# EMULSION POLYMERISATION
# IN A CONTINUOUS FLOW STIRRED REACTOR

by

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Submitted for a Degree of
Doctor of Philosophy of
Loughborough University of Technology

1982

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To Mum and Dad

# ACKNOWLEDGMENTS

I wish to thank my supervisor, Dr. B.W. Brooks, for his assistance and advice during the course of this research. One is indeed fortunate in knowing such a person with whom he can discuss his work.

My special thanks to Messrs. Andy Milne, Frank McKeown, Hugh Peters, David Smith for their assistance during the experimental work. My thanks also to F. Page for his assistance in all the photographic work.

My gratitude to Messrs. T. Bogunjoko, Michael Gyamerah, B.O. Makanjuola (fellow research students) for their useful suggestions on this work and words of encouragement.

I wish to thank my typist, Christine Sharpe, whom I am grateful to for learning to read my writing and also for excellent typed scripts.

## SUMMARY

An investigation of the emulsion polymerisation of styrene in an isothermal continuous flow stirred reactor has been carried out. The important phenomena of sustained oscillations and large conversion overshoot after start-up have been studied.

Experimental studies have shown that conversion, number of polymer particles, molecular weights, and all other related properties often oscillate widely with time, and a steady state was not always achieved. The effect of start-up procedures in continuous emulsion polymerisation reactors have not previously been investigated in detail.

Different start-up procedures were studied to determine their effect on the behaviour of the reactor. The effects of the initial concentration of soap and initiator, and the initial reaction temperatures have been studied experimentally in relation to the mean residence time of the reactor. Changes in start-up procedures were found to have a significant effect not only on the transients before a steady state, but also on the ultimate state achieved.

Evidence was obtained supporting the theory that monomer droplets can be a locus of initiation and propagation in emulsion polymerisation of styrene in a CFSR at high level of conversion. Two possible mechanisms have been proposed to explain the phenomena of the high levels of conversion in the CFSR.

Special reactor design was used to minimize aeration and to allow the variation of the average residence time without varying the pump settings.

# CONTENTS

## Nomenclature

| | |
|---|---|
| $A_p$ | Surface area of Latex particles per litre of emulsion ($\mathring{A}^2/\ell$) |
| $a_s$ | Adsorption area of an emulsifier molecule ($cm^2$) |
| $C$ | Constant |
| $c$ | Concentration (g/100 ml) |
| $C_1$ | Concentration of monomer in all forms (g/g-emulsion) |
| $C_F$ | Concentration of monomer in the feed (g/g-emulsion) |
| $C_o$ | Initial concentration of monomer in the reactor (g/g-emulsion) |
| $C_R$ | Concentration of radicals in unit volume of emulsion(g-mole/$\ell$) |
| $D$ | Diffusion coefficient ($cm^3/s$) |
| $\overline{D}$ | Average diameter of particles ($\mathring{A}$) |
| $D_N$ | Number average diameter ($\mathring{A}$) |
| $D_S$ | Surface average diameter ($\mathring{A}$) |
| $D_V$ | Volume average diameter ($\mathring{A}$) |
| $D_W$ | Weight average diameter ($\mathring{A}$) |
| $d_p$ | Density of particles ($g/cm^3$) |
| $F$ | Total volumetric feed rate ($\ell$/s) |
| $F_d$ | Fractional dissolved solids |
| $F_s$ | Fractional solids |
| $f$ | Initiator efficiency |
| $f_H$ | Inhibitor efficiency |
| $g(\tau)$ | Correlation function |
| $H$ | Inhibitor concentration (g-model/$\ell$) |
| $\|I\|$ | Initiator concentration (g-mole/$\ell$) |
| $K'$ | A constant in equation 5.5 |
| $k_d$ | Decomposition rate constant of initiator ($S^{-1}$) |
| $k_o$ | Radical desorption rate constant (cm/s) |
| $k_p$ | Propagation rate constant ($\ell$/s.mole) |
| $K_t$ | Termination rate constant ($\ell$/s.mole) = $k_{tc}+k_{td}$ |
| $K_{tc}$ | Mutual termination rate constant ($\ell$/s.mole) |
| $K_{td}$ | Termination rate constant by disproportionation ($\ell$/s. mole) |
| $k$ | Boltzman constant ($J/^oK$ mole) |
| $k_o'$ | Overall rate constant of persulphate decomposition ($S^{-1}$) |
| $M$ | Molecular weight of polymer |
| $\|M\|$ | Concentration of monomer (g-mole/$\ell$) |
| $M_p$ | Concentration of monomer in particles (g-mole/$\ell$) |
| $M_{MW}$ | Molecular weight of monomer |

| | |
|---|---|
| m | Mass capacity of the reactor (g) |
| $m_F$ | Feed mass flow rate (g/min) |
| N | Number of radicals per unit volume of emulsions ($\ell^{-1}$) |
| $N_A$ | Avogadro's number ($6.023*10^{23}$) |
| $N_R$ | Total number of radicals per litre of emulsion ($\ell^{-}$ ) |
| $\bar{q}$ | Average number of radicals per particles |
| $R_p$ | Overall rate of polymerisation (g-mole/ s.$\ell$) |
| $R_t$ | Overall rate of termination (g-mole/s.$\ell$) |
| $R_i$ | Rate of initiation ($s^{-1}$ $\ell^{-1}$) |
| $R_{i,eff}$ | Effective initiation rate ($s^{-1}$ $\ell^{-1}$) |
| S | Emulsifier concentration (g-mole/$\ell$) |
| T | Absolute Temperature ($^{o}K$) |
| t | Time (s, min, hour) |
| V | Total volume of particles per unit volume of emulsion ($\ell$) |
| v | Volume of a particle ($cm^3$, $\ell$) |
| $v_m$ | Specific volume of monomer ($cm^3$/g) |
| $v_p$ | Specific volume of polymer ($cm^3$/g) |
| x | Fractional conversion |
| y | Number of primary radicals |
| { } | Indicate concentration |
| $\alpha$ | A constant in equation (5.5) |
| $\eta$ | Viscosity (poise) |
| $\vert\eta\vert$ | Limiting viscosity number |
| $\eta_o$ | Viscosity of pure solvent (poise) |
| $\phi_m$ | Volume fraction of monomer in particles |
| $\rho$ | $\rho_i/N$ ($s^{-1}$) |
| $\mu$ | dv/dt, volumetric growth rate of particles ($cm^3$/s) |
| $\rho'_i$ | Rate of radical generation per unit volume of emulsion($s^{-1}$ $\ell^{-1}$) |
| $\theta$ | Space time (min) |
| $\tau$ | Delay time ($\mu$ s) |

# CHAPTER 1

## 1.1 Introduction

Of the three major techniques used in free radical polymerisation and copolymerisation, emulsion polymerisation is the most complex, requiring many interacting ingredients. The complexity of the reaction is however offset by its flexibility, since emulsion polymerisation provides the advantages of high reaction rates, high molecular weight polymer and an easy to handle low viscosity latex which is suitable for many direct applications. The major disadvantage however, is that the product is not a pure polymer.

Since polymers produced via emulsion polymerisation have been found to be very useful in many applications over the years, interest has been directed towards designing efficient and reliable chemical reactors to carry out the emulsion process. Though at present many industrial emulsion polymerisation processes are carried out in batch reactors, continuous processes are coming into use. Batch reactors are more commonly used because they are better understood and are easier to handle. As the physical and chemical behaviour of various species in emulsion systems and the kinetics of emulsion polymerisation are becoming better understood, newer and better reactors are being developed.

It is in pursuit of a better understanding of emulsion polymerisation processes, especially with continuous flow stirred emulsion polymerisation reactors that this project was conceived. The general theory of the mechanism of emulsion polymerisation was formulated by Harkins (97) while this formulation was placed on a quantitative basis by Smith and Ewart (137). Since the publication of Smith and Ewart many modifications of their theories have been made. The main feature of most of the theories developed for the emulsion polymerisation process is the segregation of growing polymer radicals within small polymer particles.

Although continuous reactor systems are widely used, most published research work on emulsion polymerisation kinetics is based on batch reactor data. The reasons for not employing continuous reactors for research are numerous. The equipment is usually more complex, more costly, and less flexible. Experimental run times are lengthened, and larger amounts of reactants are consumed.

As the need for high production rates of emulsion polymers increase, economic considerations dictate the use of continuous reactors or a chain of such reactors. The feasibility of commercial production of polymer and co-polymer latices in continuous reactors is closely related to the control of the polymer properties of the latex. The manner in which continuous flow stirred emulsion polymerisation reactors are started-up can have a very significant influence, not only on the transients before steady state is achieved, but also on the nature of the ultimate state obtained after all the transient effects die out.

Since the effect of the start-up procedures on the behaviour of the continuous emulsion polymerisation reactors have not previously been investigated in detail, it has become desirable to know what effect these procedures have on the reaction kinetics and performance of the reactor.

In the present study emulsion polymerisation of styrene was carried out in a continuous flow stirred reactor. The influence of soap and initiator concentrations in both the initial charge and, the feed to the reactor have been studied in relation to the temperature and the average residence time of the reactor. Different types of feasible start-up procedures were employed under a variety of space times and temperatures.

The results of the present work show clearly why models which do not take the start-up procedures into account may be unapplicable to experimental results under different conditions.

## 1.2 *Polymerisation Methods* (17)

There exist two well-recognized types of polymerisation reactions, Addition and Condensation. In addition polymerisation the monomers simply add on to one another; while in condensation polymerisation a small molecule, such as water, is split out. In condensation polymerisation reactions functional groups of two bifunctional molecules react one at a time, and further growth occurs through successive reactions of this type. The rate of each successive reaction is virtually independent of the molecular weight of the reacting molecules.

Addition polymerisation reactions proceed stepwise with the intermediate formation of a partially satisfied, and thus extremely reactive, functional group, such as a free radical. In addition to the free radical mechanism of addition polymerisation, ionic (cationic and anionic) mechanisms are also significant. Whether addition polymerisation takes place by a free radical or an ionic mechanism, at each step a functional group is partially satisfied. One new bond is formed, and one atom is left either in an odd valence state (free radical) or with a deficiency or surplus of a single electron (cationic or anionic).

It is customary to characterize a polymerisation further by the nature of the phase, or system of phases, in which the reactants and products are found. Polymerisation can either be carried out under homogeneous or hetrogeneous conditions(119). This classification is based on whether the initial reaction mixture is homogeneous or hetrogeneous even though some homogeneous systems turn hetrogeneous as polymerisation progresses.

Generally, four methods of polymerisation are used commercially: bulk (or mass), solution, suspension, and emulsion polymerisation.

In bulk polymerisation, the only phase initially present is the pure monomer, in which a small amount of initiator, and chain-transfer agent, may also be dissolved. The polymer formed may be soluble in the monomer, in this case the liquid becomes extremely viscous after a portion of the monomer has polymerised. The exothermic nature of radical chain polymerisation and the difficulty of transferring heat from the viscous medium account for the rapid temperature rise of the system. Another type of bulk polymerisation is that in which the polymer is insoluble in the monomer.

