MATHEMATICAL MODELLING IN BATCH EMULSION POLYMERIZATION

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SUMMARY

Emulsion polymerisation, suspension polymerisation and the dispersion processes of styrene in water have been carried out at 50°C in a stainless steel, stirred batch reactor of 3.6 dm^3 capacity. The reactor was fitted with a temperature control facility and could be operated with or without internal baffles.

A mathematical model covering stages I,II and III of emulsion polymerisation has been proposed and its predictions have been compared with experimental data.

Classical models do not present satisfactory predictions for the case of low soap concentrations or for the case of high impeller speed at low or intermediate soap concentrations. The model presented here overcomes this problem by taking into account the amount of soap adsorbed onto the dispersed monomer droplet interface. An existing relationship between monomer droplet size, impeller speed and impeller diameter for an unbaffled vessel and a new relationship for a baffled vessel were incorporated into the model.

During stage III the increase in monomer particle viscosity reduces the translational mobility of the radicals with the result that the reaction rate increases dramatically (the gel-effect). Analogous behaviour in suspension polymerisation of styrene has been investigated and a relationship between the termination rate constant and the level of monomer conversion has been developed. This relationship is incorporated into the model for emulsion polymerisation.

The predictions of the current model incorporating the soap adsorption and the gel effect amendments are in good agreement with experimental data for emulsion polymerisation of styrene at 50°C across the whole of the conversion.

KEY WORDS: Emulsion polymerisation, styrene, dispersion, modelling, gel-effect.

To

My Motherland

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SECTION I

INTRODUCTION 1

SECTION II

THE LITERATURE SURVEY 9

2.1 The Qualitative Theory of Emulsion Polymerization 10

2.2 Mathematical Model 13

2.2.1 Smith-Ewart Model 13

2.2.2 Gardon Model 15

2.2.3 Harada Model 19

2.2.4 Min and Ray Model 21

2.3 Gel-Effect 22

2.4 Dispersion 25

2.5 Determination of Particle Size

SECTION III

EXPERIMENTAL EQUIPMENT AND TECHNIQUES 32

3.1 Flow Chart and Equipment 33

3.2 Experiment of Emulsion Polymerization 39

3.3 Experiment of Suspension Polymerization 40

3.4 Dispersion Tests 41

SECTION IV

INTRODUCTION AND DEVELOPMENT OF ANALYTICAL TECHNIQUE 42

4.1 Droplet Size Analysis 43

4.1.1 Photomicrographic 43

4.1.2 Coulter Counter 44

4.2 Determination of Monomer Conversion 51

4.2.1 Precipitation with Methanol 53

4.2.2 Precipitation with Aluminium Chloride 53

4.2.3 Direct Drying 54

4.2.4 Comparison of Techniques 54

4.3 Development of the Technique for the Measurement of Particle Size Using Light Transmission 55

4.3.1 General Description 55

4.3.2 Setting up the Technique for Measuring Particle Size in Emulsion Latex 56

4.3.3 Determination of Particle Size Using Extinction Method 61

4.3.3.1 Collecting Basic Data 61

4.3.3.2 Diluting 62

4.3.3.3 Estimating the Mass Concentration of the Particles in the Diluted Latex 63

4.3.3.4 Finding the Density of Particles in the Diluted Latex 64

4.3.3.5 Estimating the Refractive Index 65

4.3.3.6 Measuring the Extinction Coefficient 65

4.3.3.7 Evaluating the Parameter K/α and the Average Radius of Particles 65

4.3.3.8 Correcting the size of Particles 66

4.3.4 Comparison between the Results from this Technique and the Electron Microscopic Method 67

SECTION V

		THE MATHEMATICAL MODEL	69
5.1		Setting us the Model for Stage I	70
	5.1.1	General Description	71
	5.1.2	Setting up the Differential Equation for Particle Nucleation	73
	5.1.3	Derivation of the Equation for the Surface Area of Monomer Droplets	74
	5.1.4	Estimating the Parameters of Monomer Droplets	75
	5.1.5	Derivation of the Equation for Estimating the Surface Area of Particles	76
	5.1.6	Derivation of the Equation for Estimating the Volume of Polymer Particles	78
	5.1.7	Derivation of the Equation for Estimating the Fractional Monomer Conversion	79
	5.1.8	Derivation of the Equation for Estimating the Number of Particles	80
5.2		Setting up the Model for Stage II	80
5.3		Setting up the Model for Stage III	

SECTION VI

		THE RESULTS AND DISCUSSION	87
6.1		Determination of the Dependence of Termination Rate Constant on Monomer Conversion	88
6.2		Formulation of the Dispersion Data in Baffled Reactor	93
6.3		Capabilities of the Model	97
	6.3.1	The prediction of the Model for Particle Nucleation	97
	6.3.2	Conversion-versus-Time Plots for Baffled Reactor	103
	6.3.3	The effect of Stirring Rate	107
	6.3.4	The Gel-Effect	110
	6.3.5	Baffled Reactor	117

SECTION VII

CONCLUSIONS 121

SUGGESTIONS FOR FURTHER WORK 130

NOMENCLATURE 132

REFERENCES 134

APPENDIX 138

Appendix I Computer Program for Determination of Particle Size Using Extinction Method 139

Appendix II Computer Programs for the Computation of the Dependence of Termination Rate Constant on Monomer Conversion 143

(1) DEFF1 The Computation of dX_p/d_t from t-X_p Data Using Differentiation Method 144

(2) REG3 The Formulation of K_t and X_p Using Multiple Regression Method 145

(3) XKT The Evaluation of K_t against X_p 147

Appendix III Computer Programs for Formulation of the Dispersion Data in Baffled Reactor 148

(1) DISPER The Evaluation of the Average Diameter of Monomer Droplets for the Various Sample from the Dispersion Data 149

(2) The Formulation of D_d^o So and N Using Regression Method 150

Appendix IV Computer Program for Smith-Ewart Model 151

Appendix V Computer Program for Stage I and Stage II in Unbaffled Reactor 155

Appendix VI Computer Program for Gel-Effect 161

Appendix VII Computer Program for Baffled Reactor 165

SECTION I

INTRODUCTION

SECTION 1

INTRODUCTION

Emulsion polymerization is one of the most important methods for effecting the process of addition polymerization. It is carried out in a system which includes a monomer (or monomers) and a dispersion medium, generally water, in which the monomer is either virtually insoluble, or else sparingly soluble. A micelle-generating substance, namely the emulsifier, is usually present and a water soluble initiator is generally used. The polymerization takes place, in the main, within the monomer swollen polymer particles which according to the Harkins model for emulsion polymerisation are nucleated within the micelles.

The emulsion polymerization process offers significant advantages over bulk, solution or suspension polymerization. Although the internal viscosity of the particles is extremely high, the viscosity of the emulsion remains low during the process of emulsion polymerization. Heat transfer therefore is no real problem and good temperature control can often be achieved thus avoiding the "runaway reaction" which is often observed in bulk polymerisations. The combination of highly effective surface active agents, very mild agitation and the small size of the polymer particles minimizes the tendency of the particles to coalesce so that, in contrast to suspension polymerization, emulsion polymerization is suitable for the production of sticky, rubbery polymers. Furthermore, the

polymer is produced in latex form and this is an obvious advantage in certain industrial applications.

Emulsion polymerization polymers are characterised by a very high molecular weight. The reason for this follows from the fact that free radicals are not formed within the particles but enter into the particle from the surrounding aqueous phase in which the initiator is dissolved. When a free radical enters a non-growing particle, polymerization is initiated and continues until it is terminated by the entry of another radical into the particle. Therefore, the average life time of growing polymer radicals in emulsion polymerization is much longer than for the other polymerization processes. Thus, it is possible for a growing molecule to grow to a very high molecular weight before being terminated. This growth of the polymer chain can proceed simultaneously in a large number of particles, which are isolated from each other by the intervening water phase. A growing polymer molecule in one particle cannot terminate one in another particle. This means that the total number of radicals in unit emulsion volume is larger in emulsion polymerization than in other polymerization processes, therefore, the overall rate of polymerization is high. These two important characteristics of emulsion polymerization make it a valuable commercial process. High product molecular weight for instance is especially necessary when producing synthetic rubber with satisfactory elastomer properties. High conversion rate of course leads to

reduced production costs.

For the reasons mentioned above, the emulsion polymerization process is of increasing importance to commercial polymer production. In both batch and continuous reactor systems it has become a major processing step in the manufacture of polymer products such as paints inks, coatings, adhesives, flocculants, synthetic rubbers, plastics, high impact strength copolymers and so on. Current latex production by emulsion polymerization throughout the world is of the order of a million tons per year. In spite of its great economic importance however and although emulsion polymerization has been carried out for at least 5o years, the detailed quantitative behaviour of these reactions is still not well understood. For this reason, it is considered of considerable benefit to develop a reliable, efficient predictive mathematical model for emulsion polymerization reactors.

The emulsion polymerization system is heterogeneous in that it consists of several phases which change in character during the polymerization process. The behaviour of an emulsion polymerization reactor also differs for the different monomers that may be polymerised by this process. In addition, the purities of the monomer and of the other ingredients, the gas space atmosphere, the geometry of the reactor and its accessories, the impeller speed and the reaction conditions all affect the progress of an emulsion polymerization.

Consequently, the modelling of emulsion polymerization is extremely complex. In spite of this, a number of workers have devoted themselves to the study of emulsion polymerization science. Since the classical work of Smith-Ewart (1) on the modelling of emulsion polymerization, a great number of papers have appeared which have either modified the classical model or have proposed their own new models.

It is apparent from the literature that none of the numerous previous models for emulsion polymerization have considered the effect on the reaction of the adsorption of emulsifier onto the surface of the monomer droplets. In many instances the amount of this adsorbed emulsifier may be ignored because it is a relatively small proportion of the total emulsifier concentration. However, if the emulsifier concentration is low, or if the impeller speed is high enough, the proportion of the adsorbed emulsifier on the monomer droplet surface will be comparable with that of the micellar soap. In this case the effect of the adsorbed soap must clearly be taken into account. Several workers have studied the effects of stirring on the process of emulsion polymerization. Shunmukham (2) noted that violent agitation would reduce the polymerization rate and increase the induction time. Schoot et al (3) suggested that the increase in induction time is associated with inhibition by trace oxygen in the nitrogen atmosphere used and the decrease in polymerization rate is due to increasing mass transfer between the gas and liquid

phases as agitation becomes more severe. Evans et al (4) Omi et al (5) and Nomura et al (6) pointed out that, under a highly purified nitrogen atmosphere, the decrease in the rate of polymerization and in the number of polymer particles with increased agitation may be due to the fact that the micelle population is a function not only of the soap concentration, but also of the amount of soap adsorbed onto the surface of the monomer droplets, i.e. a function of the degree of dispersion which is directly dependent on the agitation. In this work, a mathematical model for Stage I and Stage II of emulsion polymerization is established which takes into account the soap adsorbed on the surface of monomer droplets. The soap adsorption model is described in detail in Section VI.

In modelling Stage III of the reaction difficulties are encountered which are associated with the auto-acceleration of the conversion rate with increasing monomer conversion. This phenomenon is often known as the Trommsdoff effect, or gel-effect. Friis et al. (7-10) carried out experimental emulsion and bulk polymerizations of polymethylemthacrylate (7, 8) and polyvinyl acetate (7, 9). By using a steady state model they were able to model the gel-effect. They also compared their model (10) with the experimental data obtained by Grancio (11). They also looked at styrene polymerization and the relationship which they used to relate the termination constant to monomer conversion for polystyrene was based on Hui's work (12) on the thermal polymerization of styrene in bulk which was

carried out over the temperature range of 100-200°C. It was found, at-least at 50°C, that this relationship overestimates the termination rate constant if it is used for modelling the emulsion polymerization reaction, particularly at high levels of conversion. Gardon (13,14) developed a mathematical model based on a non-steady state assumption for Stage II. Unfortunately, it does not extend to Stage III because the relationship between termination rate constant and monomer concentration in the particles was not known. In the present work, a functional dependence of monomer conversion has been generated using experimental suspension polymerization data. A non-steady state mathematical model for Stage III has been developed, which is combined with the model for Stage I and Stage II mentioned above to construct a general model over the whole conversion range of the emulsion polymerization. A comparison has been made between the predicted and the experimental data. It is described in Section VI.

The flow pattern of the liquid in a baffled reactor is significantly different from that in an unbaffled reactor. The velocity distribution in the former is more uniform than in the latter (15) and the extent of monomer dispersion in the baffled reactor is much greater than that in the unbaffled one. Vermeulen et al (16) presented a correlation from their work for a baffled reactor, in which the Sauter mean diameter of the droplets is directly proportional to the impeller speed to the power (-1.2). Unfortunately, their formula is

only valid for the system in the absence of emulsifier. Merry obtained an empirical formula (17) for the dispersion of styrene in an emulsifier solution in water, in which the mean diameter of droplets was shown to be proportional to the impeller speed to the power (-1.08). This formula however can only be used for the unbaffled reactor. Harada et al (32) presented a correlation for the dispersion of styrene in an emulsifier solution in water for a baffled reactor, and in this case average diameter of the dispersed monomer droplets is proportional to impeller speed to the power (-0.75) and to the emulsifier concentration to the power (-1.5) for a lower limit of the emulsifier concentration of 3.13 g/dm^3 water, which is above the emulsifier concentration range used in the current study. Therefore, in the present work, the dependence of the average droplet diameter upon emulsifier concentration and impeller speed in a baffled reactor has been investigated and it has been included in the mathematical model for emulsion polymerization mentioned above. The results predicted from the model are compared with the experimental data as described in Section VI.

Apart from setting up the mathematical model for emulsion polymerisation, a technique, with which particle sizes as small as 0.09 micron may be measured, has been developed, this technique has been based on Mie's theory(19) on the work of Bateman(20) and of Merry (17).

SECTION II

LITERATURE SURVEY

2.1 The Qualitative Theory of Emulsion Polymerization

2.2 The Mathematical Model

2.2.1 The Smith-Ewart Model

2.2.2 The Gardon Model

2.2.3 The Harada Model

2.2.4 The Min and Ray Model

2.3 Gel-Effect

2.4 Dispersion

2.5 Determination of Particle Size.

2.1 The Qualitative Theory of Emulsion Polymerization

In the 1940's Harkins proposed an important qualitative theory (21-24) which laid a solid foundation for the modelling of emulsion polymerization. The main features of this theory are best illustrated diagrammatically as in Figure 2.1.

Figure 2.1 (a) shows the system before initiation has occurred. The emulsifier molecules are present mainly in the form of micelles, a small amount is adsorbed onto the surface of the monomer droplets, and a further small amount is dissolved in the water in the form of free molecules whose saturated concentration is defined as the critical micelle concentration (c.m.c.). Micelles are able to concentrate monomer at their centres so that monomer can be solubilised by emulsifier. Only a very small amount of monomer is dissolved in the water as free molecules. Compared with the micelles, the monomer droplets are relatively large. Generally speaking, the diameter of the droplets is about 10 micron but the micelles about 0.01 micron. In a typical case, the number of monomer droplets would be about 10^{12} $1/cm^3$, but for micelles the number would be about 10^{18} $1/cm^3$ (25).

Figure 2.1 (b) shows the system after the initiator is charged. Free radicals are generated in the aqueous phase and these diffuse into the micelles to initiate the polymerization. The micelles in which initiation takes place become polymer particles. The monomer

droplets act as reservoirs from which the monomer migrates constantly into particles through the aqueous phase, thus supplying the growing particles.

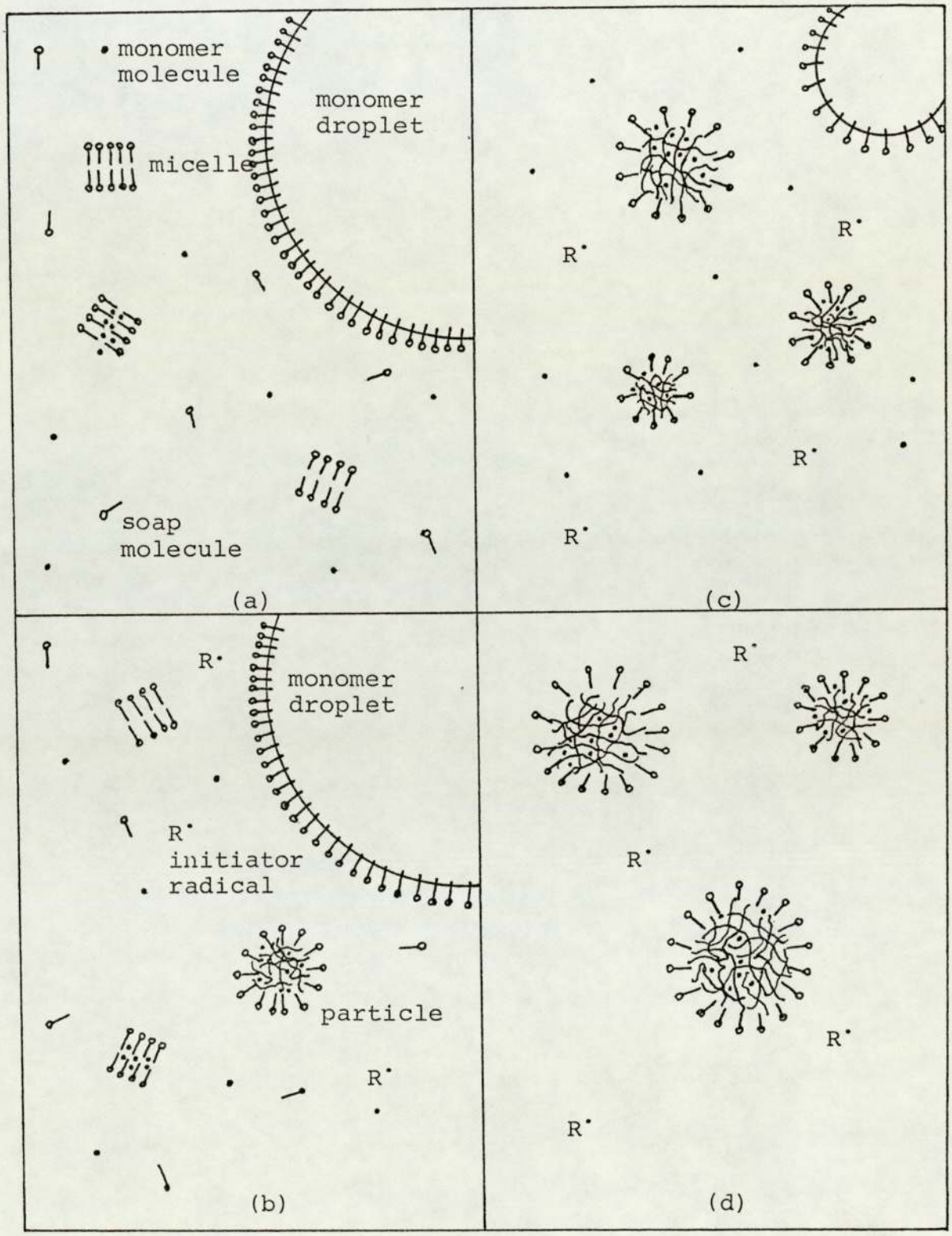


Figure 2.1 A physical picture of emulsion polymerization (a) dispersion stage, (b) Stage I (c) Stage II (d) Stage III

Particle nucleation and growth of the particles lead to an increase in the specific surface area of the particles. There is therefore a tendency to adsorb more free molecules of the emulsifier from the true aqueous phase onto this new surface and this in turn tends to lead to the destruction of micelles. Thus, as polymerization proceeds, the micellar emulsifier tends continuously to change into adsorbed emulsifier so that the micellar emulsifier eventually disappears. The period of the reaction from the charging of the initiator to the disappearance of the micelles is known as Stage I.

Figure 2.1 (c) shows the system after all the micelles have disappeared. The emulsifier is found in three forms, namely, adsorbed onto the particle surface, adsorbed onto the droplets surface and dissolved in the aqueous phase. Monomer is continually diffusing from the droplets to the particles through the aqueous phase to supply the particles as they increase in size. The number of particles, that is the number of reaction loci, remains constant once all the micelles have disappeared and so, therefore, as the polymerization rate is a function solely of the number of particles the rate also remains constant. As polymerization proceeds, eventually the monomer droplets also disappear. The period of the reaction from the disappearance of micelles to the disappearance of monomer droplets is known as Stage II.

Figure 2.1 (d) shows the system after the droplets have disappeared. At this stage the emulsifier exists in two forms only, namely adsorbed onto the surface of the particles and dissolved in the aqueous phase in free solution. The rate of polymerization gradually falls off due to the monomer depletion at the reaction loci. In normal cases, the final diameter of the particles is about 0.1 micron and the number of particles is about 10^{16} $1/cm^3$.

2.2 Mathematical Model

2.2.1 The Smith-Ewart Model

Smith and Ewart (1, 26, 27) treated Harkins' physical model quantitatively for Stage I and Stage II of emulsion polymerization. They provided two experimentally verifiable equations for Stage I and predicted that the final particle number should be proportional to the 0.4 power of the initiator concentration and to the 0.6 power of the emulsifier concentration. In addition, they also provided recurrence equations based on the steady-state assumption for Stage II. Most of the models presented after Smith and Ewart modified or extended this classical model. The model may be summarized as follows:

For Stage I, it was assumed that all free radicals are generated in the aqueous phase and then migrate into micelles and particles. Smith and Ewart assumed the two following possible cases:

(1) When all radicals enter only into micelles and generate new particles there. In this case, the number of particles per cc of water at the end of Stage I can be described using the following equation

$$N_p = 0.53 \left(\frac{R}{\mu}\right)^{0.4} S^{0.6} \qquad (2\text{-}1)$$

where N_p = number of particles per cc of water, 1/cc water

R = rate of radical generation, 1/cc water min.

μ = volume growth rate of particles, $\mu = (K_p/N_A)$ (dm/dp) $\{\emptyset m/(1-\emptyset m)\}$, cm^3/min. particle

S = area provided by emulsifier, cm^2/cc water.

(2) When radicals enter into both micelles and polymer particles, the ratio of entry into one or the other depending only on the ratio of the external surface area of micelles and particles. In this situation, the equation becomes:

$$N_p = 0.37 \left(\frac{R}{\mu}\right)^{0.4} S^{0.6} \qquad (2\text{-}2)$$

For Stage II, Smith and Ewart made a population balance on N_i the number of particles per cc of water containing i radicals, and obtained the following non-steady state recurrence equation:

$$\frac{R}{N_p}(N_{i-1} - N_i) + \frac{K_o a}{\bar{v}}\{N_{i+1}(i+1) - N_i i\} + \frac{K_t}{\bar{v}N_A}$$

$$\{N_{i+2}(i+2)(i+1) - N_i i(i-1)\} = 0 \qquad (2\text{-}3)$$

where K_o = radical desorption rate constant, cm/min.

a = average surface area of one particle at a given time, cm^2/particle

$\bar{V}$ = average volume of one particle at a given time, cm^3/particle.

K_t = termination rate constant, cm^3/mole min

N_A = Avogadro number

The first term of equation (2-3) considers the transfer of the radicals from the aqueous phase to the particles. (R/N_p) represents the rate of this transfer into a single particle.

The second term considers the transfer of radicals from particles into the aqueous phase. $(K_o ai/\bar{V})$ represents the rate of this transfer out of a single particle.

The third term considers the loss of free radicals by mutual termination of the radicals. $\{K_t i\ (i-1)/\bar{V}\}$ denotes the rate of this loss of radicals from a single particle.

2.2.2 The Gardon Model

The definitive exposition of the Gardon theory of emulsion polymerization was published in six papers which appeared in 1968 (13, 14, 28-31). He recalculated and extended the Smith-Ewart model. He used a different mathematical method from Smith and Ewart and he derived the equations for calculating the surface area of the particles, the reaction time, the number of particles, the

molecular weight and the monomer conversion for Stage I. He considered the case of slow termination of radicals instead of Smith and Ewart's fast termination, and he obtained an equation relating reaction time to monomer conversion. The model is described briefly below:

For Stage I. Gardon considered that each particle absorbs radicals at a rate proportional to its surface area $4\pi r_i^2$. If n_i is the number of radicals per cc of water whose radius is r_i and N_t is the number of particles per cc of water, the differential equation of particle nucleation is

$$\frac{dN_t}{dt} = \frac{R}{S}\{S - 4\pi(\Sigma n_i r_i^2)_t\} \qquad (2\text{-}4)$$

He derived the equation below based on equation (2-4) by using a numerical method.

$$y(x) = 0.318\, x^{\frac{5}{3}} - 0.701\, x^{\frac{5}{3}}\, y(\tfrac{x}{z}) \qquad (2\text{-}5)$$

$$u(x) = 0.279\, x\{1.91 - y(x) - 4y(\tfrac{x}{z})\} \qquad (2\text{-}6)$$

$$Z(x) = 0.265x^2 - 0.047x^{3.55} \qquad (2\text{-}7)$$

where y = dimensionless surface area

$$y = \frac{4}{S}\,\Sigma n_i r_i^2 \qquad (2\text{-}8)$$

x = dimensionless time

$$x = (\frac{12\pi}{5})^{\frac{3}{5}}\, K^{\frac{2}{5}}\, (\frac{R}{S})^{\frac{3}{5}} \qquad (2\text{-}9)$$

K = the relative rate of volume growth of particle.

$$K = \frac{3}{4\pi} \frac{Kp}{N_A} \frac{dm}{dp} \frac{\phi}{1-\phi m} \qquad (2\text{-}10)$$

u = dimensionless particle number

$$u = 4\left(\frac{5}{12\pi}\right)^{\frac{2}{5}} S^{-\frac{3}{5}} \left(\frac{K}{R}\right)^{\frac{2}{5}} N_t \qquad (2\text{-}11)$$

Z = dimensionless conversion

$$Z = 4\left(\frac{12\pi}{5}\right)^{\frac{1}{5}} S^{-\frac{6}{5}} \left(\frac{R}{K}\right)^{\frac{1}{5}} \left(\Sigma n_i r_i^3\right) \qquad (2\text{-}12)$$

Kp = propagation rate constant, cm^3/mole min.

dm = density of monomer, gram/cm^3

dp = density of polymer, gram/cm^3

ϕm = volume fraction of monomer in particles.

When polymerization has proceeded to the end of Stage I equations (2-5), (2-6) and (2-7) become:

$$t_{I-II} = 0.365\left(\frac{S}{R}\right)^{0.6} K^{-0.4} \qquad (2\text{-}13)$$

$$N_p = 0.208 S^{0.6} \left(\frac{R}{K}\right)^{0.4} \qquad (2\text{-}14)$$

$$Z_{I-II} = 0.3016$$

where t_{I-II} = reaction time elapsed at the end of Stage I, min.

Z_{I-II} = the value of parameter Z at the end of Stage I.

For Stage II , Gardon derived a set of differential equations based on a non-steady state assumption which is described as follows:

$$I\frac{df_0}{dZ} = 3.81(-f_0) + \frac{Q_3}{Z}(zf_i)$$

$$I\frac{df_i}{dZ} = 3.81(f_0-f_i) + \frac{Q_3}{Z}(6f_3)$$

$$I\frac{df_2}{dZ} = 3.81(f_1- f_2) + \frac{Q_3}{Z}(12f_4 - 2f_2)$$

$$I\frac{df_i}{dZ} = 3.81(f_{i-1}- f_i) + \frac{Q_3}{Z}\{(i+2)(i+1)f_{i+2} - i(i-1)f_i\} \quad (2\text{-}15)$$

$$\Sigma f_i = 1 \quad (2\text{-}16)$$

$$\Sigma i f_i = I \quad (2\text{-}17)$$

$$\frac{dZ}{dx} = 0.372I \quad (2\text{-}18)$$

where f_i = number fraction of the particles each of which contains i radicals.

I = average number of radicals in one particle

Q_3 = dimensionless termination parameter

$$Q_3 = \frac{K_t}{Kp} \cdot \frac{dp}{dm} \cdot \frac{1-\phi_m}{\phi_m} \quad (2\text{-}19)$$

Gardon fitted the numerical solution of the above equations to the following quadratic equation which is the relationship between conversion and reaction time.

$$Z = \frac{0.05464}{Q_3^{0.94}} x^2 + 0.186x + 0.0721\left(1 - \frac{1.14}{Q_3^{0.94}}\right) \quad (2\text{-}20)$$

2.2.3 Harada Model

Harada et al (32) developed a model of emulsion polymerization with the assumption that there is not more than one radical in each polymer particle. In this model they considered the effect of radical transfer both to the monomer droplet and to the transfer agent and the effect of the ratio of the amount of radicals diffusing into micelles to that diffusing into the polyer particles. They obtained several differential equations as follows:

$$\frac{dNp}{dt} = \frac{R}{1+ K_2Np/K_1m_s} \qquad (2\text{-}21)$$

$$\frac{dN_1^*}{dt} = K_1m_sR^* - Kp\{M\}N_1^*+K_2NR^* - K_2N_1^*R^*+ K_{fm}\{M\}N^* - K_{fm}\{M\}N_1^* + K_{fT}\{T\} - K_{fT}\{T\}N_1^* \qquad (2\text{-}22)$$

$$\frac{dN_j^*}{dt} = K_p\{M\}N_{j-1}^* - Kp\{M\}N_j^*-K_2N_j^*R^* - (K_{fm}\{M\}+K_{fT}\{T\})N_j^* \qquad (2\text{-}23)$$

$$\frac{dN^*}{dt} = K_1m_sR^* + K_2(Np - 2N^*)R^* \qquad (2\text{-}24)$$

$$\frac{dPj}{dt} = K_2N_j^*R^* + K_{fm}\{M\} + K_{fT}\{T\})\ N_j^* \qquad (2\text{-}25)$$

where N_p = number of particles per cc of water, particles/cc water $N_p = N + N^*$

N = number of inactive polymer particles per cc of water, particles/cc water

N^* = number of growing polyer particles per cc of water, particles/cc water

R^* = concentration of radicals in aqueous phase, radicals/cc water

R = rate of radical generation, radicals/cc water, min.

m_s = number of micelles per cc of water, micelles/cc H_2O

K_1 = radical diffusion coefficient from aqueous phase to micelles, cc water/molecule min.

K_2 = radical diffusion coefficient from aqueous phase to particles, cc water/molecule min.

N_j^* = number of particles containing a polymer radical with j monomer units, particles/cc water

N^* = number of active polymer particles, particles/cc water

$\{M\}$ = monomer concentration in particles, g.mole/cm^3

$\{T\}$ = concentration of transfer agent in particles, g.mole/cm^3

K_{fm} = transfer rate constant to monomer, cm^3/g.mole.min.

K_{fT} = transfer rate constant to transfer agent, cm^3/g.mole.min.

Pj = dead polymer containing j units, molecules/cc water

Harada et al solved the equations mentioned above for two limiting cases. One case is that for which the radicals generated in the aqueous phase preferentially enter the micelles, the other is that for which almost all the radicals generated in the aqueous phase are captured by the particles present. For these two cases, they obtained the

equation for calculating the number of particles and derived the correlation relating monomer conversion to time. Their model gives excellent agreement with the experimental results.

2.2.4 The Min and Ray Model

Recently, a more comprehensive detailed mathematical model was formulated for emulsion polymerisation reactors by Min and Ray(33,34). This model consists of complex multivariate population balance equations coupled to material and energy balances for the reactor. It includes all previous models as special cases. They also demonstrated the computer simulations of the model both for batch emulsion polymerisation reactors for the polymerisation of methyl methacrylate(35) and for semi-batch emulsion polymerisation for the polyvinyl chloride system(36). They showed that the model predictions are shown to be in good agreement with laboratory experimental data and with pilot plant data. To model emulsion polymerisation systems they made;

1) a particle size distribution balance
2) an individual particle balance
3) a micelle balance
4) a monomer droplet balance
5) an aqueous phase balance
6) a general material balance
7) a general energy balance

In this model they took into consideration the following factors:

(1) water-soluble initiators will decompose

and form free radicals in the aqueous phase while monomer-soluble initiators will form free radicals in the monomer droplets, in the dissolved monomer in the aqueous phase, and in the polymer particles.

(2) Particles can be formed both from micelles and from oligmers in the aqueous phase.

(3) Shorter chains and radicals can be desorbed from particles, micelles and monomer droplets.

(4) Coalescence between polymer particles will occur.

(5) Both homogeneous and heterogeneous particles morphology can be treated.

(6) The gel-effect is considered

(7) The model can describe both continuous well-stirred and batch emulsion polymerization reactors.

(8) The particle size distribution will influence the behaviour of emulsion polymerization reactors.

(9) The aqueous phase polymerization will contribute to the total polymerization rate.

(10) The polymer particle may be stabilised by both emulsifier and polymer chain ends.

2.3 Gel-effect

As mentioned above, the Smith-Ewart model was based on the instantaneous termination assumption (1). This approximation seems to be reasonable for describing Stage I and Stage II but is not valid for Stage III because of the Trommsdorff effect (37), i.e. the gel-effect.

Harada claimed (18) that their model, which is based on the instantaneous termination assumption, is in excellent quantitative agreement with the experimental results except in the range where autoacceleration occurs. As Gardon (28) pointed out, in Stage III, polymer concentration in the particles increases with increasing monomer conversion. Thus as termination is known to be a diffusion-controlled process the termination rate constant must decrease with increasing conversion during Stage III, this is what is normally described as the Trommsdorff or gel-effect. It would follow that the Smith-Ewart assumption of instantaneous termination becomes very questionable for Stage III even for small particle sized latexes with low initiation rate.

Friis et al. published several papers to deal with the gel-effect in emulsion polymerization (7-10, 41). They suggested that in bulk polymerization the termination reaction becomes diffusion controlled and the termination rate constant decreases by 3 to 4 orders in the conversion interval 0-100%. This decrease in termination rate constant, which will be referred to as the gel-effect, always causes a significant increase in the rate of polymerization and can also shift the molecular distribution to higher molecular weights. They pointed out that in emulsion polymerization a single polymer particle can be regarded as a locus of bulk polymerization with intermittent initiation. A decrease in the termination rate which is observed in bulk polymerization should therefore also occur in a single polymer particle. Therefore, the increase

in rate due to the gel-effect in emulsion polymerization of various monomers can be accounted for quantitatively by means of data from bulk polymerization.

The relationships between termination rate constant and monomer conversion that they suggested for various monomers are shown as follows:

Methylmethacrylate (valid temperature range, 40-90°C)

$$\frac{K_t}{K_{to}} = \{\frac{1}{1-x_p} \exp(BXp + C x_p^2)\}^2 \qquad (2\text{-}26)$$

$$B = -41.54 + 0.1082\ T$$

$$C = 23.46 - 0.0785\ T$$

Styrene (valid temperature range, 50-200°C)

$$\frac{Kt}{K_{to}} = \{\exp\{-(BX_p + CX_p^2 + DX_p^3)\}\}^2 \qquad (2\text{-}27)$$

$$B = 2.57 - 5.05 \cdot 10^{-3}.T$$

$$C = 9.56 - 1.76 \cdot 10^{-2}.T$$

$$D = -3.03 + 7.85 \cdot 10^{-3}\ T$$

Vinyl acetate (valid temperature, 50°C)

$$\frac{Kt}{K_{to}} = 2\exp(B + CXp + DX_p^2 + EX_p^3) \qquad (2\text{-}28)$$

$$B = 17.6620$$

$$C = -0.4407$$

$$D = -6.7530$$

$$E = -0.3495$$

where K_t = termination rate constant at $x_p = x_p$, cm^3/mole min.

