaction progress.

Figure 8.19 shows that the intensity of peak at 1450 cm^{-1} due to CH_2 , CH_3 deformations does not vary much in the course of a reaction, as expected, as the concentration of these groups remain constant throughout the reaction. Therefore, this peak was used for normalizing the C=C peak in calculating the conversions, and the results are shown in figure 8.22 for the same reaction set as that used in figure 8.21. Using this procedure of normalization, the scatter in the data was reduced significantly. Some deviations from the smooth nature of the curve over certain short time intervals were observed for some of these reactions. More importantly, the final conversion values are improved and match well with the gravimetric results. Hence, normalization with band at 1450 cm^{-1} was used throughout for analyzing the spectra.

Once the procedure for calculating the conversion profiles from Raman spectra was determined, the best fitting of these profiles were done exactly as that for the gravimetric data. Figure 8.23 shows the results of best fitting the data for reactions

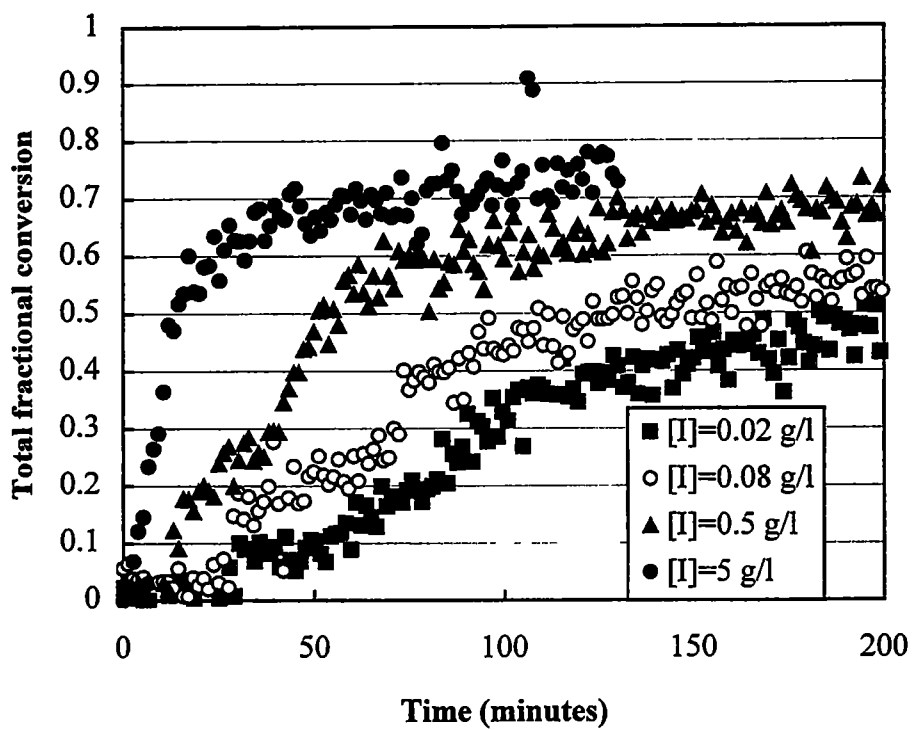


Figure 8.21 Total monomer conversions calculated using normalization of C=C peak with C=O peak

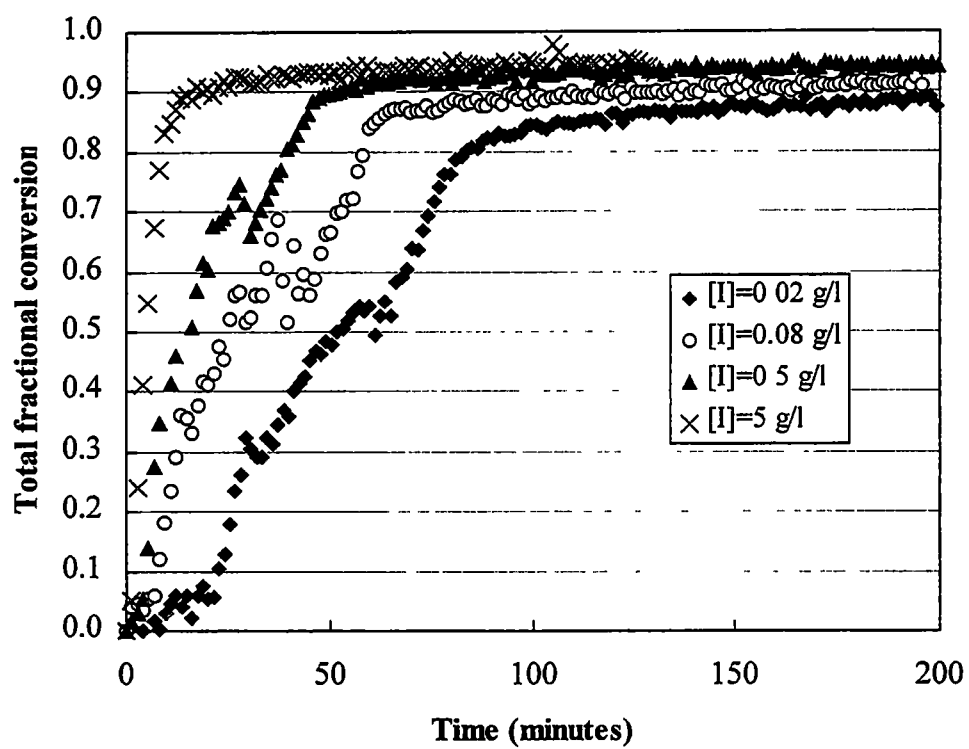


Figure 8.22 Total monomer conversions calculated using normalization of C=C peak with CH₂, CH₃ deformations peak

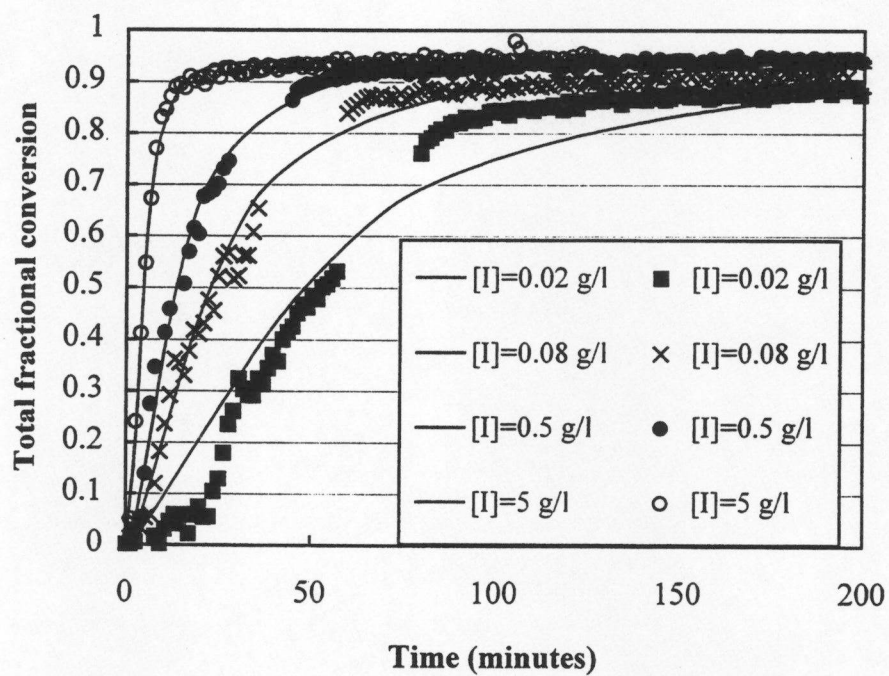


Figure 8.23 Best fitting the conversion profiles obtained from analysis of Raman spectra for reactions with varying initiator concentrations

with varying initiator concentration. The values of N_0 that best fit the individual reaction data are given in table 8.5 along with the average absolute errors in the best fitting. The small parts of conversion profiles where deviations from smooth nature of curve were observed, were omitted while best fitting the data of some of the reactions (see figure 8.23). In any of these reactions, these parts accounted for less than 10 percent of the total data. The power law fits well in correlating the number of particles with initiator concentration as is shown in figure 8.24. The power of dependence of N_0 on initiator concentration was 0.49 as compared to 0.45 that was obtained using the gravimetric data. Figure 8.25, figure 8.26, and table 8.6 show the results of a similar best fitting done on the data of the reactions with varying surfactant concentrations.