Although the viscosity of the liquid phase is not greatly altered by the separation of the polymer phase, the mixture or slurry becomes stiff and difficult to agitate. Bulk polymerisations usually, produces a polymer which is inhomogeneous with regard to molecular weight and other properties, as a result of having been formed at different temperatures and in media of different viscosities.

In solution polymerisation the monomer is dissolved in an appropriate solvent and polymerisation is brought about by the addition of an initiator. In other cases gaseous monomers are dispersed as bubbles in the solvent. As in bulk polymerisation, the polymer may be soluble in the liquid or may precipitate. The viscosity of the reaction medium is much lower than in bulk polymerisation and heat transfer is thereby improved. The choice of solvent is important as it may affect both the properties of the polymer formed and the rate of reaction.(49) A drawback exists in the requirements of evaporating and condensing large quantities of solvent, particularly if the solvent is in any way hazardous, and complete removal of the solvent from the polymer may also be difficult.

In suspension polymerisation, vigorous agitation is used to disperse the monomer in form of fine droplets in a medium (generally water) in which it is virtually insoluble, although systems in which the monomer is partially soluble in the suspending medium are also known. Suspension polymerisation is some time referred to as pearl or bead polymerisation because the polymer product is in the form of small granular spheres, with few exceptions suspension polymerisation in water require small amounts of substances that hinder the coalescence of monomer droplets and prevent beads sticking together during the course of polymerisation. They are generally called suspension stabilizers or suspending agents. Particle size can be controlled by the type and amount of stabilizer and by the agitation to give beads in sizes that can be easily separated from water 146 The tendency of the sticky droplets to coalesce, with the ultimate formation of alarge lump of coagulum, makes suspension attractive only in the production of plastics and fibers, but not of rubbers, which remain sticky throughout most of the polymerisation. The initiator used is soluble in the (dispersed) organic phase rather than in the aqueous phase. Since the polymerisation is initiated, propagated and terminated in the monomer droplets, the kinetics are identical to those in bulk polymerisation.

In emulsion polymerisation the monomer is emulsified in a medium, generally water, with the aid of emulsifying agents such as soaps, alkyl sulfonates, etc. Emulsion polymerisation differs primarily from suspension polymerisation in that the initiator is maintained in the aqueous phase. The principal distinction between these two is therefore the polymerisation process rather than the presence of an emulsifier. Polymer particles formed in emulsion polymerisation are usually much smaller than those produced in suspension polymerisation. Compared to the other polymerisation techniques the main advantage of emulsion polymerisation is that high molecular weight polymers can be produced while a high reaction rate is maintained simultaneously, these two factors can not be increased simultaneously in the other polymerisation techniques discussed. Though the presence of emulsifier and other additives in the final product, and the need for purification of the polymer, limit its use.

The latex can, in some instances, be employed directly without further separation or purification.

## 1.3 *Historical Review*

In a modern society synthetic polymers have gained widespread usage. Synthetic polymers have provided economic alternatives and in some cases more useful products to materials made from naturally occurring substances.

The rapid use of synthetic polymers began during the second world war with the only supply of natural rubber being cut off from Europe and North America. Although many polymers were developed, a good alternative to natural rubber latex was found to be an emulsion mixture of styrene - butadiene polymer. As the interest in emulsion polymerisation increased theories and kinetics started to be developed. Hohenstein(83)drew attention to papers by the Russian Balandina(3) and Berezan(11)in 1936, who thought that the polymerisation took place within the monomer droplets. Two years later in 1938 Firkentscher(45)postulated that the reaction occurred in the aqueous phase with the monomer droplet acting as reservoirs ofmonomer, making monomer available to the aqueous phase as required. Fryling et al(53)published a paper in 1944 containing the major features of emulsion polymerisation theory as that attributed to Harkins(77-80). Hohenstein and his colleagues(32, 52,136) found that the rate of polymerisation was roughly proportional to the solubility of the monomer in water, which seems to agree with the idea that primary locus is within the aqueous phase. Standinger (140) agreed with previous authors that the most probable locus for initiation is the monomer in solution which may also be a site for a small degree of propagation, however he suggested that the primary locus for the propagation is the micelles containing solubilized monomer. As propagation proceeds these micelles swell with polymer. The propagation stage of polymerisation occurs in a state of high polymer concentrations and therefore high viscosity. Under these conditions the termination stage is discouraged in favour of the propagation stage. Hence a high degree of polymerisation combines with a high rate of polymerisation.

By far the most important contribution to the development of the mechanism of emulsion polymerisation comes from Harkins(80) his theory was published in a long paper in 1950 although short publication had preceded it (78,79,116)The theory was a qualitative one and its the basis of what is called micellar, or heterogeneous, mechanism.

At about the same time Baxendal et al (10) working with methylmethacrylate, both in the absence and presence of a cationic surface active agent, reported that the polymerisation was characterized by homogenous solution kinetics, inspite of the fact that the polymer precipitated as a separate phase. The increase of rate of polymerisation upon the addition of surfactant was attributed to the reduction in the rate of mutual termination as a result of retardation of the rate of coagulation of particles. Priest (127) laid out the basic qualitative features of the theory of homogenous nucleation in emulsion polymerisation. Napper and Alexander (116) in studying the kinetics of vinyl acetate polymerisation in the presence of different types of emulsifiers arrived at the same conclusions as Priest's. The view that the interfacial region between particles and aqueous phase plays an essential part in the initiation reaction as well as providing reaction loci, has for many years been maintained by a group of Russian workers led by Medevedev (109) . To explain their experimental results on styrene using potassium laurate as the soap, Roe and Brass (128) put forward the hypothesis that the predominant process by which the radicals enter the particles is by the dissociation of initiator in the immediate vicinity of the particle - aqueous phase interface. Dissociation within the bulk of the aqueous phase, followed by diffusion to the particles was discarded as being of minor importance only.

## *1.4 Polymerisation Modelling*

With the increase in computer facilities during the 1950's, the modelling of polymerisation reactions became popular. During these years, optimization and control problems of polymerisations were studied for various types of reactors under various conditions The work in general was divided into three steps:

1. Mathematical simulation,
2. Stability problems and
3. Control techniques.

All of these works however, dealt only with bulk or suspension polymerisation and not emulsion reactions.

The neglect of emulsion polymerisation was due to several reasons. The kinetics of emulsion polymerisation is much more complex than bulk kinetics and as a result more difficult to model. In emulsion it is possible to have control over both the rate of polymer growth and the molecular weight distributions whereas in bulk polymerisation only one of these variables can be controlled at a time. Thus control studies on emulsion reactions are more complex.

Initial on line computer control for emulsion polymerisation reactons was very difficult because, other than temperature and pressure, it was impossible to measure rapidly any of the important variables. Even modern equipment such as on line gel permeation chromatographs, density meters and surface tension meters(17) do not provide sufficient and/or rapid enough measurements to permit overall on line computer control because accurate model of the emulsion systems is lacking. Instantaneous readings are crucial in emulsion polymerisation since the reaction is a fast one and the final results can vary even if the same initial feed is used and the temperature and pressure are maintained through the reaction.

A great deal of information has been published on the simulation of bulk free radical polymerisation. A true simulation of bulk polymerisation results in a long series of simultaneous differential equations. These equations can be simplified somewhat by making some approximations to the general solution which allows the number of equations to be greatly reduced.

Although emulsion polymerisation in essence consists of free radical addition polymerisation occurring in small polymer particles the initiator decomposition and initiation steps occur outside the polymer particles, while the remaining steps occur within. And although these kinetic equations are relatively simple and generally accepted, emulsion polymerisation reactors are complicated by the necessity of including the diffusion of both monomer and free radicals to and within the polymer particles as well as the influence of the emulsifier on the generation and stabilization of the particles. These physical processes are not well understood and are perhaps most fundamental in determining some of the peculiar phenomena observed in emulsion polymerisation reactors.

## 1.5 *Radical polymerisation kinetics*

The kinetics of free radical-chain polymerisation in homogeneous solutions are given in most standard textbooks on polymerisation (49,72) They consist mainly of four steps: initiation, propagation, transfer and termination.

The initiation step consists of two reactions

A) decomposition of Initiator $I \xrightarrow{k_d} 2R^{\cdot}$

decomposition rate $R_d = 2k_d |I|$ (1.1)

(note that in some literature, $R_d = k_d |I|$ )

B) initiation $R^{\cdot} + M \xrightarrow{k_i} RM^{\cdot}$

initiation rate $R_i = k_i |M| |R^{\cdot}|$ (1.2)

The propagation step consists of the growth of RM˙ by successive addition of a large number of monomer molecules

C ) propagation

$$RM^{\cdot} + M \xrightarrow{k_p} M_2^{\cdot}$$
$$M_2^{\cdot} + M \xrightarrow{k_p} M_3^{\cdot}$$
$$\vdots$$
$$M_n^{\cdot} + M \xrightarrow{k_p} M_{n+1}^{\cdot}$$

propagation rate $R_p = k_p |M| |M_n^{\cdot}|$ (1.3)

In transfer reactions a propagating polymer radical may react with another molecule to form a 'dead' polymer with a simultaneous creation of a radical which may be new center of growth.

D) transfer to monomer $M_n^{\cdot} + M \xrightarrow{k_{tm}} M_n + M^{\cdot}$

monomer transfer rate $R_{tm} = k_{tm} |M_n^{\cdot}| |M|$ (1.4)

E) transfer to polymer $M_n^{\bullet} + M_m \xrightarrow{k_{tp}} M_n + M_m^{\bullet}$

polymer transfer rate $R_{tp} = k_{tp} |M_n^{\bullet}| |M_m|$ (1.5)

F) transfer to modifier $M_n^{\bullet} + Z \xrightarrow{k_{tz}} M_n + Z^{\bullet}$

modifier transfer rate $R_{tz} = k_{tz} |M_n^{\bullet}| |Z|$ (1.6)

G) transfer to any suitable species $M_n^{\bullet} + G \xrightarrow{k_{tg}} |M_n| \; |G^{\bullet}|$ (1.7)

A polymer radical continues to grow until the termination process occurs. Termination usually takes place by a bimolecular reaction between growing radicals or between a growing radical and a primary radical.

H) termination by combination $M_n^{\bullet} + M_m^{\bullet} \xrightarrow{k_{tc}} M_{n+m}$

combination termination rate $R_{tc} = k_{tc} |M_n^{\bullet}| |M_m^{\bullet}|$ (1.8)

I) termination by disproportionation $M_n^{\bullet} + M_m^{\bullet} \xrightarrow{k_{td}} M_n + M_m$

disproportionation termination rate $R_{td} = k_{td} |M_n^{\bullet}| \; |M_m^{\bullet}|$ (1.9)

Where I, $M^{\bullet}$, $R^{\bullet}$, $M_n^{\bullet}$, $M_n$, Z, G, represent initiator, monomer primary radicals, growing polymer, dead polymer, modifier, and any other molecule present in the system respectively. The R's and k's represent the appropriate rates and rate constants.