K_{to} = termination rate constant at $x_p = o$, cm^3/mole min.

X_p = fractional monomer conversion

T = absolute temperature, ^oK.

Friis fitted the values of K_t estimated from equation (2-26) (2-27) and (2-28) to a steady state model as presented in equation (2-3) to obtain the relationship between X_p and time. They have compared the predicted results from the model with the experimental data. It seems to be in good agreement.

2.4 Dispersion

In the past twenty-five years a number of workers have studied liquid/liquid dispersions in both baffled vessels and unbaffled vessels. Vermeulen et al. (43) presented a correlation for a baffled reactor.

$$\frac{\overline{ds}}{D} = kf(\phi) - \left(\frac{N^2 D^3 \rho}{\sigma_i}\right)^{-0.6} \qquad (2\text{-}29)$$

where D = impeller diameter

N = impeller speed

σ_i = surface tension

ρ = fluid density

k = constant

ϕ = phase ratio

$\overline{ds}$ = Sauter diameter

$$\overline{ds} = \frac{\Sigma n_i d_i^3}{\Sigma n_i d_i^2} \qquad (2\text{-}30)$$

Dt = Reactor diameter

f(Ø) = a function of Ø whose value is presented by various workers as follows:

Worker	f(Ø)
Calderbank (44)	1+3.75Ø (for D/Dt = 2/3)
	1+9Ø (for D/Dt = 1/3)
Scully (45)	1+3.3Ø
Brown and Pitt (46)	1+3.14Ø
Mylnek and Resnik (47)	1+5.4Ø
Coulaloglou (48)	1+4.47Ø

Merry (17) carried out dispersion tests on the system water, styrene in the presence of soap (Nansa) in an unbaffled reactor. The tests were carried out under different emulsifier concentrations and impeller speeds and in reactors of differing diameters. The droplet sizes were determined by use of a Coulter Counter. The power dissipated by the impeller was measured by using a pully-balance system. He obtained the following correlations for unbaffled reactors.

$$D_d = D_d^i \left(\frac{N}{N_i}\right)^{-1.08} \left(\frac{D}{D_i}\right)^{-0.185} \qquad (2\text{-}31)$$

For $Re < 8 \times 10^3$

$$N^{0.61-0.24\ln Re} Re^{0.07-0.12\ln Re} = \text{const} \qquad (2\text{-}32)$$

For $Re > 8 \times 10^3$

$$N^{1.22-0.24\ln Re} Re^{1.19-0.12\ln Re} = \text{const} \qquad (2\text{-}33)$$

where N = impeller speed

D = impeller diameter

N_i = reference impeller speed

D_i = reference impeller diameter

D_d = mean droplet diamter

D_d^i = reference mean droplet diameter

Re = Reynolds number

$$R = \frac{ND^2\rho}{\mu} \qquad (2\text{-}34)$$

ρ = density of fluid

μ = Dynamic viscosity

Nomura et al. (6) also developed an empirical formula for the system water, styrene and sodium lauryl sulphate though for a baffled reactor.

$$D_d = 1.05(0.15 + 1.4S^{-3/2})(N^3D^2)^{-1/4} \qquad (2\text{-}35)$$

where S = emulsifier concentration

This formula is only valid however in the range of emulsifier concentration $S > 3.13$ g/Dm^3 water which is higher than the soap levels to be used in the current study.

2.5 Determination of particle size

The most important fundamental property of a latex is the particle size and the particle size distribution. In emulsion polymerization, the reaction rate, molecular weight and its distribution and the polymer properties all relate to the particle size and to the number of particles. Five methods have been used in the past for finding the value of the particle size: (i) electron microscopy (ii) soap titration (iii) light scattering (iv) centrifugation and (v) turbidity. Methods (i) and (v) can yield particle size distribution, from which the average values can be deduced. Methods (ii) (iii) and (v) give only average values.

(i) Electron microscopy:

This method can give a complete picture of the particles present in a latex. Size analysis is carried out by measuring the diameter of images of the polymer particles printed on an electron micrograph (49).

(ii) Soap titration

The soap titration method for the determination of particle sizes is based upon the concept that the soap is adsorbed on the surface of polymer particles until the surface is entirely covered by a monomolecular film of emulsifier molecules, each of which covers a definite area (for sodium lauryl sulphate $A_s = 3.5 \times 10^{-15}$ cm^2/one molecule (18)). If the latex contains less soap than is required for saturation of the particles, then virtually no free soap is present in the true aqueous phase. When

the soap is added beyond the point of saturation then the free soap will appear. When this free soap concentration reaches the critical micelle concentration, micelles are formed and at this point sudden changes in the properties of the latex, such as surface tension, conductance ratio, adsorption of the coloured or fluorescent dye, etc., will occur. If these properties are measured the final point of the titration may be found. According to the amount of the emulsifier added up to this point, the surface area of the particles is easily calculated (50-53).

(iii) Light scattering (54)

Light scattering is based upon the measurement of the angle between a beam of incident light and the angle of maximum intensity of scattered light. The angular dependence of intensity depends upon the relative refractive indices of the particles, the medium, the wavelength of the light and the size of the particles.

(iv) Centrifugation (55)

An ordinary centrifuge can be adapted to determine the particle size of a latex. Firstly the latex is diluted to a solid content of 2% and then centrifuged at 2700 r.p.m. while the temperature is kept fairly constant by use of dry ice. Samples are removed at various times by means of a hypodermic syringe with the needle inserted to a depth of 2 cm. The concentrations of these samples are determined. A roughly quantitative particle size contribution curve can be calculated from these data.

(v) Turbidity

Measurement of light transmission is one of the most popular methods available for measuring the particle size. It is based on the dependence of the turbidity of a dilute latex upon the particle size and on the other parameters. Barns and La Mer (56-58) did much work in this area both theoretically and in the development of the technique for the determination of the size of colloidal particles using Mie's theory (19). Of more direct use to the measurement of polystyrene latex is the method developed by Bateman et al. (20). They published a table (see Table 2-1) of theoretically determined values of total Mie scattering coefficient against wavelengths and particle radii. It is valid for the case of particle diameters more than 0.2 micron. Merry (17) extended Bateman's measurement range to smaller diameters using an interpolation method. The data he obtained seems to be reasonable in the region of particle diameter greater than 0.14 micron, but it results in a significant error if the particle size is smaller than 0.14 micron.

Table 2-1 Total Mie Scattering Coefficients for Polystyrene Spheres in Water

r(A)..... 800		1320	1940	2555	3300	4070	5000	5855	7000
λ_0		K							
3700	0.232	0.802	1.703	2.595	3.438	3.743	3.352	2.637	1.863
4300	0.144	0.526	1.185	1.945	2.792	3.450	3.723	3.458	2.710
5000 =	0.0891	0.333	0.809	1.387	2.147	2.864	3.466	3.698	3.474
5600	0.0614	0.232	0.611	1.084	1.730	2.400	3.084	3.500	3.691
6500	0.036	0.153	0.416	0.767	1.275	1.843	2.515	3.031	3.520
7500	0.0211	0.102	0.276	0.543	0.935	1.400	1.936	2.506	3.090
8500	-	0.0705	0.193	0.397	0.701	1.086	1.581	2.055	2.642
9500	-	0.0490	0.144	0.293	0.548	0.852	1.275	1.689	2.247

Dispersion equations assumed: for water, $n = 1.324_0 + 3.046 \times 10^{-11}/\lambda_0^2$; for polystyrene, $n_p = 1.5683 + 10.087 \times 10^{-11}/\lambda_0^2$

SECTION III

EXPERIMENTAL EQUIPMENT AND TECHNIQUES

3.1 Flow diagram and Equipment specification

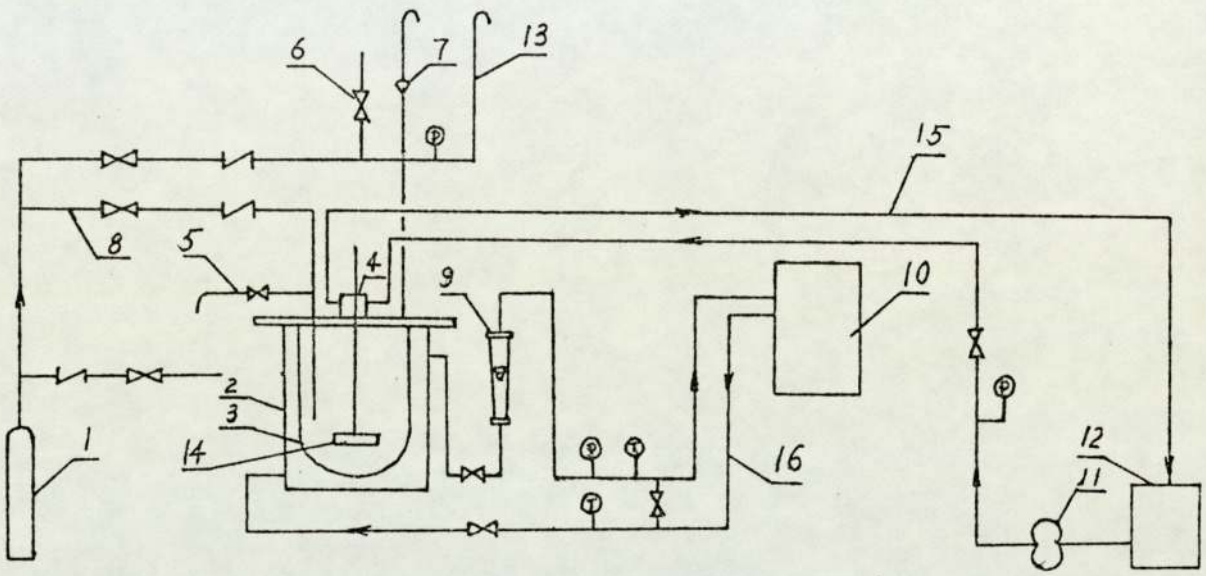
3.2 Emulsion polymerization - Experimental technique

3.3 Suspension polymerisation - Experimental technique

3.4 Droplet dispersion tests

3.1 Flow Diagram and Equipment Specification

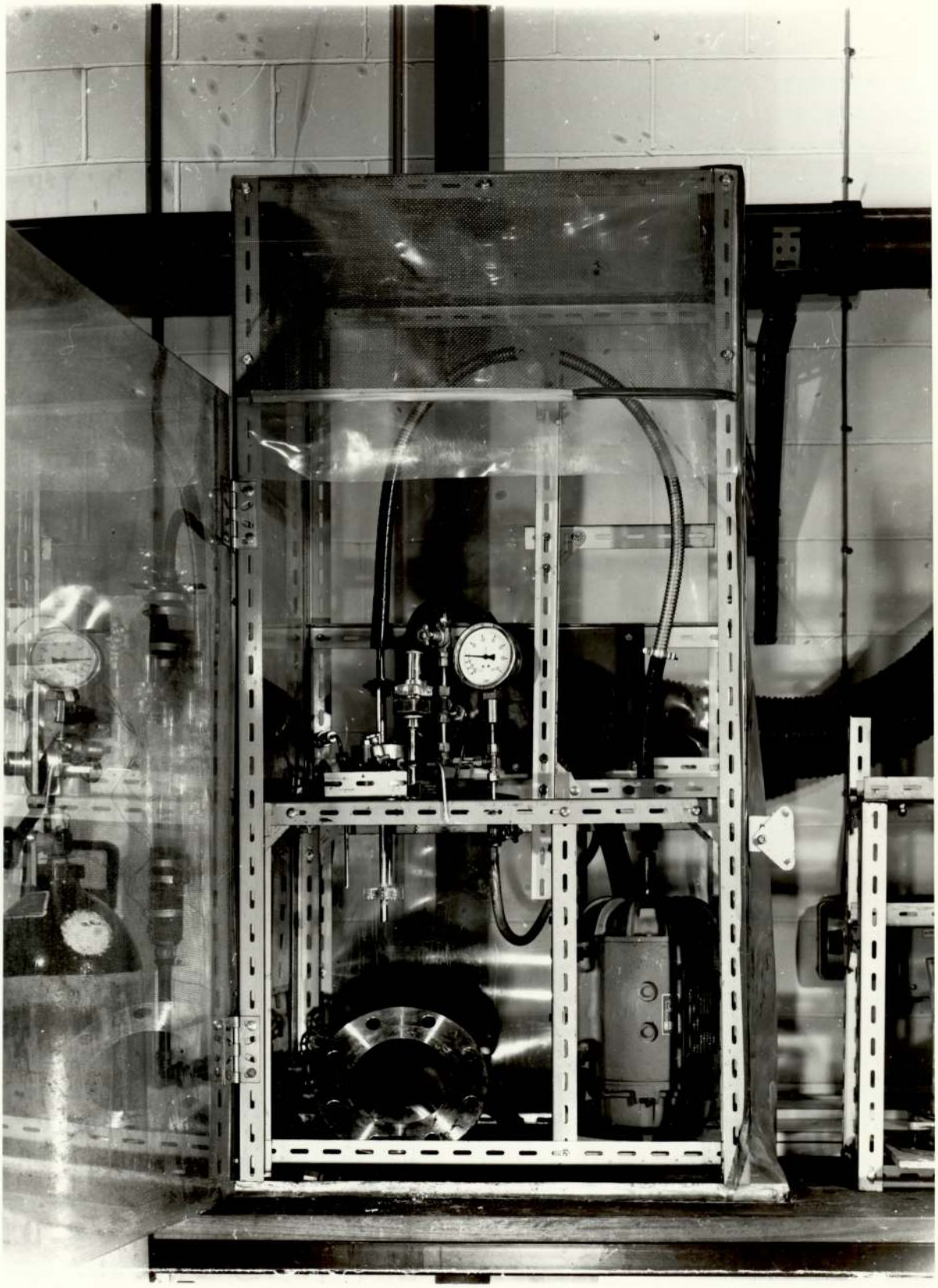
The flow chart for the emulsion polymerization, suspension polymerization and monomer dispersion runs is shown in Figure 3.1.



1. nitrogen cylinder
2. jacketed heat exchanger
3. reactor vessel
4. axial seal
5. sample line
6. charge line
7. safety valve
8. purge pipe
9. flow indicator
10. Churchill temperature controller
11. gear pump
12. lubricant reservoir
13. overpressure vent line
14. impeller
15. lubricant circulation line
16. heat exchange fluid line

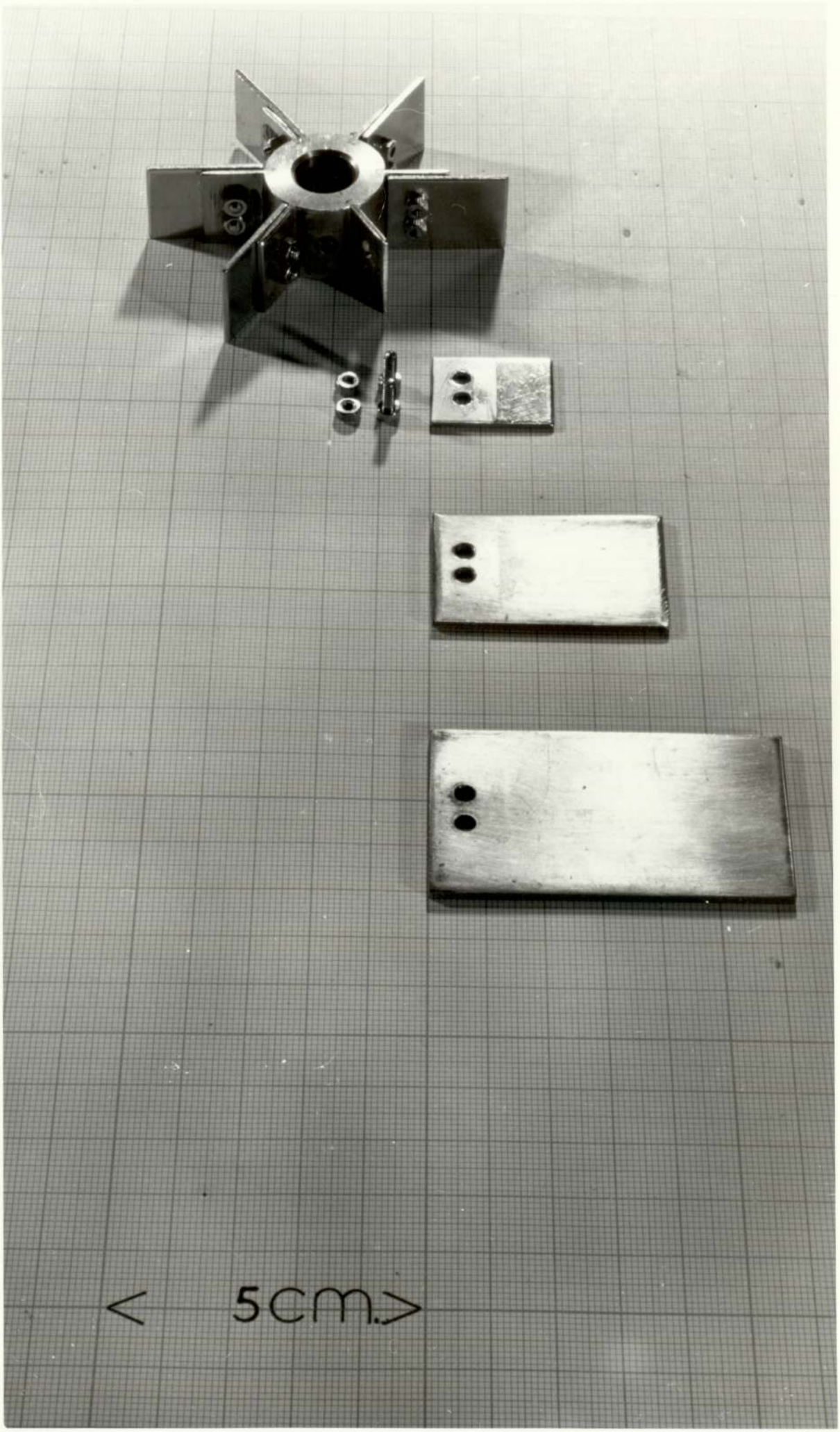
Figure 3.1 Flow Diagram

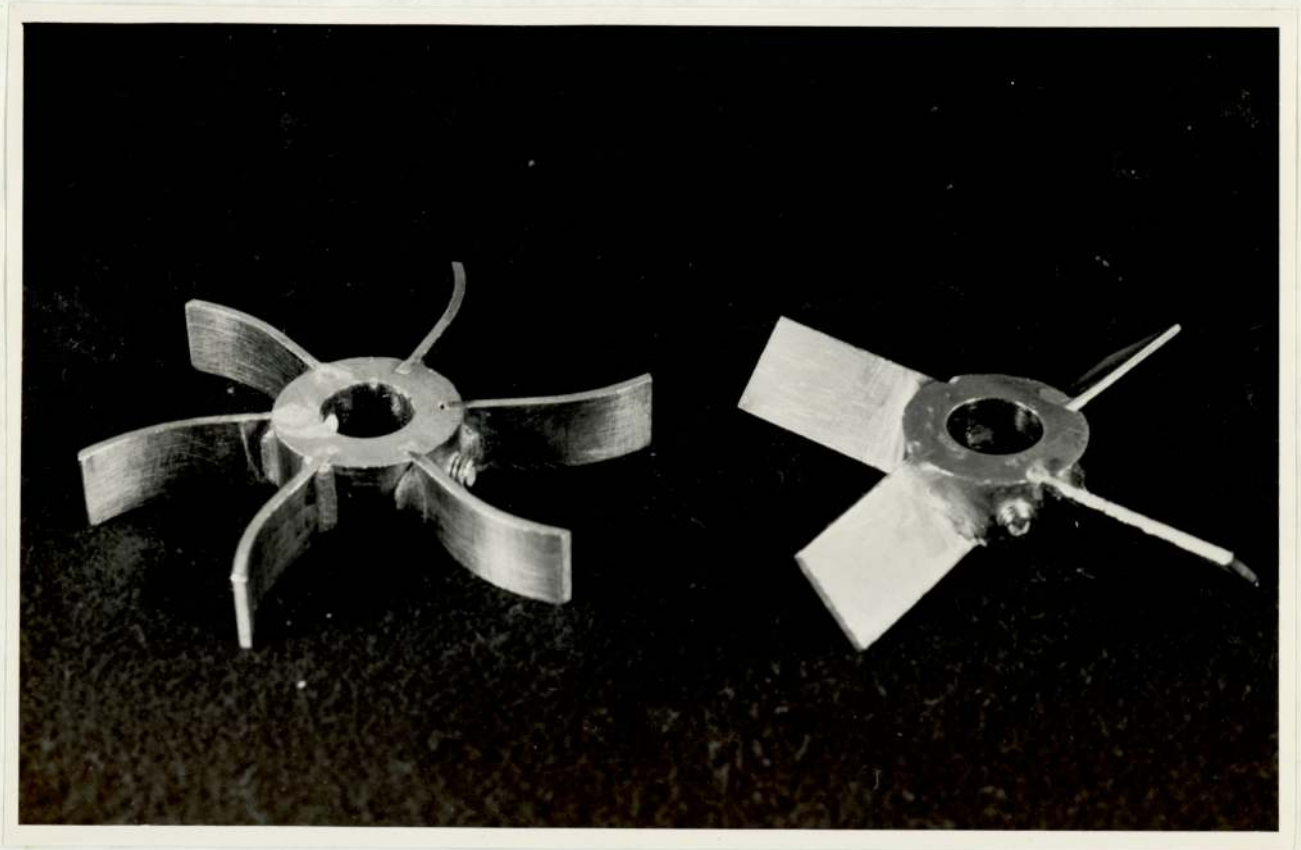
The reactor used in this work was designed and equipped by Merry(17) of this department. The reactor system is shown in figure 3.2.



As shown in the photograph, the main body of the reactor was a cylindrical stainless steel vessel with a dished bottom. It was of 152 mm bore and had a wall thickness of 6.5 mm. The vessel was secured to its lid by means of a flange which was again made of stainless steel. The lid of this reactor was constructed from a mild steel flange lined with a sheet of stainless steel to ensure that the contents of the vessel contacted only with the stainless steel. The lid was secured to the vessel with eight 3/4 inch mild steel bolts. The lid,also carried the charge line, purge line,sample line overpressure vent line, safety valve and bearing. The maximum working pressure of the reactor was 10 bar. In order to allow temperature control, the reactor was fitted with a jacket through which water as the heat exchange medium was circulated. The temperature of the circulating water was controlled by a Churchill Captain unit, which has both a heating and cooling facility. The impeller for emulsion polymerisation was a six-bladed turbine type of 75mm. diameter as shown in Fig2.3 and a combination of impellers of 75 mm diameter for suspension polymerization as is shown in Figure 3.3. The combined impeller consisted of a 4-bladed inclined turbine and a 6-bladed swept-back turbine mounted on the same shaft, the inclined turbine being mounted 96 mm above the swept-back. They are shown in Figure 3.4.

Figure 3.3 Turbine type impeller for emulsion polymerization


< 5cm.>



(a) (b)

Figure 3.4 The impellers for suspension polymerization

(a) 6-bladed back-swept turbine

(b) 4-bladed inclined turbine

Figure 3.5. The Baffle

Another possible adaption to the reactor were the stainless steel baffles which consisted of eight vanes running parallel to the axis of the vessel and located at 45° intervals along the vessel wall. Each of the vanes had a width of 20 mm. The baffle is shown in Figure 3.5.

3.2 Emulsion Polymerization Experiments

Prior to a polymerization run, the reactor vessel and all the accessories in the reactor were thoroughly cleaned. The cleaning involved scouring with an abrasive cloth or brushing with a wire brush, then washing thoroughly with a 1% solution of sodium lauryl sulphate and distilled water and finally rinsing with redistilled water.

The required volumes of redistilled water and styrene were measured using a graduated cylinder and the required masses of sodium lauryl sulphate and potassium persulphate were weighed accurately. The emulsifier and the initiator were then dissolved in the water and both this solution and the styrene were charged into the reactor. The vessel was then firmly bolted to its lid. To exclude the oxygen from the reactor, the contents of the reactor were purged 5 times with nitrogen by successively pressuring the reactor to approximately 3 bar and then venting to atmosphere. On the fifth venting, the pressure was dropped down to about 1.5 bar, the operating pressure.

After purging, the temperature at which the reaction was to be performed was selected on the Churchill Captain unit. Then stirring was started and heating began. When the reaction temperature was reached, timing was started. The samples for analysis were drawn off through the dip pipe the end of which was located in the middle position of the emulsion depth in the reactor. The interval between sampling was arranged to be 15 or 20 minutes depending on the run. The reaction continued until the monomer conversion was greater than 90%.

3.3 Suspension Polymerization Experiments

The reactor cleaning operation for suspension polymerization was the same as that for emulsion polymerization as detailed above.

After cleaning and bolting the vessel to the lid, the required volume of redistilled water and styrene were measured using a graduated cylinder and the required amount of polyvinyl alcohol as stabilizer and β,β'-azobisiobutyronitrile as initiator were weighed accurately. Then the stabilizer was dissolved into the water by heating and stirring while the initiator was dissolved into the styrene.

These two solutions were then charged into the reactor. The process of purging with nitrogen was the same as that for emulsion polymerization.

After purging, stirring and heating were started When the reaction temperature was reached timing was started. The samples for analysis were drawn off through the dip pipe. The intervals between sampling were arranged to be 30 minutes.

3.4 Dispersion Tests

After cleaning according to an identical procedure as above the vessel was secured to its lid. The defined volumes of distilled water and styrene were measured using a graduated cylinder such that the phase ratio of water to monomer was the same as in the emulsion polymerizations. The required mass of sodium lauryl sulphate was weighed accurately, this was then dissolved in water, thereafter both this solution and the styrene were charged into the reactor. Each batch used in the dispersion tests was subjected to five impeller speeds of 450, 550, 650, 750 and 850 r.p.m. The procedure was to start at 450 r.p.m. and to stir at this speed for one hour and then to increase to the next speed. A sample for analysis was withdrawn at the end of each hour long interval and these were analysed immediately after withdrawal. The method of analysis is described in Section 4.

SECTION IV

ANALYTICAL TECHNIQUES

4.1 Droplet size analysis

4.1.1 Photomicrographic technique

4.1.2 The Coulter Counter

4.1.3 Comparison between Photomicrographic Method and Coulter Counter Method

4.2 Determination of degree of monomer conversion

4.2.1 Precipitation with methanol

4.2.2 Precipitation with aluminium chloride

4.2.3 Direct drying

4.2.4 Comparison of Techniques

4.3 Development of the technique for the measurement of particle size using light transmission

4.3.1 General description

4.3.2 Setting up the technique for measuring particle size in an emulsion latex

4.3.3 Determination of particle size using extinction method.

In this section, the methods of both droplet size analysis and the determination of monomer conversions are introduced and the technique of the measurement of very small particle sizes is developed.

4.1 Droplet Size Analysis

Two methods of droplet size analysis, namely a photomicrographic technique and the Coulter Counter method, were employed in this study. They are described briefly below.

4.1.1 Photomicrographic

In this technique, photographs of the dispersion were taken though a microscope. The numbers of droplet images within the different size intervals on the photographs were counted. Thus the distribution and the Sauter mean droplet diameter could be calculated.

The photographs of monomer droplets using the microscope were obtained using the following procedure. Firstly, the latex sample was diluted. The bottle containing the latex sample was shaken gently, two drops of the sample were extracted from the middle position of the depth of the contents in the bottle into the syringe and then 4cc of redistilled water was also taken into the syringe. The syringe was shaken gently to mix the contents. A slide for holding the sample was made up of two glass plates and two small spacers of perspex sheet having a thickness of about 0.1mm. These two

spacers were put between the two glass plates to make a narrow slit, as is shown in Figure 4.1.

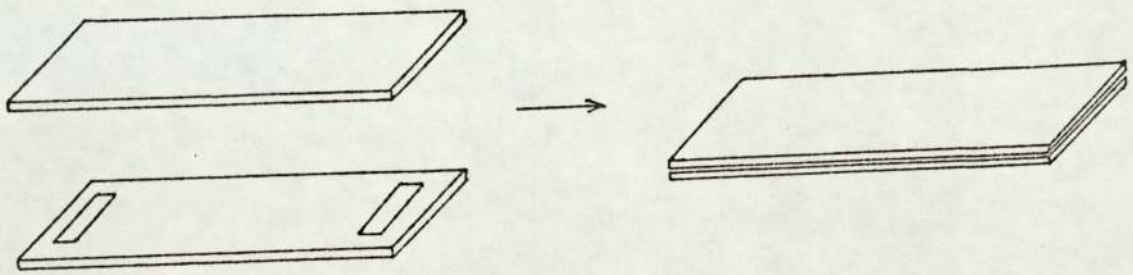


Figure 4.1 The Slide

The dilute sample in the syringe was injected slowly into the slit. It was found that in this way the droplets could be evenly distributed across the slide between the two glass plates, without observing swarming of the drops and without fear of evaporation.

The slide was placed under the microscope, three to five photographs of different parts of the slide were taken using a Miranda Sensorex 30 mm still camera. The microscope is shown in Figure 4.2 and a typical photograph of monomer droplets taken through the microscope is shown in Figure 4.3.

4.1.2 The Coulter Counter

The Coulter Counter is a widely used piece of equipment for the analysis of particle sizes of solid materials in the size range 2 to 300 micron but it is also used in the analysis of liquid droplets in dispersion. Figures 4.4 and 4.6 show the equipment

Figure 4.2 The Microscope

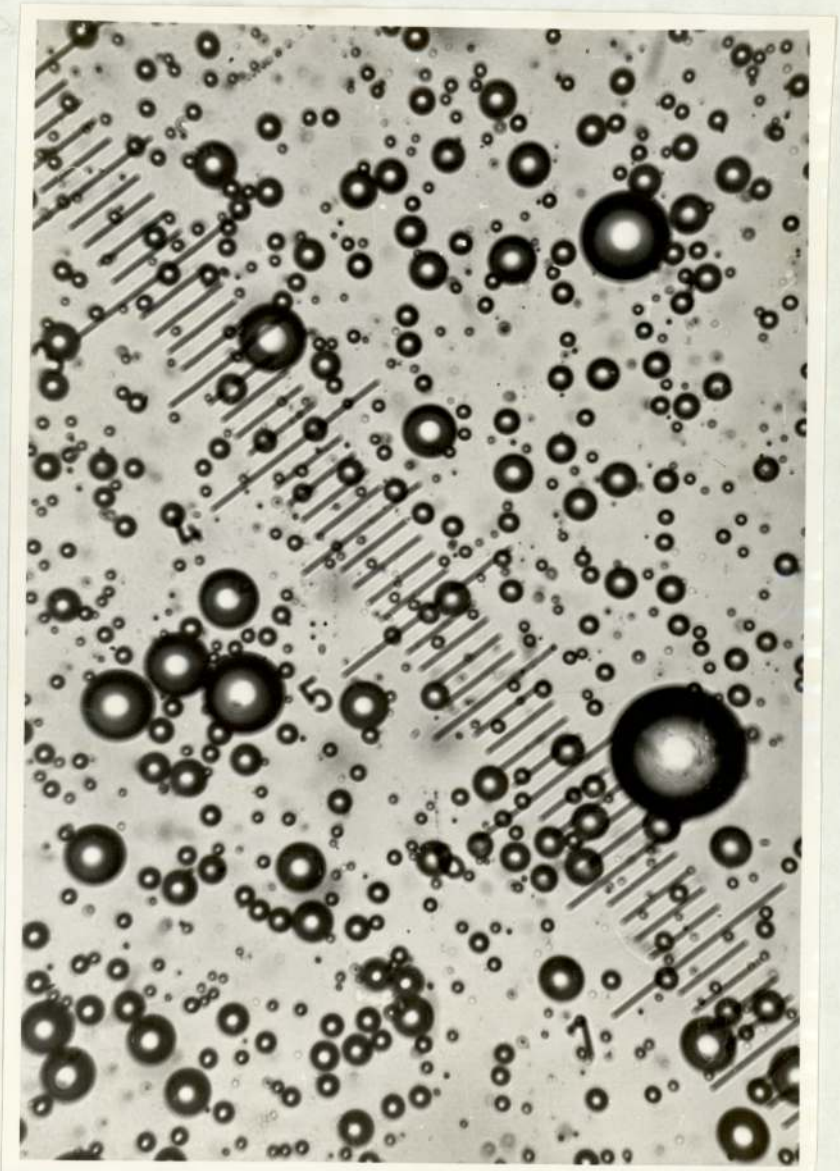


Figure 4.3 Droplets in the dispersion x 635

and Figure 4.5 shows a simplified diagram of the Coulter Counter cell. As is seen in these figures, an orifice tube (B) which is filled with the electrolyte solution in water is immersed into the same electrolyte solution in a cup (A) containing the particles or droplets. The only contact between the electrolyte solution volumes inside and outside of the tube is through an orifice of known diameter in the wall of the tube. On the horizontal section of the mercury manometers (D), two electrodes are installed. The volume of the tube between the two electrodes is fixed and known. Thus the volume of the electrolyte solution passing through the orifice in a given time may be determined. If the electric circuit is connected, then an electric current will pass between the two electrodes (C), one inside the tube and another outside the tube both placed near to the orifice. The electrolyte solution will flow through the orifice by virtue of the pressure between the outside of the tube and the inside of the tube. When the droplets dispersed in the electrolyte solution pass through the orifice the area for current to flow is reduced and thus the resistance between the electrodes changes.

The electrical signal resulting from the resistance fluctuations is fed into the analysis section of the Coulter Counter where it is decoded. A threshold setting is manually selected which relates to a certain particle size. After successively monitoring the whole range of particle sizes, the droplet size distribution and average droplet size may be obtained.