A comparison of table 8.3 and table 8.5 shows that the errors in the best fitting of conversion profiles obtained from Raman spectroscopy are smaller than those in the best fitting of conversion profiles of the same reactions using gravimetric analysis. The same conclusion can be drawn by comparing table 8.4 and table 8.6 for reactions with varying surfactant concentrations. This indicates that conversion profiles obtained from Raman spectra analysis are smoother than those obtained from gravimetric analysis. This does not really reflect on the accuracy of the two techniques. It merely indicates the accuracies of the techniques to provide experimental data that could be used for the specific kinetic model under consideration. In the following section, the ability of the model to predict the kinetic behavior of reactions with known test values of initiator and surfactant concentrations will be discussed.

Table 8 5 Values of N_0 that best fit the conversion profiles obtained from Raman spectroscopy data for reactions with varying initiator concentrations

Initiator concentration (g/l)	Number of particles ($\times 10^{17}$)	Average absolute error
0.02	7.65	0.0293
0.08	16.95	0.0200
0.5	30.35	0.0093
5.0	126.4	0.0094

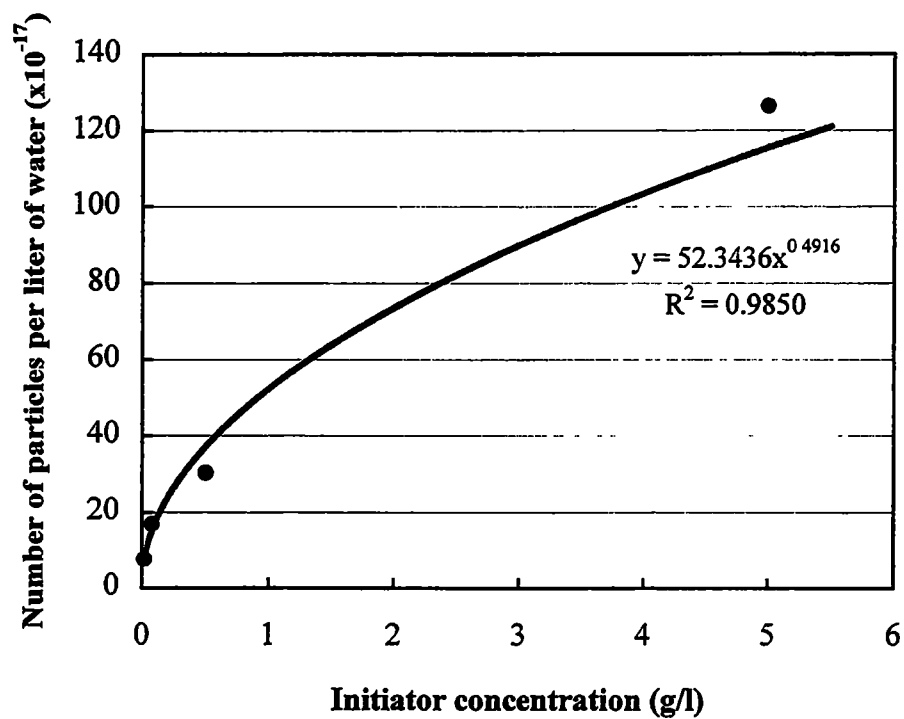


Figure 8.24 Correlation between the number of particles, N_0 , initiator concentration based on Raman spectra analysis

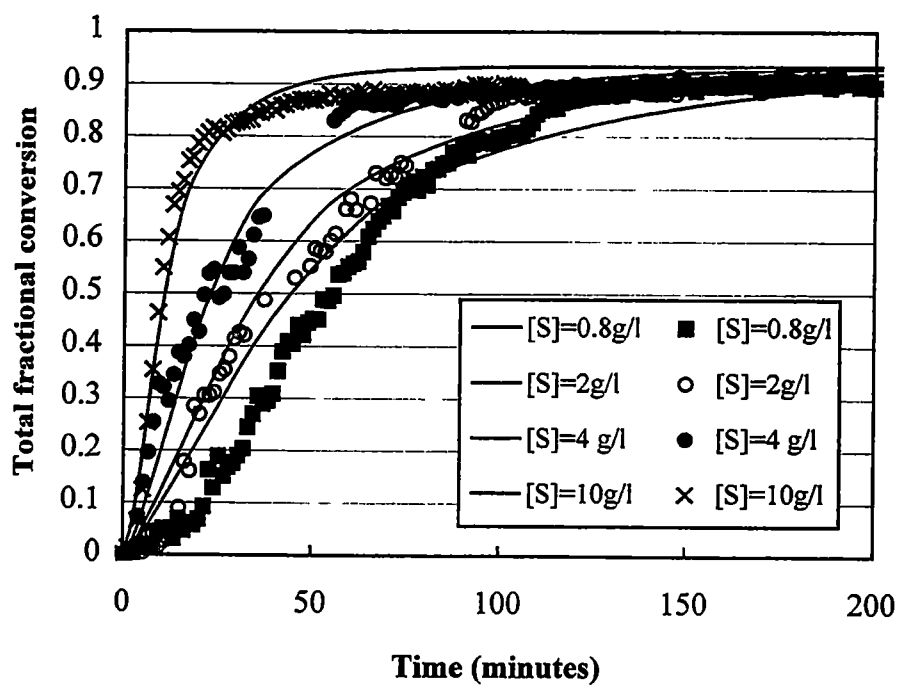


Figure 8.25 Best fitting the conversion profiles obtained from analysis of Raman spectra for reactions with varying surfactant concentrations

Table 8 6 Values of N_0 that best fit the conversion profiles obtained from Raman spectroscopy data for reactions with varying surfactant concentrations

Surfactant concentration (g/l)	Number of particles ($\times 10^{17}$)	Average absolute error
0.02	8.3	0.0437
0.08	10.45	0.0285
0.5	16.95	0.0257
5.0	40.85	0.0375

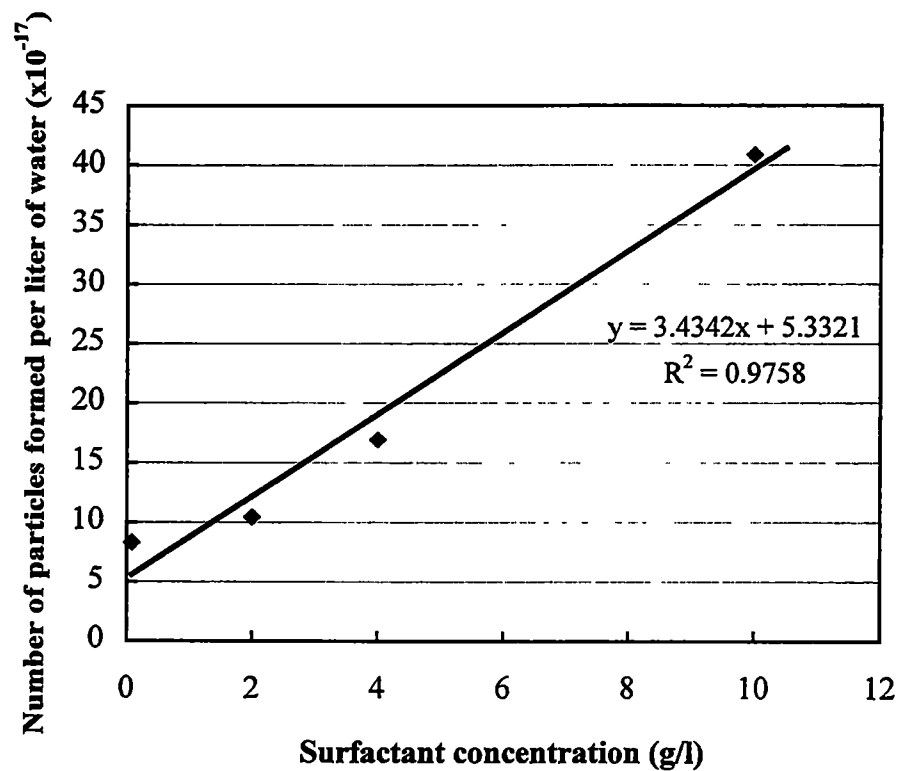


Figure 8.26 Correlation between the number of particles, N_0 , and surfactant concentration based on Raman spectra analysis

8.3 Model Predictions for Reactions with Known Test Values of Initiator and Surfactant Concentration

In section 8.2, best fitting of experimental data was done by varying only one parameter i.e. N_0 . Separate equations describing the dependence of N_0 on both initiator concentration and surfactant concentration were developed. In order to check the predictive ability of the kinetic model, four reactions were carried out at the same temperature, stirrer speed, amounts of water and monomers, and amount of chain transfer agent as those used in the reaction set for model-building. Only the initiator and surfactant concentrations were varied. Known amounts of initiator and surfactant were added and the conversion profiles were obtained using both the techniques as described in section 8.2.1 and section 8.2.2. Table 8.7 shows the recipes for prediction reactions (P-1 to P-4). In calculating the conversion profiles using the kinetic model, effects of initiator concentration and surfactant concentration were assumed to be multiplicative. Thus, for given values of surfactant and initiator concentrations, values of N_0 were calculated first, followed by generation of conversion profiles using these values. These model predictions were then compared with the experimental data obtained by both gravimetric and Raman spectra analysis.