The kinetics also apply to emulsion polymerisation with steps A) and B) occurring in the water or organic phase depending upon the initiator chosen, and the remaining occurring only in the organic phase. Step F) only occurs when modifier is added to the initial recipe. In general steps D), E) and G) have much lower rates than step C) and are often not considered except for very high molecular weight polymer. Termination processes in vinyl monomers may be either wholly combination, step H), as in styrene or a mixture of steps H) and I), as in methyl methacrylate. Since both steps lead to radical destruction and the same kinetic effect, in this work the terms $k_t$ and $R_t$ are going to be used as termination rate constant and the rate of termination respectively, where $k_t = k_{tc} + k_{td}$.

## 1.6 *Theory and Mechanism of Emulsion Polymerisation*

It is not easy to give an entirely satisfactory definition of an emulsion polymerisation reaction. A reasonable definition used by Blackly (15) is "a polymerisation reaction which produces polymer in the form of a stable lyophobic colloid". According to this definition, an emulsion polymerisation is recognised by the nature of the end-product of the reaction, rather than by the occurrence of any particular reaction mechanism that has led to the formation of the end-product.

The general emulsion mixture consists of monomer or monomers, dispersion medium, usually water, initiator, emulsifier, and modifier, (although many commercial recipes contain electrolytes as well). Emulsion polymerisation is generally divided into two classes: those in which the monomer is very soluble in the medium (e.g. vinyl acetate 2.5 wt % at 28°C) and those in which the monomer is only slightly soluble in the medium (e.g. styrene 0.039wt % at 50°C) Other factors also affect the emulsion conditions such as the emulsifier and whether the initiator is soluble in the medium or/and monomer phase. Since much of the published experimental work has been done with styrene as the monomer in batch reactors, the primary theories developed for emulsion polymerisation have the following properties. The monomer is slightly soluble in the continuous phase, the initiator is water soluble and the polymer is soluble in the monomer.

The emulsifier consist of molecules which are hydrophobic at one end and hydrophilic at the other. Owing to attractive forces between hydrophobic ends, the emulsifier molecules form aggregates, so called micelles, when their concentration exceeds a certain critical value, the critical micelle concentration, CMC. A dynamic equilibrium is assumed to exist between the micelles and the molecularly dissolved soap in aqueous phase. The structure of the micelles are not definitely known but it is supposed to be rod or sandwich-like in shape(14, 18). The micelles are able to dissolve a certain amount of monomer, a phenomenon which is often referred to as solubilization. Thus the monomer can be found in these different loci, before the polymerisation begins. The major part of the monomer is in droplets of 1-10 μm diameter. A much smaller amount is solubilized in the micelles, being of 50 - 100 Å in diameter.

Finally, a certain amount of monomer is present as an actual solution in the aqueous phase. In a batch reactor the course of a conventional emulsion polymerisation reaction is divided into the following three more-or-less distinct intervals.

Interval I, where the entities which will later grow into the particles of the eventual polymer colloid are thought to be brought into existence. It is often referred to as 'particle nucleation'. The end of this interval is not dependent upon the degree of conversion, but on the total amount of polymer formed. With usual recipes, it ends at about 1 - 5% conversion, and usually with the depletion of the emulsifier from aqueous phase.

Interval II, lasts from the end of interval I until monomer disappears as a separate phase, and during this interval polymerisation occurs within the loci formed during interval I.

Interval III, is the final stage where the monomer only exists in the monomer swollen polymer particles, and as dissolved monomer in the aqueous phase.

In emulsion polymerisation reactions there are four possible initial reaction loci, namely, the emulsifier micelles, the aqueous phase, the adsorbed emulsifier layer, and the monomer droplets. The miceller theory which was advanced by Harkins (79) received much of the attention in the bulk of the work in the field. Recently the homogeneous nucleation theory, the aqueous phase nucleation, has started to receive more attention (46-48,75,116,127,129,130,151,152). The view that the interfacial region between particles and aqueous phase plays the essential part in the initiation reaction has been put forward by Medevedev (109) and Roe(128) . The possibility that polymerisation only takes place at the surface of the monomer-polymer particles in some systems has also been suggested (107) and it has been supported by studies in which the polymerisation rate was shown to be related linearly to the total surface area of all the particles (20) Ugelstad et al (149-151,153) have described methods of preparing finely dispersed monomer emulsion and how this may bring about initiation in monomer droplets. One method of preparing such finely dispersed monomer emulsion involves the use of emulsifier system which is a mixture of an ionic emulsifier and a long-chain fatty alcohol. Ugelstad et al argued that with the more finely dispersed emulsion of the monomer with the same amount of emulsifier, the monomer droplets will become more competitive for radical capture in two ways. First, the total surface of the monomer droplets is increased, which increases the chance of radical capture; second the increase in surface area of the droplets leads to more emulsifier adsorption on the surface of droplets, leaving less emulsifier phase to facilitate particle nucleation there. It is important to point out here that the assumption of constant monomer concentration in the reaction site does not hold for droplet polymerisation as the monomer concentrations fall continuously through the course of the reaction owing to the conversion of monomer to polymer within the droplet.

### 1.61 *The Harkins Theory* (77-80)

Harkins based his qualitative theory on the information gathered by the U.S. Rubber Reserve Board during and just after the World War II. He postulated that the initiator in the solution decomposes and forms active free radicals. These free radicals react with the monomer in the solution to produce larger radicals containing monomer. In spite of the repulsive forces between micelles and polymer radical ions the radicals enter the micelles through diffusion. Once a radical enters a micelle the probability that it leaves is very small. Thus polymerisation continues until another radical enters to terminate the reaction. Once monomer begins to polymerize in the micelle it forms a polymer particle which adsorbs soap to maintain stability. Originally this soap comes from the micelle containing the particle, but as the polymer grows more soap is required. This soap comes from the surrounding micelles which have not yet been initiated. Thus, the number of polymer particles in the reaction is much less than the number of micelles present initially. The polymer in the particles is soluble in the contained monomer so there is sufficient monomer in the particle to carry on the reaction. As polymerisation occurs, monomer is added to the particle by diffusion from the aqueous solution. The aqueous solution is replenished in dissolved monomer by diffusion from the monomer droplets.

The Harkins theory thus proposes that the locus of polymerisation is first the soap micelles and then the monomer-polymer particle. It is implicit in this theory that the final particle population is a function of the micelle population which itself is a function of the initial soap concentration, critical micelle concentration and surrounding condition. The soap in the reaction has a three fold function. First, to increase the amount of monomer in the aqueous phase (solubilization), second to form micelles in which particle growth begins, and third to stabilize the particles once they are formed.

It is important here to note that if the initial soap concentration is below the critical micelle concentration, no micelles are formed and only two phases are present, i.e. the micellar phase is absent. This condition is not considered true emulsion polymerisation by Harkins.

This very simple description by Harkins forms the basis of most of the quantitative theories presented in the literature.

### 1.62 *Smith-Ewart Model* (134, 138, 139)

Smith and Ewart were able to express Harkins description quantitatively for intervals I and II. Assuming 1) the interfacial area of an emulsifier molecule is the same for the micelles and polymer particles, 2) a constant rate of polymerisation within a growing particle, 3) the critical micelle concentration (CMC) and the amount of emulsifier stabilizing monomer drops is negligible. To predict the number of polymer particles generated in interval I, two idealized situations were considered. One gives an upper limit and the other a lower limit for the particle number.

In the upper limit the rate of particle generation is proportional to the rate of radical production, and it implies that radicals only enter micelles.

$$\frac{dN}{dt} = \rho_i \tag{1.10}$$

This rate of particle nucleation is constant up to the time when the total area of polymer per litre of emulsion is equal to the total surface area of soap $a_s$ S, where S is the total amount of soap in the system and $a_s$ the specific area per unit amount of soap. In the lower limit both the particles and micelles are assumed to absorb radicals at a rate proportional to their surface area, $A_p$ This is expressed by

$$\frac{dN}{dt} = \rho_i \left(1 - \frac{A_p}{a_s S}\right) \tag{1.11}$$

The solution of equations (1.10) and(1.11) yield the following equation:

$$N = C \left(\frac{\rho_i}{\mu}\right)^{0.4} (a_s S)^{0.6} \tag{1.12}$$

where $\mu$ is the volume growth rate, $\mu = \frac{k_p}{N_A} \cdot \frac{d_m}{d_p} \cdot \frac{\phi_m}{1-\phi_m}$

for the total number of polymer particles at the end of interval I, where C = 0.53 for the upper case and C = 0.37 for the lower case. The number of particles given by the upper limit should be two large since necessarily some radicals will enter existing particles; whereas the number given by the lower limit should be too small since simple diffusion theory predicts that small particles have a greater radical capture efficiency per unit area than the large particles.

For interval II, Smith and Ewart considered the pseudo-steady state balance on $N_q$ the number of particles containing exactly q radicals:

$$\frac{d}{dt} N_q = \rho \left(N_{q-1} - N_q\right) + \frac{k_o a}{v} \left((q + 1) N_{q+1} - q N_q\right)$$
$$+ \frac{k_t}{vL} \left((q + 2)(q + 1) N_{q+2} - q(q-1) N_q\right) \qquad (1.13)$$

Setting $\frac{dN_q}{dt} = 0$ and neglecting the rate of desorption from the particles gives:

$$N_{q-1} + N_{q+2} \frac{k_t/v}{\rho} (q+2)(q+1) = N_q \left\{1 + \frac{k_t/v}{\rho} (q)\ (q-1)\right\} \qquad (1.14)$$

where the various parameters are defined in the Nomenclature.

Three limiting cases were discussed by Smith and Ewart:

Case I: $\bar{q} \ll 1$. Under this condition $N_o \gg N_1 \gg N_q$ and accordingly equation (1.14) becomes:

$$N_1 k_d' = \rho_i \left(\frac{N_o}{N}\right) \approx \rho_i \qquad (1.15)$$

Assuming that the radicals may diffuse freely out as well as into the particles, the steady state treatment gives (151)

$$\bar{q} = \left(\frac{\rho_i}{2Nk_d'}\right)^{\frac{1}{2}} \qquad (1.16)$$

Case 2: $\bar{q} = 0.5$. This case considers that desorption may be neglected which in turn, if termination in the water phase is neglected, implies $\rho_i' = \rho i$ . The solution for this case is treated in a large number of references for emulsion polymerisation.

Case 3: $\bar{q} \gg 1$. This represents the case for which more than one radical can coexist in the particle.

The rate of polymerisation is

$$R_p = \frac{k_p M_p}{N_A} \sum_{q=0}^{\infty} q N_q \equiv \frac{k_p M_p}{N_A} \bar{q} N \qquad (1.16)$$

### 1.63 *Homogeneous Particle Nucleation Theory* .

Priest(127) published a paper based upon his studies of particle size distribution in vinyl acetate polymerisation initiated by potassium persulphate in the presence of varying amounts of different stabilizers and inhibitors at several temperatures. His theory consists of eight points and these are,

1. "polymerisation in solution is the initial process",
2. "with the growth of a given polymer chain, a point is reached at which the polymer is no longer soluble",
3. "the number of primary particles would be sensibly equivalent to the number of chains initiated in solution",
4. "the number of particles which would otherwise be formed may be reduced by compination of incompletely developed chains with polymer droplets before the former are stabilized",
5. the number of particles may be reduced further by coagulation, depending upon "the quantity and efficiency of the material employed as an emulsion stabilizer".
6. "the ultimate particle size is a function of the relative number of sulfate groups per particle",
7. "the primary particle size would be of the order of $10^{-20}$ $cm^3$",
8. "almost all of the polymerisation (99.9%) occurs within the swollen polymer droplets, and only a maximum of 0.1% may be identified with primary particles".