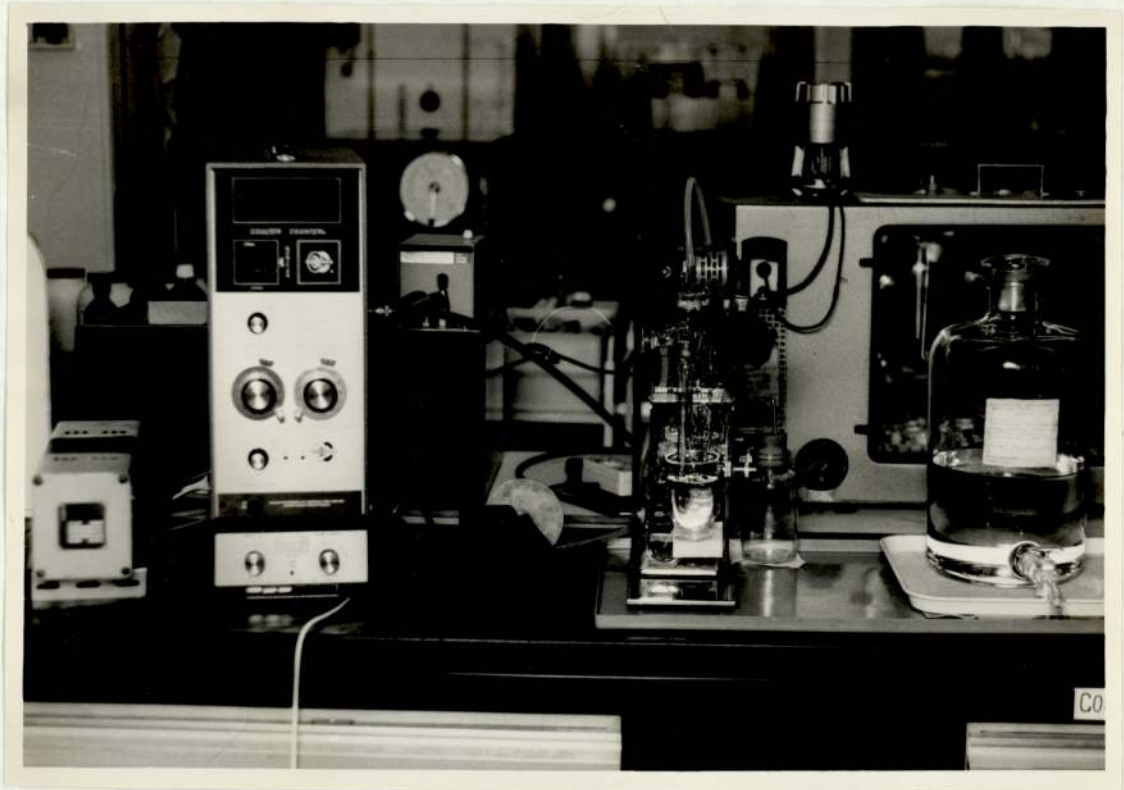


Figure 4.4 The Coulter Counter

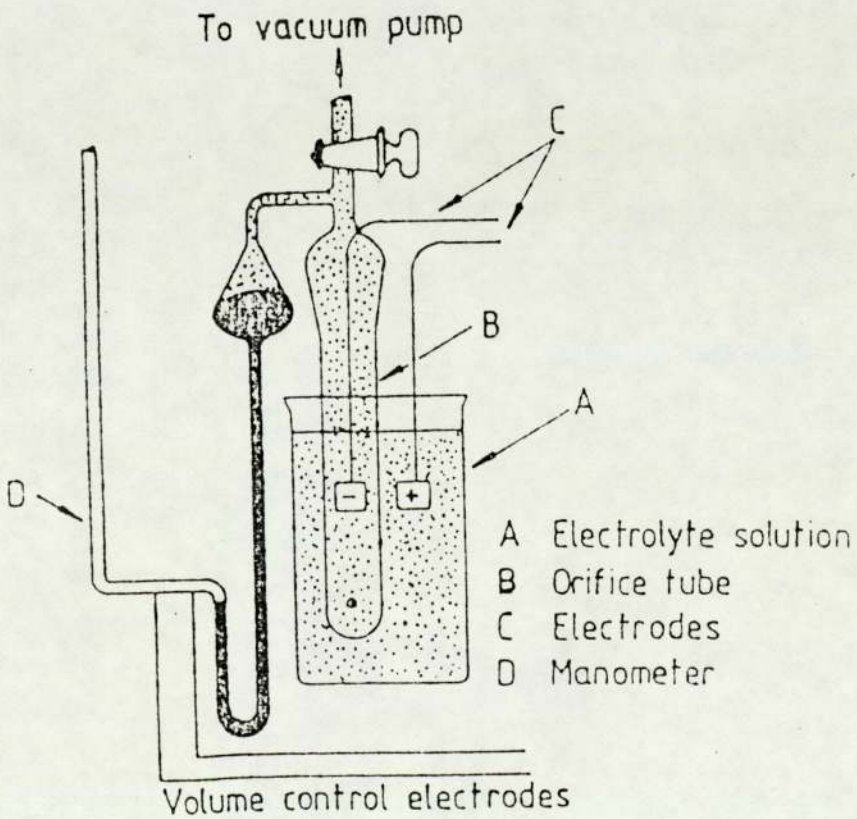


Figure 4.5 Test Cell of Coulter Counter

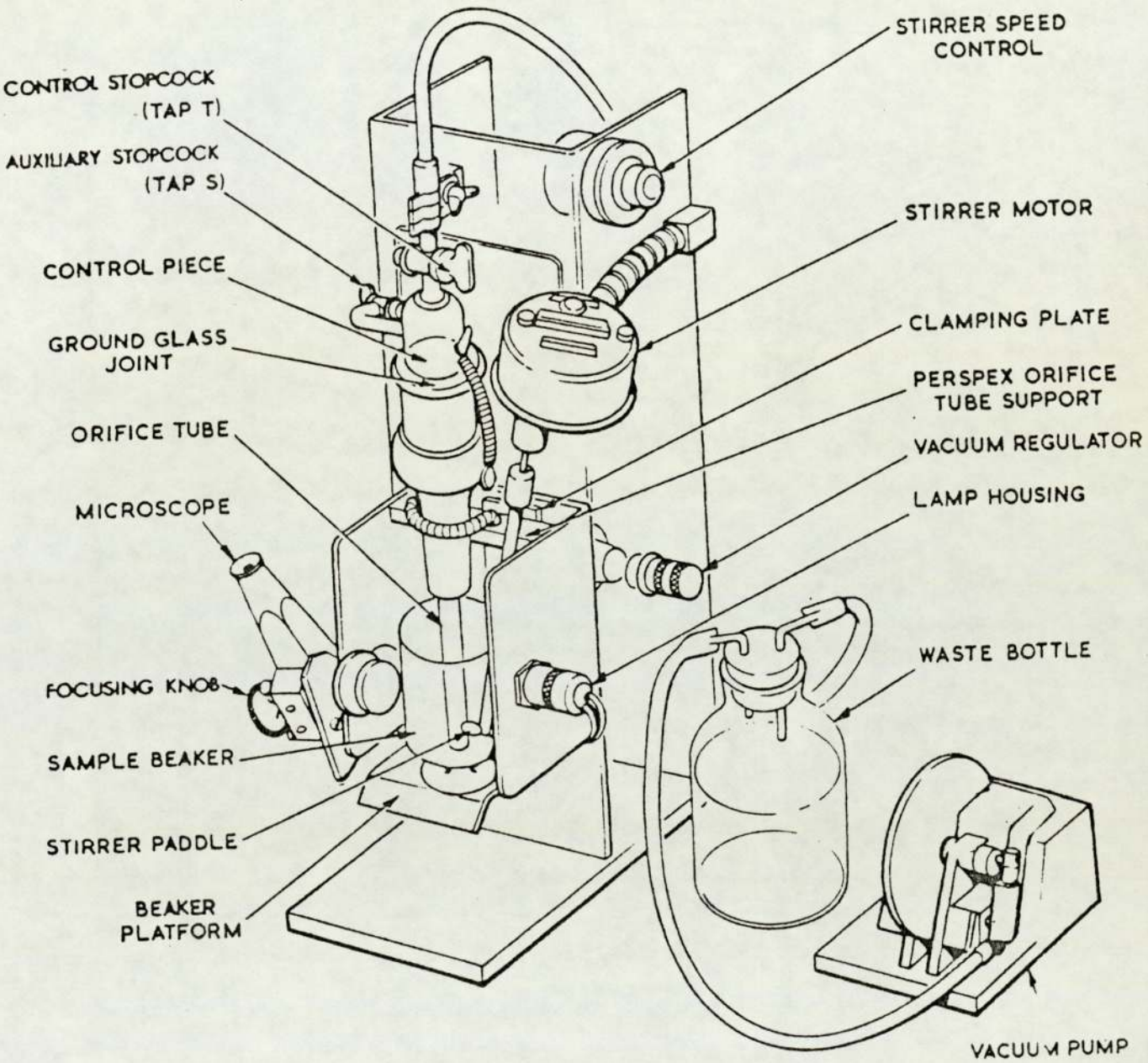


Figure 4.6 Glassware and Stand Assembly of Coulter Counter

The simplified procedure for operation of this equipment is briefly introduced below.

Prior to using the Coulter Counter for measuring the droplet size, the following preparation work should be done.

(i) Make up 0.9% of sodium chloride solution in water and filter it by passing through a 0.8 micron membrane twice.

(ii) Because the droplet sizes in the system treated in this work are less than 56 micron and the manometer volume of 2 ml is used, the tube with 140 micron orifice diameter should be selected.

After preparation, a control test is needed in order to obtain the background counts on the filtered electrolyte. Then a calibration is performed using smooth particles of known density monosized particles to obtain the calibration constant K. Finally the suspension of the samples in the filtered electrolyte solution are analysed. The whole range of the droplet diameters is divided into 16 intervals by changing the lower threshold dial setting, t_L the upper threshold dial setting, t_U aperture current setting, I, and the reciprocal amplification, A. For each interval, the number of droplets is counted and displayed on the oscilloscope of the Coulter Counter numerically, the average diameter of the droplets, D_d, is calculated using the following equation:

CONVERSION CHART

TECHNIQUE - SINGLE THRESHOLD

Sample - Polystysene | Source - | Electrolyte - NaCl | Dispersant - | Date - 14/2/81

Aperture - 100 μm Diameter | Manometer - 2ml Volume | Calibration - 2.1121 Factor, K | Matching - Switch | Operator - Cao

Aperture - Resistance | Gain - Control | Coincidence - 0.625 Factor, P | Calibration - 1.85 μm Data

t_L	I	A	n' (raw counts)				$\bar{n}'$	$n''=P(\frac{\bar{n}'}{1000})^2$	B	$n=\bar{n}'+n''-B$	$V=t_L.I.A$	$d_L=K\sqrt[3]{\bar{V}}$	Δn	$\bar{v}$	$\Delta n.\bar{v}$	$\Sigma(\Delta n)^{\bar{v}}$	Wt%
20	8	64	1,0	1,0	0,0	0	0.29	0	0	0.29	10240	45.9	0.15	5120	768	768	2.51
20	8	32	3,2	1,2	3,2	1	2	0	0	2	5120	36.4	1.7	7680	13056	13824	45.15
20	8	16	7,3	6,4	2,4	2	4	0	0	4	2560	28.9	2.0	3840	7680	21504	70.24
20	8	8	2,5	2,2	2,4	1	2.6	0	1	1.6	1280	22.9	0	1920	0	21504	70.24
20	8	4	6,2	3,4	6,1	3	3.6	0	1	2.6	640	18.2	1.0	960	960	22464	73.37
20	8	2	4,10	4,3	3,3	3	4.3	0	2	2.3	320	14.4	0	480	0	22464	73.37
20	4	2	11,10	7,11	9,10	11	10.0	0	3	7.0	160	11.5	4.7	240	1128	23592	77.06
20	2	2	18,15	23,21	18,12		14.3	0	6	8.3	80	9.1	1.3	120	156	23748	77.56
20	1	2	20,21	19,21	26,29		22.7	0	9	13.7	40	7.2	5.4	60	324	24072	78.62
20	1	1	49,64	44.52	67.48		54	0	12	41.0	20	5.7	27.3	30	819	24891	81.30
20	1	1/2	135,145	145,130			138.8	0	25	133.8	10	4.6	72.8	15	1092	25983	84.86
20	1	1/4	335,326	293,292			311.5	0	55	246.5	5	3.6	132.7	7.5	995	26978	88.11
20	1/2	1/4	586,659	628,629			625.5	0	119	506.5	2.5	2.9	260	3.75	975	27953	91.30
20	0.354	1/4	943,959	976,1013			972.8	1	178	795.8	1.725	2.5	289	2.11	610	28563	93.29
20	0.354	1/8	1419	1403			1411	1	282	1130.0	0.863	2.0	334	1.29	431	28994	94.70
20	1/4	1/8	2155	2162			21585	3	497	1682.5	0.625	1.8	553	0.744	411	29405	96.19
20	0.171	1/8	3253	3088			31705	6	824	2352.5	0.443	1.6	670	0.534	358	29763	97.21
20	1/8	1/8	7291	7892			75915	36	3015	4612.5	0.313	1.4	2260	0.378	854	30617	100.00

$$D_d = K(t_L IA)^{1/3} \qquad (4\text{-}1)$$

Therefore the droplet size distribution and the average droplet diameters can be obtained. A sample table illustrating the treatment of the data is shown in Table 4.1.

4.1.3 Comparison between the Photomicrographic Methodand the Coulter Counter Method

Compared with the photomicrographic method, the technique using the Coulter Counter is rapid and convenient, but it was found from experiment that the data obtained showed considerable scatter and the reproducibility was rather low for determining the droplet sizes of styrene. This is suggested to be because the droplets suspended in the electrolyte solution are not stable, some of the droplets coalesce together and the styrene can evaporate during the analysis for greater accuracy, although the photomicrographic technique is time- consuming and tedious, it was used for most of the dispersion tests in this study.

4.2 Determination of Monomer Conversion

Monomer conversion is one of the most important parameters for emulsion polymerization studies. In this work, it was measured using the following procedure.

At timed intervals from zero time (15 or 20 minute intervals) the samples were taken from the reactor and each of the samples was put into a bottle of known

weight. The bottle containing the sample was weighed. According to the weight of the sample in the bottle, a definite amount of inhibitor, namely benzoquinone, was added to the bottle to give a concentration of 0.5% in the sample. The role of benzoquinone is to prevent further polymerization of the unreacted monomer. In this work, the monomer conversion was determined by using three methods which are briefly described below.

4.2.1. Precipitation with Methanol

For each of the samples, a certain amount (3-5 gram) was taken from the bottle containing the stopped sample mentioned above. The polymer was precipitated by adding it to a bottle containing about 50 ml of methyl alcohol. The precipitate was then filtered on a weighed sintered glass filter. The precipitate was washed in turn with methanol and hot water five times then finally with methanol. The precipitate was then dried to constant weight. From the weight of the dried precipitate the weight of sample and the recipe of the run of the polymerisation, the fractional conversion based on styrene could be calculated.

4.2.2 Precipitation with Aluminium Chloride

For each of the samples a certain amount was taken (3-5 gram) from the bottle containing the stopped sample mentioned above. The bottle was placed in an ice bath to cool it for fifteen minutes. 5 ml of cool hexane was added and was shaken gently. The mixture was then diluted 6o times with cooled distilled water.

Ten drops of 27% w/w aluminium chloride solution in water was then added to the dilute sample in order to precipitate the polymer. The precipitate was filtered on a weighed sintered glass filter. The precipitate was washed with hot water five times. The precipitate was then dried to constant weight. From the weight of the dried precipitate, the weight of the sample and the recipe of the run of the polymerization the fractional monomer conversion could be calculated.

4.2.3 Direct Drying

For each of the samples, a certain amount was taken (0.5-1.0 gram) from the bottle containing the sample and it was put onto an aluminium plate of known weight which was heated for half an hour prior to use. The plate was then placed in an oven to dry at 70^{o}C overnight to constant weight. From the weight of the remains on the plate, the content of the inhibitor, the weight of the sample and the recipe of the run of the polymerization the fractional monomer conversion could be calculated.

4.2.4 Comparison of Techniques

The results from the technique using the precipitation with methanol seem to be more accurate than the other methods, but it is too time-consuming and wastes a large amount of methanol. The technique using the precipitation with aluminium chloride solution is economical in regard to the use of the solvent and can deliver reasonable results, but it is also time-consuming and the precipitate tends to agglomerate so that it is hard to dry if the

extraction of styrene with hexane is not complete. The technique of direct drying gives the most acceptable results. A major advantage of this method is that it is very convenient and it needs no organic solvent. So in this work, the latter technique was used for most of the test runs of both emulsion polymerization and suspension polymerization.

4.3 Development of the Technique for the Measurement of Particle Size Using Light Transmission

4.3.1 General Description

An important characteristic of a latex is its particle size. In emulsion polymerization, the reaction rate, molecular weight of polymer and its distribution and the polymer properties all relate to the particle size and the number of particles. The light transmission technique is one of the methods available for measuring these parameters. This technique is based on the dependence of the turbidity of a dilute latex upon the particle size and upon the other parameters. Many previous workers have devoted themselves to the development of the light transmission technique to measure the size of colloidal particles (56-58). Of more direct use to the measurement of polystyrene latex is the light transmission method developed by Bateman et al. (20). Unfortunately, Bateman's method is only valid for the case where the diameter of the particles is greater than 0.2 micron. The latex produced by emulsion polymerization, however, contains very small particles with an average

diameter much smaller than 0.2 micron, particularly in the early stages of the reaction. Merry (17) extended Bateman's measurement range to a smaller diameter range using an interpolation method. The data he obtained seems to be reasonable in the region of particle diameters greater than 0.14 micron, but it results in a significant error if the particle size is smaller than 0.14 micron.

In the current project, a light transmission technique for measuring particle sizes whose diameters are even smaller than 0.1 micron has been developed and the results obtained are compared with those determined by electron microscopy.

4.3.2 Setting up the Technique for Measuring Particle Size in Emulsion Latex.

According to Mie's theory, the total Mie scattering coefficient, K can be evaluated using the following equation.

$$K = \frac{2.303\ E}{\pi r_p^{\,2} N_p l} \qquad (4\text{-}2)$$

where E = light extinction, $E = \ln I/I_o$

I_o = incident light intensity

I = transmitted light intensity

r_p = average radius of particles, em

l = Length of scattering cell, cm

Np = number of particles per cm^3

If the mass concentration of the particles is denoted by C, g/cm^3, then - $C = Np\ \frac{4}{3}\pi r_p^3 D_{sw}$. So

$$K = \frac{3.0707 E r_p d_{sw}}{Cl} \qquad (4\text{-}3)$$

where d_{sw} = the density of particles, g/cm^3

On the other hand, α is defined as size parameter.

$$\alpha = \frac{2\pi n r_p}{\lambda_0} \qquad (4\text{-}4)$$

where λ_0 = wavelength of the incident light in the air, cm.

n = refractive index, which is given by the equation as follows:

$$n = a + b/\lambda_0^2 \qquad (4\text{-}5)$$

a and b are constants, a = 1.3240, b = 3.040×10^{-11} for water (59) and a = 1.5683, b = 10.087×10^{-11} for polystryene (60).

From equation (4-3) and 4-4) the following formula can be obtained.

$$\frac{K}{\alpha} = \frac{0.4887\ d_{sw} E \lambda_0}{ncl} \qquad (4\text{-}6)$$

In this project, several samples were used in which the particle sizes and the mass concentration of the particles were known. The values of E were measured using a Pye Unicon SP1800 ultraviolet spectrophotometer see Figure 4.6 within the wavelength range from 3700 Å to 6500Å . The values of n were determined by equation

(4-5). Therefore, the dependence of r, K and λ_0 could be found from equation (4-3), (4-4) and (4-6). The results computed from the original data are listed in Table 4-2, Table 4-3 and Table 4-4. Five formulae which represent the relationship between the parameter K/α and r_p were obtained as follows by using polynomial regression method:

$$r_{3700} = 0.04387 + 0.1751X + 0.9485X^2 - 1.3463X^3$$

$$r_{4300} = 0.04294 + 0.4171X - 1.2214X^2 + 11.1013X^3$$

$$r_{5000} = 0.04254 + 0.7329X - 5.6351X^2 + 45.2569X^3$$

$$r_{5600} = 0.04211 + 1.0947X - 13.7433X^2 + 122.572X^3$$

$$r_{6500} = 0.04218 + 1.6546X - 29.9384X^2 + 336.231X^3$$

where X stands for K/α

Table 4-2 The values of the size parameter for various particle radii and wavelengths.

r(Å)	0.046	0.055	0.0645	0.0698	0.0771	0.0821	0.0958
λ_0(Å)				α			
3700	1.0516	1.2575	1.3463	1.5960	1.6204	1.8781	2.1900
4300	0.9010	1.0774	1.1843	1.3674	1.3875	1.6091	1.8763
5000	0.7724	0.9236	1.0152	1.1722	1.1889	1.3794	1.6085
5600	0.6884	0.8231	0.9048	1.0447	1.0592	1.2293	1.4335
6500	0.6919	0.7078	0.7780	0.8983	0.9016	1.0571	1.2327

Table 4-3 - Total Mie scattering coefficients of polystyrene sphere in water for smaller particles

r(Å)	0.046	0.055	0.0645	0.0698	0.0771	0.0821	0.0958
λ_o(Å)				K			
3700	0.01634	0.05295	0.10380	0.16270	0.20540	0.24280	0.38200
4300	0.00827	0.02843	0.05820	0.09573	0.12480	0.14890	0.22970
5000	0.00451	0.01552	0.03244	0.05584	0.07538	0.09505	0.14500
5600	0.00301	0.00991	0.02103	0.03749	0.05347	0.06743	0.10390
6500	0.00169	0.00553	0.01185	0.02234	0.03010	0.04292	0.06527

Table 4-4 - The values of parameter k/α for various particle radii and the wavelengths

r(Å)	0.046	0.055	0.0645	0.0698	0.0771	0.0821	0.0958
$-\lambda_o$ (Å)				K/α			
3700	0.01553	0.04210	0.07710	0.10190	0.12680	0.12930	0.17440
4300	0.00918	0.02639	0.04910	0.07000	0.09885	0.09254	0.12240
5000	0.00584	0.01680	0.03195	0.04764	0.06340	0.06891	0.09015
5600	0.00437	0.01204	0.02324	0.03589	0.05049	0.05485	0.07248
6500	0.00286	0.00781	0.01523	0.02486	0.03306	0.04060	0.05295

Figure 4.6 Pye Unicon sp1800 ultravoilet spectrophotometer

4.3.3 Determination of Particle Size using Extinction Technique

This technique involves measuring the turbidity of a diluted latex and estimating the values of mass particle concentration, C, and the refractive index, n. Then the parameter K/α can be calculated by means of equation (4-6). The average radius of the particles in the latex can, therefore, be found according to equation (4-7). The computer programme for this calculation is shown in Appendix I. The procedure below can be followed.

4.3.3.1 Collecting Basic Data

In order to perform this calculation, the recipe for the emulsion polymerization needed to be known. Then based on the recipe the following parameters may be estimated.

$$MAXT = \frac{W_{mono} + W_{soap} + W_I}{W_{total}} \qquad (4\text{-}8)$$

$$MAXP = \frac{W_{mono}}{W_{total}} \qquad (4\text{-}9)$$

where W_{mono}, W_{soap}, and W_I denote the weight of monomer, soap and initiator charged, respectively. W_{total} stands for the total weight of the contents in the reactor, and MAXT and MAXP are the maximum theoretical solid contents and the maximum theoretical polymer content, respectively.

Another important parameter TSC, the total solid content, can be determined gravimetrically.

4.3.3.2 Diluting

Because the original latex contains so many particles, the turbidity goes beyond the scope of the spectrophotometer. Therefore it had to be diluted twice to reduce the concentration of the particles in the latex.

For the first dilution, an amount of emulsion sample in a bottle (say, about 0.5 gram) was accurately weighed. The weight of this sample is denoted by g_1. Distilled water was then added to this bottle (say 100 gram) and it was again weighed. The weight of the sample after the first dilution is called G_1. Thus the following parameters after the first dilution may be easily calculated:

$$TSC_1 = TSC \frac{g_1}{G_1} \qquad (4\text{-}10)$$

$$MAXT_1 = MAXT \frac{g_1}{G_1} \qquad (4\text{-}11)$$

$$MAXP_1 = MAXP \frac{g_1}{G_1} \qquad (4\text{-}12)$$

where TSC_1, $MAXT_1$, and $MAXP_1$ are the solid content, maximum theoretical solid content and the maximum theoretical polymer content after the first dilution.

In the second dilution, a sample of first dilution (say , about 10 gram) was weighed accurately. The weight of this sample is denoted by g_2. It was diluted again (say, till about 100gram). The weight of the second diluted latex is known as G_2. Thus, the following formulae can be used for finding the parameters after the second

dilution:

$$TSC_2 = TSC_1 \frac{g_2}{G_2} \tag{4-13}$$

$$MAXT_2 = MAXT_1 \frac{g_2}{G_2} \tag{4-14}$$

$$MAXP_2 = MAXP_1 \frac{g_2}{G_2} \tag{4-15}$$

4.3.3.3 Estimating the Mass Concentration of the Particles in the Diluted Latex

Firstly, the monomer conversion, X_p, may be found using the equation as follows:

$$X_p = \frac{MAXP - (MAXT-TSC)}{MAXP} \tag{4-16}$$

Therefore, the weight fraction of polymer in the diluted latex, FPL, can be found.

$$FPL = MAXP_2 X_p \tag{4-17}$$

The weight of polymer in the diluted latex, W_p, should be

$$W_p = G_2 \, FPL \tag{4-18}$$

and the weight of monomer in the diluted latex, W_s, should be

$$W_s = (MAXT_2 - TSC_2) \, G_2 \tag{4-19}$$

The weight of water in the diluted latex, W_A, should be

$$W_A = (1 - MAXT_2) G_2 \tag{4-20}$$

It may be imagined that the monomer would exist

both in the aqueous phase and in the particle phase according to the partition law. If W_{sA} denotes the weight of monomer in the aqueous phase and M the partition coefficient, then:

$$M = \frac{\frac{W_{sA}}{W_A}}{\frac{W_s - W_{sA}}{W_p}}$$

or $$W_{sA} = \frac{MW_A W_s}{W_p + MW_A} \qquad (4\text{-}21)$$

For a system made up of polystyrene, styrene and water, $M = 2.2393 \times 10^{-4}$.

Consequently, the weight of monomer in the particle phase, W_{sp}, can be obtained.

$$W_{sp} = W_s - W_{sA} \qquad (4\text{-}22)$$

Therefore, the mass particle concentration, C, can be written as

$$C = \frac{W_p + W_{sp}}{G_2} \qquad (4\text{-}23)$$

4.3.3.4 Finding the Density of Particles in the Diluted Latex, d'_{sW}

Because the particles are swollen by monomer, the density of the particles should have a value between the density of polymer, d_p, and the density of monomer, d_m. Thus, the following equation may be used for finding the value of d'_{sW} approximately,

$$d'_{sW} = \left(\frac{W_p}{W_p + W_{sp}}\right) d_p + \left(\frac{W_{sp}}{W_p + W_{sp}}\right) d_m \qquad (4\text{-}24)$$

4.3.3.5 Estimating the Refractive Index, n.

The value of the refractive index of water, n_A, and the refractive index of polymer, n_p, are first found using equation (4-5), under the different wavelength conditions (say, 3700Å, 4300Å, 5000Å, 5600Å, and 6500Å). Then the equation below is used to evaluate the average refractive index approximately.

$$n = Cn_p + (1-C)n_A \qquad (4\text{-}25)$$

4.3.36 Measuring the Extinction Coefficient, E.

The values of E are measured by the spectrophotometer for predetermined wavelengths. To be accurate, the zero point should be adjusted each time because zero drift affects the results.

4.3.3.7 Evaluating the Parameter K/α and the Average Radius of Particles

In accordance with the parameters computed or measured above, the values of K/α may be determined by means of equation (4-6) for the predetermined wavelengths. Then from the value of K/α obtained above, the average radius of particles for each wavelength can be obtained according to equation (4-7). If we take these radii on average, the average radius of the particles in the diluted latex is finally determined.

4.3.3.8 Correcting the Size of Particles

As is mentioned above, the monomer in the latex is partitioned between the aqueous phase and the polymer phase according to the partition law. In this case, equilibrium between the two phases is actually achieved. After diluting, the equilibrium is upset and some monomer will be transferred from the polymer phase to the aqueous phase. A new equilibrium will be achieved. Because the samples adopted for measuring the particle size here are much more dilute than the latex in the reactor, the content of the monomer in the polymer phase in the diluted sample is less than that in the reactor, in other words, the size of the particle measured in this case is smaller than the actual particle size in the reactor. So the particle size measured above should be corrected to return the particle size to that under the reaction conditions. The following equation is used for this correction:

$$D_p = D'_p \{\frac{d'_{sW}}{d_{sW}}(1 + \frac{W_{sA}}{W_p + W_{sp}})\}^{1/3} \qquad (4\text{-}26)$$

where D'_p = the average diameter of particles measured above

D_p = the average diameter of particles in the reactor

d'_{sW} = the density of the particles in the latex after the second dilution

d_{sW} = the density of the particles in the ractor

For Stage I and Stage II of emulsion polymerization,

$$d_{sW} = d_p x_{p,II\text{-}III} + d_m(1 - x_{p,II\text{-}III}) \qquad (4\text{-}27)$$

For Stage III

$$d_{sW} = d_p x_p + d_m(1-X_p) \qquad (4\text{-}28)$$

where $x_{p,II-III}$ is the monomer conversion at the end of stage II.

4.3.4 Comparison between the Results from This Technique and the Electron Microscopic Method.

This technique has extended Bateman's data to a smaller particle diameter range than Merry achieved previously (17). It seems that the technique is valid for measuring the particle diameter down to 0.09 micron. The data determined with this technique are similar to those measured using an electron microphotographic method. Some results analysed by these two techniques are compared in Table 4-5. Further evidence for the validity of this method is that the results under the various wavelengths for the same sample are quite close to each other, as shown in Table 4-6.

Sample	average particle radius, micron	
	electron microscope	light extinction
N5	0.043	0.0443
N7	0.0502	0.0450
N16	0.070	0.0633
N11	0.075	0.0701

Table 4.5. Comparison of the results from the light transmission technique with those from electron microscopy.

Table 4-6 Change in radius of particles with wavelength

Sample	N5	N7	N16	N11
λ_0 (Å)	r, micron			
3700	0.0448	0.0453	0.0650	0.0671
4300	0.0447	0.0452	0.0631	0.0676
5000	0.0444	0.0451	0.0621	0.0678
5600	0.0437	0.0450	0.0638	0.0688
6500	0.0440	0.0447	0.0629	0.0735

SECTION V

THE MATHEMATICAL MODEL

5.1 Setting up the Model for Stage I.

5.1.1 General description of the model.

5.1.2 Setting up the differential equation for particle nucleation

5.1.3 Derivation of the equation for the surface area of monomer droplets

5.1.4 Estimating the parameters of monomer droplets

5.1.5 Derivation of the equation for estimating the surface area of particles

5.1.6 Derivation of equation for estimating the volume of polymer particles

5.1.7 Derivation of the equation for estimating the fractional monomer conversion

5.1.8 Derivation of the equation for estimating the number of particles

5.2 Setting up the model for Stage II

5.3 Setting up the model for Stage III

5.1 Setting up the Model for Stage I

Since the classical work of Smith-Ewart[1] on modelling emulsion polymerization , a great number of papers have appeared which either modified the classical model or proposed new models. None of these papers considered the effect of the adsorption of emulsifier onto the surface of monomer droplets. In the normal case, the amount of this adsorbed soap may be ignored because it is relatively small compared with the total soap concentration. However, if the soap concentration is low or if the impeller speed is high enough, then the proportion of the adsorbed soap on the monomer droplet surface will be comparable with that of the micellar soap. In this case, the effect of the adsorbed soap must be taken into account.

Several workers have studied the effects of stirring on the process of emulsion polymerization. Shunmukham[2] noted that violent agitation would reduce the polymerization rate and increase the induction time. Schoot et al[3] suggested that the increase in induction time is associated with inhibition by trace oxygen in the nitrogen atmosphere used and the decrease in polymerization rate is due to increasing mass transfer between the gas and liquid phases as agitation becomes more severe. Evans et al[4], Omi et al[5] and Nomura et al[6] pointed out that, under a highly purified nitrogen atmosphere, the decrease in the rate of polymerization and in the number of polymer particles with increased agitation may be due to the fact that the micelle population is a function not only of the soap concentration, but also of the amount of soap adsorbed onto the surface of the monomer droplets, i.e. a function of the degree of dispersion which is directly dependent on the agitation.

In this project, a mathematical model for emulsion polymerization is established which takes into account the soap adsorbed on the surface of monomer droplets. The computed results are compared with experimental data.

5.1.1 General Description.

For a batch emulsion polymerization, definite amounts of water, monomer and soap are first charged into the reactor before charging the initiator. The soap charged will, in the main, dissolve in the water. The limiting concentration of soap up to which value the soap is in solution as single free molecules at a given reaction temperature is known as the critical micelle concentration, $[S]_{cmc}$, and any soap added above this value goes into solution but forms into aggregates known as micelles which play a significant part in the mechanism of emulsion polymerization. A proportion of the initial soap will of course be adsorbed onto the surface of the monomer droplets. The proportions of the soap distributed amongst these various forms may be easily computed. If S stands for the total area provided by soap, [S] the initial soap concentration, A_d^o the initial surface area of monomer droplets, A_m^o the initial area of micelles and A_s the surface area occupied by one soap molecule, then

$$S = ([S]-[S]_{cmc})\, N_A A_S \tag{5.1}$$

$$A_m^o = S - A_d^o \tag{5.2}$$

As the degree of dispersion increases it is clear that as A_d^o becomes larger, then A_m^o becomes proportionately smaller for a definite total amount of soap.

When the initiator is charged and the contents of the reactor reach the reaction temperature, the initiator starts to dissociate into radicals

and the reaction begins after a short induction period. The rate of radical generation, R, may be calculated from the following equation

$$R = 2k_i f[I]N_A \qquad (5.3)$$

where k_i = the decomposition rate constant of initiator.

f = the efficiency of initiator decomposition.

[I] = the initial initiator concentration.

The classical mechanism for emulsion polymerization[21,23] assumes that the soap micelles, which have the ability to solubilise monomer by concentrating it in solution at their centres, are the loci for the initiation and polymerization. A radical is assumed to migrate into the centre of a micelle and to initiate polymerization there. As polymerization proceeds, the micelle becomes a monomer swollen polymer particle. More monomer migrates from the droplets to the particle to sustain the reaction. As more and more particles are formed and increase in size, more soap is adsorbed onto the particle surface, thus depleting the number of micelles. When the micellar soap is completely depleted, generally speaking, particle nucleation stops. At this point, the final number of particles is fixed. The period from the beginning of the reaction to micelle depletion is often referred to as Stage I. In this period, if the surface area of particles is denoted by A_p and the area of micelles by A_m at a given time, then

$$A_m = S - A_p - A_d \qquad (5.4)$$

After Stage I, the reaction proceeds into Stage II, during which the soap can be found in three loci, namely, free soap in solution, the soap on the surface of particles and that on the surface of monomer droplets. As polymerization proceeds, the particle size will become larger, whilst

that of the monomer droplets becomes smaller and smaller. So some soap will be set free from the droplets and move to the polymer particle surface. When the monomer droplets disappear, Stage II finishes and enters into Stage III.

In Stage III, because of the disappearance of micelles and monomer droplets, the soap is present either in free solution at a concentration at or below $[S]_{cmc}$ or is adsorbed onto the surface of the polymer particles which are thus rendered stable.

5.1.2 Setting up the Differential Equation for Particle Nucleation.

Gardon[28] recalculated and extended successfully the Smith-Ewart model for emulsion polymerization by using a different mathematical approach. Neither Smith and Ewart nor Gardon considered the effect of both the critical micellar soap and the soap adsorbed on monomer droplet surface on the progress of the reaction. In the present paper, a mathematical model is set up using the same mathematical method as Gardon with the critical micellar soap and the soap adsorbed on the monomer droplet surface being allowed for.

Suppose during Stage I, the process of emulsion polymerization proceeds from time o to time t. To derive the differential equation, we may subdivide the time t into m very small intervals, 1, 2, 3, . . . , i-1, i, i+1, . . . , m-1, m. At the beginning of the subinterval i, the time is τ and at the end of it, the time is $(\tau+d\tau)$. If $N_p(\tau)$ denotes the number of particles which have been nucleated during period from time o to time τ, $A_p(\tau)$ the surface area of polymer particles at time τ and $A_d(\tau)$ the surface area of monomer droplets at time τ, then the differential equation of particle nucleation can be set up as

follows :

$$\frac{dN_p(\tau)}{d\tau} = \frac{R}{s}\,[s-A_p(\tau)-A_d(\tau)] \qquad (5.5)$$

5.1.3 Derivation of the Equation for the Surface Area of Monomer Droplets.

Two simplifying assumptions are adopted for this purpose:

(1) The Sauter Mean diameter of monomer droplets is taken for calculating their surface area at any given moment.

$$\overline{ds} = \frac{\Sigma n_i d_i^3}{\Sigma n_i d_i^2} \qquad (5.6)$$

(2) The number of monomer droplets, N_d, remains constant throughout Stage I and Stage II.