8.3.1. Comparison of Model Predictions with Experimental Results

Figure 8.27 shows the comparison of model predictions with gravimetric data. Prediction reactions P-1 and P-3 were found to have very high reaction rates and the experimental points of the two reactions were too close for a neat visual comparison.

Table 8.7 Recipes for the reactions carried out to check the model predictions

Ingredients	Amounts in gm			
	P-1	P-2	P-3	P-4
Water	650	650	650	650
2-ethylhexyl acrylate	58.5	58.5	58 5	58 5
Acrylic acid	6 5	6 5	6 5	6.5
Potassium persulfate	2.2765	0.0487	0.4256	0.2165
Sodium lauryl sulfate	2.9238	0.6260	1.9499	0.7228
n-dodecyl mercaptan	0 175	0 175	0 175	0.175
Total	720.38	715 85	717 55	716 11

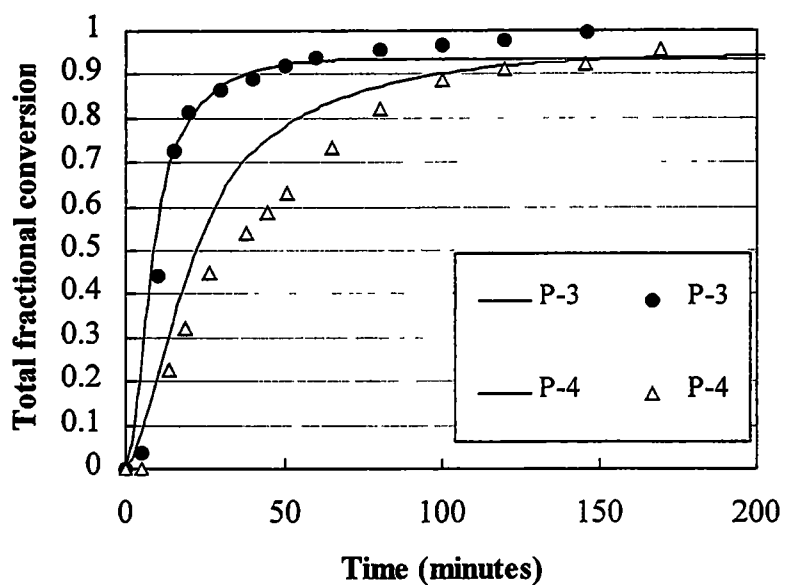
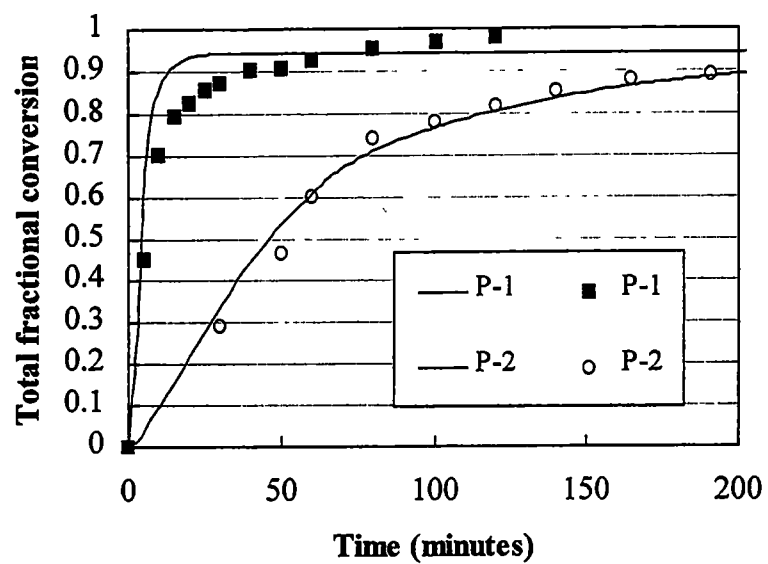


Figure 8.27 Comparison of model predictions with the experimental results obtained by gravimetric analysis

Thus, two separate charts are shown in figure 8.27, upper one for reactions P-1 and P-2, and the lower one for reactions P-3 and P-4. Figure 8.28 shows the comparison of model predictions with conversion profiles obtained from Raman spectra of the reactions. Figure 8.27 and figure 8.28 show that model predictions match well with the experimental conversion profiles calculated using both gravimetry and Raman spectroscopy.

8.3.2. Model Predictions of Individual Monomer Conversions and Particle Size

The proposed kinetic model can also predict individual conversions of 2-EHA and AA, however, only total conversion could be compared with experimental results. Figure 8.29 and figure 8.30 show the individual conversions of 2-EHA and AA for the four prediction reactions (P-1 to P-4). Figure 8.29 shows smooth curves for conversion profiles of 2-EHA, which are almost similar to the corresponding total conversion curves. The profiles for conversion of AA however, show a rapid increase initially, followed by an abrupt stoppage in AA consumption at about 85 percent of AA conversion. This is the final value of conversion of AA achieved in all the predictions. The reason for this abrupt behavior in prediction of AA conversion is that the exact concentrations of monomers in polymer particles are not known. The difficulties in calculating the values of individual monomer concentrations in polymer particles are discussed in section 6.3 in chapter 6. In the proposed kinetic model, concentrations of both the monomers are assumed to be constant in interval II, and are assumed to follow a decrease in interval III as given by equation 6.6 in chapter 6. The start of

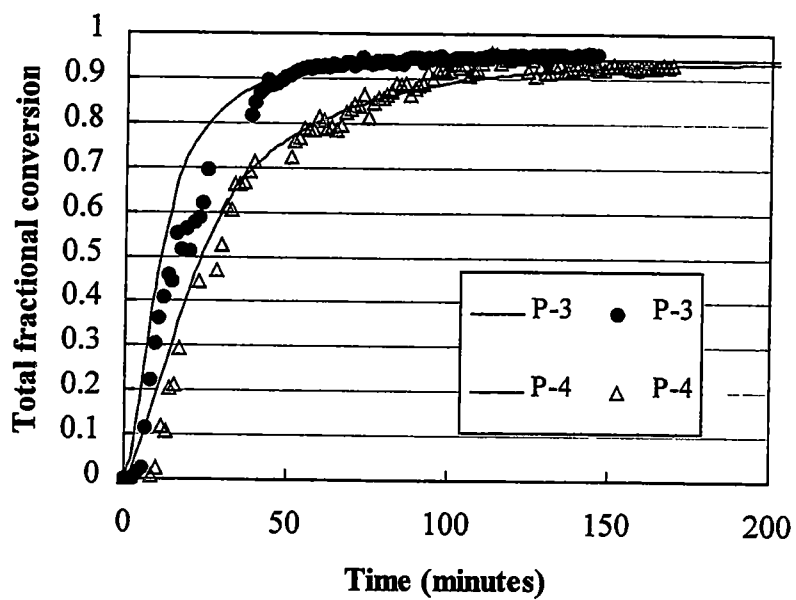
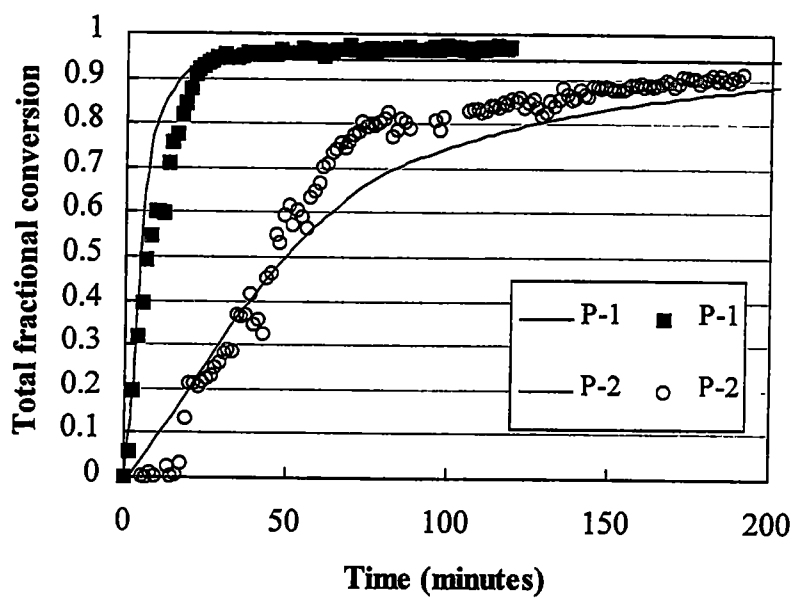