These are the main basic feature similar to those on which Roe (129) and later Fitch (46) build their quantitative homogeneous theories.

### 1.631 *Roe's Theory.*

Roe (129) , for the emulsion polymerisation of styrene, pointed out that at lower than critical micelle concentrations of emulsifier, an appreciable number of polymer particles can be generated in apparent contradiction to Harkins' miceller initiation hypothesis. This phenomenon has been observed by a number of experimenters, both for styrene and other monomers more soluble in water. The distinguishing feature of Roe's theory is that the ultimate particle population is determined, with respect to emulsifier, by the total amount of emulsifier available and its intrinsic effectiveness, and not by the presence of micelles. Although the micelle initiation hypothesis has been discarded, the same quantitative relationship developed by Smith and Ewart still applies where now the value $(a_sS)$ is simply interpreted as the "effective" covering capacity of soap.

### 1.632 *Fitch's Theory* 48

The idea of homogenous nucleation was further developed by Fitch and Tsai (46) in 1971, and was based primarily on the scheme of Priest(127) with an idea from Gardon. Gardon suggested that the rate of capture of oligomeric radicals in solution by pre-existing particles, should be proportional to the collision cross-section, or the square of the radius of the particles. This idea was updated and the rate of capture of oligomeric radicals was taken to be proportional to the first power of the radius as predicted by Fick's theory of diffusion instead of the collision theory. In 1973 Fitch extended his theory to water-insoluble monomers(47) The theory of particle nucleation by precipitation of oligomeric radicals from the aqueous phase and a model based on the diffusion, propagation and termination steps is discussed by Hansen and Ugelstad(75) . They also presented a theory for the simultaneous nucleation and fluctuation of primary particles, which may take place after interval I in an emulsion polymerisation is finished. According to this theory, when the primary particles are formed, they may start to coagulate with each other. The stability of the particles will be dependent upon their surface charge, their size, and the electrolyte concentration. When the particles coagulate, the surface charge will increase, as most of the surface active groups stay on the surface. When the particles become sufficiently large, they will have enough charge groups to prevent further coagulation. Bataile et al(31) in the study of emulsion polymerisation of styrene in a batch reactor found that coagulation of particles releases surfactant, which generates fresh particles even at high conversion in accordance with the limited coagulation theory.

## *1.64 Contributions and Extensions of the Emulsion Polymerisation Theory*

Alteration and improvements have been made to the Smith-Ewart model by Stockmayer(142) who presented a general analytical solution to equation (1.14). Various workers (14, 123,128,154) had solved in different ways the Smith-Ewart recussion equations. The mathematical treatment of the equations involved so many assumptions and approximations that the physical value of the results are somehow obscure. Brooks and Qureshi (25) solved equation (1.14) for the case where $\bar{q} \not> 1$ by assuming that $q < 4$, and this assumption made it possible to solve the resultant set of linear equations exactly for given values of the variables involved in the equations.

A set of six papers giving an extensive description of emulsion polymerisation in batch reactor was presented by Gardon (54-59) in 1968. He re-examined and re-calculated the Smith-Ewart theory and added his own development to it. These predictions were then compared to his experimental data and to data published previously. Gardon in his model considers the monomer-polymer particle as the system and the remainder of the reactor ingredients as a reservoir. Gardon solved numerically the non steady state expression (1.13) for the number of particles containing $\bar{q}$ radicals without making the quasi-steady state assumption and neglecting radical desorption. However, his results showed the validity of the quasi-steady state approximation. The results showed that due to the increase in the size of the polymer particles, $\bar{q}$ would increase with conversion so that both the rate of polyerisation and average molecular weight would increase with conversion in interval II. Considering the consequences of slow termination rate within the particles he concluded that the decrease in termination rate in interval II with increasing conversion is not due to gel effect, since the concentration of monomer at the locus of polymerisation is constant but because the larger the particle the longer the time needed for two radicals to find each other for cross-termination. Summaries of the Gardon treatments with few modification have appeared in the literature (14,60,62) Recently some workers directed their attention to the emulsion polymerisation which proceeded with a small number of radicals per particle ($q \ll 1$). Brooks(26) solved the equation presented by

Birtwistle and Blackley (13) (which is similar to equation 1.13) for $N_o$, $N_1$, and $N_2$ as function of time. His treatment is much simpler and applies to a wider range of $\bar{q}$ than the treatments of Birtwistle and Blackley (13) . He assumed that a single polymer particle contains a maximum of 2 radicals simultaneously and was able to justify the correctness of this assumption later in the paper. He also allowed for radical combination in the particle where Birtwistle et al, without justification, assumed $k_t$ to be zero. Brooks 28 in a recent paper went a step further by assuming the source of new radicals may decay with time, he expressed the average rate of entry of radicals into particles, $\rho_i$, as:

$$\rho_i = A. \exp(-Bt) + \frac{k_o a}{v} \sum_1^q q N_q \qquad (1.17)$$

where A and B are constant

The volume growth rate of particles, μ, was expressed as:

$$\mu = \frac{dv}{dt} = m \sum_1^q q N_q \qquad (1.18)$$

where m depends on the propagation coefficient for the monomer concerned and the monomer-polymer composition of the particles. dv/dt is a function of time. A numerical technique was used to solve the resultant differential equations.

A mechanism assuming preferential radical capture by latex particles has been incorporated in a model by Harada et al (76) and this model was found to fit their experimental data for styrene quite well. Katz and Saidel (87) presented both a stochastic and deterministic model for the rate of polymerisation and polymer size distribution in interval II. In 1974 a review of the theoretical approaches and a complex kinetic model for emulsion polymerisation reactors has been published by Min and Ray (112). The approach taken by Min and Ray focusses on the size distribution of the particles. They claimed that their model can be simplified to other people's models by suitable assumptions. The large number of parameters required to describe the variety of mechanisms incorporated in the model makes the use of this general framework difficult and unattractive. Kiparissides and Ponnuswramy (91) used the general population balance equations to predict the polymer particle size distribution in a batch polymerisation reactor.

Solution of the resulting partial differential equations was achieved by a finite difference method.

Other contributions to the subject of stability of the latices and to the design a scale up of the reactors are available in the literature. Brooks (23) discussed the design criteria for polymerisation reactors in general. Attention has been given to the effect of reactor type on average molecular weights, molecular weight distribution, copolymer composition, and reaction rates. The special features of hetrogeneous processes such as emulsion polymerisation have also been discussed. Wilson and Merry (158) have recently reviewed problems of modelling and scale-up in emulsion polymerisation. Ottewill (122) has given a brief review of the factors controlling the stability and instability of polymer latices while Vanderhoff (155) discussed the formation of coagulum in emulsion polymerisation and the problems which could result from this.

### 1.65 *Particle Morphologies*

In the Harkins-Smith-Ewart theory of emulsion polymerisation, the polymer particle structure is homogeneous and consists of a uniform mass of monomer-polymer solution. There are some workers in the field which suggest that there is a definite structure to the polymer particles.

### 1.651 *Thermodynamics of Particle Swelling by Monomer*

Gardon (58) has shown that the prediction of monomer concentration in swelled polymer particle from the thermodynamic theory is consistent with experimental results obtained by either a static method or a kinetic method and concluded that polymer particles remain in their state of equilibrium, swelling up to the conversion at which monomer droplets disappear. This does not mean that monomer concentration is necessarily constant because the emulsifier concentration on the particle surface, the particle radius, and surface tension are all varying with conversion. Morton et al (114) suggested that a swelling equilibrium is reached when the change in the free energy of mixing and the change in the surface energy are balanced.

Since monomer is transferred from the monomer droplets into the monomer-polymer particles by diffusion through the aqueous phase, some mass transfer resistance will be expected. Brooks (22) discussed this phenomenon in detail and concluded that sweeping generalisations cannot be made about the nature of this and the interfacial phenomena or about the effects that they will exert. He also concluded that simple diffusional resistance will not affect the course of polymerisation, however, the polymerisation rate can be affected by diffusional processes that occur within the polymer particles, since conditions are such that radical-radical reaction within these particles may be "diffusion controlled". Interfacial resistance to the transfer of both monomer molecules and free radicals from the aqueous phase to the particles appear to have the most far-reaching effects.

### 1.652 *Non-uniform Particles Theories*

Experimental evidence to support the view of a non-uniform particle has been presented by Williams and Co-workers (70, 88). They show that the monomer concentration in the particle decreases with conversion in interval II, while the rate remains constant. Their explanation of this effect takes the form of a core-shell model (a polymer-rich core with relatively little monomer and shell practically pure monomer). Keusch and Williams (88) showed that in seed batch polymerisation additional monomer did not penetrate from the monomer-rich shell to the core even when 48 hours was allowed for the swelling of the latex particles. William and co-workers (70,88) further supported their model by showing electron-microscope photographs of polymer particles having such a core-shell structure. Napper (115) rejected Grancio and Williams's (70) model and proposed an inverse of it, with monomer rich core and a polymer rich shell. Further studies by Chung-li et al (36) showed that when particles with a diameter of 2140 nm were employed, no swelling of the latex polymer took place after 12 hours at 60°C. Even after 60 hours, equilibrium swelling had not been attained. According to Ham (73), such swelling data provide a strong indication that polymer emulsion particles do polymerise at high conversions when at equilibrium. It is of interest to notice that the core-shell theory of Williams has been heavily criticised by Gardon (61)

It is difficult to establish if the homogeneous or hetrogeneous models is the correct one since there are evidence for both, but the work done by Brooks and co-workers (30) on seeded latexes indicate that the structure and the way the seed is prepared may have a significant effect on the behaviour of the seed in farther polymerisation reactions.

### 1.66 Gel Effect Theories

In the later stages of a polymerisation reaction, a rapid increase in the polymerisation rate may be observed. This phenomenon is well known as the Trommsdörf , or gel effect and can be attributed to the decrease in termination rate constant, $k_t$, with increasing viscosity of the reaction mixture as the reaction proceeds towards complete conversion. In emulsion polymerisation (batch reactor), this auto-acceleration in the polymerisation rate normally occurs in interval III which begins when the monomer drops disappear.

Although some theories for the gel effect have been advanced in the literature, few applications of these theories to emulsion polymerisation systems have appeared. This perhaps is due to the inherent complexity of this effect in such systems. Whereas in bulk polymerisation, the isothermal gel effect is almost independent of experimental conditions in emulsion polymerisation conditions such as number of particles, particle size, and initiator concentration must be taken into account.