Based on these assumptions and defining V_d^o as the initial volume of monomer droplets per cc of water, $r_d(\tau)$ as the radius of monomer droplets at time τ, $V_p(\tau)$ as the volume of particles per cc of water at time τ, d_{sw} as the density of particles swollen by monomer and d_m as the density of monomer, the mass balance over the monomer at time τ can be expressed as

$$V_d^o d_m = \frac{4\pi}{3}(r_d(\tau))^3 N_d d_m + V_p(\tau) d_{sw} \qquad (5.7)$$

$$r_d(\tau) = \left(\frac{3}{4\pi N_d}\right)^{1/3}\left(V_d^o - \frac{d_{sw}}{d_m}V_p(\tau)\right)^{1/3}$$

$$A_d(\tau) = 4\pi(r_d(\tau))^2 N_d =$$

$$[3(4\pi N_d)^{1/2}\, V_d^o - 3(4\pi N_d)^{1/2}\frac{d_{sw}}{d_m}V_p(\tau)]^{2/3}$$

Let $B_2 = 3(4\pi N_d)^{1/2}\, V_d^o$

$$B_3 = 3(4\pi N_d)^{1/2}(d_{sw}/d_m)$$

So $A_d(\tau) = (B_2 - B_3 V_p(\tau))^{2/3}$ (5.8)

Substituting equation(5.8) into equation (5.5), we obtain:

$$\frac{dN_p(\tau)}{d\tau} = \frac{R}{S}\{s - A_p(\tau) - (B_2 - B_3 V_p(\tau))^{2/3}\} \quad (5.9)$$

5.1.4 Estimating the Parameters of Monomer Droplets.

If A_d^o and D_d^o are the initial surface area per cubic centimeter of water and the initial Sauter diameter of monomer droplets, respectively, then

$$A_d^o = 6V_d^o/D_d^o \quad (5.10)$$

$$N_d = (6/\pi)\{V_d^o/(D_d^o)^3\} \quad (5.11)$$

The initial volume of monomer droplets, V_d^o, can be obtained from the initial charge. The initial droplet diameter, D_d^o, can be calculated by using Merry's emprical formula (17) for an unbaffled reactor:

$$D_d^o = D_d^i (N/N_i)^{-1.08}(H/H_i)^{-0.185} \quad (5.12)$$

where N and H are the impeller speed and impeller diameter used in the experiment, respectively, and N_i and H_i are the impeller speed and impeller diameter used in the dispersion test, respectively. D_d^i is the Sauter mean diameter of monomer droplets which had been measured by use of a Coulter Counter in the dispersion test.

Use of this formula assumes linearity between Sauter mean droplet diameter and the term $N^{1.08}\ N^{0.185}$ for the system under study. Preliminary dispersion tests in the presence of sodium lauryl sulphate in concentrations in excess of the c.m.c. were seen to display such linearity.

For a baffled reactor, the empirical formula, the derivation for which is presented in Section VI, can be used.

$$D_d^o = 2.42 S_o^{0.013} N^{-1.86} \quad (5.13)$$

Where S_o is the total soap concentration gram /dm^3 of water.

5.1.5 Derivation of the Equation for Estimating the Surface Area of Particles.

Firstly, it is necessary to find the relationship between the time and the radius of the particles. For a single growing particle, the rate of volume increase can be described by the following equation:

$$\frac{4\pi}{3}\frac{dr_p^3}{dt} = \frac{K_p}{N_A}\frac{d_m}{d_p}\frac{\phi_m}{1-\phi_m}$$

where K_p is the rate constant for polymer propagation

d_p is the density of the polymer

ϕ_m is the monomer volume fraction in the particles.

$$\text{Let} \quad K = \frac{3}{4\pi} \cdot \frac{K_p}{N_A} \cdot \frac{d_m}{d_p} \cdot \frac{\phi_m}{1-\phi_m} \tag{5.14}$$

$$\text{So} \quad \frac{dr_p^3}{dt} = K \tag{5.15}$$

If this particle is formed at time τ , then r_p=o at time τ and $r_p = r_p$ at time t. Hence, the following integration can be obtained.

$$\int_o^{r_p^3} dr_p^3 = K \int_\tau^t dt$$

$$r_p^3 = K(t-\tau) \tag{5.16}$$

$$r_p^2 = K^{2/3}(t-\tau)^{2/3} \tag{5.17}$$

Where $(t-\tau)$ is the lifetime of the growing particle from its generation to time t.

The number of polymer particles which are formed during the interval from τ to $(\tau+d\tau)$ is denoted by $dN_p(\tau)$. Each of these particles at time t will be of the radius of r_p and surface area of $4\pi r_p^2 = 4\pi K^{2/3}(t-\tau)^{2/3}$. So at time t, the surface area of all the particles which have been formed in the interval from τ to $(\tau+d\tau)$ in one cc of water can be written as:

$$dA_p(t) = 4\pi K^{2/3}(t-\tau)^{2/3}dN_p(\tau) \tag{5.18}$$

where the $dA_p(t)$ is the increment of total surface area of the particles per cc of water at time t owing to the nucleation of $dN_p(\tau)$ particles from time τ to $(\tau+d\tau)$.

Based on equation (5.9) and (5.18), we obtain:

$$dA_p(t) = 4\pi K^{2/3}\frac{R}{S}(t-\tau)^{2/3}[S-A_p(\tau)-(B_2-B_3V_p(\tau))^{2/3}]d\tau \tag{5.19}$$

Let $B_1=4\pi K^{2/3}(R/S)$ and integrate equation (5.19) over the range from time $\tau=o$ to $\tau=t$, we obtain

$$A_p(t) = B_1\int_o^t(t-\tau)^{2/3}[S-A_p(\tau)-(B_2-B_3V_p(\tau))^{2/3}]d\tau \tag{5.20}$$

According to Simpson's rule

$$F(a) - F(b) = \int_b^a f(x)dx = \frac{a-b}{6}\left[f(a)+ 4f\left(\frac{a+b}{2}\right) + f(b)\right] \tag{5.21}$$

To use equation 5.21 to estimating equation 5.20 we set a=t, b=o, x= τ, $F(a)=A_p(t)$, $F(b)=o$, $f(x)=f(\tau)=B_1(t-\tau)^{2/3}[S-A_p(\tau)-(B_2-B_3V_p(\tau))^{2/3}]$, $f(a)=f(t)=o$, $f(b)=f(o)=B_1(S-A_d^o)t^{2/3}$, $f(\frac{a+b}{2})=$

$$f(\frac{t}{2}) = B_1[S-A_p(\frac{t}{2})-(B_2-B_3V_p(\frac{t}{2}))^{2/3}](\frac{t}{2})^{2/3}.$$

Substituting these into equations (5.21), the following formula can be obtained:

$$A_p(t) = \frac{B_1}{6}t^{5/3}[3.52S-A_d^o - 2.52A_p(\frac{t}{2})-2.52(B_2-B_3V_p(\frac{t}{2}))^{2/3}]$$

Let $B_4 = 3.52S - A_d^o$, the above equation becomes

$$A_p(t) = \frac{B_1}{6} t^{5/3}[B_4-2.52A_p(\frac{t}{2})-2.52 (B_2-B_3V_p(\frac{t}{2}))^{2/3}] \qquad (5.22)$$

When time t tends to zero, the following equation is used for calculating the surface area of polymer particles approximately.

$$A_p(t) = 0.587B_1(S-A_d^o)t^{5/3} \qquad (5.23)$$

5.1.6 Derivation of Equation for Estimating the Volume of Polymer Particles.

For one single particle generated at time τ, in terms of equation (5.16), the volume at time t should be $(4\pi/3)r_p^3 = (4\pi/3)K(t-\tau)$.

For $dN_p(\tau)$ particles generated during the interval from τ to $(\tau+d\tau)$, the volume at time t should be

$$dV_p(t) = \frac{4\pi}{3} K(t-\tau)\, dN_p(\tau)$$

From equation (5.9), it becomes

$$dV_p(t) = \frac{4\pi}{3} K \frac{R}{S} (t-\tau)[S-A_p(\tau)-(B_2-B_3V_p(\tau))^{2/3}]d\tau \qquad (5.24)$$

Let $C_1 = (4\pi/3)K(R/s)$ and Integrate equation (5.24) over the range from $\tau=o$ to $\tau=t$, then

$$V_p(t) = C_1 \int_o^t (t-\tau)[S-A_p(\tau) - (B_2-B_3 V_p(\tau))^{2/3}]d\tau \qquad (5.25)$$

Using the same method as that mentioned above, from equation (5.21) and (5.25), the following equation can be obtained

$$V_p(t) = \frac{C_1}{6} t^2[3S-A_d^o-2A_p(\frac{t}{2})-(B_2-B_3V_p(\frac{t}{2}))^{2/3}]$$

Let $C_2 = 3S-A_d^o$, then the above equation becomes

$$V_p(t) = \frac{C_1}{6} t^2[C_2-2A_p(\frac{t}{2})-2(B_2-B_3V_p(\frac{t}{2}))^{2/3}] \qquad (5.26)$$

When the time t tends to zero, the following equation is used for calculating the particle volume, $V_p(t)$, approximately

$$V_p(t) = \frac{C_1}{2} t^2(S-A_d^o) \qquad (5.27)$$

5.1.7 Derivation of the Equation for Estimating the Fractional Monomer Conversion.

The relationship between fractional monomer conversion, $X_p(t)$, and the volume of particles per cc of water, $V_p(t)$, at a time t can be written as

$$X_p(t) = V_p(t)(1-\phi_m)\frac{d_p}{M_o} \qquad (5.28)$$

Where M_o is the amount of monomer charged initially.

Substituting equation (5.26) into equation (5.28), we get

$$X_p(t) = \frac{C_1 d_p(1-\phi_m)}{6M_o} t^2 [C_2 - 2A_p(\frac{t}{2}) - 2(B_2 - B_3 V_p(\frac{t}{2}))^{2/3}]$$

Let $D_1 = C_1 d_p(1-\phi_m)/6M_o$, then above equation becomes

$$X_p(t) = D_1 t^2 [C_2 - 2A_p(\frac{t}{2}) - 2(B_2 - B_3 V_p(\frac{t}{2}))^{2/3}] \qquad (5.29)$$

5.1.8 Derivation of the Equation for Estimating the Number of Particles

Integrating equation 5.9 over the range from time $\tau=o$ to $\tau=t$

$$N_p(t) = \frac{R}{s} \int_o^t [s - A_p(\tau) - (B_2 - B_3 V_p(\tau))^{2/3}] d\tau \qquad (5.30)$$

According to equation (5.21) and (5.30), we obtain the formula as follows

$$N_p(t) = \frac{R}{6S} t[6S - A_d^o - A_p(t) - (B_2 - B_3 V_p(t))^{2/3} - 4A_p(\frac{t}{2}) - 4(B_2 - B_3 V_p(\frac{t}{2}))^{2/3}]$$

Let $Z_1 = R/6S$ and $Z_2 = 6S - A_d^o$, then

$$N_p(t) = Z_1 t[Z_2 - A_p(t) - (B_2 - B_3 V_p(t))^{2/3} - 4A_p(\frac{t}{2}) - 4(B_2 - B_3 V_p(\frac{t}{2}))^{2/3}] \qquad (5.31)$$

5.2 Setting up the Model for Stage II.

The following equation is used for calculating the conversion rate in Stage II

$$\frac{dx_p}{dt} = \frac{K_p}{N_A} d_m N_p \phi_m I \frac{1}{M_o} \qquad (5.32)$$

where I is the average number of radicals in one particle.

In Stage II, there is good evidence that the ratio of monomer to polymer in the particle, ϕ_m, remain constant. The number of particles per cc water, N_p, also remains a constant as particle nucleation has

stopped by the end of Stage I and the value may be calculated using the model proposed above.

In the Smith-Ewart model, the average number of radicals in one particle, I, is considered equal to 1/2. This may be true if the particles are infinitely small. In that case, the diffusion path for radicals is so short that on entry of a second radical into an active particle termination is instantaneous. However, as is well known, the concentration of macromolecules is very high in the monomer swollen particles and the viscosity inside is relatively large. Consequently, the termination process is controlled by diffusion. When a radical enters into an active particle if the particle is large as in the latter half of Stage II, then the collision between two radicals is not instantaneous. In this case, two or more radicals may co-exist in the same particle for some time. As a result, the parameter I is greater than 1/2 and the larger the particles, the greater the value of I will be. In our case, we are dealing with rather low soap concentrations, thus the particle size is much larger than in the normal case and therefore we must take this 'volumetric' effect into account.

Now the question is how to find the parameter I at a given conversion. Gardon[11,12] has established a mathematical model for this purpose based on the non-steady state assumption. Here we use a similar method for solving this problem.

To simplify, an assumption of all the particles having the same size at a given time during Stage II is used.

If i denotes the number of radicals in a particle, f_i the number fraction of the particles each of which contains i radicals, $\bar{V}$ the average

volume of a particle, a the average surface area of a particle and K_o the radical desorption rate constant, thus the non-steady state population balance of particles in one cc of water can be described as follows

$$\frac{df_i}{dt} = \frac{R}{N_p}(f_{i-1}-f_i) + \frac{K_o a}{\bar{V}}[f_{i+1}(i+1)-f_i i] + \frac{K_t}{N_A \bar{V}}$$

$$[f_{i+2}(i+2)(i+1)-f_i i(i-1)] \qquad (5.33)$$

Divide equation (5.33) by equation (5.32) and let

$$G_1 = RM_o N_A/(k_p N_p{}^2 d_m \phi_m)$$

$$G_2 = (K_o/K_p)\pi^{1/3} N_A (6M_o/N_p)^{2/3}(d_p{}^{1/3}/d_m)(1-\phi_m)^{1/3}/\phi_m$$

$$G_3 = (K_t/K_p)(d_p/d_m)(1-\phi_m)/\phi_m$$

the following set of equations can be obtained

$$\frac{df_i}{dx_p} = \frac{G_1}{I}(f_{i-1}-f_i) + \frac{G_2}{X_p{}^{1/3} I}[f_{i+1}(i+1)-f_i i]$$

$$+ \frac{G_3}{X_p I}[f_{i+2}(i+2)(i+1)-f_i i(i-1)] \qquad (5.34)$$

$$\Sigma f_i = 1 \qquad (5.35)$$

$$I = \Sigma i f_i \qquad (5.36)$$

Fortunately, the ratio of polymer to monomer in particles is a constant during Stage II and thus the diffusional resistance does not change with conversion, i.e. both the termination rate constant, K_t, and the value of G_3 are conversion independent throughout Stage II. The value of Kt in Stage II should be equal to that in bulk polymerization at the same conversion as at the end of Stage II, $X_{p,I-II}$, in emulsion

polymerization. It is to be calculated using the following empirical formula which is formulated in Section VI.

$$K_t = \exp(A_1 + A_2 X_{p,II-III} + A_3 X_{p,II-III}^2 + A_4 X_{p,II-III}^3 + A_5 X_{p,II-III}^4) \quad (5.37)$$

where $X_{p,II-III}$ is the functional monomer conversion at the end of Stage II. A_1, A_2, A_3, A_4 and A_5 are constants.

K_{to} = the termination rate constant in pure styrene.

T = the absolute temperature.

Thus, a set of the simultaneous equations (5.34), (5.35) and (5.36) which consists of (i+2) equations has been set up. As we know, the duration of Stage I is rather short. Therefore, the particle size is relatively small at the end of Stage I and at this point the termination process might be considered as virtually instantaneous. Thus all of f_i in which $i \geq 2$ would be zero and the value of I tends to $\frac{1}{2}$. So we would choose the threshold between Stage I and Stage II as a starting point. In this case, the initial conditions for solving the above set of equations would be $x_p = X_{p,I-II}$, $f_o = 0.5$, $f_1 = 0.5$, $I = 0.5$, $f_2 = f_3 = f_4 = \ldots = 0$ The value of I is determined by solving this set of equations at various conversions and the relationship between t and Xp can be found using equation (5.32).

5.3 Setting up the Model for Stage III

In Stage III, it is found that the autoacceleration effect of the conversion rate becomes important. This phenomenon is known as the Trommsdoff effect or gel-effect, and is extremely significant in emulsion polymerization modelling. If it is not taken into account, a significant deviation of the predicted results from the experimental results will be encountered in Stage III of the reaction Friis et al carried out experimental emulsion and bulk polymerizations of polymethylmethacrylate (7, 9) and polyvinyl acetate (7, 10) and by using a steady state model they were able to model the gel-effect. They also compared their model with experimental data for the emulsion polymerization of styrene. The relationship which they used to relate the termination constant to monomer conversion for polystyrene was based on Hui's work (12) on the thermal polymerization of styrene in bulk which was carried out over the temperature range of 100 - 200°C. It was found, at least at 50°C, that this relationship overestimated the termination rate constant when itis used for calculating the emulsion polymerization particularly at high levels of conversion.

Gardon (13,14) developed a mathematical model based on a non-steady state assumption for Stage II. Unfortunately, it was not extended to Stage III because the relationship between the termination rate constant and the monomer concentration in the particles was not known.

In this project, the dependence of the termination rate constant upon monomer conversion has been generated using experimental suspension polymerization data (see Section VI), a non-steady state mathematical model for Stage III has been developed. When it is combined with the model developed for Stages I and II above, a mathematical model covering the whole conversion range of an emulsion polymerization is the result.

In Stage III, the ratio of monomer to polymer in the particles is no longer a constant. As polymerization proceeds, the volume fraction of monomer, $\phi(Xp)$, will increase gradually with the monomer conversion, X_p.

$$\phi(Xp) = \frac{1-X_p}{(1-X_p)+(d_m/d_p)X_p} \qquad (5-38)$$

and thus the value of K_t will also decrease with X_p. This may be described by the following equation which is developed in section VI.

$$K_t = \exp\ (A_1 + A_2X_p + A_3X_p^2 + A_4X_p^3 + A_5X_p^4\ ) \qquad (5.39)$$

The model for Stage III can be presented as follows:

$$I\frac{df_i}{dX_p} = H_1J_1(X_p)(f_{i-1}-f_i)+H_2J_2(X_p)\{f_{i+1}(i+1)-f_i i\} + H_3J_3(X_p)\{f_{i+2}(i+2)(i+1)-f_i i(i-1)\} \qquad (5-40)$$

$$\Sigma f_i = 1 \qquad (5-41)$$

$$\Sigma f_i i = I \qquad (5-42)$$

where

$$H_1 = RN_A M_O/(K_p N_p^2 d_m)$$

$$H_2 = (K_O/K_p)(\pi^{1/3} N_A)(6M_O/N_p)^{2/3}(d_p^{1/3}/d_m)$$

$$H_3 = 1/K_p$$

$$J_1(X_p) = 1-d_m X_p / d_p(1 - X_p)$$

$$J_2(X_p) = (d_m/d_p)^{1/3}\{(1-X_p)+d_m X_p/d_p\}^{2/3}/(1-X_p)$$

$$J_3(X_p) = \frac{1}{1-X_p}\exp(A_1+A_2X_p+A_3X_p^2+A_4X_p^3+A_5X_p^4)$$

The initial condition is

$$X_p = X_{p,\text{II-III}}, \quad I = I_{\text{II-III}}$$

$$f_i = f_{i,\text{II-III}}, \quad (i=0,1,2,3,.....)$$

$$\text{at } t = t_{\text{II-III}}$$

In the computation, the values of f_i and I can be found by solving equations (5-40), (5-41) and (5-42) at various conversions and the corresponding dependence of X_p upon t may be determined by solving the following equation:

$$\frac{dX_p}{dt} = \frac{K_p d_m}{N_A M_O} N_p I \phi(X_p)$$

SECTION VI

RESULTS AND DISCUSSION

6.1 Determination of the Dependence of Termination Rate Constant on Monomer Conversion

6.2 Formulation of Dispersion Data for the Baffled Reactor

6.3 Scope of the Model

6.3.1 Predictions of the model for Particle nucleation

6.3.2 Conversion-versus-time plots for the unbaffled reactor

6.3.3 The effect of stirring rate

6.3.4 The gel-effect

6.3.5 The Baffled reactor

6.1 Determination of the Dependence of Termination Rate Constant on Monomer Conversion

There is clear evidence[38] that the termination rate constant, K_t, for styrene polymerization is extremely large, and is about 5 orders larger than the propagation rate constant, K_p. The termination rate is therefore diffusion controlled even for the smallest radicals even in the early stage of reaction. As polymerization proceeds, the polymer chains entangle with each other and this causes the monomer-polymer solution to increase in viscosity and therefore the translational mobility of the radical chains will be decreased. Thus, K_t decreases dramatically with monomer conversion. Furthermore the reduction of K_t depends only upon the extent of this entanglement of the polymer chains and upon the environmental conditions in the polymerization loci regardless of whether the reaction is occurring in bulk, in the droplets of suspension polymerization or in the polymer particles of emulsion polymerization. As Friis pointed out[10], in emulsion polymerization a single polymer particle can be regarded as a tiny locus of bulk polymerisation with intermittent initiation. A decrease in the termination rate which is observed in bulk(or suspension) polymerisation should therefore also be observed in a single polymer particle in emulsion polymerisation. Thus it seems reasonable that the relationship between K_t and monomer conversion obtained from either bulk or suspension polymerisation may be used for the emulsion polymerisation model.

According to Hui's theory, the dependence of K_t upon monomer conversion may be described by the following formula.

$$\frac{K_t}{K_p^2} = \frac{K_{to}}{K_{po}^2} \exp\left(A_2X_p+A_3X_p^2+A_4X_p^3+A_5X_p^4\right) \qquad (6\text{-}1)$$

In the case of the reaction temperature being above the glass transition point, T_g, monomer molecules or chain segments can move so freely that the propagation reaction is not controlled by diffusion. Therefore, the value of Kp always maintains a fixed value as long as the temperature is not less than T_g. For polymerization of styrene if the monomer concentration is more than 2.6%, T_g will be lower than 50°C. In other words, Kp remains a constant at 50°C within the range of monomer conversion from zero to 97.4%. Consequently for the normal case, equation (6-1) becomes:

$$K_t = \exp(A_1+A_2X_p+A_3X_p^2+A_4X_p^3+A_5X_p^4) \qquad (6\text{-}2)$$

For bulk and suspension polymerization, the propagation rate may be described as follows[40]:

$$\frac{dX_p}{dt} = K_p(1-X_p)\left(\frac{K_i f\{I\}}{K_t}\right)^{\frac{1}{2}} \qquad (6\text{-}3)$$

where $K_i f\{I\}$ is the decomposition rate of the initiator, which can be regarded as a constant during the reaction. This approach has been made by a number of authors previously[13].

Figure 6.1 shows the interdependence between conversion and time obtained from the experimental suspension polymerization of styrene at 50°C.

For polymerization of styrene K_p is set at 1.27×10^7 cm^3/mole. min[32], and $K_i f$ at 1.782×10^{-4} l/min[39]. From fig 6.1 a series of values of (dXp/dt) may be found using numerical differentiation, then the value of A_1, A_2, A_3, A_4 and A_5 may be estimated by means of multiple regression. The computer programmes for this calculation are shown in Appendix II.

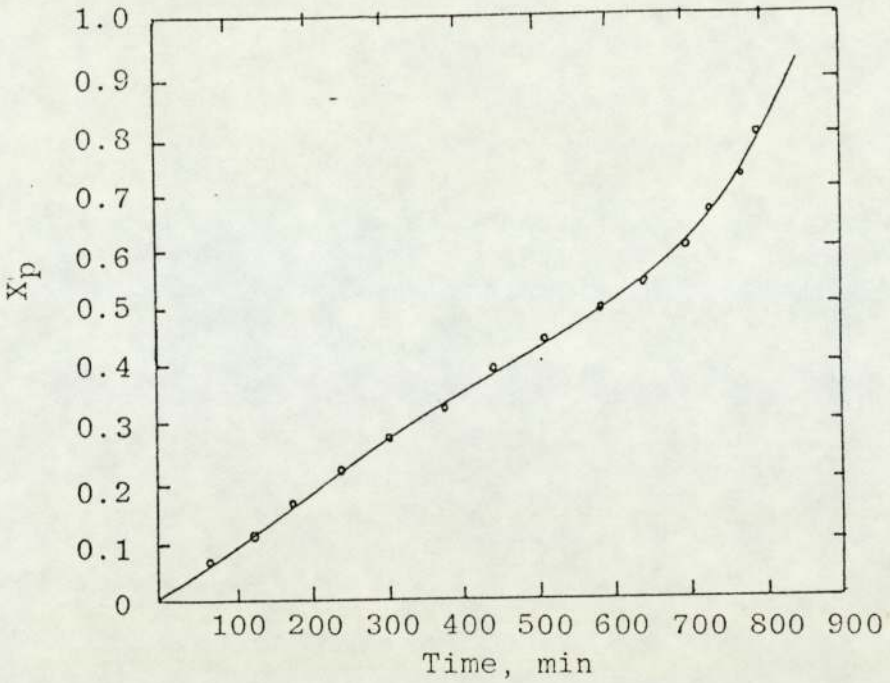


Fig. 6.1 Dependence of conversion upon the time for suspension polymerization of styrene at 50°C: {AIBN} = 0.216 mole/dm^3 monomer, the phase ratio: water/monomer = 6 (volume), stabiliser (polyvinyl alcohol) concentration: 2.6% (in water)

The values obtained are presented below:

A_1 = 29.5873

A_2 = -7.4332

A_3 = 45.8577

A_4 = -95.9184

A_5 = 47.4095

When X_p = 0, K_t = 7.073 x 10^{12} cm^3/mole. min. This value agrees with that in the literature (Olive[42], 6.9 x 10^{12} cm^3/mole.min).

Figure 6.2 shows the dependence of K_t upon conversion for suspension polymerization of styrene at 50°C. It may be seen that in the early stages K_t changes only slightly, but in the later stages, the decrease in K_t with increasing conversion is dramatic.

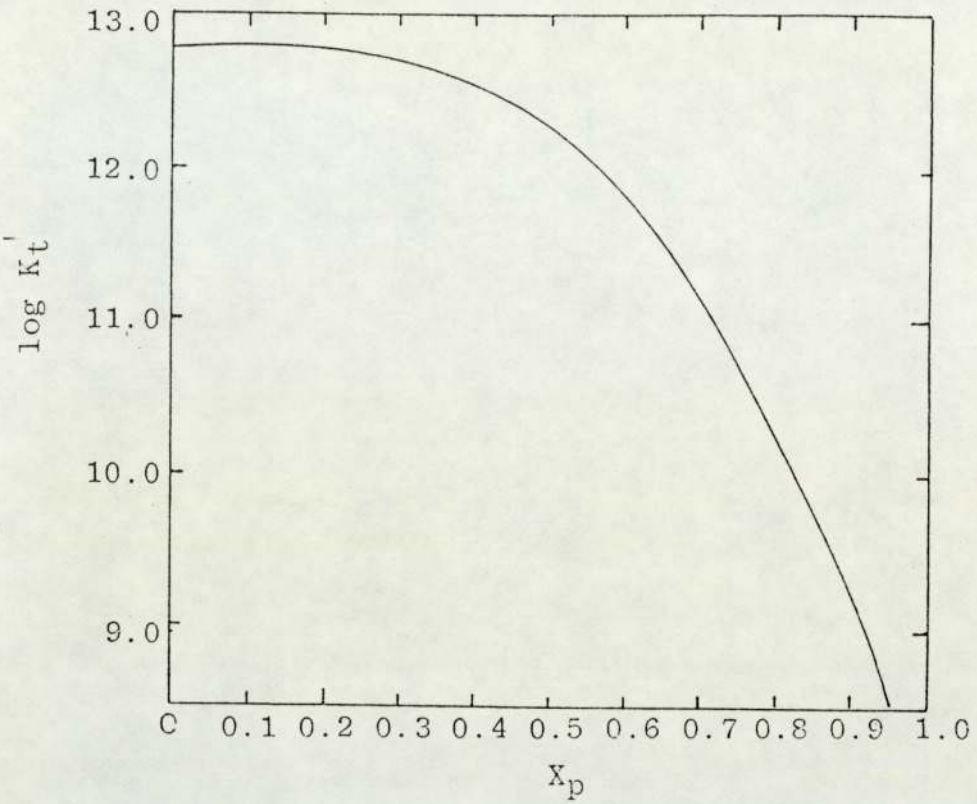


Figure 6.2 Dependence of termination rate constant upon conversion for suspension polymerization of styrene at 50°C.

6.2 Formulation of Dispersion Data for the Baffled Reactor.

To prove the validity of the model proposed above, for baffled reactors, the interdependence of the average initial diameter of monomer droplets, D_d^o (micron), total soap concentration, S_o (gram/Dm^3 water), and impeller speed (r.p.m.) is needed in the computation. In this section it is shown how this relationship was derived.

The flow pattern of the liquid in a baffled reactor is far different from that in unbaffled reactors; the velocity distribution in the former is more homogeneous than in the latter[15]. Differences in the dispersion characteristics between baffled and unbaffled reactors would be expected and, in fact, experiment has shown that the extent of monomer dispersion in the baffled reactor is much greater than that in the unbaffled one. Vermeulen et al[16] presented a correlation from their experimental data for baffled reactors, in which the Sauter mean diameter of the droplets is shown to be directly proportional to impeller speed raised to a power of -1.2. Unfortunately, their formula is only valid for a system in the absence of an emulsifier. Merry[17] obtained an empirical formula for the dispersion of styrene in an emulsifier solution in water, in which the mean diameter of monomer droplets is shown to be proportional to the impeller speed raised to the power of -1.08 This formula, however, was developed for unbaffled reactors. Harada et al[32] proposed a

correlation for baffled reactors in which the average diameter of the dispersed monomer droplets was shown to be proportional to the impeller speed raised to the power of -0.75 and to the emulsifier concentration raised to the power -1.5. In this formula, however the lower limit of the emulsifier concentration is 3.13 gram/dm^3 water, which is beyond the emulsifier concentration range that was dealt with in this project. Therefore, to model emulsion polymerization in a baffled reactor for the case of low soap concentration a correlation is needed relating the average initial monomer droplet diameter to the impeller speed and to soap concentration.

To obtain this relationship three batches of styrene/water/sodium lauryl sulphate were tested. The emulsifier concentrations for the three batches were assigned 3.75, 2.75 and 1.75 gram per cm^3 of water. Five impeller speeds were set for each batch, namely, 450, 550, 650, 750 and 850 r.p.m. The average droplet diameter was obtained using the microphotographic technique described in Section IV. The results for each sample are listed in Table 6-1. The computed results from that data in Table 6-1 are listed in Table 6-2. The computer programme for this computation is shown in Appendix III (1).

Table 6.1 The experimental data of dispersion test.

diameter of particle cm	number of droplets														
	S.= 3.75					S.= 2.75					S.= 1.75				
	Impeller Speed														
	450	550	650	750	850	450	550	650	750	850	450	550	650	750	850
2	99	93	51	-	66	29	61	25	42	14	125	20	60	41	56
3	111	114	37	78	45	23	53	37	52	58	91	36	61	33	39
4	103	91	33	27	21	11	27	21	18	22	26	9	77	24	33
5	112	70	22	22	23	7	27	23	20	26	19	5	29	12	29
6	64	42	25	10	10	7	16	11	11	17	17	10	24	23	15
7	50	28	23	12	6	9	13	8	12	17	10	3	16	11	14
8	48	26	9	7	5	6	3	9	15	9	5	4	12	5	6
9	19	17	7	2	3	2	5	5	3	4	8	4	3	7	2
10	24	7	11	2	3	2	7	4	3	-	6	1	4	1	-
11	15	11	5	3	-	3	5	2	1	-	5	-	3	1	-
12	16	11	4	-	-	2	2	2	-	-	-	-	3	1	-
13	9	3	3	1	-	1	2	-	-	-	3	-	-	1	-
14	6	2	1	-	-	1	-	-	-	-	1	3	2	-	-
15	3	3	2	-	-	1	1	1	-	-	1	2	2	-	-
16	4	4	3	-	-	-	-	-	-	-	3	1	-	-	-
17	3	-	-	-	-	2	2	-	-	-	1	1	-	-	-
18	3	3	-	-	-	-	-	-	-	-	-	2	-	-	-
19	4	2	-	-	-	2	-	-	-	-	-	-	-	-	-
20	3	-	-	-	-	2	1	-	-	-	2	-	-	-	-
21	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-
22	1	-	-	-	-	1	-	-	-	-	-	-	-	-	-
23	2	-	-	-	-	1	-	-	-	-	1	-	-	-	-
24	-	-	-	-	-	1	-	-	-	-	1	1	-	-	-
25	-	-	-	-	-	2	-	-	-	-	3	-	-	-	-
26	1	-	-	-	-	-	-	-	-	-	1	-	-	-	-
27	1	-	-	-	-	1	-	-	-	-	-	-	-	-	-
28	-	1	-	-	-	-	-	-	-	-	1	-	-	-	-
30	-	-	-	-	-	-	-	-	-	-	1	-	-	-	-
31	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-
32	-	1	-	-	-	-	-	-	-	-	-	-	-	-	-
38	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-
40	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-
41	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-
50	-	-	-	-	-	-	-	-	-	-	1	-	-	-	-
56	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Table 6-2 Average diameter of monomer droplets computed from the data in Table 6-1 for the various emulsifier concentration and impeller speed.

S_o, g/cm^3 water	3.75	2.75	1.75
N, r.p.m.		D_d^o, micron	
450	29.63	27.83	34.64
550	18.35	14.92	21.07
650	17.94	12.20	11.94
750	10.59	10.43	11.04
850	9.34	9.60	8.88

In accordance with the data obtained above, the following empirical exponential correlation was fitted using a multiple regression method.

$$D_d^o = 2.42\, S_o^{0.013}\, N^{-1.86} \qquad (6\text{-}4)$$

The computer programme for this formulation is shown in Appendix III (2).

It may be seen from formula (6-4) that in a baffled reactor, impeller speed affects the values of the average diameter of the dispersed monomer droplets more seriously than in an unbaffled reactor.

6.3 Capabilities of the Model

To illustrate the capabilities of the model proposed above, more than 30 test runs were performed under various emulsifier concentrations, initiator concentrations and impeller speeds both in the baffled reactor and in the unbaffled reactor. The experimental results are shown in figures 6.3 to 6.12, in Table 6.3 to 6.6 and in Appendix IV and V.

In the computation, the following values of the constants for emulsion polymerization of styrene are used $K_p = 1.27 \times 10^7$ $cm^3/mole.min$ [32], $K_i f = 5.7 \times 10^{-5}$ $1/min$ [61], $d_m = 0.879 g/cm^3$, $dp = 1.049 g/cm^3$, $d_{sw} = 0.934 g/cm^3$, $\phi_m = 0.605$, $A_s = 3.5 \times 10^{-15}$ cm^2/one molecule [32] and $\{S\}_{cmc} = 1.8382 \times 10^{-3}$ $mole/Dm^3$ water [6].