Figure 8.28 Comparison of model predictions with the experimental results obtained by Raman spectra analysis

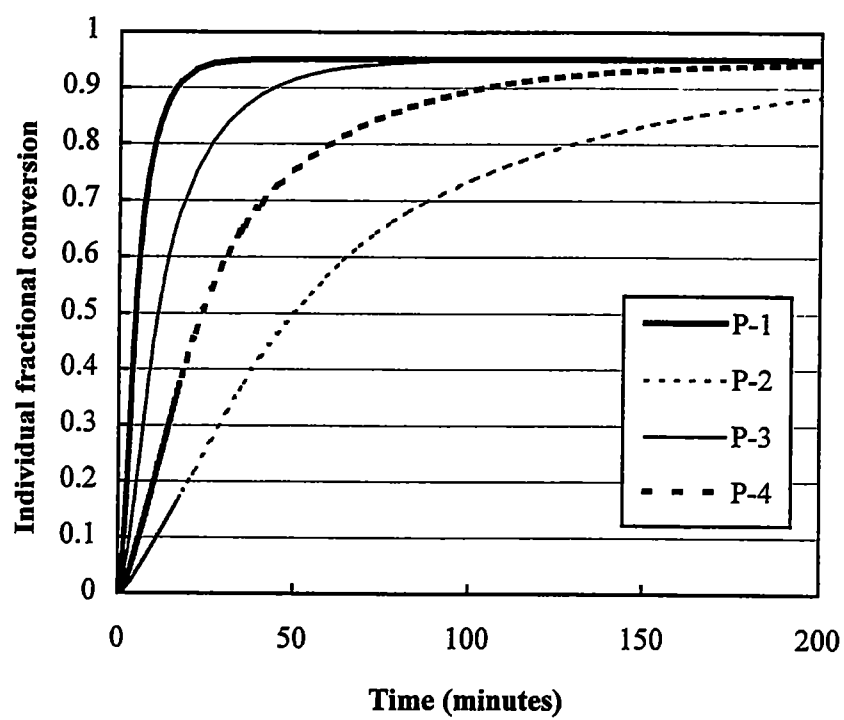


Figure 8.29 Model predictions of individual conversions of 2-EHA

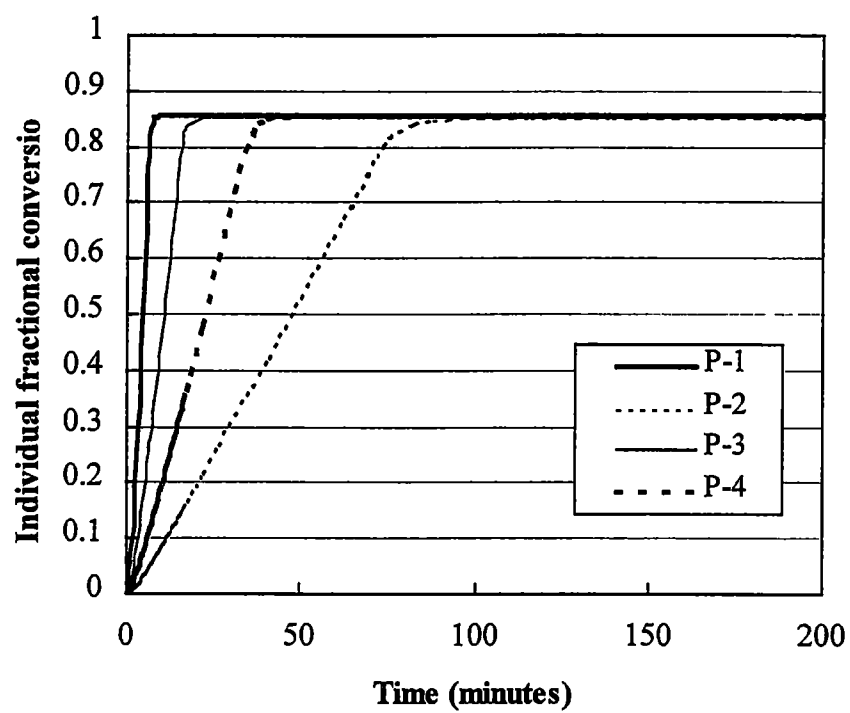


Figure 8.30 Model predictions of individual conversions of AA

interval III, and the constant values of monomer concentrations in interval II, are assigned in the model so as to have an agreement between experimental values and model predictions of total conversions. As fraction of AA in the monomer mixture is only 10 percent, the individual conversion of AA hardly has any effect on the total monomer conversion. Thus, in the absence of experimental data for individual monomer conversions and the actual profiles of monomer concentrations in polymer particles, the model cannot predict unique profiles for individual monomer conversions. It can however, give various combinations of individual monomer conversion profiles that combine to give the same total conversion profile. Only one of these several combinations, is the one actually occurring in the reaction.

One more thing to note is that the individual conversions of both 2-EHA and AA saturate at fixed conversion values which are, 95 percent for 2-EHA and 85 % for AA. The reason for this behavior can be explained by looking at figure 8.31 and figure 8.32. Figure 8.31 and figure 8.32 show respectively the concentrations of 2-EHA and AA inside the polymer particles. As we can see, the concentrations of both the monomers remain constant for a certain amount of time that corresponds to the interval II of emulsion polymerization. When the interval II ends, the concentrations of monomers inside the particles start decreasing and become zero after a while, due to which their individual conversion profiles show a saturation value. The final conversion value is however not 100 percent which means there is some monomer left, that does not enter the polymer particle, and hence remains unreacted. The