A number of empirical relationships for the termination rate constant have appeared in the literature, most of which made use of the data available from bulk polymerisation. Sundberg et al (143) used the free volume concept to remove the empirical nature of the $k_t$ dependency discussed above. Cao et al(33) used suspension polymerisation data to generate the dependence of the termination rate constant upon monomer conversion. They also developed a non-steady state model for stage III. This model combined with their previous model (32) for stage I and II gave good agreement with their experimental data.

Considering that as much as 50% of the monomer, in a batch reactor, may be polymerised during interval III, it is surprising that so little attention has been directed to it.

### 1.67 *Effect of Stirring on Emulsion Polymerisation Reactions*

It is often observed that the polymerisation rate and the quality of the polymer produced in agitated emulsion polymerisation reactors are affected by the stirring conditions. The effect of stirring in emulsion polymerisation is not well understood, and that may explain why this effect has largely been overlooked. Shunmukhan et al (134) noted that the increase in agitation resulted in a decrease in the polymerisation rate. Schoot et al (133) argued that the observation of Shunmukham (134) might have been due to traces of oxygen contained in the nitrogen atmosphere in the reactor. Evans et al (44) noted that the rate of polymerisation of vinylidene chloride was influenced by stirring. The decrease in the polymerisation rate was attributed to the reduction of the effective emulsifier concentration caused by the adsorption of emulsifier molecules onto monomer droplets dispersed finally by stirring. Omi et al (120) came to the conclusion that it is the level of agitation at the start of the reaction which affects the reaction rate during the later stages. Nomura et al (118) studied the effect of stirring on styrene emulsion polymerisation and found that 1) stirring affected significantly the course of reaction with nitrogen containing some oxygen. 2) at very high stirring speeds, more particle agglomeration has been observed where at lower stirring speeds, the reaction rate may be controlled by monomer transport from monomer droplets to the aqueous phase, 3) stirring can contribute to a reduction in the number of micelles in accordance with Evans's explanation. This is specially important at low emulsifier concentration near the C.M.C.. Kiparissides et al (93) studied the effect of stirring on the behaviour of the continuous emulsion polymerisation reactor of vinyl acetate. They noted that by increasing the agitation rate, a larger-liquid-air interface is generated and this would increase the amount of oxygen in the water and thus reduce the radical generation rate, which in turn results in a reduction in the polymerisation rate.

# CHAPTER 2

## INITIATION AND INITIATOR EFFICIENCY

2.1 Decomposition of Persulphate in Aqueous Solutions
  2.1.1 Mechanisms of the Hydrogen Ion Independent Reaction
  2.1.2 Mechanism of the Acid Catalysed Reaction
2.2 Decomposition of Persulphate in Presence of Additives
  2.2.1 In the Presence of Hydrocarbons or Monomers
  2.2.2 In the Presence of Inorganic Salts
  2.2.3 In the Presence of Emulsifier
2.3 Initiator Efficency

# CHAPTER 2

## INITIATION AND INITIATOR EFFICIENCY

Chain-initiation can occur by several mechanisms; thermal, photo-chemical, and chemical initiation. The thermal collision of the monomer molecules may result in a small proportion of them being raised to an activated state by a bimolecular process which may generate a very energetic molecule or often a free radical. Polymerisation can also be initiated by electro-magnetic radiation, but the most important type of initiation is that in which a chemical, or a chemical system, other than the monomer itself, acts as a source of free radicals, which in turn attack the monomer and initiate polymerisation. The simplest case of chemical initiation involves the dissociation of a single compound into free radicals (dissociative initiation), while, in more complicated systems, two or more compounds react to form radicals (redox initiation).

In the present study the initiator of interest is the persulphate ion ($S_2O_8^{2-}$). The term "peroxydisulphate" is used by Chemical Abstract, although the International Union of Pure and Applied Chemistry has recommended the name "peroxodisulphate". The trivial name "persulphate" is also in common use.

The rate of thermal decomposition of persulphate in pure water has been examined by Kolthoff and Miller (96) . It has been shown that the rate of disappearance of persulphate is greatly increased by the presence of various organic and inorganic compounds, such as alcohols (4,7,99,132) monomers (113) emulsifying agents (38, 97, 111, 118) and metal ions (9) .

### *2.1 Decomposition of Persulphate in Aqueous Solutions* (8)

A detailed investigation of the kinetics of thermal decomposition of persulphate in aqueous solution was made by Kolthoff and Miller (96). It was shown that persulphate ion decomposition in aqueous phase is first order (7, 96) . In neutral and alkaline solutions, a lowering of the pH has been found to increase slightly the decomposition rate, (2, 19, 96) while it is independent of the ionic strength (96) . In acid solution the decomposition of persulphate is catalysed by hydrogen ion and there is a negative salt effect. (96) Liegeois (104) reported a marked decrease of the decomposition rate of persulphate when oxygen was present.

The hydrolysis of the persulphate ion in neutral or alkaline solution is represented by the equation:

$$S_2O_8^{2-} + H_2O \longrightarrow 2HSO_4^- + \tfrac{1}{2}O_2 \qquad (2.1)$$

in dilute acid by

$$S_2O_8^{2-} + 2H_2O \longrightarrow 2HSO_4^- + H_2O_2 \qquad (2.2)$$

and in concentrated acid by

$$S_2O_8^{2-} + H_2O \longrightarrow H_2SO_5 + SO_4^{2-} \qquad (2.3)$$

### *2.1.1Mechanism of the Hydrogen Ion Independent Reaction* (7, 37, 96)

$$S_2O_8^{2-} \xrightarrow{k_1} 2\ SO_4^{\cdot-} \qquad (2.4)$$

$$SO_4^{\cdot-} + H_2O \xrightarrow{k_2} HSO_4^- + OH^{\cdot} \quad \text{slow} \qquad (2.5)$$

$$S_2O_8^{2-} + OH^{\cdot} \xrightarrow{k_3} HSO_4^- + SO_4^{\cdot-} + \tfrac{1}{2}O_2 \quad \text{fast} \qquad (2.6)$$

$$SO_4^{\cdot-} + OH^{\cdot} \xrightarrow{k_4} HSO_4^- + \tfrac{1}{2}O_2 \quad \text{chain termination} \qquad (2.7)$$

The primary step (2.4) is characteristic of all persulphate oxidation and may be initiated by impurities in the solution, dust, or light, as the aqueous decomposition of persulphate is known to be photosensitive. An alternative mechanism where step (2.8) replaces (2.6) and (2.7) is suggested (7)

$$2OH^{\cdot} \longrightarrow H_2O + \tfrac{1}{2}O_2 \qquad (2.8)$$

Application of the steady state hypothesis to the radicals in the above scheme (See Appendix I) leads to the rate law

$$\begin{aligned} -d\,|S_2O_8^{2-}|/dt &= (k_1k_2k_3/k_4)^{\frac{1}{2}}\ |S_2O_8^{2-}| \\ &= k_o'\ |S_2O_8^{2-}| \qquad (2.9) \end{aligned}$$

where $k_o'$ is the observed rate constant.

Crematy (37) followed the decomposition of persulphate by a pH state continuous potentiometric technique. The experiments were done in the presence and absence of styrene monomers as a free radical scavenger. He found that in the presence of the scavenger, the initial rate of acid formation is zero. This emphasises that the increased acidity with time is due to reaction (2.5) and not to any direct reaction between the persulphate ion and water.

### *2.1.2 Mechanism of the Acid Catalysed Reaction* (9, 96)

$$S_2O_8^{2-} + H^+ \longrightarrow HS_2O_8^- \qquad (2.10)$$

$$HS_2O_8^- \longrightarrow SO_4 + HSO_4^- \qquad (2.11)$$

$$SO_4 \longrightarrow SO_3 + \tfrac{1}{2}O_2 \qquad (2.12)$$

$$SO_3 + H_2O \longrightarrow H_2SO_4 \qquad (2.13)$$

In strong acid

$$SO_4 + H_2O \longrightarrow H_2SO_5 \qquad (2.14)$$

Rather fewer data have been published on this aspect of the decomposition and the evidence for the sulphur tetroxide molecule as an intermediate, rests on the detailed study made by Kolthoff and Miller (96) . They studied the kinetics of the decomposition in water enriched with oxygen-18 at varying pH, and found that in acid solution (0.5 M $HClO_4$), all the oxygen produced came from the persulphate, but in alkaline solution (0.1M NaOH), the oxygen came from water. This observation led them to postulate different mechanisms for hydrogen ion catalysed and uncatalysed decomposition. For example the following mechanism which may take place, the oxygen produced from the persulphate decomposition in acid medium is not explained.

$$SO_4^{\bullet -} + H^+ \longrightarrow HSO_4^{\bullet} \qquad (2.15)$$

$$HSO_4^{\bullet} + H_2O \longrightarrow HSO_4^- + OH^{\bullet} + H^+ \qquad (2.16)$$

For acid solution of concentration of more than 2M measurements have been made to determine the amounts of peroxy monosulphuric acid and hydrogen peroxide produced(96) . These indicate that the peroxydisulphate first decomposes to give peroxydisulphuric acid which hydrolyses further to hydrogen peroxide as follows:

$$H_2SO_5 + H_2O \longrightarrow H_2O_2 + H_2SO_4 \qquad (2.17)$$

$$H_2O_2 \longrightarrow H_2O + \tfrac{1}{2}O_2 \qquad (2.18)$$

Step (2.10) is rate determining and the reaction between two oppositely charged ions accounts for the negative salt effect. From the evidence presented here the observed overall persulphate reaction rate can be given by

$$-d|S_2O_8^{2-}| /dt = k_1' \, |S_2O_8^{2-}| + k_2'|H^+| \, |S_2O_8^{2-}| \qquad (2.19)$$

and the rate constant can be split into two parts, one is acid catalysed:

$$k_o' = k_1' + k_2' \, |H^+| \qquad (2.20)$$

It can be concluded that in the systems discussed till now, sulphate radical production rate remains unchanged even when catalysed reactions (with $H^+$) is taking place, provided the same initial peruslphate concentration is present.

## *2.2 Decomposition of Persulphate in Presence of Additives*

In an emulsion polymerisation system, apart from persulphate ions, there are present polymer particles, emulsifier (soap), monomer and probably ionic salts and mercaptan. So in a thorough study of the kinetics of emulsion polymerisation it is of great importance to know the effect of these components on the production rate of persulphate radicals.

Direct comparison of results of different workers is difficult because of various conditions of temperature and pH. Several reports have appeared of increased rate of decomposition of persulphate ion in polymerising systems based on increased rates of polymerisation under various conditions, e.g. with different soap concentrations (16, 100, 111). It is felt that some caution should be exercised in drawing conclusions about the rate of decomposition of persulphate from observations of a rate of polymerisation in a polymerizing reaction. For example, a faster rate of polymerisation in the presence of soap may result from the formation of a more finely divided latex rather than from an increased rate of decomposition of persulphate. A brief discussion of the persulphate decomposition in the presence of different substances follows and for wider coverage see House (84) and Baddar (2) .

### *2.2.1 In the Presence of Hydrocarbons or Monomers*

The rate of disappearance of persulphate is greatly increased in the presence of vinyl acetate or methyl acrylate (70, 113) No explanations were advanced for these observations except that decomposition products of persulphate in the presence of these monomers may have an effect on the decomposition process (113) Liegeois(104) found that the rate of decomposition was not affected by vinyl acetate.