The desorption of radicals from particles to the aqueous phase for emulsion polymerization of styrene is ignored because the solubility of styrene is relatively low so that their escape from the particles is insignificant. Thus K_O is set equal to zero and so is the value of G_2.

6.3.1 Predictions of the Model for Particle Nucleation

The accepted mechanism for emulsion polymerization assumes that the particles are initiated in micelles, thus the number of particles and the reaction rate at a given time are functions of the amount of micellar soap. Because some soap is adsorbed onto the surface of the

monomer droplets, the micellar soap will be reduced, accordingly the number of particles, the conversion rate, the size of particles and the duration and final conversion of Stage I vary with the degree of dispersion which in turn depends on the soap concentration and the impeller speed.

Figures 6.3 and 6.4 show the computed results of the conversion and the number of particles versus time in Stage I for polystyrene.

It can be found that the conversion rate, the particle nucleation rate, final conversion at the end of stage I and the number of particles decrease with decreasing soap concentration and increasing impeller speed along the conversion history of Stage I. It can also be seen that the duration of Stage I increases with soap concentration but is affected little by the impeller speed. This is perhaps because as the reaction proceeds, the monomer droplets would shrink slightly and some soap would be set free from the droplets, therefore the duration of particle nucleation is slightly postponed especially in the case of a high degree of dispersion.

Table 6.3 shows a comparison of the results obtained by experiment and the predictions both from the classical model and from the present model. It is found that under the various soap concentrations and impeller speeds, the

present model is in acceptable agreement with experimental data. Most importantly, under low soap conditions, the classical model deviates significantly from the experimental results owing to the fact that it does not allow for the soap adsorbed onto the surface of the monomer droplets and the critical micellar soap and the advantage of the present model is thus clearly demonstrated.

The computer programme for Smith-Ewart model is shown in Appendix IV. And the program simulating the present model for the unbaffled reactor is shown in Appendix V.

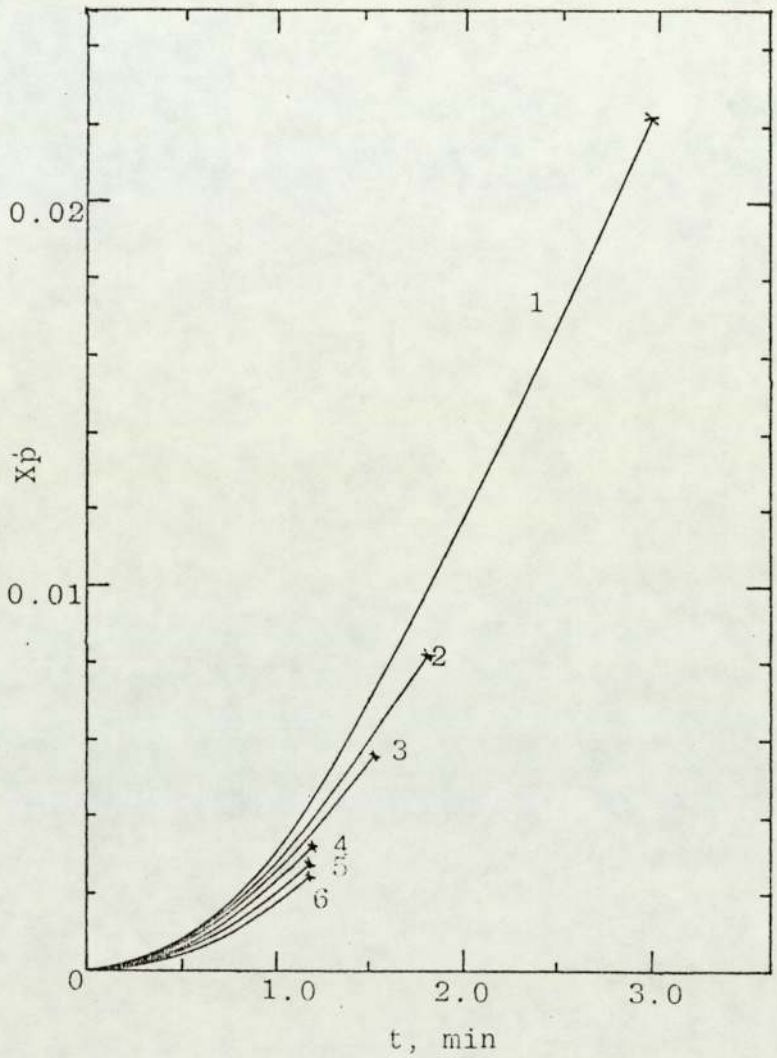


Figure 6.3 Conversion-vs-time plots computed according to the present model: [I]=0.00463mole/dm^3.water,

(1) So=5g/dm^3,water, N=410 r.p.m.,
(2) So=2.5g/dm^3.water, N=410 r.p.m.,
(3) So=2,Ig/dm^3.water, N=410 r.p.m.,
(4) So=1.5g/dm^3.water, N=410 r.p.m.,
(5) So=1.5g/dm^3.water, N=600 r.p.m.,
(6) So=1.5g/dm^3.water, N=800 r.p.m.

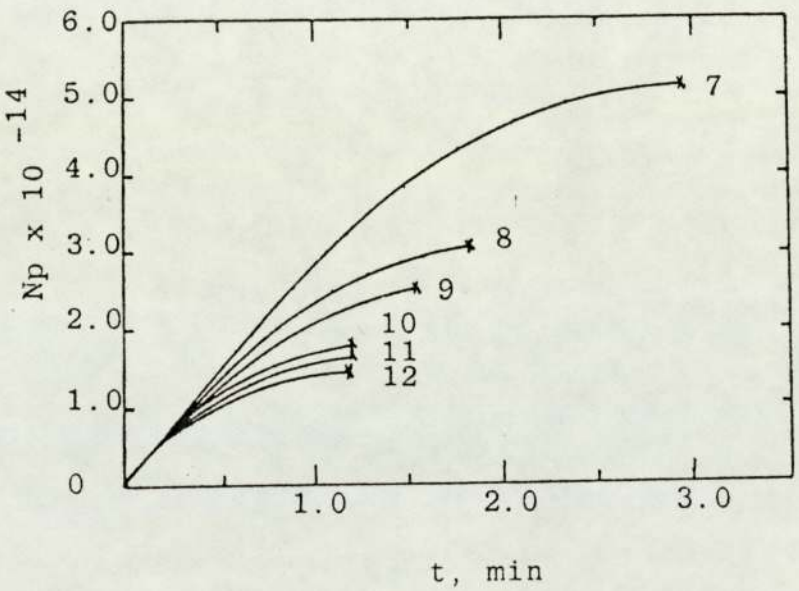


Figure 6.4 Number of particles-vs time plots computed according to the present model:

[I]=0.00463mole/dm^3,water,

(7) So=5.0g/dm^3.water, N=410 r.p.m.,

(8) So=2.5g/dm^3.water, N=410 r.p.m.,

(9) So=2.0g/dm^3.water, N=410 r.p.m.,

(10) So=1.5g/dm^3.water, N=410 r.p.m.,

(11) So=1.5g/dm^3.water, N=600 r.p.m.,

(12) So=1.5g/dm^3.water, N=800 r.p.m.

Table 6.3 Final number and diameter of particles obtained by experiment and theory.

Total amount of soap g/dm^3 H_2O	Concen. of initiator g/dm^3 H_2O	Impeller speed rmp	Present Model		Experimental		Smith-Ewart Model	
			Number of particles x 10^{-14} parti./ $cc H_2O$	Final diameter of parti. micron	Number of particles x 10^{-14} parti./ $cc H_2O$	Final diameter of parti. micron	Number of particles x 10^{-14} parti./ $cc H_2O$	Final diameter of parti. micron
* 7.50	2.50	410	8.085	0.1046	6.5313	0.1130	9.371	0.1023
* 3.75	2.50	410	5.552	0.1216	5.2070	0.1227	6.259	0.1169
* 2.25	2.50	410	3.607	0.1403	3.6040	0.1384	4.562	0.1298
5.00	1.25	500	5.031	0.1255	5.1834	0.1216	5.583	0.1204
2.50	1.25	410	3.034	0.1487	3.1218	0.1438	3.746	0.1386
2.00	1.25	410	2.483	0.1585	2.4514	0.1559	3.289	0.1446
1.50	1.25	410	1.809	0.1764	1.9514	0.1679	2.756	0.1532
1.50	1.25	600	1.647	0.1819	1.7215	0.1775	2.756	0.1532
1.50	1.25	800	1.484	0.1883	1.5312	0.1846	2.756	0.1532

* Baffled reacto-

6.3.2 Conversion-versus-time plots for unbaffled reactor

Figures 6.5,6.6,6.7 and 6.8 show a comparison between the classical model, the present model and the experimental results of conversion against time and the effect of emulsifier concentration on the behaviour of emulsion polymerization reactors. If the soap level is high (Figure 6.5), the present model (Curve 14), the classical model (Curve 13) and experimental conversion-versus-time data are closer to each other compared with the case of low soap concentration. The difference between the classical model and the experimental data at this high soap level is well within the experimental error encountered and consequently, many authors simply neglected the effect of the emulsifier adsorbed on the surface of the monomer droplets. If the soap concentration is reduced, however, the fraction of the soap adsorbed on the monomer droplets increases and its effect is enhanced. As is shown in Figures 6.6, 6.7 and 6.8 the classical model deviates significantly from the experimental results but they are in good agreement with the present model which takes into account the soap adsorbed on the surface of monomer droplets.

The computer program for the classical model is shown in Appendix IV and the program simulating the present model is shown in Appendix V.

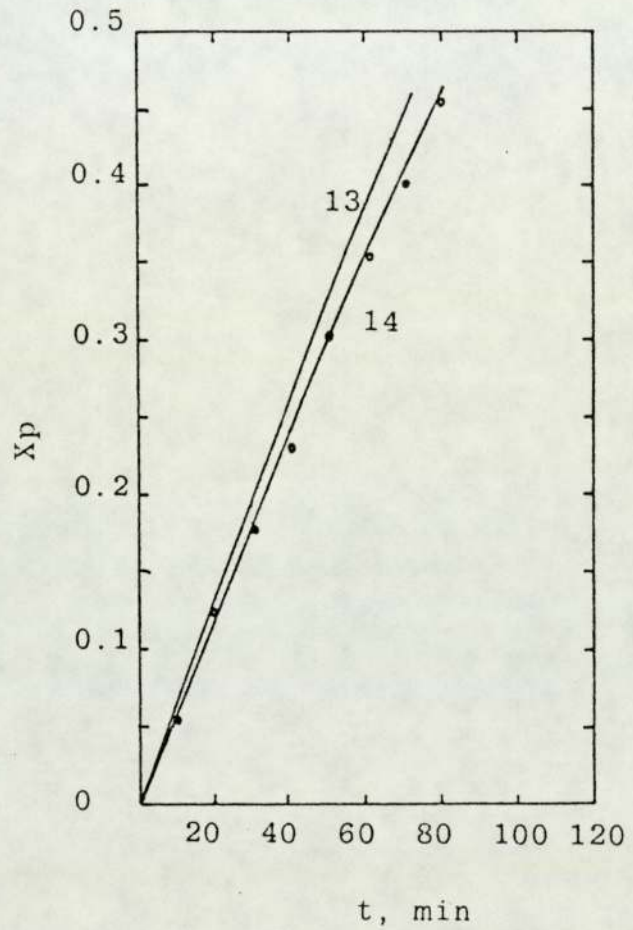


Figure 6.5 Comparison between theoretical and experimental conversion versus time plots : S_o= 5.0 g/dm^3.water, {I}=0.00463 mol/dm^3.water, N= 410 r.p.m. (13) Smith and Ewart model (14)present model, (.)experimental points.

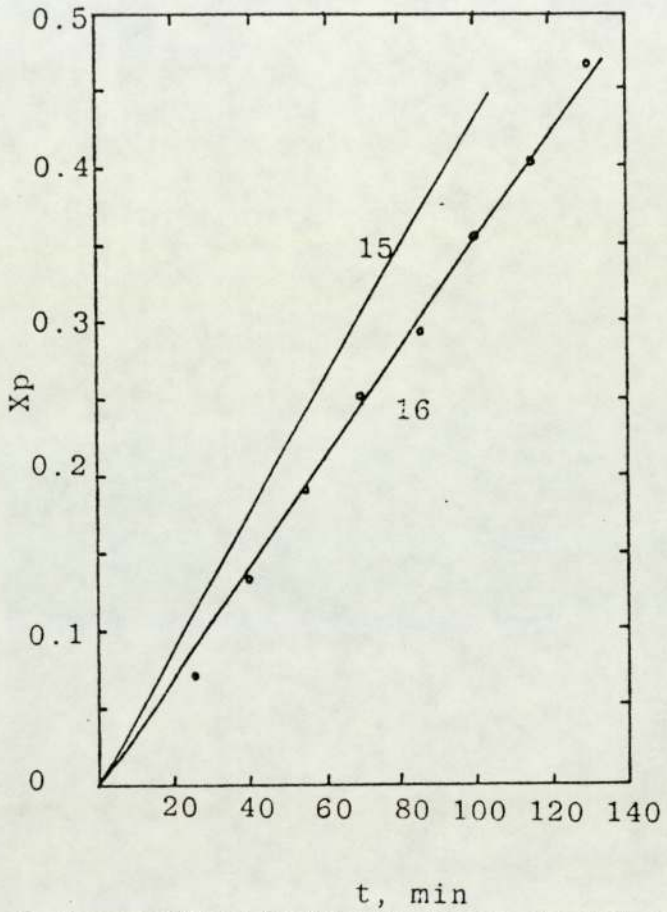


Figure 6.6 comparison between theoretical and experimental conversion versus time plots : S_o= 2.5 g/dm^{3}water,N=410 r.p.m. {I}= 0.00463 mol/dm^{3}water. ; (15) Smith and Ewart model, (16) present model,(.)experimental points.

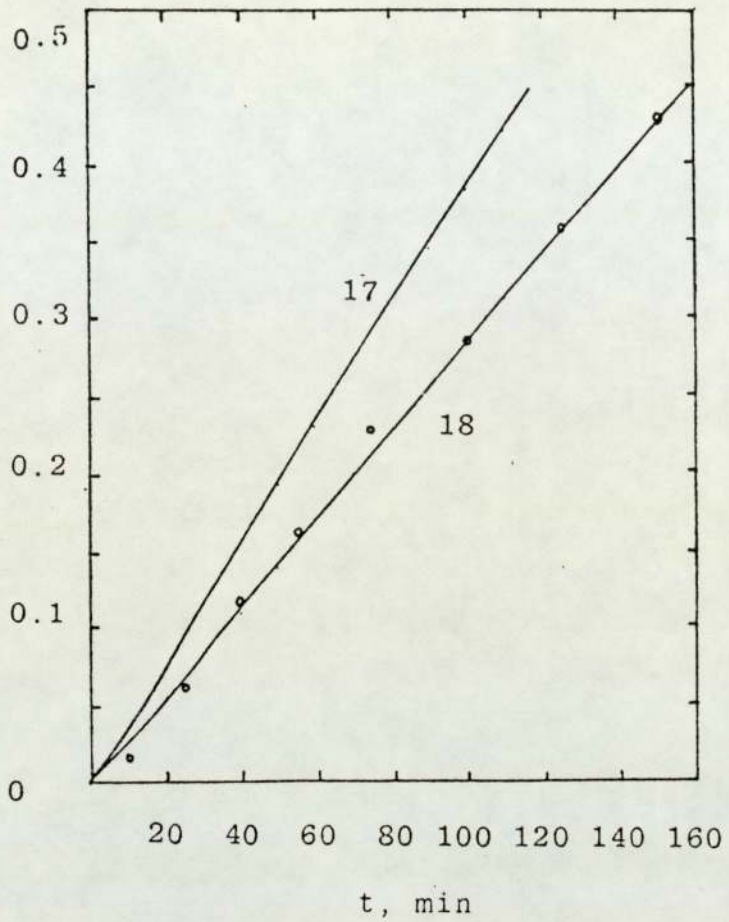


Figure 6.7 Comparison between theoretical and experimental conversion-vs-time plots: N=410 r.p.m., So=2.0g/dm^3.water, [I]=0.00463 mol/dm^3.water, (17) Smith Ewart model, (18) present model, experimental points

6.3.3 The effect of stirring rate

As has already been pointed out, violent agitation will result in a high degree of dispersion with the consequence that more soap will be adsorbed onto the monomer droplets and more micelles will be destroyed so that the final number of particles will be reduced, the size of particles will be increased and the conversion rate will be reduced. Figure 6.8 shows that under low soap concentrations the present model reflects dependence on impeller speeds and the predictions are in reasonable agreement with experimental results. It can be seen from Table 6.3 that under the same emulsifier and initiator concentration conditions, if the impeller speed increases from 410 r.p.m. to 800 r.p.m., then the number of particles will decrease from 1.809×10^{14} to 1.484×10^{14} while the final particle diameters will increase from 0.1764 micron to 0.1883 micron. These predictions of the present model are in excellent agreement with the experimental results.

It can be seen in Table 6.3 that the Smith-Ewart theory predicts that impeller speed has no effect on the number of particles and on the final particle diameter. If this were true for the system indicated, the number of particles should be 2.756×10^{14} and the final particle diameter should be 0.1532 micron. These values are in fact far from the true experimental values which are seen to be dependent on impeller speed. This dependence is clearly reflected in the computer predictions of the present model.

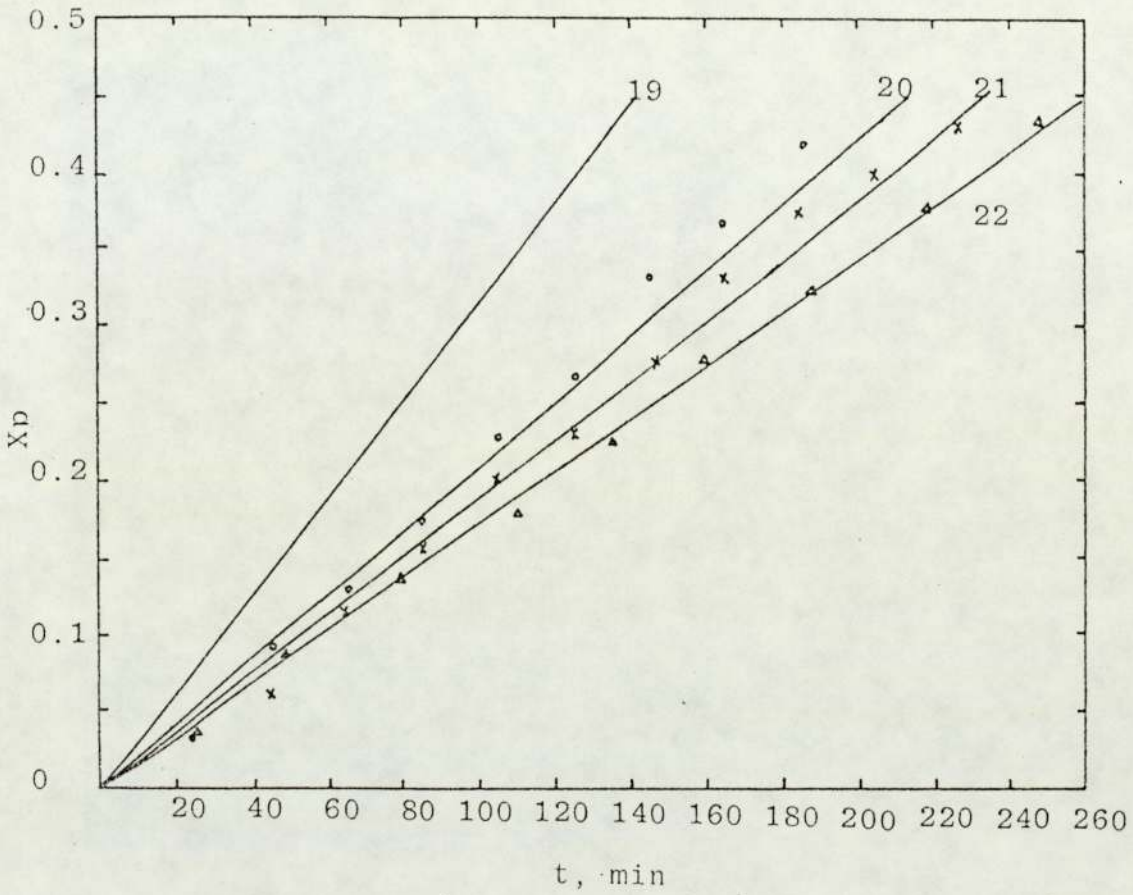


Figure 6.8 Comparison between theoretical and experimental conversion-vs-time plots: So=1.5g/dm^3.water, [I]=0.00463 mol/dm^3.water, (19) Smith-Ewart model, (20) present model, N=410 r.p.m., (21) present model, N=600 r.p.m., (22) present model, N=800 r.p.m., "o" experimental, N=410 r.p.m., "x" experimental, N=600 r.p.m., "Δ" experimental, N=800 r.p.m.

6.3.4 The Gel-Effect

The predicted results from the classical model and the present model over the whole range of the monomer conversion and the corresponding experimental data are shown in Table 6.3. and Figure 6.9. to 6.11. The computer program for this calculation is shown in Appendix IV.

Table 6.3 shows predicted results from the present model for a typical case. It is clear that K_t will maintain a constant value when $X_p \leq 0.43$ because up to this point, which represents the end of Stage II, the ratio of monomer to polymer in the particles maintains a fixed value. During Stage II, however, the average number of radicals in one particle, I,slightly increases due to the particles increasing in size. When the conversion is beyond 0.43 i.e. Stage III, the value of K_t increases dramatically and the rate of increase in the value of I will accelerate owing to the gel-effect.

Figure 6.9 shows the distribution of radicals among particles at different monomer conversions for a single case. It indicates clearly that the distribution is broadened and the average number of radicals is increased along with increasing monomer conversion.

Figures 6.10 to 6.11 show conversion-versus-time plots computed by both the present model and the classical model and the experimental results. It may be seen that the

theoretical simulation is a far better prediction than the classical model in Stage I and Stage II. This is particularly evident at low initial soap concentrations. This improvement over the classical model comes from the fact that the present model has taken into consideration the emulsifier adsorbed onto the surface of monomer droplets. In Stage III, it is found that the present model (the solid lines) which allow for the gel-effect is in much better agreement with the experimental results (symbols) than the case which neglects this effect (the dashed lines). The validity of the present model is clearly demonstrated.

From Figure 6.10 and Figure 6.11, it can be seen that in Stage I and Stage II, the deviation of the experimental data and the present model from the classical model becomes more serious if the initial soap concentration is decreased. This is because the fraction of the emulsifier that is adsorbed onto the surface of monomer droplets increases with the reduction of emulsifier concentration at a given impeller speed. In other words, in these low initial soap conditions the adsorbed emulsifier will play a significant role in decreasing the number of particles and consequently in the polymerization rate.

From Figures 6.10 and 6.11 it may also be seen that the severity of the gel-effect increases as initial soap concentration decreases for a given impeller speed. There is no easily tested explanation for this but it might be

proposed that it may be associated with the observation that the radicals in the surface layer of the particles are terminated more readily than those in the body of the particles because the diffusion paths for radicals in the surface layer are short. When the initial soap concentration is low, fewer particles will be generated and thus the surface area of particles per cc of water will be smaller, and therefore fewer radicals will be able to take advantage of the fast termination zone.

Table 6.4 Interdependence between the conversion, the termination rate constant and the average number of radicals in one particle:
S_o=2.25 g/dm^3 water, R_o=2.5 g/dm^3 water, N=410 r.p.m.
Reaction temperature: 50°C.

X	I	K_t, cm^3/mol min
0.10	0.500101	3.4340×10^{12}
0.20	0.500203	2.4340×10^{12}
0.30	0.500305	3.4340×10^{12}
0.40	0.500407	3.4340×10^{12}
0.43	0.500448	3.4340×10^{12}
0.50	0.500749	1.9687×10^{12}
0.60	0.502582	5.6610×10^{11}
0.70	0.514133	1.0089×10^{11}
0.80	0.599936	1.3133×10^{10}
0.85	0.758931	4.5729×10^{9}
0.90	1.081800	1.6483×10^{9}
0.95	1.608270	6.4814×10^{8}
0.97	1.871540	4.6323×10^{8}

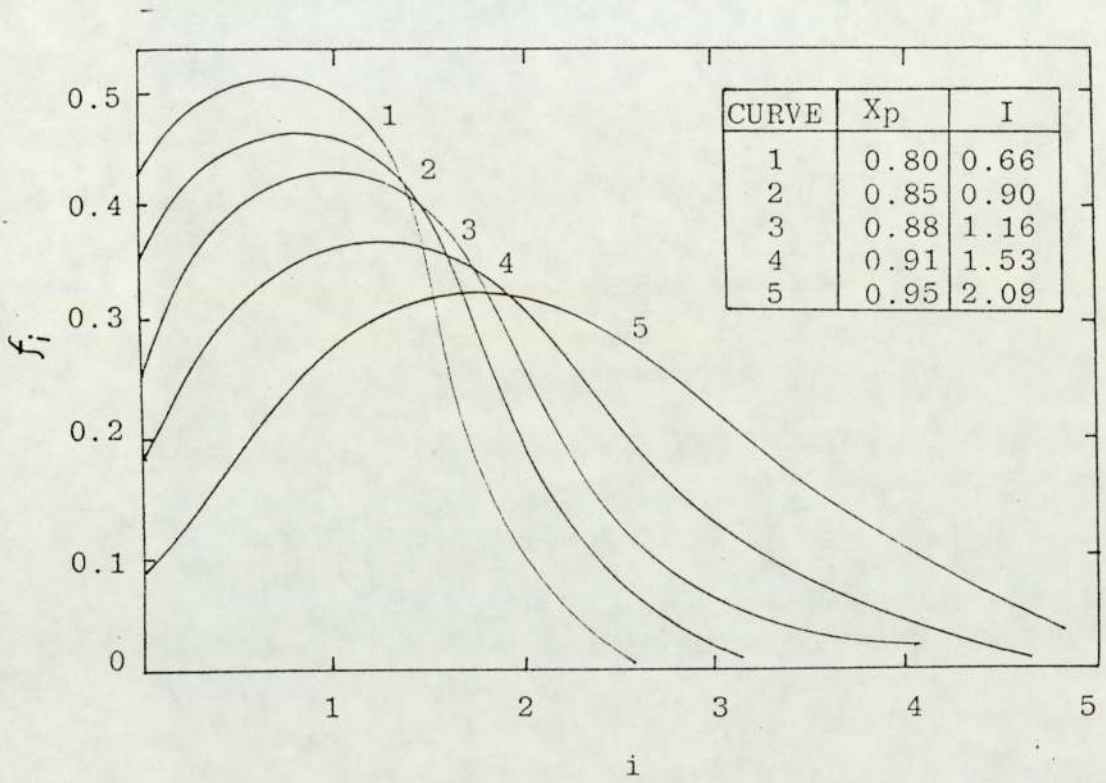


Figure 6.9 Distribution of radicals among the particles at different monomer conversions: S_o=2.25 g/dm^3 water, R_o=2.5 g/dm^3 water, N=410 r.p.m., reaction temperature: 50°C.

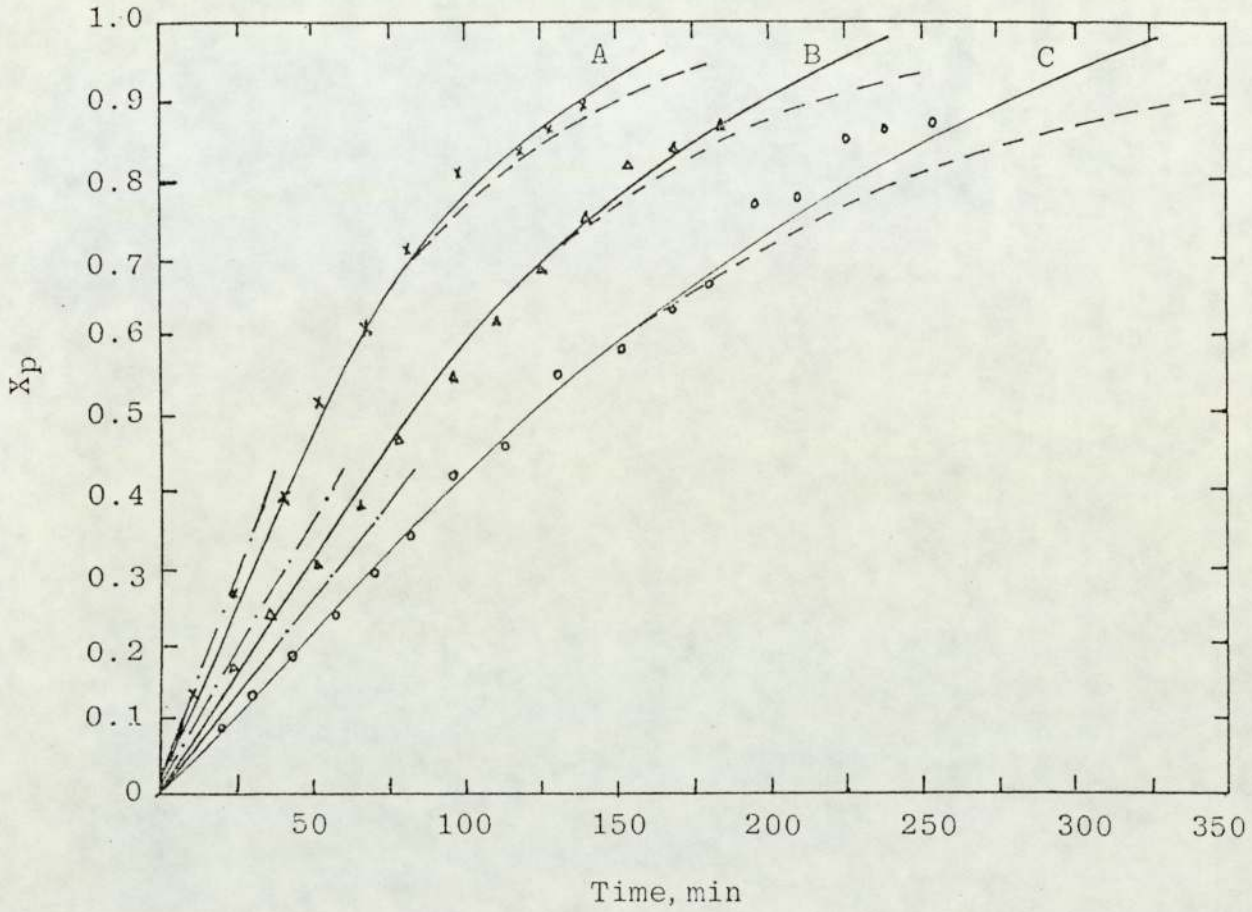


Figure 6.10 Comparison between theory and experimental data: " ____" present, " ----" the model without considering gel-effect, "___.___" the Smith-Ewart model, M_o=0.5 g/g water, R_o=2.5 g/dm^3 water, "A" S_o=7.5 g/dm^3 water, "C" S_o=2.25 g/dm^3 water.

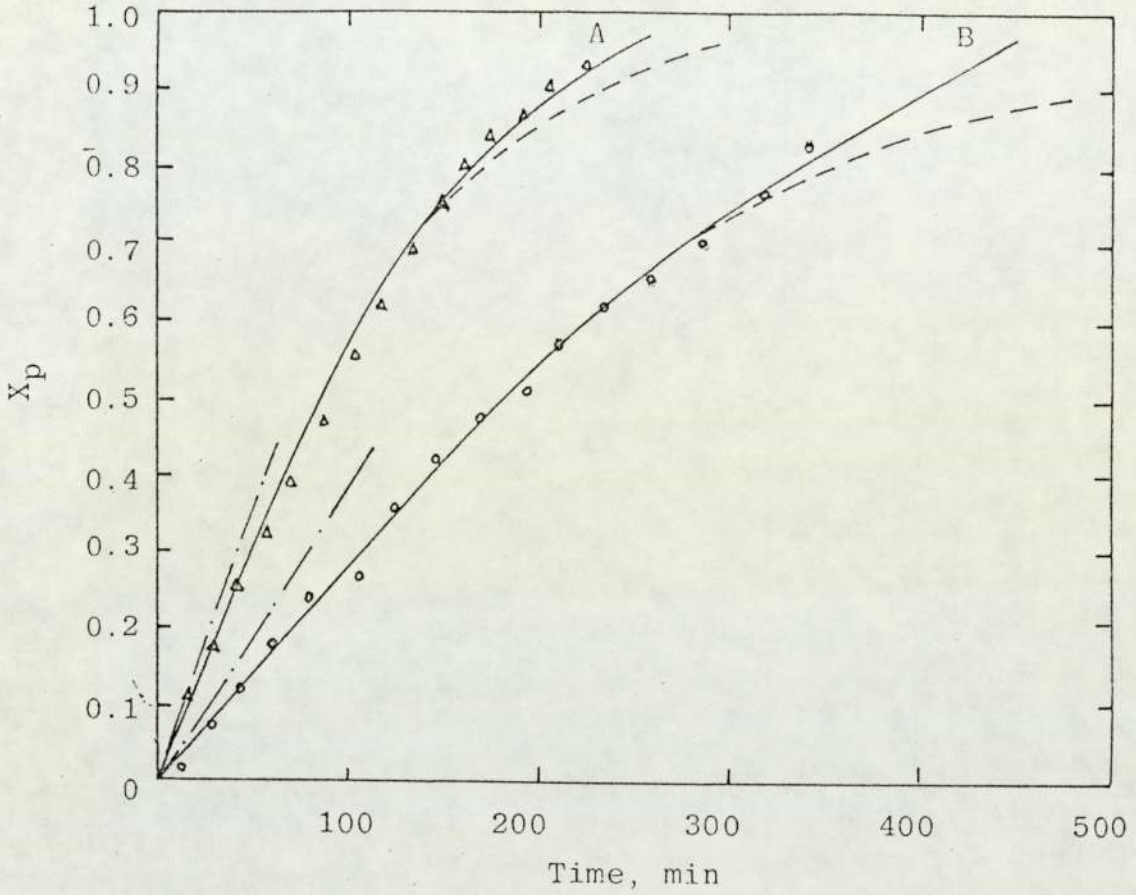


Figure 6.11 Comparison between theory and expermental data: "___" present model, "---" the model without considering gel-effect, "___.____" Smith-Ewart model, M_o=0.5 g/g water, R_o=1.25 g/dm^3 water, "A" S_o=5 g/dm^3 water, N=500 r.p.m., "B" S_o=2.0 g/dm^3 water, N=410 r.p.m.

6.3.5 The Baffled Reactor

To test the validity of the model for the baffled reactors, further test runs of emulsion polymerization were carried out in the reactor fitted with baffles as described in Section 3.1 In the computation, the dispersion formula derived above (equation 6.4) was used instead of Merry's empirical dispersion formula (equation 5.12). The results are shown in Figure 6.12 and 6.13. The computer program for this calculation is shown in Appendix VII.

Figure 6.12 and 6.13 show comparisons of conversion-versus-time plots computed by both the present model and the classical model with the experimental results across the whole range of the conversion. It indicates that the present model comes far closer to predicting the experimental data than the classical model. This is due to the fact that the present model has considered both the emulsifier adsorbed onto the surface of the monomer droplets and the gel-effect, both of which factors are ignored in the classical model. Therefore, the validity of the present model for the baffled reactor is also clearly demonstrated.