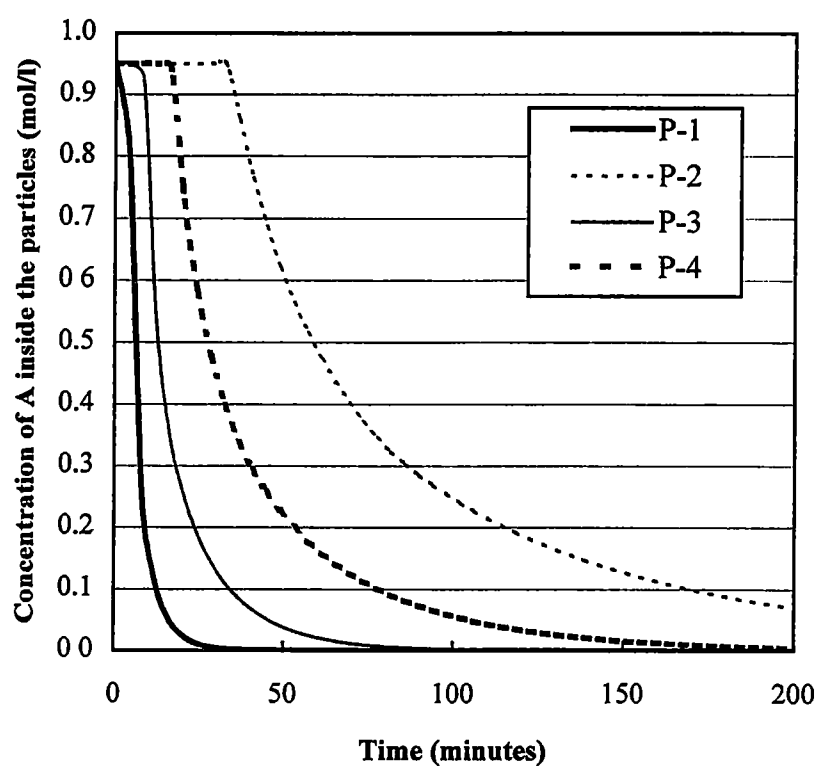


Figure 8.31 Profiles of concentration of 2-EHA inside the polymer particle

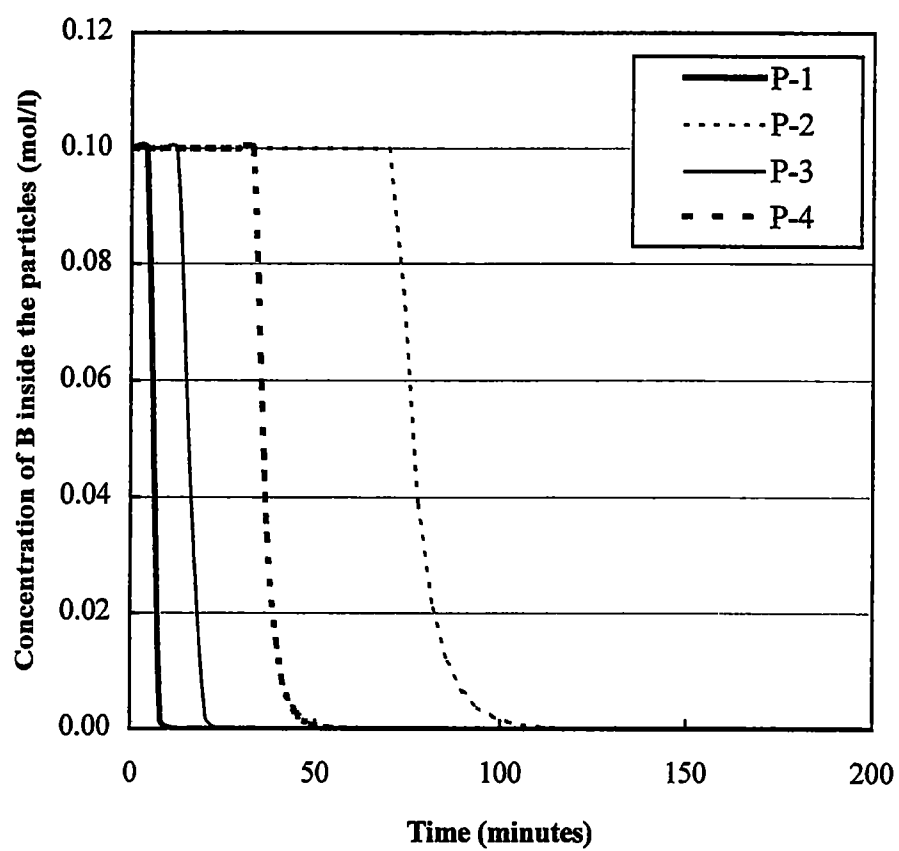


Figure 8.32 Profiles of concentration of AA inside the polymer particle

limiting conversion value remains constant as long as the assumed value of initial concentration of monomer inside the polymer particle is same. This is the reason why model predicts the same limiting conversion value for all the reactions shown in figure 8.29 or in figure 8.30. For a higher value of initial monomer concentration inside the particle, the limiting conversion value will be higher and so on.

The prediction of particle size evolution is shown in figure 8.33. The final particle sizes vary from 50 nm to 140 nm, which falls in the range of 5 to 500 nm reported by F. Loncar (58) from his particle size measurement using TEM. As discussed in section 8.2.1, no experimental data is available on particle size evolution for the reactions under consideration. It should be remembered that this model involves a number of unknown parameters, values of which are assigned in the simulations. Of these parameters, values of the exit rate coefficients of A and B radicals (ρ_A and ρ_B) significantly affect the model predictions. As discussed earlier, the changes in the shapes of conversion profiles are modeled by varying only one parameter, N_0 . It turns out that for a different combination of ρ_A and ρ_B , a different set of N_0 values may give the same profiles for total conversion, but different profiles for particle size evolution. In the absence of the experimental data on particle size for comparison, one set of values of N_0 is as good as another. Thus, the set of particle size evolution profiles shown in figure 8.33 is one of the many that the model can predict for this set of reactions, only one of which is the one actually occurring in the reaction.

The details of the calculations involved in the model simulations for the estimation of unknown parameters and for the predictions of reaction kinetics are

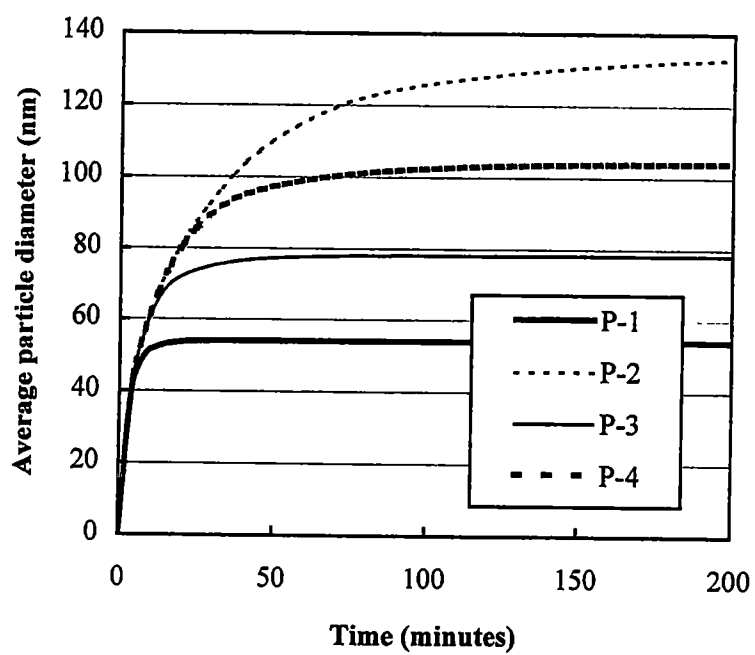


Figure 8.33 Model predictions of particle size evolution during copolymerization of 2-EHA and AA

described in Appendix A The MATLAB[®] codes developed for performing the simulations are shown in Appendix B

CHAPTER 9

CONCLUSIONS

In this research, a simple kinetic model based on the generalization of Smith-Ewart homopolymerization theory to emulsion copolymerization was developed. The model does not consider any specific mechanism for particle nucleation, rather it describes the possibilities of various microscopic events that take place in interval II and interval III (i.e. intervals in which no new particles are generated), and the effect of these events on the conversion of monomers. The model equations were developed earlier by Ballard et al (40) for a general emulsion copolymerization reaction. In this work, these equations were applied for the copolymerization of 2-EHA and AA. The values of a number of parameters viz., entry and exit rate coefficients of radicals, the transfer rate coefficients, the number of particles initially formed, and the concentrations of each monomer in polymer particles were not known for the monomers studied. Hence, the values of these parameters were assigned as those that best fit the experimental data. Separate kinetic models were built using the primary data obtained from both gravimetry and Raman spectroscopy

Normalization (ratio of peak intensities) of the intensity of C=C peak at 1640 cm^{-1} with CH_2 , CH_3 deformations band at 1450 cm^{-1} was used in calculating the conversions from the raw Raman spectra of the reaction mixture. This procedure of normalization resulted in less scatter in the data as compared to that observed in the data using normalization with C=O peak at 1730 cm^{-1} . Also, the final conversion

values matched better with the gravimetric results using the former method of normalization.

A detailed parameter sensitivity analysis of the model simulations showed that the number of particles initially formed, N_0 , was the key factor affecting the shape of conversion-time curve. The concentrations of monomers in the polymer particles were found to be the main factors affecting the final value of conversion. Since both initiator concentration and surfactant concentration in an emulsion polymerization reaction affects the number of particles produced, reactions were carried out by varying the initiator concentration and the surfactant concentration, one at a time, keeping all the other reaction conditions same. The experimental data was then best fitted using a range of N_0 values in model simulations. The best fit values of N_0 thus obtained were then correlated to the actual concentrations of initiator and emulsifier used in the reactions. Total conversion profiles obtained from both gravimetric analysis and Raman spectra analysis were best fitted. It was observed that data obtained from both the techniques was well fitted by varying only N_0 values. The average percent errors in the best fitting were in the range of 1% to 6%. The errors in the best fitting of the conversion profiles obtained from Raman spectra analysis were smaller than those obtained from gravimetric analysis. However, in both the cases, the number of particles was found to be proportional to about 0.5 power of initiator concentration, and the dependence of number of particles on surfactant concentration was found to be linear.

Predictions of the model were then compared to the experimental data (both gravimetry and Raman spectra) for a set of prediction reactions carried out with known test values of initiator and surfactant concentrations. Model predictions matched equally well with the experimental data obtained using both the techniques. Thus, a kinetic model has been developed for emulsion copolymerization of 2-EHA and AA that can predict the total conversion profiles, i.e. the copolymerization rate, for a range of initiator concentrations (0.02 g/l to 5 g/l) and a range of surfactant concentrations (0.8 g/l to 10 g/l). The kinetic model can also predict the individual conversions of monomers and the evolution of particle size with time.