Bartlett and Cotman (7) found the decomposition rate is 3/2 order in persulphate and 1/2 order in methanol and it was accelerated by a factor of about twenty five. Khachatryan et al (89) claimed that ethanol does not participate in the initial step which is first order in persulphate. This has been reported by Kolthoff et al (99) where they found that the alcohol does not accelerate decomposition rate in the presence of allyl acetate which is an efficient radical trap.

### *2.2.2 In the Presence of Inorganic Salts*

An increased rate of disappearance of persulphate has been reported with a wide range of inorganic salts. These reactions have been reviewed by House (84) . Bawn and Margerison (9) have reported on the catalysis of potassium persulphate decomposition by heavy-metal ions. Baddar (2) attributed the somewhat higher rate of decomposition of persulphate in aqueous solutions, compared with those reported by workers who recrystalysed the persulphate before use, to the presence of impurity ions which catalysed the reaction. The same effect was reported by Ball et al (4) . He claimed that careful recrystallisation from conductivity water, or addition of a small amount of the complexing agent "EDTA", caused a significant decrease in the rate.

It is of interest to point out that metal ions which can exist in more than one valency state can catalyse the decomposition of persulphate ions. Such ions may enter into industrial emulsion polymerisation systems, either as impurities in the water or from defective reactor lining. The result of such impurities may give rise to erratic persulphate decomposition rates, and therefore to erratic initiation rates.

### *2.2.3 In the Presence of Emulsifier*

Decomposition of persulphate in the presence of emulsifiers had been widely studied (2, 84, 96, 97, 111, 113, 156) and the general conclusion is that emulsifiers accelerate the decomposition even though the extent depends on the particular emulsifier. Morris and Part (113) found an acceleration produced by sodium lauryl sulphate and sodium hexadecyl sulphate, but not by a fluorinated soap. Kolthoff and Miller (96) found that in 10% sodium laureate solution the rate of disappearance of persulphate was increased about three-fold and effectively independent of the laureate concentration in the range 0.01 - 0.07 M. Vinogradov et al (156) found that potassium oleate, ammonium oleate, sodium dibutyl napthalene sulphonate and rozin soap accelerated the decomposition of persulphate to varying extents. Crematy (38) found the first order decomposition rate was increased by cationic surfactants. Grancio and Williams (70) found the decomposition rate in the presence of acetylphenoxyethyl, a non-ionic soap, and sodium dodecyl sulphate increased by a factor of about four.

Baddar (2) postulated a probable (though incomplete) sequence that is consistent, of both his results and the results of other workers (9, 37, 96, 113)

$$S_2O_8^{2-} \xrightarrow{k_1} 2\ SO_4^{\cdot -} \qquad \text{(I)}$$

$$SO_4^{\cdot -} + H_2O \xrightarrow{k_2} HSO_4^- + OH^{\cdot} \qquad \text{(II)}$$

$$R\text{-}OSO_3^- + OH^{\cdot} \xrightarrow{k_3} H_2O + R^{\cdot}\ \text{-}OSO_3^- \qquad \text{(III)}$$

$$R^{\cdot}\ \text{-}OSO_3^- + S_2O_8^{2-} \xrightarrow{k_4} SO_4^{\cdot -} + SO_4^{2-} + \text{reactive intermediate} \qquad \text{(IV)}$$

$$R^{\cdot}\ \text{-}OSO_3^- + SO_4^{\cdot -} \xrightarrow{k_5} SO_4^{2-} + \text{(reactive intermediate and/or products)} \qquad \text{(V)}$$

The rate law derived from such a sequence by the steady state hypothesis and further assumptions that $k_1$ is small compared to the other rate coefficients involved in the law (see Appendix I) is:

$$-d|S_2O_8^{2-}|\ /dt = (k_1k_2k_4/k_5)^{\frac{1}{2}}|S_2O_8^{2-}|$$

$$= k_o'\ |S_2O_8^{2-}|$$

where $k_o'$ is the observed rate constant.

$R\ \text{-}OSO_3^-$ is an alkyl sulphate ion

## *2.3 Initiator Efficiency*

The efficiency of an initiator is generally defined as the fraction of the radicals produced in the decomposition reaction which initiate polymer chains(119). If the decomposition of initiator, I, can be represented as:

$$I \xrightarrow{k_d} 2R^{\cdot}$$

then the rate of initiation, $R_i$, is given by:

$$R_i = 2f\ k_d|I| \qquad (2.22)$$

where f is the initiator efficiency and $|I|$ is the concentration of the initiator.

In setting up equation (2.22) it was assumed that only thermal decomposition results in the production of initiating radicals while other side reactions do not(119) , (this is not always true). The quantity f, then, is a measure of the wastage of radicals initially formed that do not successfully initiate polymerisation, but are destroyed by other reactions. For an initiator giving y primary radicals

$$f = \frac{\text{rate of initiation of polymer chains}}{y * \text{rate of decomposition of initiator}} = \frac{R_i}{yk_d|I|} \qquad (2.23)$$

If an inhibitor is present in a batch reactor, it simply delays the start of the polymerisation and after the inhibitor is consumed the polymerisation proceeds normally. When an inhibitor is present in a feed stream to a continuous system, the effect can be quite different. The rate of free radical generation in a CFSR is given by $k_d|I|$ V where V is the volume of the reacting mixutre. The rate of initiation in the absence of inhibitor, $R_i$, is usually given by equation (2.22). The rate of inhibitor input to the reactor can be expressed as FH, where F is the volumetric feed rate and H is an effective inhibitor concentration in the mixed stream. If one molecule of inhibitor destroys the effectiveness of one free radical, the inhibitor will reduce the initiation rate as follows:

$$R_{i,eff} = f \{k_d|I| - H/(\theta f_H)\} \qquad (2.24)$$

where $R_{i,eff}$ is the effective initiation rate, and $f_H$ is the initiator effectiveness in its reactions with the inhibitor.

If $H > k_d |I| \theta f_H$, no polymerisation will take place

If $k_d |I| \theta f_H > H$, polymerisation will proceed with lower initiation rate given by equation (2.24). The influence of inhibitor on the performance of a single CFSR can be seen by replacing $R_i$ with $R_{i,eff}$ in the appropriate equations.

From the available experimental evidence in the literature it is not established that an increase in the rate of decomposition of persulphate ions in the presence of additives does not result in an increase in the rates of production of sulphate radicals or vice versa.

# CHAPTER 3

## CONTINUOUS EMULSION POLYMERISATION REACTORS

# CHAPTER 3

# CONTINUOUS EMULSION POLYMERISATION REACTORS

## *3.1 Introduction*

Chemical reactors are specially designed vessels inside which controlled chemical reactions can be carried out. In general, chemical reactors are broadly of three types(101, 124) , batch, semicontinuous, and continuous reactors. In the batch systems all the reactants are fed into the reactor before the start of the reaction. During reaction no material is either introduced or withdrawn, (except for sampling). This is an unsteady state operation where composition changes with time. Most of the earlier theories were developed in batch reactors, and this could be attributed to the ease of handling.

A reactor into which reactants are added continuously after a part of the recipe has been charged, while no product withdrawal takes place during reaction, is classified as a semicontinuous reactor. Another type of semicontinuous reactor is available where all reactants are fed initially but one or more of the products is removed continuously. This technique gives certain advantages in altering the polymer structure and is more efficient in reactor utilisation. In emulsion polymerisation it offers the advantage of easily controlling reaction rates for exothermic reactions, (almost all vinyl polymerisation reactions are exothermic), particle size, molecular properties, and particle morphology in the case of copolymer products. It is also capable of producing a stable, high solids latex.

Gerrens (63) investigated the semicontinuous emulsion polymerisation of styrene and methyl methacrylate to determine the effect of monomer feed rate and emulsion feed rate on the rate of polymerisation, the degree of polymerisation, and particle size. Variations in the particle size distribution could be accomplished without changing the overall recipe.

There are extensive experimental investigations on semicontinuous reactors, but there have been few theoretical treatments of this type of system, and so it will not be discussed further.

For processes which require high rates of production of a single material (or closely related materials) of uniform product quality, economic considerations make continuous flow reactors particularly attractive. In this type reactants are introduced and products withdrawn simultaneously during the reaction. The two commonly used flow reactors are; stirred tank reactors and plug flow reactors. The main differences between these reactors are the flow patterns and shapes of the equipment. The former are usually operated in series. The plug flow reactors are hardly used in emulsion polymerisation reactions except on occasions when introduced as a first reactor in a series, to function as a 'seeder' or pre reactor.

### *3.2 Tubular Reactor*

The tubular flow reactors have been used to increase the heat transfer area and thus improve temperature control and generally give lower equipment cost. Initially it was thought that the emulsion polymerisation should be conducted in the turbulent flow regime as a condition necessary to obtain satisfactory heat transfer and mixing. However, experiments showed that turbulent flow gave rise to the formation of a pre-coagulum. This resulted in an accummulation of polymer particles on the walls of the tube and finally the reactor plugged. (131)

Ghosh and Forsyth (67) examined the continuous emulsion polymerisation of styrene in a tubular reactor, where they restricted the operation to a maximum Reynolds number of 210 and used very high soap concentrations and thus were able to obtain operation without plugging and conversions as high as 90%. In their attempt to model the tubular reactor, they assumed that the number of polymer particles remained constant during the polymerisation. Rollin et al 131 found experimentally that the emulsion Reynolds number had a large effect on the conversion of styrene in a tubular emulsion polymerisation reactor. They observed that when operating in the turbulent flow region, the final conversion decreased as the Reynolds number was increased. They also found that the rate of polymerisation was maximum when the flow was at the point of the laminar-turbulent transition. Lynch and Kiparissides (106) attempted to predict Rollin et al (131) experimentally obtained results by developing a mathematical model of the system. They assumed Smith-Ewart case 2 kinetics to apply at all conversions ($\overline{q} = \frac{1}{2}$) and also a plug flow operation with a constant axial velocity, which is not true in the turbulent flow region. They claimed that their model successfully simulated Rollin's data. Lee and Forsyth (102) investigated the feasibility of using a tubular reactor for the seeded polymerisation of vinyl acetate, and the effect of process variables on conversion and latex properties. From their study they arrived at the conclusion that complete monomer conversion is possible with high concentrations of initiator and mixed emulsifier. They also found that the use of seed improves the latex stability, which was found generally poor even at high levels of emulsifier concentration for tubular reactors. Alse phase separation occurred at low monomer conversion.

### 3.3 *Continous Flow Stirred Reactor*

In this thesis the continuous flow stirred reactor is going to be referred to as CFSR or continuous reactor. A number of mathematical models and considerable experimental data (at least for styrene) have been published for a single continuous flow stirred reactor (CFSR) and short trains. These models can be classified as to being either steady state or dynamic models and they are usually obtained either from Smith-Ewart relationships, where particle size is uniform, or, from the ideal residence time distribution of CFSR, or, from a population balance around a CFSR. Since the way in which continuous emulsion polymerisation reactors are started up can have a significant influence, not only on the transient behaviour before steady state is achieved, but also on the nature of the ultimate state obtained after all transient effects die out, the following section is going to be allocated to the start-up procedures in a CFSR.