It is seen again from Figure 6.13 how impeller speed affects the behaviour of emulsion polymerization reactors. As discussed above, for the baffled reactor the extent of monomer dispersion is much more severe than that in the unbaffled reactor so that a much greater effect on the number of particles and on the polymerization rate by the level of agitation can be expected. It is clear from Figure 6.13

that the slope of the conversion-versus-time curve for the case of high impeller speed (Curve C) is much lower than that for the case of low impeller speed(Curve B). If Curve B in Figure 6.12 is compared with Curve 21 in Figure 6.8 for the unbaffled reactor of the same impeller and soap concentration it is clearly seen that the baffled reactor gives rise to a much reduced reaction rate and particle number as may be expected from the higher specific monomer surface area available for soap adsorption in baffled systems.

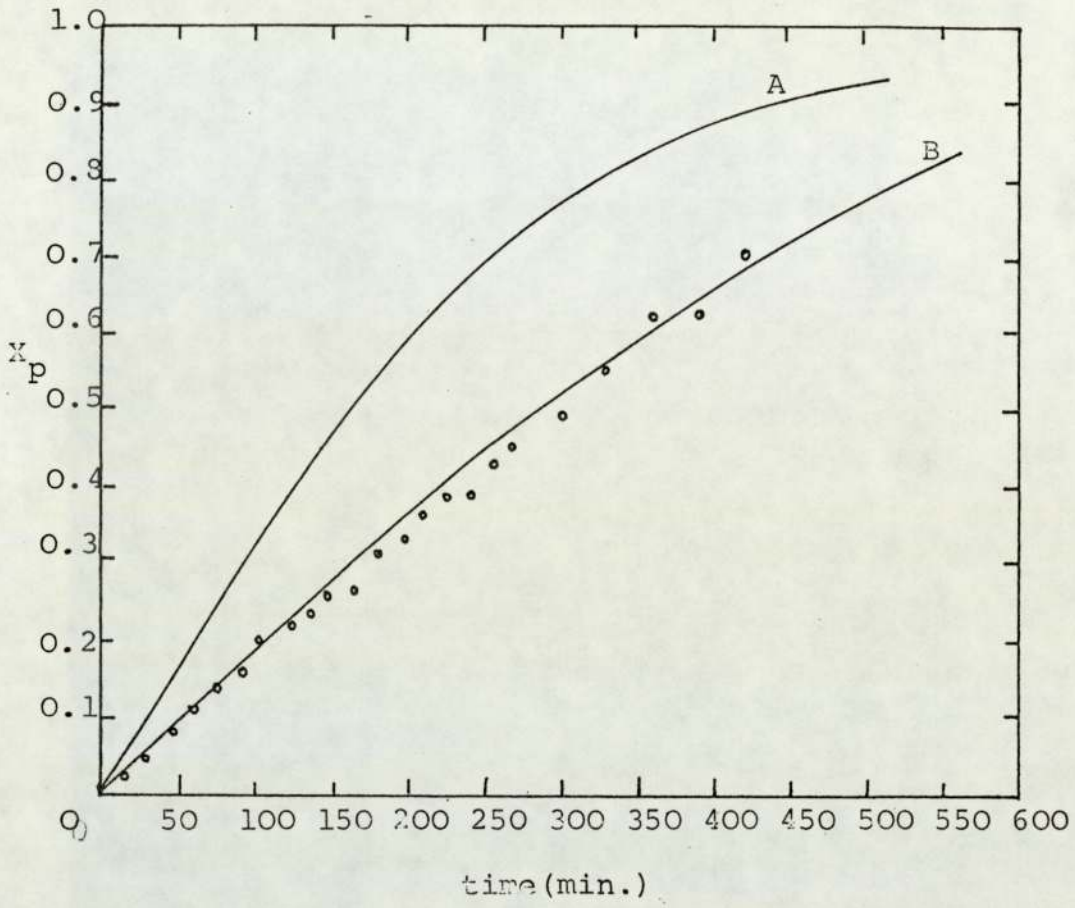


Figure 6.12 Comparison between theory and experimental data for baffled reactor S_o= 1.5 g/dm^3 water, R_o=1.25 g/dm^3 water. Mo= 0.5 g/g water, N=600 r.p.m. "A" Smith-Ewart model, "B" present model. Reaction temperature 50^{o}C.

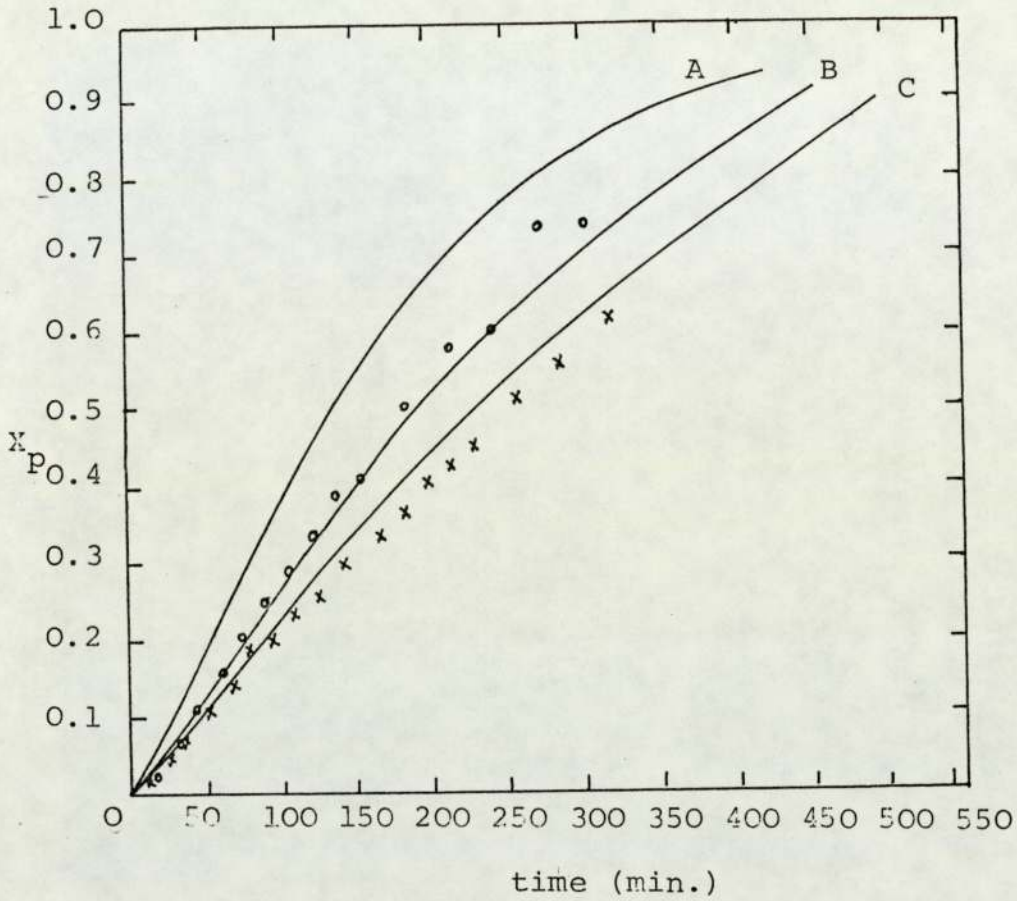


Figure 6.13 Comparison between theory and experimental results for baffled reactor R_o=1.25 g/dm^3 water, M_o=0.5 g/g water, "A" Smith-Ewart model, "B"present model, S_o= 2 g/dm^3 water, N=600 r.p.m., "C" present model, N=800 r.p.m., S_o= 2 g/dm^3 water, Reaction temperature 50^{o}C.

SECTION VII

CONCLUSIONS

1) The classical models for emulsion polymerization as presented by Smith and Ewart and by Gardon do not present satisfactory predictions for stages I and II of the reaction for the case of low soap concentrations and for the case of high impeller speeds at intermediate and low soap concentrations. This is recognised in this project to be due to the fact that these two models fail to take into account the adsorption of a proportion of the emulsifying soap onto the surface of the dispersed monomer droplets. This adsorption clearly reduces the number of micelles available for polymer particle nucleation. Not surprisingly, therefore, the classical models predict more, though smaller, polymer particles and higher reaction rates than are observed in practice and this deviation becomes increasingly severe as the initial soap concentration is reduced.

2) The increase in viscosity within the polymer particles during Stage III of the emulsion polymerization reaction gives rise to a reduction in the translational mobility of the radicals within the particles. This is suggested to progressively reduce the effective termination constant of the reaction as the polymer concentration increases through Stage III. The classicial models do not take this 'gel-effect' into account and thus they predict a declining reaction rate during Stage III whereas in practice the reaction rate is often observed to increase.

(3) The field of study of this project has been the effects upon the behaviour of the emulsion polymerization reaction of the adsorption of emulsifier onto the surface of monomer droplets and of the gel-effect. A mathematical model for predicting these effects in both unbaffled and baffled stirred batch reactors has been established. It is summarized below.

Stage I

$$A_p(t) = \frac{B_1}{6} t^{5/3}\{B_4 - 2.52A_p(\tfrac{t}{2}) - 2.52(B_2 - B_3V_p(\tfrac{t}{2}))^{2/3}\}$$

$$V_p(t) = \frac{C_1}{6} t^2 \{C_2 - 2A_p(\tfrac{t}{2}) - 2(B_2 - B_3V_p(\tfrac{t}{2}))^{2/3}\}$$

$$X_p(t) = D_1 t^2 \{C_2 - 2A_p(\tfrac{t}{2}) - 2(B_2 - B_3V_p(\tfrac{t}{2}))^{2/3}\}$$

$$N_p(t) = Z_1 t \{Z_2 - A_p(t) - (B_2 - B_3V_p(t))^{2/3} - 4A_p(\tfrac{t}{2}) - 4(B_2 - B_3V_p(\tfrac{t}{2}))^{2/3}\}$$

where

$$B_1 = 4\pi K^{2/3}(R/s)$$

$$B_2 = 3(4\pi N_d)^{\frac{1}{2}} V_d^o$$

$$B_3 = 3(4\pi N_d)^{\frac{1}{2}}(d_{sw}/d_m)$$

$$B_4 = 3.52S - A_d^o$$

$$C_1 = (4\pi/3)K(R/S)$$

$$C_2 = 3S - A_d^o$$

$$D_1 = C_1 d_p (1-\phi_m)/6M_o$$

$$Z_1 = R/6S$$

$$Z_2 = 6S - A_d^o$$

$$K = (3/4\pi)\ (K_p/N_A)(d_m/d_p)\phi_m/(\ 1 - \phi_m)$$

$$R = 2K_i f\ \{I\}N_A$$

$$S = (\ \{S\} - \{S\}_{cmc})N_A A_S$$

$$N_d = (6/\pi)\{V_d^o/(D_d^o)^3\}$$

$$A_d^o = 6V_d^o/D_d^o$$

$$D_d^o = D_d^j \{\frac{N}{N_i}\}^{-1.08}\ \{\frac{H}{H_i}\}^{-0.185}$$

Stage II

$$\frac{d_{fi}}{dX_p} = \frac{G_1}{I}\ (f_{i-1} - f_i) + \frac{G_2}{X_p^{1/3} I}\{f_{i+1}(i+1) - f_i i\} + \frac{G_3}{X_p I}$$

$$\{f_{i+2}(i+2)(i+1) - f_i i(i-1)\}$$

$$\Sigma f_i = 1$$

$$\Sigma f_i i = I$$

where

$$G_1 = RM_o N_A/(K_p N_p^2 d_m \phi_m)$$

$$G_2 = (K_O/K_p)\ (\pi^{1/3}N_A)(6M_O/N_p)^{2/3}(d^{1/3}/d_m)\ (1-\phi_m)/\phi_m$$

$$G_3 = (K_t/K_p)\ (d_p/d_m)\ (1-\phi_m)/\phi_m$$

$$K_t = \exp(A_1+A_2X_p,\text{II-III}+A_3X_p^2,\text{II-III}+A_4X_p^3,\text{II-III}+A_5X_p^4,\text{II-III}$$

$$\frac{dX_p}{dt} = \frac{K_p}{N_A}.\frac{d_m}{M_O}.N_p\phi_m I$$

Stage III

$$I\frac{df_i}{dx} = H_1J_1(X_p)(f_{i-1}-f_i)+H_2J_2(X_p)\{f_{i+1}(i+1)-f_i i\} +$$

$$H_3J_3(X_p)\{f_{i+2}(i+2)(i+1)-f_i i(i-1)\}$$

$$\Sigma f_i = 1$$

$$\Sigma f_i i = I$$

where

$$H_1 = RN_AM_O/(K_pN_p^2d_m)$$

$$H_2 = (K_O/K_p)(\pi^{1/3}N_A)\ (6M_O/N_p)^{2/3}(d_p^{1/3}/d_m)$$

$$H_3 = 1/K_p$$

$$J_1(X_p) = 1-d_mX_p/d_p(1-X_p)$$

$$J_2(X_p) = (d_m/d_p)^{1/3}\{(1-X_p)+d_mX_p/d_p\}^{2/3}/(1-X_p)$$

$$J_3(X_p) = \frac{1}{1-X_p}\exp(A_1+A_2X_p+A_3X_p^2+A_4X_p^3+A_5X_p^4)$$

$$\frac{dX_p}{dt} \quad \frac{K_p d_m}{N_A M_O} \quad N_p I \; \phi(X_p)$$

$$\phi(X_p) = \frac{1-X_p}{(1-X_p)+(d_m/d_p)X_p}$$

4) The model for Stage I of the reaction demands a knowledge of the specific surface area of the monomer dispersion. A relationship relating Sauter mean droplet diameter, impeller speed and impeller diameter has been presented by Merry (17) for styrene in an aqueous solution of emulsifying soap in an unbaffled reactor. This has been incorporated into the model for Stage I of the reaction for emulsion polymerization of styrene in an unbaffled reactor. A relationship between Sauter mean droplet diameter, soap concentration and impeller speed for the dispersion of styrene in an aqueous solution of sodium lauryl sulphate in a baffled reactor has been determined during the current study. This relationship is presented below. It has been incorporated into the model for Stage I of emulsion polymerization of styrene in a baffled reactor.

$$D_d^o = 2.42 \; S_o^{0.013} \; N^{-1.86}$$

Internal dia.of the vessel = 152 mm, impeller combination diameter 75 mm.

5) The model for Stage III of the reaction demands a knowledge of the termination rate constant of the polymerization and its dependence on polymer concentration.

An empirical formula which relates radical termination constant, K_t, to monomer conversion, X_p, has been formulated from conversion against time data of suspension polymerization of styrene at 50°C. It is shown as follows:

$$K_t = \exp(A_1 + A_2 X_p + A_3 X_p^2 + A_4 X_p^3 + A_5 X_p^4)$$

where $A_1 = 9.5873$

$A_2 = -7.4332$

$A_3 = 45.8577$

$A_4 = -95.9184$

$A_5 = 47.4095$

This relationship is incorporated into the model for emulsion polymerization.

6) Emulsion polymerization of styrene at 50°C has been successfully carried out under a range of initial sodium lauryl sulphate concentrations from 1.5 → 7.5 gms dm^{-3} and for impeller speeds in the range 410-850 r.p.m. The progress of the reaction has been monitored gravimetrically and the final particle size has also been determined.

7) A technique for the measurement of particle size using a light transmission method has been developed based on Mie's light scattering theory. This technique is valid for measuring particle diameters down to 0.09 micron. The following set of equations relating particle radius to the Mie light scattering coefficient for various wavelengths have been

formulated and used in the current work.

$$\gamma_{3700} = 0.04387+0.1751X+0.9485X^2-1.3463X^3$$

$$\gamma_{4300} = 0.04294+0.4171X-1.2214X^2+11.1013X^3$$

$$\gamma_{5000} = 0.04254+0.7329X-5.6351X^2+45.2569X^3$$

$$\gamma_{5600} = 0.04211+1.0947X-13.7433X^2+122.572X^3$$

$$\gamma_{6500} = 0.04218+1.6546-29.9384X^2+336.231X^3$$

where X stands for k/α

The data determined with this technique have been shown to be in good agreement with that obtained measured using an electron microphotographic method.

8) Predictions of the computer model for stages I, II and III of emulsion polymerization of styrene at 50°C are in excellent agreement with experimental results. The model is clearly able to represent the dependence of the reaction on impeller speed, a facility that was not available in the use of the Smith and Ewart or Gardon models. The model also allows the progress of Stage III of the reaction to be successfully predicted in that it takes into account the

gel-effect. Particle size, particle number, reaction rate and the mean number of radicals per particle are predicted with good accuracy across the whole of the conversion, or at least up to the point at which the glass transition point falls above the temperature of the reaction (in this case this was 97.4% conversion). This excellent agreement is found both for unbaffled and baffled reactor operation.

Suggestions for Future Work

i) The validity of the present model is demonstrated only for the case of styrene as monomer under rather limited conditions, for instance it is a very simple recipe with no transfer agent, no electrolytes, no incremental soap and it has been tested only at one temperature. Future work should focus on testing different kinds and combinations of monomers under different phase ratios, initiator concentrations, emulsifier concentrations, impeller speeds, temperature and different sized reactors with or without baffles to further test the capabilities of the model and to expand its applications.

ii) In the present model, it has been assumed that the heat transfer in the system is perfect so that the reactor remains isothermal. For the real system however especially for large reactors, this will not be achieved in practice. To model the emulsion polymerization reactor more effectively, heat transfer in the reactor must be investigated and incorporated into the model.

iii) Molecular weight and its distribution directly affect the properties and application of the polymer. For the emulsion polymerization processes, these characteristics in turn relate to the number of particles, the initiator concentration, the purity of the contents in the reactor, environmental conditions and so on. A successful mathematical model of emulsion polymerization reactors should

correctly predict the molecular weight and its distribution of polymer.

(iv) In fact, the molecular weight of products produced by emulsion polymerization can be too high for some practical applications. For this reason, it is sometimes necessary to include within the recipe a chain transfer agent in order deliberately to reduce the molecular weight. In a further investigation this factor should be taken into account.

(v) Gel-effect is a very important phenomenon for emulsion polymerization. Although in the present work the model has given good results, this has only been possible using an empirical formula which clearly is only applicable to this single case. Future work starting from the study of the morphology of the polymer molecules, the structure of the polymer itself and the structure of the polymer solution could be directed towards determination of the dependence of the radical termination rate constant upon the monomer conversion which would be applicable to all polymers under different conditions.

(vi) Although the light transmission technique for measuring the particle size developed in the present work can determine the particle diameter down to 0.09 micron, it is still not adequate for the investigation at the whole course of the emulsion polymerization. Thus, it is necessary to further extend the technique down to an even smaller size range.

NOMENCLATURE.

a	Average surface area of one particle at a given time, cm^2
A_1	Constant
A_2	Constant
A_3	Constant
A_4	Constant
A_5	Constant
A_d^o	Initial surface area of monomer droplets, cm^2/cc water
A_p	Surface area of particles, cm^2/cc water
A_s	Surface area provided by one soap molecule, cm^2
B_1	Constant, $B_1=4\pi K^{2/3}(R/S)$
B_2	Constant, $B_2=3(4\pi N_d)^{\frac{1}{2}}V_d^o$
B_3	Constant, $B_3=3(4\pi N_d)^{\frac{1}{2}}(d_{sw}/d_m)$
B_4	Constant, $B_4=3.52S-A_d^o$
C_1	Constant, $C_1=(4/3)k(R/S)$
C_2	Constant, $C_2=3S-A_d^o$
d_m	Density of monomer, g/cm^3
d_p	Density of polymer, g/cm^3
d_{sw}	Density of monomer swollen particles, g/cm^3
D_1	Constant, $D_1=C_1d_p(1-\phi_m)/6M_O$
D_d^o	Initial Sauter diameter of monomer droplets, cm
D_d^i	Reference Suater diameter of monomer droplets, cm
f	Efficiency of initiator decomposition, fraction
f_i	Number fraction of the particles each of which contain i radicals
$f_{i,II-III}$	Number fraction of the particles each of which contains i radicals by the end of Stage II.

G_1	Constant, $G_1=RM_ON_A/(K_pN_p^2d_m\phi_m)$
G_2	Constant, $G_2=(K_O/K_p)(\pi^{1/3}N_A)(6M_O/N_p)^{2/3}(d_p^{1/3}/d_m)(1-\phi_m)^{1/3}/\phi_m$
G_3	Constant, $(K_t/K_p)(d_p/d_m)(1-\phi_m)/\phi_m$
H	Impeller diameter, cm.
H_1	Constant, $H_1=RN_AM_O/(K_pN_p^2d_m)$
H_2	Constant, $H_2=(K_O/K_p)(\pi^{1/3}N_A)(6M_O/N_p)^{2/3}(d_p^{1/3}/d_m)$
H_3	Constant, $H_3=1/K_p$
H_i	Reference impeller diameter, cm.
i	Number of radicals in one particle
$[I]$	Initial initiator concentration, mole/dm^3 water
I_{II-III}	Average number of radicals in one particle by the end of Stage II
$J_1(X_p)$	Function of X_p
$J_2(X_p)$	Function of X_p
$J_3(X_p)$	Function of X_p
K	Constant, $K=(3/4\pi)(K_p/N_A)(d_m/d_p)\phi_m/(1-\phi_m)$
K_i	Rate constant of initiator decomposition, 1/min
K_p	Rate constant of polymer propagation cm^3/mole.min
K_{pO}	Rate constant of polymer propagation in pure monomer cm^3/mole.min
K_t	Termination rate constant, cm^3/mole.min
K_{tO}	Termination constant in pure monomer, cm^3/mole.min
K_O	Radical desorption rate constant, cm/min
M_O	Ratio of monomer to water in initial charge, g/g
N	Impeller speed, rpm
N_A	Avogadro number
N_d	Number of monomer droplets, 1/cc water

N_i	Reference impeller speed, rpm
N_p	Number of particles, 1/cc water
r_d	Radius of monomer droplets, cm
r_p	Radius of polymer particles, cm
R	Rate of radical generation, 1/cc water
R_O	Initial initiator charged, g/dm^3 water
S	Total area provided by soap, cm^2/cc water
S	Initial soap charged, mole/cc water
$[S]_{cmc}$	Critical micelleiconcentration, mole/cc water
S_O	Initial soap charged, g/dm^3 water
t	Time, min
t_{I-II}	Time passed by the end of Stage I.
T_g	Glass transition temperature of the polymer, ^oC.
V_d^o	Initial volume of monomer droplets, cm^3/cc water
V_p	Volume of particles, cm^3/cc water
$\bar{V}$	Average volume of one particle, cm^3
X_p	Fractional monomer conversion.
$X_{p,I-II}$	Fractional monomer conversion by the end of Stage I.
$X_{p,II-III}$	Fractional monomer conversion by the end of Stage II.
Z_1	Constant, $Z_1=R/6S$
Z_2	Constant, $Z_2=6S-A_d^o$
ϕ_m	Volume fraction of monomer in particles during the Stage I and Stage II.
$\phi(X_p)$	Volume fraction of monomer in particles during Stage III

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APPENDICES

APPENDIX I

COMPUTER PROGRAM FOR DETERMINATION OF PARTICLE SIZE USING EXTINCTION METHOD.

```
50 REM THIS PROGRAMME CALCULATES THE DIAMETER OF POLYMER PARTICLES
60 REM USING LIGHT TRANSMISSION TECHNIQUE.
100 READ M
110 FOR I=1 TO 5
120 READ L[I]
130 NEXT I
140 FOR I=1 TO 5
150 FOR J=1 TO 5
160 READ A[I,J]
170 NEXT J
180 NEXT I
182 FOR I=1 TO 5
184 READ B[I]
186 NEXT I
190 FOR I=1 TO 5
200 READ E[I]
210 NEXT I
220 READ T,P,S
230 FOR I=1 TO 2
240 READ V[I],D[I]
250 NEXT I
255 PRINT "BATCH: PS-12; NO: 12; SO=5GRAM/L.WATER; N=410RPM; UNBAFFLED"

256 PRINT "**************************************************************"
257 PRINT
258 PRINT "THE DATA"
259 PRINT "========="
260 PRINT "AMAXT=",T
270 PRINT "AMAXP=",P
280 PRINT "TSC=",S
281 PRINT "V1=",V[1]
282 PRINT "D1=",D[1]
283 PRINT "V2=",V[2]
284 PRINT "D2=",D[2]
285 PRINT
287 PRINT "WAVE LENGTH: 3700   4300   5000   5800   6500"
288 PRINT "    [illegible] :     4.915  0.53   0.3    0.196  0.1125"
290 K1=T-S
300 K2=P-K1
310 K3=1-T
320 K4=K2/P
330 FOR I=1 TO 2
340 S9=S
350 S=S9*D[I]/V[I]
360 P=P*S/S9
370 T=T*S/S9
380 IF I>1 THEN 470
390 IF K4>.43 THEN 470
400 P5=D[I]*K2
410 S5=D[I]*K1
420 P6=P5/.43
430 S6=P6-P5
440 S7=S5-S6
450 P=P-S7/V[I]
460 T=T-S7/V[I]
470 NEXT I
480 K5=P-(T-S)
490 P1=V[2]*K5
500 S1=(T-S)*V[2]
510 M2=(1-T)*V[2]
520 S2=M*M2*S1/(P1+M*M2)
530 S3=S1-S2
540 C=(P1+S3)/V[2]
542 PRINT
543 PRINT "THE RESULTS"
544 PRINT "==========="
545 PRINT "C=",C
550 D5=(1.0949*S3*.957/(S3+P1))+(1-1.0949*S3/(S3+P1))*1.057
560 FOR I=1 TO 5
570 N[I]=1.5683-1.[illegible]7E-10/(L[I]*1.E-08) ** 2
580 C[I]=1.329+3.[illegible]45E-11/(L[I]*1.E-08) ** 2
590 [illegible]=.99995*[illegible]+.00005*[illegible]
```

```
600  L1=1
610  X(1)=.4337*D5*E(1)*L(1)*1.E-03/(R(1)*D*L1)
612  FOR J=1 TO 5
614  R(J)=A(1,J)
616  NEXT J
618  X6=X(1)
620  GOSUB 1500
622  R(1)=Y6
630  NEXT I
640  H=0
650  FOR I=1 TO 5
660  H=H+R(I)
670  NEXT I
680  R1=H/5
690  D1=2*R1
700  IF (4>.43 THEN 730
710  D=D1*((D5*(1-S3/(S3+P1)))/.4176) ** (1/3)
720  GOTO 770
730  D6=(4*1.257+(1-(4)*.925
740  D=D1*((1+S2/(P1+S3))*D5/D6) ** (1/3)
750  J=6*((1+(2)/(3.14159*(3*D6*(D*.2881) ** 3)
760  GOTO 780
770  J=4.5979*(2/(3/(D*.2881) ** 3
780  PRINT "(3700=",X(1),"R3700=",R(1)
790  PRINT "(4300=",X(2),"R4300=",R(2)
800  PRINT "(5000=",X(3),"R5000=",R(3)
810  PRINT "(5600=",X(4),"R5600=",R(4)
820  PRINT "(6500=",X(5),"R6500=",R(5)
830  PRINT "R1=",R1
840  PRINT "D1=",D1
850  PRINT "DP=",D
860  PRINT "JP=",J
870  PRINT "(P=",(4
880  DATA 2.2393E-04
890  DATA 3700,4300,5000,5600,6500
895  DATA .4155,.3567,.1269,.2653,.334
900  DATA .4292,.2362,.892,.2034,.3113
910  DATA .2853,.2227,.3663,.1502,.2434
920  DATA .2844,.2147,.2513,.1175,.2185
930  DATA .3829,.2187,.835,.0781,.1665
940  DATA .346,.255,.83,.132,.194
950  DATA .915,.53,.3,.196,.1135
960  DATA .3414,.3306,.3263
970  DATA 100,.454,100,.45,10
980  END
1500  J6=5
1505  J7=J6
1507  J6=J6-1
1510  FOR J=1 TO J6
1520  D6=((6-R(J))*((6-R(J+1))
1530  IF D6>0 THEN 1560
1540  I6=J
1550  GOTO 1620
1560  NEXT J
1570  D7=ABS((6-R(1))-ABS((6-R(J6))
1580  IF D7 >= 0 THEN 1610
1590  I6=1
1600  GOTO 1620
1610  I6=J6-1
1620  IF ((6-J6+1) <> 0 THEN 1650
1630  I6=I6-1
1640  GOTO 1690
1650  IF I6-1=0 THEN 1690
1660  D8=ABS((6-R(I6))-(ABS((6-R(I6+1)))
1670  IF D8 >= 0 THEN 1690
1680  I6=I6-1
1690  Y6=0
1700  IF I6-J6<2 THEN 1720
1710  I6=I6-1
1720  L6=I6+2
1730  FOR X6=I6 TO L6
1740  J6=S((5)
1750  FOR J=I6 TO L6
1760  IF J-X6=0 THEN 1790
1770  J6=((6-R(J))/(R((6)-R(J)))*J6
1780  NEXT J
```

```
1290  V6=V6+N6
1300  NEXT X6
1310  V6=V6
1320  N6=N7
1330  RETURN
1340  END

RUN
NA

BATCH: PS-12; NO: 12; CD=50GRAM/L.WATER; N=410RPM; UNBAFFLED
*************************************************************

THE DATA
=========
AMAXT=              .3414
AMAXP=              .3346
TSC=                .3263
G1=                 100
S1=                 .454
G2=                 100.45
S2=                 10

WAVE LENTH: 3700   4300   5200   5600   6500
    E :     0.915  0.53   0.3    0.176  0.1135

THE RESULTS
===========
C=                  1.45251E-04
K3700=              3.91957E-02   R3700=            6.50530E-02
K4300=              6.03022E-02   R4300=            6.47409E-02
K5200=              3.93173E-02   R5200=            6.45739E-02
K5600=              2.91397E-02   R5600=            6.62002E-02
K6500=              1.96567E-02   R6500=            .26475
R1=                 6.57515E-02
D1=                 .130123
D2=                 .131509
NP=                 4.01423E+14
XP=                 .954326

DONE
```

APPENDIX II

COMPUTER PROGRAMS FOR THE COMPUTATION OF THE DEPENDENCE OF TERMINATION RATE CONSTANT ON MONOMER CONVERSION

1) DEFFI The Computation of dX_p/dt from $t\text{-}X_p$ data using differentiation method.

2) REG 3 The Formulation of K_t and X_p using multiple regression method.

3) XKT The Evaluation of K_t against X_p

```
LIS
DEFF1

1   REM THIS PROGRAMME IS A NUMERICAL DIFFERENTIAL METHOD TO
2   REM CALCULATE THE CONVERSION RATE FROM THE DATA OF
3   REM SUSPENSION POLYMERIZATION.
5   DIM X[27],Y[27],F[27]
10  N1=15
20  FOR I=1 TO N1
30  READ X[I]
31  NEXT I
39  FOR I=1 TO N1
40  READ Y[I]
50  NEXT I
60  H=60
65  PRINT " NO","TIME(MIN)","CONVERSION","  DY/DT"
70  FOR I=1 TO N1
80  IF I=1 THEN 140
90  IF I=2 THEN 160
100  IF I=N1 THEN 200
110  IF I=N1-1 THEN 180
120  LET F[I]=(-2*Y[I-2]-Y[I-1]+Y[I+1]+2*Y[I+2])/(10*H)
130  GOTO 210
140  LET F[I]=(-21*Y[I]+13*Y[I+1]+17*Y[I+2]-9*Y[I+3])/(20*H)
150  GOTO 210
160  LET F[I]=(-11*Y[I-1]+3*Y[I]+7*Y[I+1]+Y[I+2])/(20*H)
170  GOTO 210
180  LET F[I]=-1*(-11*Y[I+1]+3*Y[I]+7*Y[I-1]+Y[I-2])/(20*H)
190  GOTO 210
200  LET F[I]=-1*(-21*Y[I]+13*Y[I-1]+17*Y[I-2]-9*Y[I-3])/(20*H)
210  PRINT I,X[I],Y[I],F[I]
220  NEXT I
430  DATA 0,60,120,180,240,300,360,420,480,540,600
490  DATA 660,720,780,840
510  DATA 0,.0613,.1195,.1399,.2367,.2774,.3243
520  DATA .336,.4264,.4583,.5007,.5449,.6313
530  DATA .7502,.9655
550  END

RUN
DEFF1

 NO            TIME(MIN)       CONVERSION        DY/DT
 1              0               0               9.33167E-04
 2              60              .0613           1.00933E-03
 3              120             .1195           1.00250E-03
 4              180             .1399           .000914
 5              240             .2367           3.23500E-04
 6              300             .2774           7.99667E-04
 7              360             .3243           8.13333E-04
 8              420             .336            7.73167E-04
 9              480             .4264           7.03500E-04
 10             540             .4583           6.53500E-04
 11             600             .5007           .000529
 12             660             .5449           1.19150E-03
 13             720             .6313           1.39150E-03
 14             780             .7502           2.30500E-03
 15             840             .9655           3.90500E-03

DONE
```

```
RUN

 1  REM THIS PROGRAM IS FOR ESTABLISHING THE DEPENDENCE OF
 2  REM TERMINATION DATE CONSTANT UPON JUNCTION CONNECTION
 3  REM POLARIZATION OF STORAGE BY USING MULTIPLE REGRESSION
 4  REM METHOD.
100   N=4
110   M=15
119   DIM C(30,10),X(30),Z(30),B(10),L(14,10),C(10),Y(30),W(30)
130   FOR I=1 TO N
140   READ Z(I)
150   NEXT I
160   DATA 0,.0613,.1195,.1899,.2367,.2774,.3243,.386
170   DATA .4264,.4563,.5207,.5449,.6313,.7572,.9655
200   FOR I=1 TO N
210   READ Y(I)
220   NEXT I
230   DATA 9.33167E-04,1.0493E-03,1.0825E-03,.002914,3.035E-04
240   DATA 7.99667E-04,3.13333E-04,7.73167E-04,7.035E-04,6.535E-04
250   DATA .000329,1.1915E-03,1.3915E-03,2.33533E-03,3.775333E-03
290   READ X1,X2,I1
300   DATA 1.27E+07,1.032E-04,2.159E-04
310   S=X1 ** 2*X2*I1
320   FOR I=1 TO N
330   Y(I)=S*((1-Y(I))/Y(I)) ** 2
340   Y(I)=LOG(Y(I))
350   NEXT I
360   FOR I=1 TO N
370   FOR J=1 TO M
380   L(I,J)=Z(I) ** J
390   NEXT J
400   NEXT I
410   GOSUB 1000
420   GOSUB 2000
430   B=Y2
440   FOR I=1 TO M
450   B=B-C(I)*V(I)
460   NEXT I
465   PRINT "      B=";B
470   PRINT
480   PRINT " I","  B"
490   FOR I=1 TO M
500   PRINT I,C(I)
510   NEXT I
520   END
1000  Y1=0
1050  FOR I=1 TO N
1060  Y1=Y1+Y(I)
1070  NEXT I
1080  Y2=Y1/N
1090  FOR I=1 TO M
1100  V(I)=0
1110  FOR J=1 TO N
1120  V(I)=V(I)+L(J,I)
1130  NEXT J
1140  V(I)=V(I)/N
1150  NEXT I
1160  FOR I=1 TO M
1170  FOR J=1 TO M
1200  S1=0
1210  S2=0
1220  S3=0
1230  FOR R=1 TO N
1240  S1=S1+L(R,I)*L(R,J)
1250  S2=S2+L(R,I)
1260  S3=S3+L(R,J)
1270  NEXT R
1280  A(I,J)=S1-S2*S3/N
1290  NEXT J
1300  NEXT I
1310  FOR I=1 TO M
1320  S4=0
1340  FOR J=1 TO N
1350  S4=S4+L(J,I)*Y(J)
1360  NEXT J
1370  S5=V(I)*Y1
1380  C(I)=S4-S5/N
1390  NEXT I
```

```
1400  RETURN
2000  N0=N-1
2010  FOR K6=1 TO N0
2020  FOR L=K6 TO N
2030  IF L(L,K6)=0 THEN 2060
2040  L0=L
2050  GOTO 2080
2060  IF L-N=0 THEN 2410
2070  NEXT L
2080  IF L0-K6=0 THEN 2170
2090  FOR J=K6 TO N
2100  T6=L(K6,J)
2110  L(K6,J)=L(L0,J)
2120  L(L0,J)=T6
2130  NEXT J
2140  T6=C(K6)
2150  C(K6)=C(L0)
2160  C(L0)=T6
2170  N1=K6+1
2180  FOR J=N1 TO N
2190  L(K6,J)=L(K6,J)/L(K6,K6)
2195  NEXT J
2200  C(K6)=C(K6)/L(K6,K6)
2210  L=L0+1
2220  FOR I=L TO N
2230  FOR J=N1 TO N
2240  L(I,J)=L(I,J)-L(I,K6)*L(K6,J)
2250  NEXT J
2260  C(I)=C(I)-C(K6)*L(I,K6)
2270  NEXT I
2280  NEXT K6
2290  K7=N
2300  IF L(K7,K7)=0 THEN 2410
2310  C(K7)=C(K7)/L(K7,K7)
2320  N1=N-1
2330  FOR K6=1 TO N1
2340  I=N-K6
2350  L=I+1
2360  FOR J=L TO N
2370  C(I)=C(I)-L(I,J)*C(J)
2380  NEXT J
2390  NEXT K6
2400  RETURN
2410  PRINT "K6=",K6
2500  END

RUN
RESID

      B0=          29.641

  I                B
  1               -7.43325
  2                45.5635
  3               -95.9334
  4                47.419

DONE
```

```
LIS
XXT

100  DIM X(30),X(30)
110  LET N=20
120  FOR I=1 TO N
130  READ X(I)
140  NEXT I
150  READ A1,A2,A3,A4,A5
160  FOR I=1 TO N
170  S=A1+A2*X(I)+A3*X(I) ** 2+A4*X(I) ** 3+A5*X(I) ** 4
180  X(I)=EXP(S)
190  NEXT I
200  PRINT " X(S)","     XT"
210  FOR I=1 TO N
220  PRINT X(I),X(I)
230  NEXT I
240  DATA 0,.05,.1,.15,.2,.25,.3,.35,.4,.45,.5
250  DATA .55,.6,.65,.7,.75,.8,.85,.9,.95
260  DATA 29.5373,-7.4332,45.3577,-95.9134,47.4895
300  END

RUN
XXT

 X(S)              XT
 0                 7.87293E+12
 .05               5.48634E+12
 .1                4.35673E+12
 .15               4.62291E+12
 .2                5.81512E+12
 .25               5.28937E+12
 .3                5.19515E+12
 .35               4.81224E+12
 .4                4.03552E+12
 .45               3.02738E+12
 .5                1.96376E+12
 .55               1.12729E+12
 .6                5.66109E+11
 .65               2.51326E+11
 .7                1.03895E+11
 .75               3.73074E+10
 .8                1.31383E+10
 .85               4.57388E+09
 .9                1.64838E+09
 .95               6.43153E+08

DONE

LIS
```

APPENDIX III

COMPUTER PROGRAM FOR FORMULATION OF THE DISPERSION DATA IN BAFFLED REACTOR

1) DISPER The Evaluation of the average diameter of monomer droplets for the various sample from the dispersion data.