This work also emphasizes the ability of in-line Raman spectroscopy to observe changes in the reaction rates due to variations in the initiator concentration and the surfactant concentration. This is an important feature, as variations in initiator and surfactant concentrations are done to alter the particle size and morphology of the final latex. In order to have control over these properties, an in-line measurement of reaction rates that is sensitive to the changes in initiator and surfactant concentration is required. Raman spectroscopy can be very useful for this purpose.

CHAPTER 10

FUTURE WORK

The kinetic model developed in this work is based on a number of simplifying assumptions. The model does not consider a specific mechanism for particle nucleation in interval I. It describes the kinetic behavior of the system based on the microscopic events in interval II and interval III. In an actual emulsion copolymerization reaction, about 90 percent of polymer is formed in these intervals. In interval I, the precursor particles are generated at a very fast rate. In this interval, very little polymerization takes place at a much smaller rate than that in interval II.

As the kinetic model is based upon the events in interval II and III, the predictions of model are poor when compared to the experimental data, for the first few minutes in the reaction, when the interval I exists. This is shown in figure 8.12, figure 8.14, figure 8.20 and figure 8.22 in chapter 8. This discrepancy increases as the initial number of particles, N_0 , decreases. Thus, in order to obtain accurate model predictions throughout the reaction progress, the events occurring in interval I, should be considered in the modeling. This requires the knowledge of a number of parameters: the rate of radical generation, the rate of particle growth, and the adsorption area per emulsifier molecule on the surface of the polymer molecules. If the values of these parameters are known, differential equations for the number of particles can be written for interval I (33), which can improve the model predictions for the initial part of the reaction.

The other major limitation in model simulations is that the concentrations of each monomer in polymer particles are not known. This severely limits the ability of the proposed kinetic model to predict “unique” individual conversion profiles for each monomer. The concentration of monomers in polymer particles can be calculated using molecular thermodynamics as described in section 6.2.3. However, values of the thermodynamic parameters required for this calculation are not known for the copolymerization system under study. The problem can be partly solved, if the individual conversions of monomers could be obtained experimentally. One can then use this as an additional data in best fitting, which may help in determining the accurate values of individual concentrations of monomers in polymer particles.

On-line gas chromatography and densimetry have been used to measure partial conversions of monomers in emulsion copolymerization (84). In-line Raman spectroscopy could not measure the individual monomer conversions in 2-EHA/AA copolymerization because a separate peak for C=C in AA is not observed due to its very low concentration (1%) in the reaction mixture. However, in-line monitoring of individual conversions by Raman spectroscopy of copolymerization of styrene and butyl acrylate has been reported (79). The proposed kinetic model applies to any emulsion copolymerization reaction as long as the values of the model parameters are known or can be estimated by best fitting the data. Thus, a kinetic model can be built on the system styrene-butyl acrylate, making use of the additional data of individual monomer conversions in estimating the best-fit parameter values. Work in this area is

required in order to improve the model predictions of individual monomer conversions

In this work, an attempt was made to measure the latex particle size using a scanning electron microscope, which was unsuccessful. As described in section 8.3.2 in chapter 8, the absence of the experimental data on particle size limits the accuracy of estimated values of the best fit parameters, especially the number of particles. An elaborate method to measure the particle size of the latex under study is developed by F. Loncar (58), using a transmission electron microscope. Availability of the data on particle size measurements would improve the accuracy of the estimated values of the best fit parameters, and consequently the accuracy of the model predictions.

The proposed model can predict the kinetic behavior of the reactions in which the total monomer content is 10 percent of the water, and the monomers 2-EHA and AA are in the ratio 90/10. For predictions of the reactions with recipes other than mentioned above, one has to obtain the experimental conversion profiles for those reactions, and estimate the values of the unknown parameters using that data. The concentrations of monomers inside the polymer particle will change as the reaction recipe is varied. This will affect the final value of conversion. Thus, independent estimation of model parameters for each reaction recipe is required. This problem can be solved if the monomer concentrations inside the particles are calculated *a-priori* for the reaction recipe used. This requires an understanding of the thermodynamics involved in the process.

The ultimate goal of both the kinetic modeling and in-line monitoring using Raman spectroscopy of emulsion copolymerization reactions is to design a control system for the industrial reactor facility. The rate of emulsion copolymerization reaction can be calculated using this kinetic model (by simply taking the derivatives of conversion-time curve). Simultaneous material and energy balance equations can then be written for either a batch, continuous or semi continuous reactor, with the knowledge of the heat of the reaction. Thus, the proposed kinetic model can serve as a useful mathematical description of the polymerization reaction, which can be put into a transfer function chain while designing a control system.

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APPENDICES

APPENDIX A: DETAILS OF MODEL SIMULATIONS

The following discussion is intended to give a synopsis of the procedure for the estimation of the best-fit parameters using the experimental data, and simulation of the kinetic model for predictions of the reaction kinetics. The procedure of solving the differential equations in simulating the model is briefly described in this appendix and the MATLAB[®] codes for the simulations are given in appendix B.

A.1 Estimation of the Unknown Parameters by Best Fitting the Experimental Data

The experimental data obtained from both the gravimetric analysis and the analysis of the Raman spectra, is arranged in the form of a matrix containing 2 columns; the first column contains the time values, and the second column contains the corresponding total conversion values. The profiles of total conversion vs time are generated by simulating the kinetic model. The system of differential equations used in the simulation is described in section 6.1. The equations are reproduced here for a quick reference.

The equation for the number of particles containing i of A free radicals and j of B free radicals is

$$\begin{aligned}
\frac{dN_y}{dt} = & -[\rho_A + \rho_B + ik_A + jk_B + i(i-1)c_{AA} + 2jc_{AB} + j(j-1)c_{BB} + i\gamma_{AB} + j\gamma_{BA}]N_y \\
& + \rho_A N_{(i-1)j} + \rho_B N_{i(j-1)} + (i+1)k_A N_{(i+1)j} + (j+1)k_B N_{i(j+1)} \\
& + (i+2)(i+1)c_{AA} N_{(i+2)j} + 2(i+1)(j+1)c_{AB} N_{(i+1)(j+1)} \\
& + (j+2)(j+1)c_{BB} N_{i(j+2)} + (i+1)\gamma_{AB} N_{(i+1)(j-1)} + (j+1)\gamma_{BA} N_{(i-1)(j+1)}
\end{aligned} \quad .(A.1)$$

In the proposed kinetic model, it is assumed that the polymer particles do not contain more than 2 free radicals at any time. Thus, there are six types of particles, viz, N_{00} , N_{01} , N_{02} , N_{10} , N_{11} , and N_{20} , and a differential equation can be written down for each of these particles. These equations are given below, which are derived by substituting the values of i and j in equation (A.1).

$$\frac{dN_{00}}{dt} = -[\rho_A + \rho_B]N_{00} + k_A N_{10} + k_B N_{01} + 2c_{AA} N_{20} + 2c_{AB} N_{11} + 2c_{BB} N_{02} \quad .(A.2)$$

$$\frac{dN_{01}}{dt} = -[\rho_A + \rho_B + k_B + \gamma_{BA}]N_{01} + \rho_B N_{00} + k_A N_{11} + 2k_B N_{03} + \gamma_{AB} N_{10} \quad ..(A.3)$$

$$\frac{dN_{02}}{dt} = -[\rho_A + \rho_B + 2k_B + 2c_{BB} + 2\gamma_{BA}]N_{02} + \rho_B N_{01} + \gamma_{AB} N_{11} \quad .(A.4)$$

$$\frac{dN_{10}}{dt} = -[\rho_A + \rho_B + k_A + \gamma_{AB}]N_{10} + \rho_A N_{00} + 2k_A N_{20} + k_B N_{11} + \gamma_{BA} N_{01} \quad ..(A.5)$$

$$\frac{dN_{11}}{dt} = -[\rho_A + \rho_B + k_A + k_B + 2c_{AB} + \gamma_{AB} + \gamma_{BA}]N_{11} + \rho_A N_{01} + \rho_B N_{10} + 2\gamma_{AB} N_{20} + 2\gamma_{BA} N_{02} \quad .(A.6)$$

$$\frac{dN_{20}}{dt} = -[\rho_A + \rho_B + 2k_A + 2c_{AA} + 2\gamma_{AB}]N_{20} + \rho_A N_{10} + \gamma_{BA} N_{11} \quad ..(A.7)$$