#### 3.3.1 *Start-Up Procedures*

Gershberg and Longfield (66) used a three stage reactor train where the system was started up from an empty state by pumping premixed emulsion into the first stage. Nomura et al (117) on the other hand, filled their reactors with styrene emulsion and started the continuous reaction period by injecting simultaneously initiator and pumping monomer emulsion plus initiator into the reactor. Ueda et al (147) introduced the styrene and aqueous phase (of soap and initiator) into a premixer at 0°C. The reactants were then introduced to a seeder and later into the reactor. Both the seeder and the reactor operates at the required temperature. Two kinds of seeder, back mixed and plug flow type, were used. Gerrens and Kuchner (64) filled their first reactor with monomer emulsion (styrene or methyl acrylate). Polymerisation started after the addition of the required amount of initiator solution. The overflow from the first reactor gradually filled the 2nd and 3rd reactors. Brooks et al(27) used a single reactor in their study. The reactor was filled to its operating capacity with an emulsion which contain no initiator; all other ingredients were present in the desired quantities. Pumping of the soap-styrene emulsion and the initiator was started as soon as the required steady temperature of the reactor contents was reached. Gorber (69) filled his reactor with the soap-styrene emulsion and started the reaction by adding the initiator solution required and starting the flow of the aqueous soap-initiator solution and the monomer from the storage tanks. Gerrens et al (65) studied three separate start-up procedures for a three-stage, isothermal reactor train. Procedure (1) was to start with the first reactor full of monomer (styrene) emulsion and remaining reactors empty. When the first reactor had been brought to the desire temperature, initiator was injected and the continuous feed of premixed emulsion started. The second and third reactors filled and overflowed in sequence after the start-up. Procedure (2) was the same as (1) except all three reactors were initially filled with monomer emulsion, and initiator was injected as the continuous flow was started. Procedure (3) was again the same as (1), but after steady state had been achieved, the reaction temperature was increased to a new temperature. Greene and Poehlein (71) started-up their reactor with nitrogen-purged deionized water, while Kiparissides et al (93) used distilled water prior to introducing any feed stream. De Graff and Poehlein (39), Stevens and Funderburk (141), Lin et al (105) did not have a clear description of the start-up procedure.

In the present work several start-up procedures has been studied and a full description of these procedures is discussed in the experimental section of this report.

### *3.3.2 Studies and Models of CFSR's*

Wall et al (151) presented the first study of continuous emulsion polymerisation as a part of a more general study of continuous free radical copolymerisation of methyl methacrylate and styrene. No theory was advanced from these studies.

The first significant theoretical study of continuous emulsion polymerisation reactors was put forward by Gershberg and Longfield (66) in 1961. Using essentially the Smith-Ewart assumption of water insoluble monomer and a $\bar{q}$ of 0.5, they developed a steady state model for a train of reactors where the feed stream is identical to the initial recipe in each reactor (a match flow reactor), and no polymerisation between stages. The steady state rate of polymerisation in the n-th reaction $R_{pn}$, should be the same as in a batch reactor, and given by

$$R_{pn} = k_{pn} \, |M|_n \frac{N_n}{N_A} * 0.5 \qquad (3.1)$$

The steady state number of particles in the first reactor, $N_1$, was then given by two limiting cases of Smith and Ewart as

$$N_1 = \begin{cases} \rho_i \theta_1 & \text{upper case} \\ \rho_i \theta_1 (1 - \frac{A_p}{a_s S}) & \text{lower case} \end{cases} \qquad (3.2)$$

For spherical particles, the volume of a particle at time t which was initiated as a polymer particle at time ω was given as

$$v = \frac{k_{p1}}{N_A} * \frac{d_m}{d_p} * \frac{\phi_{m1}}{1-\phi_{m1}} * (t - \omega) * \bar{q} \qquad (3.3)$$

$$= \mu(t-\omega) * 0.5$$

where $\phi_{m1}$ is the monomer volume fraction of a particle in the first reactor and was assumed insensitive to conversion as long as monomer droplets were present in the reactor. Employing the ideal residence time distribution for CFSR gives

$$\frac{dN_1}{N_1} = \frac{EXP(-t/\theta_1)}{\theta_1} \, dt \qquad (3.4)$$

If it is assumed that life expectancy of a micelle is very short compared to the residence time (i.e. $\omega << \theta_1$), the steady state number of particles is given by

$$N_1 = \frac{\rho_i \theta_1}{1 + \frac{K_1 \theta_1 \rho_i}{a_s S} \{ \frac{k_{p1} |M|_1 \theta_1}{1 - k_2 |M|_1} \}^{2/3}} \qquad (3.5)$$

where

$$K_1 = 6.41 * 10^{-24} \, (v_p \, M_{mw})^{2/3} \, \overset{o}{A}{}^2 \text{ mole} \qquad (3.5a)$$

$$K_2 = 10^{-3} * (v_m \, M_{mw}) \qquad \ell/\text{mole} \qquad (3.5b)$$

For high soap concentration ($a_s S$ large)

$$N_1 = \rho_i \theta_1 \qquad (3.6)$$

For small concentration of soap ($A_p/a_s S >> 1$)

$$N_1 = \frac{a_s S}{K_1 \{k_{p1} \theta_1\}^{2/3}} * \frac{1-K_2 \, |M|_1^{\;2/3}}{|M|_1} \qquad (3.7)$$

Gershberg and Longfield studied the emulsion polymerisation of styrene. They found that at steady state there was very little free soap available in the second and third reactors, hence particle generation occurred only in the first reactor and

$$N_1 = N_2 = N_3 = \ldots\ldots. N_n \qquad (3.8)$$

From the foregoing discussion it could be concluded that for a single stage continuous reactor,or a series CFSR in which all particles are generated in the first stage, the number of latex particles in the reactor depends on $S^1$ and $\theta^{-2/3}$ and $|I|^o$.

A rather significant contribution to the modelling of a single steady state CFSR has been made by De Graff and Poehlein (39) . These authors extended the steady state model of Gershberg and Longfield (66) to account for the co-existence of more than one radical per particle and incorporated particle size distribution and molecular weight calculations into their model. In a later paper Poehlein and Dougherty(125) noted that the Stackmayer treatments for the case of no radical desorption which was used earlier does not account for $\bar{q} > 0.5$ during the early stages of growth, but it does predict accelerating growth for large particles. With their model (39, 125) Poehlein and co-workers were not only able to explain their own experimental data but also that of Gershberg and Longfield(66) and Gerrens and Kuchner (64) , especially in the region where $\bar{q}$ > 0.5. However for short mean residence time the model is in general poor.

Stevens and Funderburk (141) illustrated the use of the population balance in continuous emulsion polymerisation. Their model was capable of predicting the overall particle size distribution leaving the reactor. Free radical desorption was ignored. The main drawback of their model was that the size dependent average number of free radicals per particle had to be calculated before obtaining solutions to their population balance equation.

Thompson and Stevens (144) have used a new approach to model continuous emulsion polymerisation. The Smith-Ewart recursion equation is incorporated directly as the "rate of formation" relation for polymer particles. The mechanism of free radical desorption from polymer particles was included, and finite termination rates in particles were allowed.

Omi et al (121) were among the first to present a dynamic model of continuous emulsion polymerisation in a series of stirred tank reactors. Their model describes the particle population, free emulsifier concentration and monomer concentration during transient conditions assuming the particle generation occurs only in the first reactor,(which is not necessarily true during start-up). The particle area was assumed to be directly proportional to the number of particles as given by the Gershberg-Longfield steady state expression.

A paper published by Nomura et al (117) in 1971 presented a dynamic model for a train of continuous reactors which incorporate their batch reactor model (76) for particle generation where radicals enter polymer particles in preference to micelles. This is contrary to Smith-Ewart assumptions used by Gershberg and Longfield, which assume that radicals either enter micelles preferentially or else enter the micelles and particles proportional to their surface area. Although the proposed model predicted closely the steady state and transient number of particles and conversion, the molecular weight predictions agreed satisfactorily only at high residence times. A summary of this model and its application to new experimental data has been published in 1981.

Brooks (24) in 1973 stated that it is erroneous to assume that the particle surface is always saturated with emulsifier. He pointed out that since experimental results show that the total surface area of polymer particles is usually greater than the total adsorption area of surfactant (65,66) at steady state then the particles cannot be saturated with surfactant. In an attempt to explain this phenomenon, Gerrens and Kuchner(65) mentioned the possibility of micelles being adsorped into the surface of the particles almost immediately they enter the reactor. Instead of following this line of argument, Brooks (24) explicitly considered micelles to be participating in two competing rate processes; the nucleation of new particles and dissolution into the aqueous phase. Since micelle break-up is then a rate process, polymer particle surfaces may not necessarily be saturated with emulsifier in the presence of free soap. Taking into account the above processes he was able to obtain equations which show that N depends on S, $\theta$, and $\rho_i$. Simplified forms of the equations predict that N depends on $S^1$ and $\theta^{-y}$, where the value of y less than 2/3.

Gorber (69) has developed and experimentally tested a model for continuous emulsion polymerisation CSTR. The model assumes instantaneous radical termination within polymer particles and a constant, equilibrium monomer concentration in particles as long as monomer drops exist. The two limiting particle generation rate expressions developed by Smith and Ewart for a batch reactor are used for a CSTR. The approach taken by Gorber in developing his model was followed by Dickinson (40) to derive a mathematical model for emulsion polymerisation of styrene in a train of CSTR's. A similar approach based on an age distribution function was taken by Kiparissides et al (92, 94). On the other hand Min and Ray's(112) approach focussed on the size distribution rather than on the residence time or age distribution of particles. The principal criticism to be made is that so many parameters are introduced, reliable values for which are impossible to obtain. The inclusion of certain variables, e.g. rates of diffusion which are often so high, in a computer simulation would lead to very stiff equations, causing computation problems without significant improvement in the accuracy of the simulation. Kirillov and Ray (95) in 1976 presented results of a simulation of a continuous emulsion polymerisation reactor.

The model was developed out of the frame-work presented earlier by Min and Ray (112) . The results of the model were compared to the experimental data for the emulsion polymerisation of methyl methacrylate presented by Greene, Gonzales and Poehlein in the A.C.S. symposium series number 24 in 1976. While the comparison of steady state monomer conversion results was fair , the model failed to simulate the results of some experiments where sustained oscillations had been observed. The situation was corrected by adding a new mechanism and adjusting the value of the polymerisation rate constant. About 25 independent parameters were involved in the simulation. No particle size distribution results were shown.

### *3.3.3 Dynamic Phenomena in Continuous Emulsion Polymerisation Reactors*

Other work on the field include papers dealing with the stability of the system and with some of the extraordinary phenomena occurring in continuous emulsion polymerisation reactors. These include overshoot upon the start of the reactor, transient and sustained oscillations, and multiple steady state.