2) D Formulation of D_d^o, So and N using regression method.

```
DISPER

100  K1=15
110  K2=42
120  DIM D[42],N[42]
130  PRINT "I","DS","N"
140  FOR I=1 TO K2
150  READ D[I]
160  NEXT I
165  FOR I1=1 TO K1
170  FOR I=1 TO K2
180  READ N[I]
190  NEXT I
200  N1=0
210  A1=0
220  V1=0
230  FOR I=1 TO K2
240  D=1.6129E-06*D[I]
250  A=3.1416*D ** 2*N[I]
260  V=(3.1416/6)*D ** 3*N[I]
270  N1=N1+N[I]
280  A1=A1+A
290  V1=V1+V
300  NEXT I
305  D1=V1*6/A1
320  PRINT I1,D1,N1
330  NEXT I1
340  DATA 2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18,19,20,21
350  DATA 22,23,24,25,26,27,28,29,30,31,32,33,34,35,36,37,38
360  DATA 39,40,41
365  DATA 50,56
370  DATA 99,111,103,112,64,50,43,19,24,15,16,9,6,3,4
380  DATA 3,3,4,3,1,1,2,0,0,1,1,0,0,0,1
390  DATA 0,0,0,0,0,0,1,0,0,1,1,0,0,1
400  DATA 93,114,91,72,42,23,26,17,7,11,11,3,2,3,4
410  DATA 0,3,2,0,0,0,0,0,0,0,0,1,0,0,0
420  DATA 0,1,0,0,0,0,0,0,0,0,0,0
430  DATA 51,37,33,22,25,23,9,7,11,5,5,3,1,2,0
440  DATA 0,0,0,0,0,0,0,0,0,0,0,0,0,0,0
450  DATA 1,0,0,0,0,0,0,0,0,0,0,0
460  DATA 0,73,27,22,16,12,7,2,2,3,0,1,0,0,0
470  DATA 0,0,0,0,0,0,0,0,0,0,0,0,0,0,0
480  DATA 0,0,0,0,0,0,0,0,0,0,0,0
490  DATA 66,45,21,23,10,6,5,3,3,0,0,0,0,0,0
500  DATA 0,0,0,0,0,0,0,0,0,0,0,0,0,0,0
510  DATA 0,0,0,0,0,0,0,0,0,0,0,0
520  DATA 29,23,11,7,7,9,6,2,2,3,3,1,1,1,0
530  DATA 2,0,2,2,2,1,1,1,2,0,1,0,0,0,0
540  DATA 0,0,0,0,0,0,0,0,0,0,0,0
550  DATA 61,53,27,27,16,13,5,5,7,5,2,2,0,1,0
560  DATA 2,0,0,1,0,0,0,0,0,0,0,0,0,0
570  DATA 0,0,0,0,0,0,0,0,0,0,0,0
580  DATA 25,37,21,23,11,3,9,5,4,2,2,0,0,1,0
590  DATA 0,0,0,0,0,0,0,0,0,0,0,0,0,0
600  DATA 0,0,0,0,0,0,0,0,0,0,0,0
610  DATA 42,52,13,20,11,12,15,3,3,1,0,0,0,0,0
620  DATA 0,0,0,0,0,0,0,0,0,0,0,0,0,0,0
630  DATA 0,0,0,0,0,0,0,0,0,0,0,0
640  DATA 14,53,22,26,17,17,9,4,0,0,0,0,0,0,0
650  DATA 0,0,0,0,0,0,0,0,0,0,0,0,0,0,0
660  DATA 0,0,0,0,0,0,0,0,0,0,0,0
670  DATA 125,71,26,19,17,10,5,3,6,5,0,3,1,1,3
680  DATA 1,0,0,0,0,0,1,1,3,1,0,1,0,1,0
690  DATA 0,0,0,0,0,0,0,0,0,0,1,0
700  DATA 20,36,9,5,10,3,4,4,1,0,0,0,3,2,1
710  DATA 1,2,0,0,0,0,0,0,1,0,0,0,0,0,0
720  DATA 0,0,0,0,0,0,0,0,0,0,0,0
730  DATA 62,61,77,29,24,16,12,3,4,3,3,0,2,2,0
740  DATA 0,0,0,0,0,0,0,0,0,0,0,0,0,0,0
750  DATA 3,0,0,0,0,0,0,0,0,0,0,0
760  DATA 41,33,24,12,23,11,5,7,1,1,1,1,0,0,0
770  DATA 0,0,0,0,0,0,0,0,0,0,0,0,0,0,0
780  DATA 0,0,0,0,0,0,0,0,0,0,0,0
790  DATA 56,39,33,29,15,14,6,2,0,0,0,0,0,0,0
800  DATA 0,0,0,0,0,0,0,0,0,0,0,0,0,0,0
810  DATA 0,0,0,0,0,0,0,0,0,0,0,0
820  END
```

```
D

1   REM THIS PROGRAMME IS FOR SETTING UP THE INTERDEPENDENCE OF
2   REM AVERAGE DROPLET DIAMETER , EMULSIFIER CONCENTRATION AND
3   REM IMPELLER SPEED BY USE OF MULTIPLE REGRESSION.
110  N=15
120  DIM X[29]
130  DIM Y[29]
140  DIM Z[29]
150  FOR I=1 TO N
160  READ X[I]
165  X[I]=LOG(X[I])
170  NEXT I
180  FOR I=1 TO N
190  READ Y[I]
195  Y[I]=LOG(Y[I])
200  NEXT I
210  FOR I=1 TO N
220  READ Z[I]
225  Z[I]=LOG(Z[I])
230  NEXT I
240  LET T1=0
250  LET T2=0
260  LET T3=0
270  LET J1=0
280  LET J2=0
290  LET J3=0
300  LET F1=0
310  LET F2=0
320  LET F3=0
330  FOR I=1 TO N
340  LET T1=T1+X[I]
350  LET T2=T2+Y[I]
360  LET T3=T3+Z[I]
370  LET J1=J1+X[I]*Z[I]
380  LET J2=J2+Y[I]*X[I]
390  LET J3=J3+Y[I]*Z[I]
400  LET F1=F1+X[I] ** 2
410  LET F2=F2+Z[I] ** 2
420  LET F3=F3+Y[I] ** 2
430  NEXT I
440  LET Y1=T2/N
450  LET X1=T1/N
460  LET X2=T3/N
470  LET L1=F1-(T1 ** 2)/N
480  LET L2=J1-(T1*T3)/N
490  LET L3=F2-(T3 ** 2)/N
500  LET L4=J2-(T2*T1)/N
510  LET L5=J3-(T2*T3)/N
520  LET B1=(L4*L3-L5*L2)/(L1*L3-L2 ** 2)
530  LET B2=(L5*L1-L4*L2)/(L1*L3-L2 ** 2)
540  LET B3=Y1-B1*X1-B2*X2
545  B3=EXP(B3)
550  PRINT "B0=",B3
560  PRINT "B1=",B1
570  PRINT "B2=",B2
580  DATA 3.75,3.75,3.75,3.75,3.75
590  DATA 2.75,2.75,2.75,2.75,2.75
600  DATA 1.75,1.75,1.75,1.75,1.75
610  DATA 2.96334E-05,1.33543E-05,1.79412E-05,1.05393E-05,9.32693E-06
620  DATA 2.73325E-05,1.49247E-05,1.22083E-05,1.24334E-05,9.50256E-06
630  DATA 3.46353E-05,2.12693E-05,1.19414E-05,1.10377E-05,8.37543E-06
640  DATA 450,550,650,750,850,450,550,650,750,850
650  DATA 450,550,650,750,850
700  END

RUN
D

B0=                 2.48033
B1=                 1.29462E-02
B2=                -1.55136

DONE
```

APPENDIX IV

COMPUTER PROGRAM FOR SMITH-EWART MODEL

```
C012                -TRACE 1
C000                 TRACE 0
C001                 MASTER SWMODEL
C002           C  THIS PROGRAMME RECALCULATES THE SMITH-EWART MODEL FOR EMULSION
C003           C  POLYMERIZATION OF STYRENE
C004           C
C005                 DIMENSION T1(8)
C006                 COMMON /A/KP,KD,DM,DP,FI,NA,AS,SCMC
C007                 REAL KP,KD,NA,K,MO,N10,MI
C008           C
C009           C  INPUT DATA . KP(CC/MOLE.MIN),FI(%),NA(MOLECULES/CCW),DM(GRAM/CC),
C010           C  DP(GRAM/CC),AS(SQCM/MOLECLES),KD(1/S),SCMC(GRAM/LW),T(MIN),SO(GRAM
C011           C  /LW),MO(GRAM/CCW),RO(GRAM/LW)
C012           C
C013                 DO 9999 I1=1,3
C014                 READ(1,1) SO,MO,RO
C015               1 FORMAT(3F0.0)
C016                 WRITE(2,391)
C017             391 FORMAT(/////2X,'INITIAL DATA: AMOUNT OF SOAP SO; AMOUNT OF MONOMER
C018                *  MO;AMOUNT OF INITIATER RO'/2X,77(1H*)///10X,'SO(G/LW)',6X,
C019                *'MO(G/CCW)',7X,'RO(G/LW)')
C020                 WRITE(2,392) SO,MO,RO
C021             392 FORMAT(/,3F15.2//2X,77(1H*)//)
C022                 IF(SO.LT.2.5) GOTO 2
C023                 T9=0.025
C024                 DO 3 L=1,8
C025                 T1(L)=2.0*T9
C026                 T9=T1(L)
C027               3 CONTINUE
C028                 GOTO 8
C029               2 T9=0.01
C030                 DO 9 L=1,8
C031                 T1(L)=2.0*T9
C032                 T9=T1(L)
C033               9 CONTINUE
C034               8 CALL STAGE1(SO,MO,RO,R,T1,V10,N10,TB)
C035                 CALL STAGE2(V10,N10,TB,MO,DM,DP,FI,KP,NA,R,T2,VP)
C036                 CALL STAGE3(T2,VP,FI,KP,NA,N10,DM,DP,MO,MI,0.5)
C037            9999 CONTINUE
C038                 STOP
C039                 END

END OF SEGMENT, LENGTH   115, NAME  SWMODEL

C040                 BLOCK DATA
C041                 COMMON /A/KP,KD,DM,DP,FI,NA,AS,SCMC
C042                 REAL KP,KD,NA
C043                 DATA KP,KD,DM,DP,FI,NA,AS,SCMC/1.27E7,5.7E-5,0.906,1.057,0.605,
C044                36.023E23,3.5E-15,0.5/
C045                 END



C046                 SUBROUTINE STAGE1(SO,MO,RO,R,T1,V10,N10,TB)
C047                 DIMENSION T1(8),A1(8),T(10),A(10),V(10),N(10),D(10),SM(10),X(10)
C048                 COMMON /A/KP,KD,DM,DP,FI,NA,AS,SCMC
C049                 REAL KP,KD,NA,K,MO,N,MI,N10
C050           C
C051           C  FIX CONSTANTS
C052           C
C053                 S=NA*AS*SO/(272.0*1000.0)
C054                 R=2.0*KD*NA*RO/(270.0*1000.0)
C055                 K=(3.0/(4.0*3.14159))*(KP/NA)*(DM/DP)*(FI/(1.0-FI))
C056                 B=4.0*3.14159*K**(2.0/3.0)*R/S
C057                 C=(4.0*3.14159/3.0)*K*R/S
C058           C
C059           C  FIND THE RELATIONSHIP BETWEEN TIME T1 AND THE AREA OF PARTICLES IN ONE
C060           C  CC WATER A1
C061                 DO 400 I=1,8
C062                 IF(.NOT.I.EQ.1) GOTO300
C063                 A1(I)=0.587*B*S*T1(I)**(5.0/3.0)
C064                 GOTO400
C065             300 A1(I)=B*T1(I)**(5.0/3.0)*(0.587*S-0.42*A1(I-1))
C066             400 CONTINUE
C067           C
C068           C  FIND THE TIME TB WHEN PARTICLENUCLEATION IS JUST COMPLETE
C069           C
C070                 CALL CHAZHI(A1,T1,B,S,TB)
```

```
C
C  CALCULATE A SERIES OF VALUES OF PARAMETERS ALANG THE HISTORY OF
C  POLYMERIZATION DURINGTHE STAGE ONE
      WRITE(2,450)
  450 FORMAT(//2X,'THE RESULTSCALCULATED ALONG THE REACTION HISTORY OF
     1STAGE ONE'/2X,62(1H=)//)
      WRITE(2,500)
  500 FORMAT(//8X,'TIME(MIN)',4X,'CONVERSION(%)',3X,'S(MIC)(G/LW)',2X,
     2'AP(SQCM/CCW)',3X,'VP(CC/CCW)',4X,'DP(MICRON)',5X,'N(PARS/CCW)')
      DO 600 I=1,10
      T(I)=(TB/10.0)*FLOAT(I)
  600 CONTINUE
      DO 800 J=1,10
      CALL CHAZHI(T1,A1,B,T(J),A(J))
      TH=T(J)/2.0
      CALL CHAZHI(T1,A1,B,TH,AH)
      N(J)=(R/S)*T(J)*(S-A(J)/6.0-(2.0/3.0)*AH)
      V(J)=(T(J)**2/6.0)*(3.0*C*S-2.0*C*AH)
      D(J)=(V(J)/A(J))*60000.0
      X(J)=V(J)*(1.0-FI)*DP/MO*100.0
      SM(J)=(S-A(J))/AS/NA*272.0*1000.0
      WRITE(2,700) T(J),X(J),SM(J),A(J),V(J),D(J),N(J)
  700 FORMAT(/5X,0PF10.3,2F15.3,1P4E15.3)
  800 CONTINUE
      MI=1.44*KP*FI*DM**N(10)/R
      WRITE(2,190)
  190 FORMAT(//2X,'THE VALUES OF PARAMETERS AT THE END OF STAGE ONE',
     3//8X,'TIME(MIN)',4X,'CONVERSION(%)',3X,'S(MIC)(G/LM)',2X,'AP(SQCM/
     4CCW)',2X,'VP(CC/CCW)',4X,'DP(MICRON)',5X,'MOLEC.WT.',4X,'N(PARS/CC
     5W)'//)
      WRITE(2,191) T(10),X(10),SM(10),A(10),V(10),D(10),MI,N(10)
  191 FORMAT(//5X,F10.3,2F15.3,1P3E15.3,0PF15.0,1PE15.3)
      N10=N(10)
      V10=V(10)
      RETURN
      END
```

END OF SEGMENT, LENGTH 395, NAME STAGE1

```
      SUBROUTINE STAGE2(VI,NI,TB,MO,DM,DP,FI,KP,NA,R,T2,VP)
      REAL NI,NP,NT,NA,MO,KP,MI
      VDO=MO/DM
      VP=VI
      VD1=VDO-VP*(FI+(1.0-FI)*DP/DM)
      NT=NI
      T2=TB
      DELTAT=1.0
      WRITE(2,210)
  210 FORMAT(//2X,'THE RESULTS CULCULATED ALONG THE REACTION HISTORY OF
     2STAGE TWO'/2X,60(1H=)//8X,'TIME(MIN)',4X,'CONVERSION(%)',3X,
     3'AP(SQCM/CCW)',3X,'VP(CC/CCW)',4X,'DP(MICRON)',4X,'VD(CC/CCW)'/)
      B=0.5*(KP/NA)*(DM/DP)*FI*NT
C
C  CALCULATE A SERIES OF VALUES OF PARAMETERS ALONG THE HISTORY OF POLYMERIZATI
C  DURING THE STAGE TWO
C
      DO 240 I=1,10000
      DO 220 J=1,2
      IF(VD1.LE.0.0) GOTO250
      DELTAV=B*DELTAT/(1.0-FI)
      VP=VP+DELTAV
      DPA=(6.0*VP/(3.14159*NT))**(1.0/3.0)*10000.0
      AP=(VP/DPA)*60000.0
      VD1=VD1-DELTAV*(FI+(1.0-FI)*DP/DM)
      T2=T2+DELTAT
      X2=VP*(1.0-FI)*DP/MO*100.0
  220 CONTINUE
      WRITE(2,230) T2,X2,AP,VP,DPA,VD1
  230 FORMAT(/5X,0PF10.3,F15.3,1P4E15.3)
  240 CONTINUE
  250 MI=2.0*B*NA*DP/R
      WRITE(2,260)
  260 FORMAT(///2X,'THE VALUES OF PARAMETERS AT THE END OF STAGE TWO',
     5//,8X,'TIME(MIN)',4X,'CONVERSION(%)',2X,'AP(SQCM/CCW)',2X,'VP(CC/
     6CCW)',4X,'DP(MICRON)',4X,'VD(CC/CCW)',5X,'MOLEC.WT.',//)
      WRITE(2,270) T2,X2,AP,VP,DPA,VD1,MI
  270 FORMAT(/5X,F10.3,F15.3,1P4E15.3,0PF15.0)
      RETURN
      END
```

```
END OF SEGMENT, LENGTH_  219, NAME  STAGE2

 0147                  SUBROUTINE STAGE3(T2,VP,FI,KP,NA,NT,DM,DP,MO,MI,Q)
 0148                  REAL MO,NI,KP,NA,NT,MI
 0149                  WRITE(2,310)
 0150              310 FORMAT(//2X,'THE RESULTS CALCULATED ALONG THE REACTION HISTORY OF
 0151                 6STAGE THREE'/2X,64(1H=)//8X,'TIME(MIN)',4X,'CONVERSION(%)',2X,
 0152                 5'AP(SQCM/CCW)',3X,'VP(CC/CCW)',4X,'DP(MICRON)',4X,'VMP(CC/CCW)'/)
 0153                  VMP=VP*FI
 0154                  T3=T2
 0155                  DELTAT=1.0
 0156                  X3=0.0
 0157                  DO 360 I=1,100
 0158                  DO 340 J=1,5
 0159                  IF(X3.GE.95.0) GOTO370
 0160                  RATE=(KP/NA)*(VMP/VP)*(NT*Q)
 0161                  VMP=VMP-RATE*DELTAT
 0162                  VP=VP-RATE*DELTAT*(1.0-DM/DP)
 0163                  AP=(NT*3.14159)**(1.0/3.0)*(6.0*VP)**(2.0/3.0)
 0164                  DP3=(VP/AP)*60000.0
 0165                  X3=(1.0-VMP*DM/MO)*100.0
 0166                  T3=T3+DELTAT
 0167              340 CONTINUE
 0168                  WRITE(2,350) T3,X3,AP,VP,DP3,VMP
 0169              350 FORMAT(/5X,OPF10.3,F15.3,1P4E15.3)
 0170              360 CONTINUE
 0171              370 WRITE(2,380)
 0172              380 FORMAT(///2X,'THE FINAL RESULTS OF THE CALCULATION',/2X,36(1H=)//
 0173                 8X,'TIME(MIN)',4X,'CONVERTION(%)',2X,'N(PARTICLES)',3X,'DP3(MICRON)',
 0174                 9)',4X,'MOLECLE.WT.'/)
 0175                  WRITE(2,390) T3,X3,NT,DP3,MI
 0176              390 FORMAT(/5X,F10.3,F15.3,1P2E15.3,0PF15.1)
 0177                  RETURN
 0178                  END

END OF SEGMENT, LENGTH   192, NAME  STAGE3

 0179                  SUBROUTINE CHAZHI(A,B,N,X,Y)
 0180                  DIMENSION A(N),B(N)
 0181                  NC=N
 0182                  N=N-1
 0183                  DO 1 J=1,N
 0184                  IF((X-A(J))*(X-A(J+1))) 10,10,1
 0185               10 I=J
 0186                  GOTO 22
 0187                1 CONTINUE
 0188                  IF(ABS(X-A(1))-ABS(X-A(N))) 20,21,21
 0189               20 I=1
 0190                  GOTO 22
 0191               21 I=N-1
 0192               22 IF(I-N+1) 24,23,24
 0193               23 I=I-1
 0194                  GOTO 27
 0195               24 IF(I-1) 25,27,25
 0196               25 IF(ABS(X-A(I))-ABS(X-A(I+1))) 26,27,27
 0197               26 I=I-1
 0198               27 V=0.0
 0199                  IF(I-N) 29,28,28
 0200               28 I=I-1
 0201               29 L=I+2
 0202                  DO 2 K=I,L
 0203                  W=B(K)
 0204                  DO 3 J=I,L
 0205                  IF(J-K) 30,3,30
 0206               30 W=(X-A(J))/(A(K)-A(J))*W
 0207                3 CONTINUE
 0208                  V=V+W
 0209                2 CONTINUE
 0210                  Y=V
 0211                  N=NC
 0212                  RETURN
 0213                  END

END OF SEGMENT, LENGTH   179, NAME  CHAZHI

 0214                  FINISH
```

APPENDIX V

COMPUTER PROGRAM FOR STAGE I AND STAGE II IN UNBAFFLED REACTOR

```
C012                TRACE 1
C000                TRACE 0
C001                MASTER UNSTABLE MODEL
C002          C
C003          C  THIS PROGRAMME SIMULATES THE EMULSION POLYMERIZATION . THE MODEL
C004          C  PROPOSED TAKES INTO ACCOUNT THE SOAP ADSORBED ONTO THE SURFACE OF
C005          C  MONOMER DROPLETS. THE REACTOR USED IS UNBAFFLED. AND THE PROGRESSC
C006          C  OF STAGE TWO IS CONSIDERED AS UNSTABLE
C007          C
C008                DIMENSION T1(8)
C009                COMMON /A/KP,KD,DM,DP,FI,NA,AS,SCMC
C010                REAL KP,KD,NA,K,MO,N10,MI
C011          C
C012          C  INPUT DATA . KP(CC/MOLE.MIN),FI(%),NA(MOLECULES/CCW),DM(GRAM/CC),
C013          C  DP(GRAM/CC),AS(SQCM/MOLECLES),KD(1/S),SCMC(GRAM/LW),T(MIN),SO(GRAM
C014          C  /LW),MO(GRAM/CCW),RO(GRAM/LW)
C015          C
C016                SO=5.0
C017                MO=0.5
C018                RO=1.25
C019                H=7.5
C020                REV=410
C021                WRITE(2,391)
C022           391  FORMAT(//////2X,'INITIAL DATA: AMOUNT OF SOAP SO;AMOUNT OF MONOME
C023               * MO; AMOUNT OF INITIATOR RO; DIAMETER OF IMPELLER H; IMPELLER SPE
C024               *ED REV',/2X,118(1H*)///10X,'SO(G/LW)',6X,'MO(G/CCW)',7X,'RO(G/LW)
C025               *,8X,'H(CM)',8X,'REV(RPM)')
C026                WRITE(2,392) SO,MO,RO,H,REV
C027           392  FORMAT(/,5F15.2///2X,118(1H*)//)
C028                IF(SO.LE.2.5) GOTO 2
C029                T9=0.025
C030                DO 3 L=1,8
C031                T1(L)=2.0*T9
C032                T9=T1(L)
C033              3 CONTINUE
C034                GOTO 8
C035              2 T9=0.01
C036                DO 9 L=1,8
C037                T1(L)=2.0*T9
C038                T9=T1(L)
C039              9 CONTINUE
C040              8 CALL STAGE1(SO,MO,RO,S,R,K,T1,V10,N10,T10,TB,REV,H,X10)
C041                CALL UNSTA(N10,T10,MO,RO,X10)
C042                STOP
C043                END
```

END OF SEGMENT, LENGTH 101, NAME UNSTABLEMODEL

```
C044                BLOCK DATA
C045                COMMON /A/KP,KD,DM,DP,FI,NA,AS,SCMC
C046                REAL KP,KD,NA
C047                DATA KP,KD,DM,DP,FI,NA,AS,SCMC/1.27E7,5.7E-5,0.906,1.057,0.605,
C048               36.023E23,3.5E-15,0.5/
C049                END
```

```
C050                SUBROUTINE STAGE1(SO,MO,RO,S,R,K,T1,V10,N10,T10,TB,REV,H,X10)
C051                DIMENSION T1(8),A1(8),T(10),A(10),V(10),N(10),D(10),SP(10),X(10)
C052                DIMENSION V1(8),VD(10),DD(10),AD(10),VD1(8),DD1(8),AD1(8),AM1(8)
C053                COMMON /A/KP,KD,DM,DP,FI,NA,AS,SCMC
C054                REAL KP,KD,NA,K,MO,N,MI,NDO,N10
C055                XX=-1.03
C056                Y=-0.185
C057                REVI=845.0
C058                HI=7.5
C059                DDI=13.07
C060                S=NA*AS*(SO-SCMC)/(272.0*1000.0)
C061                R=2.0*KD*NA*RO/(270.0*1000.0)
C062                K=(3.0/(4.0*3.14159))*(KP/NA)*(DM/DP)*(FI/(1.0-FI))
C063          C
C064          C  CALCULATE DEGREE OF  DISPERTION BEFORE REACTION
C065          C
```

```
C066                VDO=MO/DM
C067                DDO=DDI*(REV/REVI)**XX*(H/HI)**Y
C068                NDO=6.0*VDO/(3.14159*DDO**3)*1.0E 12
C069                ADO=(VDO/DDO)*60000.0
C070          C
C071          C  FIX THE CONSTANTS
C072          C
C073                B1=4.0*3.14159*K**(2.0/3.0)*R/S
C074                B2=3.0*(4.0*3.14159*NDO)**(1.0/2.0)*VDO
C075                DSW=0.966
C076                B3=3.0*(4.0*3.14159*NDO)**(1.0/2.0)*(DSW/DM)
C077                B4=3.52*S-ADO
C078                C1=(4.0*3.14159/3.0)*(K*R/S)
C079                C2=3.0*S-ADO
C080                Z1=R/(6.0*S)
C081                Z2=6.0*S-ADO
C082          C
C083          C  FIND THE RELATIONSHIP BETWEEN TIME T1 AND THE AREA OF PARTICLES IN ONE CC WAT
C084          C
C085                DO 420 I=1,8
C086                IF(.NOT.I.EQ.1) GOTO410
C087                A1(I)=0.587*B1*(S-ADO)*T1(I)**(5.0/3.0)
C088                V1(I)=(C1/2.0)*(S-ADO)*T1(I)**2
C089                GOTO 481
C090            410 A1(I)=(B1/6.0)*(B4-2.52*A1(I-1)-2.52*(B2-B3*V1(I-1))**(2.0/3.0))*
C091               *T1(I)**(5.0/3.0)
C092                V1(I)=(C1/6.0)*(C2-2.0*A1(I-1)-2.0*(B2-B3*V1(I-1))**(2.0/3.0))
C093               3*T1(I)**2
C094            481 AD1(I)=(B2-B3*V1(I))**(2.0/3.0)
C095                AM1(I)=S-A1(I)-AD1(I)
C096            420 CONTINUE
C097          C
C098          C  FIND THE TIME TB WHEN PARTICLE NUCLEATION IS JUST COMPLETE
C099          C
C100                H1=10.0
C101                TB=0.365*(S/R)**0.6/K**0.4
C102                CALL CHAZHI(T1,AM1,8,TB,AMB)
C103            471 IF(AMB.GT.H1) GOTO477
C104                IF(AMB.LT.(-H1)) GOTO476
C105                GOTO436
C106            476 DO 435 I=1,1000
C107                CALL CHAZHI(T1,AM1,8,TB,AM)
C108                IF(ABS(AM).LE.H1) GOTO436
C109                IF(AM.GT.H1) GOTO478
C110                TB=TB-0.01
C111            435 CONTINUE
C112            478 H1=H1+10.0
C113                GOTO471
C114            477 DO 441 I=1,1000
C115                CALL CHAZHI(T1,AM1,8,TB,AM)
C116                IF(ABS(AM).LT.H1) GOTO436
C117                IF(AM.LT.(-H1)) GOTO478
C118                TB=TB+0.01
C119            441 CONTINUE
C120          C
C121          C  CALCULATE A SERIES OF VALUES OF PARAMETERS ALANG THE HISTORY OF
C122          C  POLYMERIZATION DURINGTHE STAGE ONE
C123          C
C124            436 WRITE (2,440)
C125            440 FORMAT(//2X,'THE RESULTSCALCULATED ALONG THE REACTION HISTORY OF
C126               1STAGE ONE'/2X,62(1H=)//)
C127                WRITE(2,444)
C128            444 FORMAT(/8X,'TIME(MIN)',4X,'CONVERSION(,%)',4X,'SM(G/LW)',3X,'AP(SQ
C129               *CM/CCW)',4X,'VP(CC/CCW)',5X,'DP(MICRON)',4X,'N(PARS/CC.)',5X,'VD(CC/CCW)/)
C130               *C/CCW)'/)
C131                DO 460 I=1,10
C132                T(I)=(TB/10.0)*FLOAT(I)
C133            460 CONTINUE
C134                DO 480 J=1,10
C135                CALL CHAZHI(T1,A1,8,T(J),A(J))
C136                CALL CHAZHI(T1,V1,8,T(J),V(J))
C137                TH=T(J)/2.0
C138                CALL CHAZHI(T1,A1,8,TH,AH)
C139                CALL CHAZHI(T1,V1,8,TH,VH)
C140                N(J)=Z1*T(J)*(Z2-A(J)-(B2-B3*V(J))**(2.0/3.0)-4.0*AH-4.0*(B2-B3*VH
C141               1)**(2.0/3.0))
```

```
C142                D(J)=(V(J)/A(J))*60000.0
C143                X(J)=V(J)*(1.0-FI)*DP/MO*100.0
C144                VD(J)=VDO-V(J)*DSW/DM
C145                DD(J)=((6.0/3.14159)*(VD(J)/NDO))**(1.0/3.0)
C146                AD(J)=(VD(J)/DD(J))*6.0
C147                SM(J)=(S-A(J)-AD(J))/AS/NA*272.6*1000.0
C148                WRITE(2,470) T(J),X(J),SM(J),A(J),V(J),D(J),N(J),VD(J)
C149             470 FORMAT(/5X,0PF10.3,2F15.3,1P5E15.3)
C150             480 CONTINUE
C151                MI=1.44*KP*FI*DM**N(10)/R
C152                WRITE(2,490)
C153             490 FORMAT(//2X,'THE VALUES OF PARAMETERS AT THE END OF STAGE ONE',
C154                3//8X,'TIME(MIN)',4X,'CONVERSION(%)',3X,'S(MIC)(G/LM)',2X,'AP(SQC
C155                4CCW)',3X,'VP(CC/CCW)',5X,'DP(MICRON)',5X,'MOLEC.WT.',5X,'N(PARS/C
C156                5W)'//)
C157                WRITE(2,494) T(10),X(10),SM(10),A(10),V(10),D(10),MI,N(10)
C158             494 FORMAT(//5X,F10.3,2F15.3,1P3E15.3,0PF15.0,1PE15.3)
C159                V10=V(10)
C160                X10=X(10)
C161                T10=T(10)
C162                N10=N(10)
C163                RETURN
C164                END

END OF SEGMENT, LENGTH   770, NAME  STAGE1


C165                SUBROUTINE CHAZHI(A,B,N,X,Y)
C166                DIMENSION A(N),B(N)
C167                NC=N
C168                N=N-1
C169                DO 1 J=1,N
C170                IF((X-A(J))*(X-A(J+1))) 10,10,1
C171             10 I=J
C172                GOTO 22
C173              1 CONTINUE
C174                IF(ABS(X-A(1))-ABS(X-A(N))) 20,21,21
C175             20 I=1
C176                GOTO 22
C177             21 I=N-1
C178             22 IF(I-N+1) 24,23,24
C179             23 I=I-1
C180                GOTO 27
C181             24 IF(I-1) 25,27,25
C182             25 IF(ABS(X-A(I))-ABS(X-A(I+1))) 26,27,27
C183             26 I=I-1
C184             27 V=0.0
C185                IF(I-N) 29,28,29
C186             28 I=I-1
C187             29 L=I+2
C188                DO 2 K=I,L
C189                W=B(K)
C190                DO 3 J=I,L
C191                IF(J-K) 30,3,30
C192             30 W=(X-A(J))/(A(K)-A(J))*W
C193              3 CONTINUE
C194                V=V+W
C195              2 CONTINUE
C196                Y=V
C197                N=NC
C198                RETURN
C199                END

END OF SEGMENT, LENGTH   179, NAME  CHAZHI


C200                SUBROUTINE UNSTA(NP,TO,MO,RO,XO)
C201                DIMENSION F(25),AM(25),AK(25),C(25),YY(25),Y1(25),Y2(25),Y3(25)
C202                COMMON G
C203                COMMON /A/KP,KD,DM,DP,FI,NA
C204                REAL NP,MO,NA,KP,MI,KD
C205                DO 610 I=1,25
C206                F(I)=0.0
C207             610 CONTINUE
```

```
0208                F(1)=X0
0209                F(2)=0.5
0210                F(3)=0.5
0211                Q=0.5
0212                WRITE(2,888)
0213              888 FORMAT(///2X,'THE RESULTS CALCULATED ALONG THE REACTION HISTOR
0214               * OF STAGE TWO'/2X,62(1H=)/)
0215                WRITE(2,999)
0216              999 FORMAT(//6X,'II',3X,'T(MIN)',8X,'Q',10X,'X(%)',10X,
0217               *'F0',13X,'F1',13X,'F2',13X,'F3'/)
0218                N=10
0219                H=0.000025
0220                C(1)=0.5
0221                C(2)=0.5
0222                C(5)=0.5
0223                C(3)=1.0
0224                C(4)=1.0
0225                EPS=1.0E-4
0226                CUSI=47691.0
0227                DO 657 I=3,N-5
0228                AK(I)=0.0
0229              657 CONTINUE
0230                AK(1)=1.0
0231                R=2.0*KD*NA*RO/(270.0*1000.0)
0232                B=0.5*(KP/NA)*(DM/DP)*FI*NP
0233                G=R*MO/(200.0*NP*B*DP)
0234                D=200.0*B*DP/MO
0235                T=TO
0236                DO 50 II=1,200000
0237              703 DO 670 KK=1,100
0238                QO=Q
0239                XO=F(1)
0240                CALL RUKB(N,H,C,EPS,F,AM,AK,Q,YY,Y1,Y2,Y3,CUSI)
0241              420 SIGMAF=0.0
0242                DO 666 M=2,N-5
0243                SIGMAF=SIGMAF+F(M)
0244              666 CONTINUE
0245                DO 660 L=2,N-5
0246                F(L)=F(L)/SIGMAF
0247              660 CONTINUE
0248                Q=0.0
0249                DO 651 M=3,N-5
0250                Q=Q+FLOAT(M-2)*F(M)
0251              651 CONTINUE
0252                T=T+(F(1)-XO)/(D*QO)
0253              670 CONTINUE
0254                WRITE(2,1000) II,T,Q,F(1),F(2),F(3),F(4),F(5)
0255             1000 FORMAT(/2X,I6,3F12.7,1P4E15.6)
0256                IF(F(1).GE.43.0) GOTO 705
0257               50 CONTINUE
0258              705 RETURN
0259                END
```