Similarly, the equations for the individual conversions of A and B can be written by substituting the values of i and j in equation (6.5) as

$$\frac{dx_A}{dt} = N_I N_A^{-1} [A]_p \left[k_{AA}^p (N_{10} + N_{11} + N_{20}) + k_{BA}^p (N_{01} + N_{11} + N_{02}) \right] \quad \text{.. (A.8)}$$

and,

$$\frac{dx_B}{dt} = N_I N_A^{-1} [B]_p \left[k_{BB}^p (N_{01} + N_{11} + N_{02}) + k_{AB}^p (N_{10} + N_{11} + N_{20}) \right] \quad \text{. (A.9)}$$

By substituting the values of i and j the equations for the concentrations of A and B in the polymer particles become

$$\frac{d[A]_p}{dt} = -[A]_p (N_A V)^{-1} \left[k_{AA}^p (N_{10} + N_{11} + N_{20}) + k_{BA}^p (N_{01} + N_{11} + N_{02}) \right] \quad \text{.. (A.10)}$$

and,

$$\frac{d[B]_p}{dt} = -[B]_p (N_A V)^{-1} \left[k_{BB}^p (N_{01} + N_{11} + N_{02}) + k_{AB}^p (N_{10} + N_{11} + N_{20}) \right] \quad \text{.(A.11)}$$

Equation (A.2) through equation (A.11) constitute the system of simultaneous differential equations that is required to solve in order to simulate the model. This system of equations is solved using an in-built differential equation solver in MATLAB[®] called “*ode15s*”. Appendix B.1 shows the MATLAB[®] code, “*bestfit m*”, for best fitting the experimental conversion profiles using the model simulations and estimating the best-fit value of N_0 , the total number of particles initially formed.

The experimental conversion-time data is saved in a file named “*bfmat*”. This data can be loaded whenever the simulations are to be done. A MATLAB[®] subroutine named “*modcal m*” does the actual model simulations. This subroutine is recalled in the main program “*bestfit m*” for a range of N_0 values from 1×10^{17} to 200×10^{17} , and the individual monomer conversions x_A and x_B are obtained along with the profiles of

number of particles and the concentrations of monomers in the particles. The total conversion is then calculated for each run as

$$X_t = \frac{M_{A_0} x_A + M_{B_0} \cdot x_B}{(M_{A_0} + M_{B_0})} \quad \dots(\text{A.12})$$

where, M_{A_0} and M_{B_0} are the moles of A and B per liter that are charged at the start of the reaction. The total conversions calculated from the model are then compared with the corresponding experimental values, and the average absolute error in the best fitting is calculated for each value of N_0 as

$$\text{Average absolute error} = \frac{\sum_{i=1}^n (|X_{ei} - X_{mi}|)}{n} \quad . (\text{A } 13)$$

where, n = number of data points

X_{ei} = experimental conversion value of data point i

X_{mi} = conversion value of data point i as calculated from the model

The value of N_0 is estimated that gives the least average absolute error in the best fitting of the experimental data. The subroutine “*modcal m*” is shown in appendix B.2.

For determining the initial conditions for simulation, it is assumed that all the particles generated at time $t=0$, contain none of the free radicals, i e ,

$$N_{00} = N_0, \text{ and}$$

$$N_{01} = N_{02} = N_{10} = N_{11} = N_{20} = \text{zero}$$

The conversions of both the monomers at $t=0$, have to be zero, i e

$$x_A = x_B = \text{zero.}$$

The initial concentrations of monomers in the polymer particles, $[A]_p$ and $[B]_p$, are assigned as 0.95 and 0.1 mol/l, respectively. These values are estimated as those that give the final conversion value of 95 percent.

The best-fit values of N_0 thus estimated using the model simulations are then correlated with the actual initiator and surfactant concentrations used. Two separate sets of reactions were carried out, by varying each of the initiator and surfactant concentrations one at a time, keeping the other value constant. Thus, separate correlations of N_0 with the initiator and surfactant concentrations are obtained, as shown in figure 8.13 and figure 8.15 respectively, from the best-fitting of the gravimetric data. Similar correlations are obtained from the analysis of Raman spectra, and are shown in figure 8.22 and figure 8.24.

A.2 Calculations for Model Predictions

For predicting the conversion profiles from the values of initiator and surfactant concentration used, the value of N_0 was first calculated using the individual correlations of N_0 with the initiator and the surfactant concentration. The combined effect of the two variables was assumed to be multiplicative. A simple procedure is used for calculating the value of N_0 for the given initiator and surfactant concentrations. The value of N_0 for the reaction I-3 given in table 8.2 is taken as the reference value for N_0 , and the reaction is called as the "reference reaction". Using the individual correlation of N_0 with the initiator concentration, the increase or decrease in

the value of N_0 compared to the reference reaction is calculated. Similarly, increase or decrease in the value of N_0 due to the change in the surfactant concentration is calculated. The value of N_0 for the given reaction is then calculated as

$$\begin{aligned}
 N_0 \text{ for the given reaction} = & \\
 & (N_0 \text{ for the reference reaction}) \times \\
 & (\text{change in } N_0 \text{ due to change in initiator concentration}) \times \dots (\text{A.14}) \\
 & (\text{change in } N_0 \text{ due to change in surfactant concentration})
 \end{aligned}$$

The conversion profiles were then calculated using the N_0 values thus generated. Since, different correlations are generated from the analysis of gravimetric data and the Raman spectra, model predictions for each of the two will be different. A MATLAB[®] subroutine named “*modpred m*” is written for performing these calculations and is shown in appendix B 3. This subroutine gives the model predictions to be compared with the conversion profiles obtained from the gravimetric analysis. A similar program is written for the model predictions to be compared with the conversion profiles obtained from the analysis of Raman spectra

The model can also calculate the total number of particles present at any time as

$$N_t = N_{00} + N_{01} + N_{02} + N_{10} + N_{11} + N_{20} \quad \dots (\text{A.14})$$

$$d_p = \left(\frac{6M_0 X_{Mf}}{\pi N_T \rho_p} \right)^{1/3} \quad \dots (\text{A.15})$$

where, d_p = the diameter of the particle.

M_0 = the total amount in gms of monomer initially charged per liter.

X_{Mt} = the total molar conversion.

ρ_p = the density of the polymer formed.

APPENDIX B: MATLAB CODES FOR MODEL SIMULATIONS

B.1 Matlab® Code for Best-Fitting the Experimental Data

```
% Program "bestfit.m"
% Program developed by Parag Patil at University of Tennessee,
% Knoxville.
% All the lines in this MATLAB® code beginning with "%" are the
% comment statements
% This MATLAB® code best fits the experimental data of total
% conversion using the kinetic model and estimates the best-fit
% values of  $N_0$ , the number of particles initially formed in an
% emulsion copolymerization reaction
% In this code A represents the monomer 2-ethylhexyl acrylate
% and B represents the monomer acrylic acid

clear all % Clears all the variables from the workspace

% In this initial part of the code, the values of some
% parameters required in the best fitting of the experimental
% data are entered

MA0=0.8653; % Moles of A initially charged per liter of water
MB0=0.1; % Moles of B initially charged per liter of water

errmin=100; % The "minimum error" value used for initializing
            % the code

load bf tspan econv; % loads the experimental conversion-time
                    % profiles pre-saved in a file "bf.mat"
n=size(tspan); % size of the time vector
cina=0.95; % Assumed values for concentrations of A and B
cinb=0.1; % inside the polymer particles

% The following part of the code does the actual best-fitting
% of the experimental data

for N0=1e17:.05e17:200e17 % the range of  $N_0$  values used in
                        % best-fitting the data

    clear t y xtotal diff error; % clears the results of the
                                % previous iteration
    [t,y]=ode15s('modcal',tspan,[N0;0;0;0;0;0;0;0;0;cina;cinb]);

    % Generates the profiles for the number of particles,
```

```

% individual monomer conversions, and the concentrations of
% monomers inside the polymer particles
% "ode15s" is the in-built differential equation solver in
% MATLAB®
% A subroutine file named "modcal.m" solves the system of
% differential equations using "ode15s" for different
% initial conditions, i.e., for different values of  $N_0$ .
% The entities in the square bracket, "[ ]" separated by
% ";" are the initial values of the different parameters
% those constitute the initial condition
% The value of  $N_{00}$  is assigned as  $N_0$ .
% The values of  $N_{01}$ ,  $N_{02}$ ,  $N_{10}$ ,  $N_{11}$ , and  $N_{20}$  are all
% assigned as zero as an initial condition
% The values of initial conversions of A and B are assigned
% as zero as well
% The values of initial concentrations of A and B are
% assigned as those input by the user

xtotal=(MA0*y(:,7)+MB0*y(:,8))/(MA0+MB0);

% Calculates of the total conversion from the individual
% monomer conversions

for i=1:n
    diff(i)=abs(econv(i)-xtotal(i));
end

% Calculates the absolute value of the difference
% between the experimental conversions and the
% conversions predicted by the model for each data
% point, and stores in a vector named "diff"

error=sum(diff)/length(diff);

% Calculates the average absolute error in the best-fit

if error<errmin
    errmin=error;
    xtotalmin=xtotal;
    N0min=N0;
end

% Replaces the previous "minimum error" with the new error
% if it less than the previous "minimum error", and stores
% it under the variable name "errmin"
% The corresponding total conversion profile and  $N_0$  value