END OF SEGMENT, LENGTH 277, NAME UNSTA

```
0260                SUBROUTINE RUKB(N,H,C,EPS,Y,AM,AK,Q,YY,Y1,Y2,Y3,CUSI)
0261                DIMENSION Y(N),AM(N),AK(N),C(N),YY(N),Y1(N),Y2(N),Y3(N)
0262                COMMON G
0263                CALL RUKU(N,Y,Y1,AM,AK,H,Q,CUSI,C)
0264              500 H=H/2.0
0265                CALL RUKU(N,Y,Y2,AM,AK,H,Q,CUSI,C)
0266                CALL RUKU(N,Y2,Y3,AM,AK,H,Q,CUSU,C)
0267                DO 197 I=2,N-5
0268                IF(Y3(I).LT.0.0.OR.Y2(I).LT.0.0) GOTO 72
0269                D=ABS(Y3(I)-Y1(I))
0270                IF(D.GT.EPS) GOTO 72
0271              197 CONTINUE
0272                GOTO 73
0273               72 DO 194 I=2,N-5
0274                Y1(I)=Y2(I)
0275              194 CONTINUE
```

```
0276                GOTO 500
0277             73 IF(D-EPS/32.0) 22,23,23
0278             22 H=4.0*H
0279                GOTO 292
0280             23 H=2.0*H
0281            292 DO 193 I=1,N-5
0282                Y(I)=Y3(I)
0283            193 CONTINUE
0284                RETURN
0285                END

END OF SEGMENT, LENGTH   187, NAME  RUKB

0286                SUBROUTINE RUKU(N,Y,YY,AM,AK,H,Q,CUSI,C)
0287                DIMENSION Y(N),YY(N),C(N),AM(N),AK(N)
0288                COMMON G
0289                DO 30 I=1,N-5
0290                AM(I)=Y(I)
0291                YY(I)=Y(I)
0292             30 CONTINUE
0293                DO 22 J=1,4
0294                CALL RKFF(N,AM,AK,Q,CUSI)
0295                DO 201 I=1,N-5
0296                W=H*AK(I)
0297                IF(J.EQ.4) GOTO 31
0298                AM(I)=W*C(J)+Y(I)
0299             31 YY(I)=W*C(J+1)/3.0+YY(I)
0300            201 CONTINUE
0301             22 CONTINUE
0302                RETURN
0303                END

END OF SEGMENT, LENGTH   138, NAME  RUKU

0304                SUBROUTINE RKFF(N,AM,AK,Q,CUSI)
0305                DIMENSION AM(N),AK(N)
0306                COMMON G
0307                A=G/Q
0308                B=CUSI/(AM(1)*Q)
0309                AK(2)=A*(-AM(2))+B*(2.0*AM(4))
0310                DO 650 L=3,N-5
0311                AK(L)=A*(AM(L-1)-AM(L))+B*(FLOAT(L*(L-1))
0312               #*AM(L+2)-FLOAT((L-2)*(L-3))*AM(L))
0313            650 CONTINUE
0314                RETURN
0315                END

END OF SEGMENT, LENGTH   115, NAME  RKFF

0316                FINISH

END OF COMPILATION -  NO ERRORS
```

APPENDIX VI

COMPUTER PROGRAM FOR GEL-EFFECT

```
0012                TRACE 1
0000                TRACE 0
0001                MASTER GELEFF1
0002                DIMENSION F(25),AM(25),AK(25),C(25),YY(25),Y1(25),Y2(25),Y3(25)
0003                DIMENSION AFO(500),AF1(500),AF2(500),AF3(500),AF4(500),AF5(500),
0004               &AQ(500),AZ(500),AT(500)
0005                COMMON /G1/A1,A2,A3,A4,A5,KP
0006                COMMON /B2/G,DP,DM,GT
0007                REAL NP,MO,NA,KP,KD
0008                DO 610 I=4,25
0009                F(I)=0.0
0010              610 CONTINUE
0011                F(1)=0.4857612
0012                F(2)=0.4999665
0013                F(3)=0.4999933
0014                F(4)=3.34648E-5
0015                F(5)=6.739512E-6
0016                Q=0.5000804
0017                T0=51.2626822
0018                N=10
0019                NP=8.08E14
0020                RO=2.5
0021                MO=0.5
0022                A1=29.5873
0023                A2=-7.43322
0024                A3=45.3577
0025                A4=-95.9184
0026                A5=47.4095
0027                KP=1.27E7
0028                NA=6.023E23
0029                FI=0.605
0030                DP=1.057
0031                DM=0.905
0032                KD=5.7E-5
0033                H=0.000025
0034                C(1)=0.5
0035                C(2)=0.5
0036                C(5)=0.5
0037                C(3)=1.0
0038                C(4)=1.0
0039                EPS=1.0E-4
0040                DO 657 I=3,N-5
0041                AK(I)=0.0
0042              657 CONTINUE
0043                AK(1)=1.0
0044                R=2.0*KD*NA*RO/(270.0*1000.0)
0045                B=.5*(KP/NA)*(DM/DP)*FI*NP
0046                G=R*(NA/NP**2)*(MO/(DM*KP))
0047                GT=G*(DM/DP-1.0)
0048                D=2.0*B*DP/MO
0049                T=T0
0050                DO 50 II=751,200000
0051                IF(F(N-5).LT.1.0E-4) GOTO 703
0052                N=N+1
0053              703 DO 670 KK=1,100
0054                QO=Q
0055                XO=F(1)
0056                CALL RUKB(N,H,C,EPS,F,AM,AK,Q,YY,Y1,Y2,Y3)
0057              429 SIGMAF=0.0
0058                DO 666 M=2,N-5
0059                SIGMAF=SIGMAF+F(M)
0060              666 CONTINUE
0061                DO 660 L=2,N-5
0062                F(L)=F(L)/SIGMAF
0063              660 CONTINUE
0064                Q=0.0
0065                DO 651 M=3,N-5
0066                Q=Q+FLOAT(M-2)*F(M)
0067              651 CONTINUE
0068                D1O=(D/FI)*F1O(F(1))
0069                T=T+(F(1)-XO)/(D1O*Q)
0070              670 CONTINUE
0071                WRITE(2,1000) II,T,Q,F(1),F(2),F(3),F(4),F(5),F(6)
0072             1000 FORMAT(/2X,I6,3F12.7,1PSE15.6)
0073                IF(F(1).GE.0.98) GOTO 705
0074               50 CONTINUE
```

```
0075              705 STOP
0076                  END

END OF SEGMENT, LENGTH   306, NAME  GELEFF1

0077
0078                  SUBROUTINE RUKB(N,H,C,EPS,Y,AM,AK,Q,YY,Y1,Y2,Y3)
0079                  DIMENSION Y(N),AM(N),AK(N),C(N),YY(N),Y1(N),Y2(N),Y3(N
0080                  CALL RUKU(N,Y,Y1,AM,AK,H,Q,C)
0081              500 H=H/2.0
0082                  CALL RUKU(N,Y,Y2,AM,AK,H,Q,C)
0083                  CALL RUKU(N,Y2,Y3,AM,AK,H,Q,C)
0084                  DO 197 I=2,N-5
0085                  IF(Y3(I).LT.0.0.OR.Y2(I).LT.0.0) GOTO 72
0086                  D=ABS(Y3(I)-Y1(I))
0087                  IF(D.GT.EPS) GOTO 72
0088              197 CONTINUE
0089                  GOTO 73
0090               72 DO 194 I=2,N-5
0091                  Y1(I)=Y2(I)
0092              194 CONTINUE
0093                  GOTO 500
0094               73 IF(D-EPS/32.0) 22,23,23
0095               22 H=4.0*H
0096                  GOTO 292
0097               23 H=2.0*H
0098              292 DO 193 I=1,N-5
0099                  Y(I)=Y3(I)
0100              193 CONTINUE
0101                  RETURN
0102                  END

END OF SEGMENT, LENGTH   173, NAME  RUKB

0103
0104                  SUBROUTINE RUKU(N,Y,YY,AM,AK,H,Q,C)
0105                  DIMENSION Y(N),YY(N),C(N),AM(N),AK(N)
0106                  DO 30 I=1,N-5
0107                  AM(I)=Y(I)
0108                  YY(I)=Y(I)
0109               30 CONTINUE
0110                  DO 22 J=1,4
0111                  CALL RKFF(N,AM,AK,Q)
0112                  DO 201 I=1,N-5
0113                  W=H*AK(I)
0114                  IF(J.EQ.4) GOTO 31
0115                  AM(I)=W*C(J)+Y(I)
0116               31 YY(I)=W*C(J+1)/3.0+YY(I)
0117              201 CONTINUE
0118               22 CONTINUE
0119                  RETURN
0120                  END

END OF SEGMENT, LENGTH   131, NAME  RUKU

0121
0122                  SUBROUTINE RKFF(N,AM,AK,Q)
0123                  DIMENSION AM(N),AK(N)
0124                  P1=FU(AM(1))/Q
0125                  P2=TK(AM(1))/Q
0126                  AK(2)=P1*(-AM(2))+P2*(2.0*AM(4))
0127                  DO 650 L=3,N-5
0128                  AK(L)=P1*(AM(L-1)-AM(L))+P2*(FLOAT(L*(L-1))*AM(L+2)
0129                 £-FLOAT((L-2)*(L-3))*AM(L))
0130              650 CONTINUE
0131                  RETURN
0132                  END

END OF SEGMENT, LENGTH   114, NAME  RKFF
```

```
0133
0134                    FUNCTION TK(X)
0135                    COMMON /G1/A1,A2,A3,A4,A5,KP
0136                    REAL KP
0137                    Y=A1+A2*X+A3*X**2+A4*X**3+A5*X**4
0138                    TK=EXP(Y)/(KP*(1.0-X))
0139                    RETURN
0140                    END

END OF SEGMENT, LENGTH    46, NAME  TK

0141
0142                    FUNCTION FU(X)
0143                    COMMON /B2/G,DP,DM,GT
0144                    FU=(G+GT*X)/(1.0-X)
0145                    RETURN
0146                    END

END OF SEGMENT, LENGTH    19, NAME  FU

0147                    FUNCTION F10(X)
0148                    COMMON /B2/G,DP,DM
0149                    F10=(1.0-X)/((X*DM/DP)+(1.0-X))
0150                    RETURN
0151                    END

END OF SEGMENT, LENGTH    20, NAME  F10

0152                    FINISH

END OF COMPILATION -  NO ERRORS
```

APPENDIX VII

COMPUTER PROGRAM FOR BAFFLED REACTOR

```
C012                TRACE 1
C000                MASTER BAFFLE
C001          C
C002          C  THIS PROGRAM SIMULATES EMULSION POLYMERIZATION OF STYRENE .IT BASED ON FAST
C003          C   TERMINATION RATE WITHIN LATEX PATICLES
C004          C
C005                DIMENSION T1(8)
C006                COMMON /A/KP,KD,DM,DP,FI,NA,AS,SCMC
C007                REAL KP,KD,NA,K,MO,N10,MI
C008          C
C009          C  INPUT DATA . KP(CC/MOLE.MIN),FI(,),NA(MOLECULES/CCW),DM(GRAM/CC),
C010          C   DP(GRAM/CC),AS(SQCM/MOLECLES),KD(1/S),SCMC(HGRAM/LW),T(MIN)SO(GRAM
C011          C  /LW),MO(GRAM/CCW),RO(GRAM/LW)
C012          C
C013                READ(1,100) (T1(I),I=1,8)
C014              100 FORMAT(8F0.0)
C015                READ(1,200) SO,MO,RO,REV,H
C016              200 FORMAT(5F0.0)
C017                WRITE(2,391)
C018              391 FORMAT(///2X,'INITIAL DATA : AMOUNT OF SAOP SO;AMOUNT OF MONOMER MO;
C019                 *O;AMOUNT OF INITIATOR RO;DIAMRTER OF IMPELLER H;IMPELLER SPEED REV
C020                 '*/2X,118(1H=)///2X,'SO(G/LW)',6X,'MO(G/CCW)',7X,'RO(G/LW)',8X,'H(CM
C021                 *)',8X,'REV(RMP)')
C022                WRITE(2,392) SO,MO,RO,H,REV
C023              392 FORMAT(//,5F15.3)
C024          C
C025          C  THE CASE OF FAST TERMINATION AND NOT CONSIDERING THE SOAP ON MONOMER DROPLET
C026          C  ***************************************************************************
C027          C
C028          C
C029          C  STAGE ONE
C030          C  =========
C031          C
C032                CALL ST1A(SO,MO,RO,R,K,T1,V10,N10,TB)
C033          C
C034          C  STAGE TWO
C035          C  =========
C036          C
C037                CALL STAGE2(V10,N10,TB,MO,DM,DP,FI,KP,NA,R,T2,VP)
C038          C
C039          C  STAGE THREE
C040          C  ===========
C041          C
C042                CALL STAGE3(T2,VP,FI,KP,NA,N10,DM,DP,MO,MI,0.5)
C043          C
C044          C  THE CASE OF FAST TERMINATION AND CONSIDERING THE SOAP ON MONOMER DROPLETS
C045          C  ***************************************************************************
C046          C
C047          C
C048          C  STAGE ONE
C049          C  =========
C050          C
C051                CALL ST1B(SO,MO,RO,R,K,T1,V10,N10,T10,TB,REV,H,X10)
C052          C
C053          C  STAGE TWO
C054          C  ===========
C055          C
C056                CALL STAGE2(V10,N10,TB,MO,DM,DP,FI,KP,NA,R,T2,VP)
C057          C
C058          C  STAGE THREE
C059          C  ===========
C060          C
C061                CALL STAGE3(T2,VP,FI,KP,NA,N10,DM,DP,MO,MI,0.5)
C062          C
C063                STOP
C064                END

END OF SEGMENT, LENGTH   127, NAME  BAFFLE

C065                BLOCK DATA
C066                COMMON /A/KP,KD,DM,DP,FI,NA,AS,SCMC
C067                REAL KP,KD,NA
C068                DATA KP,KD,DM,DP,FI,NA,AS,SCMC/1.27E7,5.7E-5,0.906,1.057,0.605,
C069               36.023E23,3.5E-15,0.5/
C070                END
```

```
C071                SUBROUTINE ST1A(SO,MO,RO,R,K,T1,V10,N10,TB)
C072                DIMENSION T1(8),A1(8),T(10),A(10),V(10),N(10),D(10),SM(10),X(10)
C073                COMMON /A/KP,KD,DM,DP,FI,NA,AS,SCMC
C074                REAL KP,KD,NA,K,MO,N,MI,N10
C075                WRITE(2,201)
C076              201 FORMAT(///2X,'THE CASE OF FAST TERMINATION AND  NOT CONSIDERING
C077                 *SOAP ON MONOMER DROPLETS'/2X,78(1H*)///)
C078          C
C079          C   FIX CONSTANTS
C080          C
C081                S=NA*AS*SO/(270.0*1000.0)
C082                R=2.0*KD*NA*RO/(270.0*1000.0)
C083                K=(3.0/(4.0*3.14159))*(KP/NA)*(DM/DP)*(FI/(1.0-FI))
C084                B=4.0*3.14159*K**(2.0/3.0)*R/S
C085                C=(4.0*3.14159/3.0)*K*R/S
C086          C
C087          C   FIND THE RELATIONSHIP BETWEEN TIME T1 AND THE AREA OF PARTICLES IN ONE
C088          C   CC WATER A1
C089                DO 400 I=1,8
C090                IF(.NOT.I.EQ.1) GOTO300
C091                A1(I)=0.587*B*SAT1(I)**(5.0/3.0)
C092                GOTO400
C093              300 A1(I)=B*T1(I)**(5.0/3.0)*(0.587*S-0.42*A1(I-1))
C094              400 CONTINUE
C095          C
C096          C   FIND THE TIME TB WHEN PARTICLENUCLEATION IS JUST COMPLETE
C097          C
C098                CALL CHAZHI(A1,T1,8,S,TB)
C099          C
C100          C   CALCULATE A SERIES OF VALUES OF PARAMETERS ALANG THE HISTORY OF
C101          C   POLYMERIZATION DURINGTHE STAGE ONE
C102                WRITE(2,450)
C103              450 FORMAT(//2X,'THE RESULTSCALCULATED ALONG THE REACTION HISTORY OF
C104                 1STAGE ONE'/2X,62(1H=)//)
C105                WRITE(2,500)
C106              500 FORMAT(//8X,'TIME(MIN)',4X,'CONVERSION(%)',3X,'S(MIC)(G/LW)',2X,
C107                 2'AP(SQCM/CCW)',3X,'VP(CC/CCW)',4X,'DP(MICRON)',5X,'N(PARS/CCW)')
C108                DO 600 I=1,10
C109                T(I)=(TB/10.0)*FLOAT(I)
C110              600 CONTINUE
C111                DO 800 J=1,10
C112                CALL CHAZHI(T1,A1,8,T(J),A(J))
C113                TH=T(J)/2.0
C114                CALL CHAZHI(T1,A1,8,TH,AH)
C115                N(J)=(R/S)*T(J)*(S-A(J)/6.0-(2.0/3.0)*AH)
C116                V(J)=(T(J)**2/6.0)*(3.0*C*S-2.0*C*AH)
C117                D(J)=(V(J)/A(J))*60000.0
C118                X(J)=V(J)*(1.0-FI)*DP/MO*100.0
C119                SM(J)=(S-A(J))/AS/NA*272.0*1000.0
C120                WRITE(2,700) T(J),X(J),SM(J),A(J),V(J),D(J),N(J)
C121              700 FORMAT(/5X,0PF10.3,2F15.3,1P4E15.3)
C122              800 CONTINUE
C123                MI=1.44*KP*FI*DM*N(10)/R
C124                WRITE(2,190)
C125              190 FORMAT(//2X,'THE VALUES OF PARAMETERS AT THE END OF STAGE ONE',
C126                 3//8X,'TIME(MIN)',4X,'CONVERSION(%)',3X,'S(MIC)(G/LM)',2X,'AP(SQCM/
C127                 4CCW)',2X,'VP(CC/CCW)',4X,'DP(MICRON)',5X,'MOLEC.WT.',4X,'N(PARS/CC
C128                 5W)'//)
C129                WRITE(2,191) T(10),X(10),SM(10),A(10),V(10),D(10),MI,N(10)
C130              191 FORMAT(//5X,F10.3,2F15.3,1P3E15.3,0PF15.0,1PE15.3)
C131                N10=N(10)
C132                V10=V(10)
C133                RETURN
C134                END

END OF SEGMENT, LENGTH   407, NAME  ST1A
```

```
      SUBROUTINE ST1B(SO,MO,RO,R,K,T1,V10,N10,T10,TB,REV,H,X10)
      DIMENSION T1(8),A1(8),T(10),A(10),V(10),N(10),D(10),SM(10),X(10)
      DIMENSION V1(8),VD(10),DD(10),AD(10),VD1(8),DD1(8),AD1(8),AM1(8)
      COMMON /A/KP,KD,DM,DP,FI,NA,AS,SCMC
      REAL KP,KD,NA,K,MO,N,MI,NDO,N10
      READ(1,250) XX,Y,REVI,HI,DDI
  250 FORMAT(6F0.0)
      WRITE(2,251)
  251 FORMAT(///2X,'THE CASE OF FAST TERMINATION AND CONSIDERING THE
     *SOAP ON MONOMER DROPLETS'/2X,73(1H*)///)
C
C  CALCULATE DEGREE OF  DISPERTION BEFORE REACTION
C
      S=NA*AS*(SO-SCMC)/(270.0*1000.0)
      VDO=MO/DM
      DDO=2.42303*SO**(0.0129)*REV**(-1.861)
      WRITE(2,3000) SO,REV,H,DDO
 3000 FORMAT(2X,'SO=',F4.2,2X,'REV=',F6.2,2X,'H=',F4.2,2X,'DDO=',E15.5
     1////)
      DDO=DDO*1.0E6
      NDO=6.0*VDO/(3.14159*DDO**3)*1.0E 12
      ADO=(VDO/DDO)*6.0000.0
      WRITE(2,2000) DDO,ADO,REV
 2000 FORMAT(/////,10X,'DDO=',E15.5,10X,'ADO=',E15.5,10X,'REV=',F6.2/)
C
C  FIX THE CONSTANTS
C
      B1=4.0*3.14159**(2.0/3.0)*R/S
      B2=3.0*(4.0*3.14159*NDO)**(1.0/2.0)*VDO
      DSW=0.966
      B3=3.0*(4.0*3.14159*NDO)**(1.0/2.0)*(DSW/DM)
      B4=3.52*S-ADO
      C1=(4.0*3.14159/3.0)*(K*R/S)
      C2=3.0*S-ADO
      Z1=R/(6.0*S)
      Z2=6.0*S-ADO
C
C  FIND THE RELATIONSHIP BETWEEN TIME T1 AND THE AREA OF PARTICLES IN ONE CC WA
C
      DO 420 I=1,8
      IF(.NOT.I.EQ.1) GOTO410
      A1(I)=0.587*B1*(S-ADO)*T1(I)**(5.0/3.0)
      V1(I)=(C1/2.0)*(S-ADO)*T1(I)**2
      GOTO 481
  410 A1(I)=(B1/6.0)*(B4-2.52*A1(I-1)-2.52*(B2-B3*V1(I-1))**(2.0/3.0))*
     *T1(I)**(5.0/3.0)
      V1(I)=(C1/6.0)*(C2-2.0*A1(I-1)-2.0*(B2-B3*V1(I-1))**(2.0/3.0))
     3*T1(I)**2
  481 AD1(I)=(B2-B3*V1(I))**(2.0/3.0)
      AM1(I)=S-A1(I)-AD1(I)
  420 CONTINUE
C
C  FIND THE TIME TB WHEN PARTICLE NUCLEATION IS JUST COMPLETE
C
      H1=10.0
      TB=0.365*(S/R)**0.6/K**0.4
      CALL CHAZHI(T1,AM1,8,TB,AMB)
  471 IF(AMB.GT.H1) GOTO477
      IF(AMB.LT.(-H1)) GOTO476
      GOTO436
  476 DO 435 I=1,1000
      CALL CHAZHI(T1,AM1,8,TB,AM)
      IF(ABS(AM).LE.H1) GOTO436
      IF(AM.GT.H1) GOTO478
      TB=TB-0.01
  435 CONTINUE
  478 H1=H1+10.0
      GOTO471
  477 DO 441 I=1,1000
      CALL CHAZHI(T1,AM1,8,TB,AM)
      IF(ABS(AM).LT.H1) GOTO436
      IF(AM.LT.(-H1)) GOTO478
      TB=TB+0.01
  441 CONTINUE
```

```
0209            C
0210            C  CALCULATE A SERIES OF VALUES OF PARAMETERS ALANG THE HISTORY OF
0211            C  POLYMERIZATION DURINGTHE STAGE ONE
0212            C
0213              436 WRITE (2,440)
0214              440 FORMAT(//2X,'THE RESULTSCALCULATED ALONG THE REACTION HISTORY OF
0215                 1STAGE ONE'/2X,62(1H=)//)
0216                  WRITE(2,444)
0217              444 FORMAT(/8X,'TIME(MIN)',4X,'CONVERSION(,%)',4X,'SM(G/LM)',3X,'AP(SQ
0218                 *CM/CCW)',4X,'VP(CC/CCW)',3X,'DP(MICRON)',6X,'N(PARS/CCW)',5X,'VD(CC/CCW)//)
0219                 *C/CCW)'/)
0220                  DO 460 I=1,10
0221                  T(I)=(TB/10.0)*FLOAT(I)
0222              460 CONTINUE
0223                  DO 480 J=1,10
0224                  CALL CHAZHI(T1,A1,8,T(J),A(J))
0225                  CALL CHAZHI(T1,V1,8,T(J),V(J))
0226                  TH=T(J)/2.0
0227                  CALL CHAZHI(T1,A1,8,TH,AH)
0228                  CALL CHAZHI(T1,V1,8,TH,VH)
0229                  N(J)=Z1*T(J)*(Z2-A(J)-(B2-B3*V(J))**(2.0/3.0)-4.0*AH-4.0*(B2-B3*VH
0230                 1)**(2.0/3.0))
0231                  D(J)=(V(J)/A(J))*60000.0
0232                  X(J)=V(J)*(1.0-FI)*DP/MO*100.0
0233                  VD(J)=VDO-V(J)*DSW/DM
0234                  DD(J)=((6.0/3.14159)*(VD(J)/NDO))**(1.0/3.0)
0235                  AD(J)=(VD(J)/DD(J))*6.0
0236                  SM(J)=(S-A(J)-AD(J))/AS/NA*272.0*1000.0
0237                  WRITE(2,470) T(J),X(J),SM(J),A(J),V(J),D(J),N(J),VD(J)
0238              470 FORMAT(/5X,0PF10.3,2F15.3,1P5E15.3)
0239              480 CONTINUE
0240                  MI=1.44*KP*FI*DM*N(10)/R
0241                  WRITE(2,490)
0242              490 FORMAT(//2X,'THE VALUES OF PARAMETERS AT THE END OF STAGE ONE',
0243                 3//8X,'TIME(MIN)',4X,'CONVERSION(%)',3X,'S(MIC)(G/LM)',2X,'AP(SQCM/
0244                 4CCW)',2X,'VP(CC/CCW)',4X,'DP(MICRON)',5X,'MOLEC.WT.',4X,'N(PARS/CC
0245                 5W)'//)
0246                  WRITE(2,494) T(10),X(10),SM(10),A(10),V(10),D(10),MI,N(10)
0247              494 FORMAT(//5X,F10.3,2F15.3,1P3E15.3,0PF15.0,1PE15.3)
0248                  V10=V(10)
0249                  X10=X(10)
0250                  T10=T(10)
0251                  N10=N(10)
0252                  RETURN
0253                  END

END OF SEGMENT, LENGTH   762, NAME  ST1B

0254                  SUBROUTINE STAGE2(VI,NI,TB,MO,DM,DP,FI,KP,NA,R,T2,VP)
0255                  REAL NI,NP,NT,NA,MO,KP,MI
0256                  VDO=MO/DM
0257                  VP=VI
0258                  VD1=VDO-VP*(FI+(1.0-FI)*DP/DM)
0259                  NT=NI
0260                  T2=TB
0261                  DELTAT=1.0
0262                  WRITE(2,210)
0263              210 FORMAT(//2X,'THE RESULTS CULCULATED ALONG THE REACTION HISTORY OF
0264                 2STAGE TWO'/2X,60(1H=)//8X,'TIME(MIN)',4X,'CONVERSION(%)',3X,
0265                 3'AP(SQCM/CCW)',3X,'VP(CC/CCW)',4X,'DP(MICRON)',4X,'VD(CC/CCW)'/)
0266                  B=0.5*(KP/NA)*(DM/DP)*FI*NT
0267            C
0268            C  CALCULATE A SERIES OF VALUES OF PARAMETERS ALONG THE HISTORY OF POLYMERIZATIO
0269            C  DURING THE STAGE TWO
0270            C
0271                  DO 240 I=1,10000
0272                  DO 220 J=1,2
0273                  IF(VD1.LE.0.0) GOTO250
0274                  DELTAV=B*DELTAT/(1.0-FI)
0275                  VP=VP+DELTAV
0276                  DPA=(6.0*VP/(3.14159*NT))**(1.0/3.0)*10000.0
0277                  AP=(VP/DPA)*60000.0
0278                  VD1=VD1-DELTAV*(FI+(1.0-FI)*DP/DM)
0279                  T2=T2+DELTAT
0280                  X2=VP*(1.0-FI)*DP/MO*100.0
0281              220 CONTINUE
0282                  WRITE(2,230) T2,X2,AP,VP,DPA,VD1
0283              230 FORMAT(/5X,0PF10.3,F15.3,1P4E15.3)
0284              240 CONTINUE
0285              250 MI=2.0*B*NA*DP/R
0286                  WRITE(2,260)
0287              260 FORMAT(///2X,'THE VALUES OF PARAMETERS AT THE END OF STAGE TWO',
0288                 5//,8X,'TIME(MIN)',4X,'CONVERSION(%)',2X,'AP(SQCM/CCW)',2X,'VP(CC/
0289                 6CCW)',4X,'DP(MICRON)',4X,'VD(CC/CCW)',5X,'MOLEC.WT.',//)
```

```
0290                  WRITE(2,270) T2,X2,AP,VP,DPA,VD1,MI
0291              270 FORMAT(/5X,F10.3,F15.3,1P4E15.3,0PF15.0)
0292                  RETURN
0293                  END

END OF SEGMENT, LENGTH =  221, NAME  STAGE2


0294                  SUBROUTINE STAGE3(T2,VP,FI,KP,NA,NT,DM,DP,MO,MI,Q)
0295                  REAL MO,NI,KP,NA,NT,MI
0296                  WRITE(2,310)
0297              310 FORMAT(//2X,'THE RESULTS CALCULATED ALONG THE REACTION HISTORY OF
0298                 6STAGE THREE'/2X,64(1H=)//8X,'TIME(MIN)',4X,'CONVERSION(%)',2X,
0299                 5'AP(SQCM/CCW)',3X,'VP(CC/CCW)',4X,'DP(MICRON)',4X,'VMP(CC/CCW)'/)
0300                  VMP=VP*FI
0301                  T3=T2
0302                  DELTAT=1.0
0303                  X3=0.0
0304                  DO 360 I=1,100
0305                  DO 340 J=1,5
0306                  IF(X3.GE.95.0) GOTO370
0307                  RATE=(KP/NA)*(VMP/VP)*(NT*Q)
0308                  VMP=VMP-RATE*DELTAT
0309                  VP=VP-RATE*DELTAT*(1.0-DM/DP)
0310                  AP=(NT*3.14159)**(1.0/3.0)*(6.0*VP)**(2.0/3.0)
0311                  DP3=(VP/AP)*60000.0
0312                  X3=(1.0-VMP*DM/MO)*100.0
0313                  T3=T3+DELTAT
0314              340 CONTINUE
0315                  WRITE(2,350) T3,X3,AP,VP,DP3,VMP
0316              350 FORMAT(/5X,0PF10.3,F15.3,1P4E15.3)
0317              360 CONTINUE
0318              370 WRITE(2,380)
0319              380 FORMAT(///2X,'THE FINAL RESULTS OF THE CALCULATION',/2X,36(1H=)//
0320                 87X,'TIME(MIN)',4X,'CONVERTION(%)',2X,'N(PARTICLES)',3X,'DP3(MICRON)',
0321                 9)',4X,'MOLECLE.WT.'/)
0322                  WRITE(2,390) T3,X3,NT,DP3,MI
0323              390 FORMAT(/5X,F10.3,F15.3,1P2E15.3,0PF15.1)
0324                  RETURN
0325                  END

END OF SEGMENT, LENGTH =  194, NAME  STAGE3


0326                  SUBROUTINE CHAZHI(A,B,N,X,Y)
0327                  DIMENSION A(N),B(N)
0328                  NC=N
0329                  N=N-1
0330                  DO 1 J=1,N
0331                  IF((X-A(J))*(X-A(J+1))) 10,10,1
0332               10 I=J
0333                  GOTO 22
0334                1 CONTINUE
0335                  IF(ABS(X-A(1))-ABS(X-A(N))) 20,21,21
0336               20 I=1
0337                  GOTO 22
0338               21 I=N-1
0339               22 IF(I-N+1) 24,23,24
0340               23 I=I-1
0341                  GOTO 27
0342               24 IF(I-1) 25,27,25
0343               25 IF(ABS(X-A(I))-ABS(X-A(I+1))) 26,27,27
0344               26 I=I-1
0345               27 V=0.0
0346                  IF(I-N) 29,28,29
0347               28 I=I-1
0348               29 L=I+2
0349                  DO 2 K=I,L
0350                  W=B(K)
0351                  DO 3 J=I,L
0352                  IF(J-K) 30,3,30
0353               30 W=(X-A(J))/(A(K)-A(J))*W
0354                3 CONTINUE
0355                  V=V+W
0356                2 CONTINUE
0357                  Y=V
0358                  N=NC
0359                  RETURN
0360                  END

END OF SEGMENT, LENGTH =  181, NAME  CHAZHI

0361                  FINISH

END OF COMPILATION -  NO ERRORS
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