```

```

    % are stored as "xtotalmin" and "N0min" respectively

end

disp(errmin) % Average absolute error in the best-fitting
disp(N0min)  % Best-fit value of  $N_0$ 
plot(t,econv,'*') % Plots the experimental conversion profiles
hold on
plot(t,xtotalmin) % Plots the best-fit conversion profiles on
                  % the same figure

```

B.2 Matlab® Subroutine for the Model Simulations

```
% Program "modcal.m"
% Program developed by Parag Patil at University of Tennessee,
% Knoxville.
% This initial part of the code assigns the values of various
% model parameters

clear all % Clears all the variables from the workspace
function dy=model(t,y); % Statement for communication between
                        % the main program and the subroutine

NA=6.023e23; % Avogadro Number
rhoa=1e-4; % Entry rate coefficient of A radical
rhob=4e-3; % Entry rate coefficient of B radical
ka=1.5e-5; % Exit rate coefficient of A radical
kb=1e-5; % Exit rate coefficient of B radical
kpaa=252; % Self-propagation rate constant of A
kpbb=1500; % Self-propagation rate constant of B
kpab=kpaa/0.93; % Cross-propagation rate constants,
kpba=kpbb/1.08; %  $k_{AB}^p$  and  $k_{BA}^p$ , calculated using the reactivity
                % ratios ( $r_A = 0.93$  and  $r_B = 1.08$ )
ktrab=12e-2; % Cross-propagation rate constant,  $k_{AB}^{tr}$ 
ktrba=8e-2; % Cross-propagation rate constant,  $k_{BA}^{tr}$ 
MS0=.8653; % Moles of A initially charged per liter of water
MM0=.1; % Moles of B initially charged per liter of water
caa=2.75e6; % Self-termination rate constant of A
cbb=2.7e6; % Self-termination rate constant of B
cab=sqrt(caa*cbb); % Cross-termination rate constant calculated
                  % as the geometric mean of  $C_{AA}$  and  $C_{BB}$ 

% The following part of the code carries out the model
% simulations

gab=(kpab+ktrab)*y(10);
gba=(kpba+ktrba)*y(9);
r0=rhoa+rhob;
r01=rhoa+rhob+kb+gba;
r02=rhoa+rhob+2*kb+2*cbb+2*gba;
r10=rhoa+rhob+ka+gab;
r11=rhoa+rhob+ka+kb+2*cab+gab+gba;
r20=rhoa+rhob+2*ka+2*caa+2*gab;
d00=-(r0*y(1)+ka*y(4)+kb*y(2)+2*caa*y(6)+2*cab*y(5)+2*cbb*y(3));
d01=-(r01*y(2)+rhob*y(1)+ka*y(5)+2*kb*y(3)+gab*y(4));
d02=-(r02*y(3)+rhob*y(2)+gab*y(5));
d10=-(r10*y(4)+rhoa*y(1)+2*ka*y(6)+kb*y(5)+gba*y(2));
```

```

d11=-(r11*y(5)+rhoa*y(2)+rhob*y(4)+2*gab*y(6)+2*gba*y(3);
d20=-(r20*y(6)+rhoa*y(4)+gba*y(5);

% "d00, ,d20" are the values of "differentials" of "N00, ,N02"
% respectively, calculated at a given time

NT=y(1)+y(2)+y(3)+y(4)+y(5)+y(6); % Total number of particles
DA=NA*MA0;
DB=NA*MB0;
q=y(9)*(kpaa*(y(4)+y(5)+2*y(6))+kpba*(y(2)+y(5)+2*y(3)))/DA;
r=y(10)*(kpbb*(y(2)+y(5)+2*y(3))+kpab*(y(4)+y(5)+2*y(6)))/DB;

% "q" and "r" are the values of "differentials" of xA and xB
% respectively

xtotal=(MA0*y(7)+MB0*y(8))/(MA0+MB0); % Total conversion
Mi=100; % Total weight of monomers (in gm) initially added
% per 1000 gm of water
vs=(Mi*xtotal)/(NT*1e3); % Volume of one polymer particle
% density of polymer = 1000 kg/m3

if xtotal<.35
    s=0;
else
    s=-q/(vs*NT);
end
if xtotal<.65
    ss=0;
else
    ss=-r/(vs*NT);
end

% The two "if statements" above specify the end of interval II
% for each monomer
% Interval II ends at 35% of total conversion for monomer A
% Interval II ends at 65% of total conversion for monomer B

dy=[d00;d01;d02;d10;d11;d20;q;r;s;ss];

% Stores the values of the "differentials" of all the variables
% at a given time t and uses them to calculate the values of
% the variables in the next iteration

```

B.3 Matlab® Code for Predicting the Total Conversions Using the Kinetic Model

```
% Program "modpred.m"
% Program developed by Parag Patil at University of Tennessee,
% Knoxville.
% In this initial part of the code, the values of the
% parameters required in the model predictions are entered

clear all % Clears all the variables from the workspace
MA0=0.8653; % Moles of A initially charged per liter of water
MB0=0.1; % Moles of B initially charged per liter of water
c1na=0.95; % Assumed values for the concentrations of A and B
c1nb=0.1; % inside the polymer particles
M1=100; % Total weight of monomers (in gm) initially added
% per 1000 gm of water

% This part of the code calculates the number of particles
% initially formed using the best-fit correlations of number
% of particles with the initiator and surfactant concentrations

c11=0.08; % Concentration of initiator used in the reference
% reaction
cs1=4; % concentration of surfactant used in the reference
% reaction
n1=25.3e17; % Value of  $N_0$  in the reference reaction

n11=75.4257*c11^0.4539;
% The value of  $N_0$  for the reference reaction calculated using
% the correlation between  $N_0$  and the initiator concentration

ns1=5.4209*cs1+2.8571;
% The value of  $N_0$  for the reference reaction calculated using
% the correlation between  $N_0$  and the surfactant concentration

c12=input('Enter the initiator concentration');
cs2=input('Enter the surfactant concentration');
% input of the initiator and surfactant concentration by the
% user

n12=75.4257*c12^0.4539;
% Value of  $N_0$  for the initiator concentration entered

ns2=5.4209*cs2+2.8571;
% Value of  $N_0$  for the surfactant concentration entered
```

```

N0=N1*(ni2*ns2)/(n11*ns1);
% Value of the number of particles calculated by assuming
% the combined effect of the initiator and surfactant
% concentrations on  $N_0$  to be multiplicative

tspan=linspace(0,12000,100);
% Generation of an equally spaced time vector

[t,y]=ode15s('modcal',tspan,[N0;0;0;0;0;0;0;0;0;c1na;c1nb]);
% Model simulation to calculate the profiles of all the
% variables

NT=y(:,1)+y(:,2)+y(:,3)+y(:,4)+y(:,5)+y(:,6);
% Total number of particles

xa=y(:,7);    % Individual conversion of A
xb=y(:,8);    % Individual conversion of B

xtotal=(MA0*y(:,7)+MB0*y(:,8))/(MA0+MB0);    % Total conversion

vs=(Mi*1e-3*xtotal)./NT;    % Average particle volume
dp=(6*vs/3.142).^(1/3);    % Average Particle diameter

```

VITA

Parag Patil was born in Mumbai, India on August 18, 1977. He attended high school at D. G. Ruparel College, Mumbai, India. He joined University Department of Chemical Technology, University of Mumbai, India in 1994 and received the Bachelor of Chemical Engineering degree in 1998. In August 1998, he joined The University of Tennessee, Knoxville and received the Master of Science degree in August 2000