Gershberg and Longfield (66) observed an initial large conversion overshoot followed by small, but apparently sustained, fluctuations of 1-5% conversion about an average value, with a period of 3 to 5 mean residence time. Gerrens and Kuchner (64) thought that these oscillations were due to the fluctuations in the feed systems. Nomura et al (117) reported overshoots in both conversion and polymer particle concentrations; however, the magnitude of the conversion overshoot was not as large as that of Gershberg and Longfield, and no sustained fluctuations of conversion about an average value were detected. Gorber (69) also observed the initial conversion overshoot and gave some evidence of separate generations of new particles. Several other workers have also reported the initial overshoot in the conversion

As Brooks (24) noted, the form of the particle and micelle conservation equations he developed for CFSR, leads to the possibility of solutions which show that the dependent variables oscillate with respect to time. Gerrens et al (65) have shown experimental verification of the theoretical predictions of multiple steady states. Dickinson (40) , and Kirillov and Ray (95) presented models to predict the phenomenon of multiple steady state. Chiang and Thompson (35) in studying theoretically the stability of continuous emulsion polymerisation reactors noted that only one steady state operating point was predicted for the case where the decrease in the termination rate constant due to the gel effect was neglected.

It is clear from the brief discussion of this chapter that there have been a large number of isolated theories developed to model emulsion polymerisation in continuous reactors. None of these provide a suitable framework for including the whole spectrum of mechanisms postulated for emulsion polymerisation. Most of the models which have been put forward by various workers for continuous reactors fit their own experimental data (if available), and not those of other workers. These models are often developed for particular monomer/surfactant systems and then generalised to include other systems.

# CHAPTER 4

# CONCLUSION FROM THE LITERATURE SURVEY

# CHAPTER 4

## CONCLUSION FROM THE LITERATURE SURVEY

The discussions in this section showed that much of the data in the literature has to be viewed individually, and to present a unifying theory is still impossible, because not enough comparative data are available. One of the reasons for this is the number and complexity of the variables. Temperature, monomer-to-water ratio, kind and amount of emulsifier, pH, and initiator vary in most of the work reported.

The influence of pH on the initiator efficiency and on the hydrolysis of some monomers and emulsifiers, which results in products which in turn may retard or accelerate the rate of polymerisation, has to be taken into account. It is still very difficult to determine accurately what the efficiency of an initiator is during polymerisation. All methods used so far have been indirect. Most of the workers in the field assumed that any reaction of the persulphate with monomer or emulsifier does not contribute to the initiation process, and the valuesfor the decomposition rate of persulphate in pure water have been used.

Batch polymerisation of emulsion systems has been widely studied both theoretically and experimentally. In emulsion polymerisation of many monomers the mechanism of the reaction can be explained by the Harkins theory, and the application of a Smith-Ewart model can be satisfactory enough to explain the reaction kinetics. On the other hand quite a number of monomers have been found not to conform to the Smith-Ewart theory and this has necessitated modification of the original theory or in some cases the proposition of entirely new reaction models. There is still uncertainty as to whether water - solubility of a monomer causes the deviant behaviour from the Smith-Ewart model of most 'soluble' monomers.

In contrast with batch reactors the continuous operation has received less theoretical and/or experimental study. The experimental studies are particularly rare. Due to the complexity of the mechanism and kinetics of continuous emulsion polymerisation, some workers had found it useful to combine batch reactor models with the theories of continuous flow stirred reactors. In general there are more theoretical than experimental studies reported for the continuous emulsion polymerisation operation, and in many cases the experimental work suffers from lack of accuracy.

Some of the main features of emulsion polymerisation are:

i) the increase in the concentration of emulsifier and initiator results in a decrease in the average particle size.
ii) the higher the reaction temperature the larger the number of particles (batch reactor)
iii) for most monomers, the polymerisation rate increases with the increase in the number of particles in emulsion.
iv) attainment of high polymerisation rates and molecular weights simultaneously.

# CHAPTER 5

# EXPERIMENTAL TECHNIQUES

# CHAPTER 5

# EXPERIMENTAL TECHNIQUES

## 5.1 Introduction

In carrying out a chemical reaction, it is desirable to learn of the fate of the reactants and the properties of the resultant product. In emulsion polymerisation the reactant of greatest concern is usually the monomer or mixture of monomers, the main product of which is the polymer. Procedures for following the course of the emulsion polymerisation are mainly concerned with the determination of conversion, unreacted monomer, soap concentration and location, initiator concentration, heat generation, concentration of modifier (if present), average particle size, particle size distribution, molecular weight and molecular weight distribution, with time. Other properties of interest are viscosity and stability of the latex. A brief discussion of some of these procedures follows in this chapter.

The factors which influenced the design and operation of the continuous reactor in this study are highlighted, and a brief discussion of on-line techniques and measurements is presented at the end of the present chapter.

## 5.2 Procedures for Following the Course of the Polymerisation

### 5.2.1 Conversion

The conversion is the fraction of monomer charged which is converted to polymer. It is often used as a percentage. There are direct and indirect methods to determine the conversion.

In the direct methods the fraction of solid polymer in a sample is determined gravametrically. There are two main gravamatic methods, the first is to heat a sample of latex of known weight to dryness and from the weight of residue and taking into account the non-volatile constituents the conversion is determined. In this method, it is essential to use a satisfactory shortstop. The other method is to coagulate the latex by the addition of acid, electrolyt, or methanol.

The polymer is then separated from the solution by filtration, dried and weighed.

The other type of direct method is the determination of the unreacted monomer, which is equivalent to determination of solid polymer, assuming no loss of monomer by side reactions or evaporation. It is more convenient to determine the polymer than the monomer, but in special cases direct determination of the monomer may be advantageous, for example in butadiene-styrene polymerisation.

Many indirect methods have been used for following the conversion in emulsion polymerisation. In reactors with high volume to surface area, i.e. industrial reactors, it is possible to follow the conversion by quantifying the heat liberated from the reactor. In some polymerising systems the change in the value of the vapour pressure can be related to the conversion. Since a decrease in volume accompanies the polymerisation, it is possible to measure the change in density and then relate this to the conversion.

### *5. 2.2 Initiator*

The discussion which follows is concerned with persulphate ions as initiator. There are three main methods for the determination of undissociated persulphate in the latex. These are volumetric, polarographic, and colourimetric. Only the volumetric method is going to be discussed. In the present study, both the iodometric and ferrometric methods proposed by Kolthoff and Carr(98) were used.

In the ferrometric method the latex is coagulated with sulphuric acid, and an excess of ferrous sulphate is added to the filtrate in order to reduce persulphate. After about 30 minutes the excess of ferrous ion is back-titrated with ceric sulphate. The presence of organic matter and oxygen interfere with this method, and leads to irreproducible high results.

The theory behind the iodometric method proposed by Kolthoff and Carr (98), with some modifications, and the calculation used for it in this study, are presented in Appendix II.

### *5.2.3 Emulsifier (Soap)*

To determine soaps which are derived from fatty or rosin acids, the latex is diluted with water and isopropyl alcohol, and the mixture is titrated conductometrically with dilute hydrochloric acid. In the case of excess alkali present with the latex, an excess hydrochloric acid is added to the diluted latex and the mixture is back titrated conductometrically with sodium hydroxide. The first break in the titration curve corresponds to neutralization of the excess hydrochloric acid, and the second to neutralization of the fatty acid.

## *5.3 Methods for the Study of the Latex and the Properties of the Polymer*

### *5.3.1 Particle Size*

The measurement of particle and particle size distribution (PSD) is one of the most necessary tasks for characterizing a latex. The importance of this physical characteristic of the system is readily realized on examination of the chemical and physical properties controlled by particle size and size distribution. The control of particle size by means of reproducible and accurate, and fairly simple, analysis is of primary importance.

Much of the literature dealing with particle size measurements fails to analyse the spectrum of techniques as to their advantages and shortcomings, their principle, and the applicability of given analytical techniques to the problem at hand.

Average diameters are usually used to describe a given particle population even when full distribution data is available. The main reasons for using particle size averages are:

1) They are convenient
11) Some methods only give an average diameter
111) The use of numerical analysis is possible

The most familiar averages are:

number average

$$D_n = \frac{\Sigma n_i D_i}{\Sigma n_i} = \frac{\text{Number of particles of } D_i}{\text{Total number of particles}} \qquad (5.1)$$

weight average, where most of the light scattering methods give a value close to it

$$D_{\bar{w}} = \frac{\Sigma n_i D_i^4}{\Sigma n_i D_i^3} = \frac{\Sigma W_i D_i}{\Sigma W_i} \tag{5.2}$$

volume average, which is obtained from the flow ultra microscope and similar devices which count the particles per unit volume of a suspension

$$D_v = \left(\frac{\Sigma n_i D_i^3}{\Sigma n_i}\right)^{1/3} \tag{5.3}$$

surface average, which can be obtained by soap titration method.

$$D_s = \frac{\Sigma n_i D_i^3}{\Sigma n_i D_i^2} = \frac{\text{Total volume of particles}}{\text{Total particle surface}} \tag{5.4}$$

It should be noted, however, that if the size distribution data is available, it is possible to compute any of the particle size averages.

Methods used to obtain the particle size distribution vary from the direct microscope analysis to the indirect methods that depend on intrinsic or optical properties of the particles themselves. Techniques for measuring particle size distribution in the submicron range tend to be either time consuming, inaccurate or limited to a portion of the total size range.

The electron microscope is useful in sizing particles below 10,000 Å and gives a complete picture of the particles present in an ordinary latex. Modern instruments have a resolving power of less than 10 Å.

One of the main problems of electron microscopy is the difficulty in obtaining a representative sample. At least a thousand particles have to be counted to give a statistical satisfactory result and this number should be larger the wider the size distribution. Another problem with the electron microscope is that the temperature of the sample can reach as high as 150°C. Under these conditions some latices may shrink and give diameters about 20% too low. Furthermore soft latices should be treated with a special hardening technique before particles can be photographed. This treatment can alter the original particle dimensions.

Ultracentrifugation theoretically should provide a simple technique for measurement of the particle size and its distribution, depending on the density. This technique is difficult to use with particles smaller than 1000 Å, because the analysis time becomes too long.

A brief description of some 'average' particle size measurement methods, their advantages and limitations follows:

(i) Light Transmission, where the transmitted momochromatic light, at a given concentration, is a function of particle size and refractive index. The size determination is in the range 500 - 3000 Å. The main advantages of this method is rapidity, simplicity, and the small sample needed for the measurement. In this method the concentration of the latex should be known accurately, and the presence of large particles will give high results. This method is also sensitive to small changes in ratio of refractive indices.

(ii) Dissymetry, where the intensity of scattered light is measured at 45° and 135°. This method is relatively simple and the concentration of the sample need not be known. Results are imprecise above 2000 Å.

(iii) Maximum-Minimum Technique, where light intensity is measured as a function of the angle of scatter, and the angle of maximum and minimum intensity are noted. This technique is relatively accurate, and a qualitative estimation of the polydispersity can be obtained. The concentration of the sample need not be known accurately. However expensive spectrophotometers must be used, and it is easy to miss an angle of maximum or minimum intensity. The refractive index must be known accurately, and the method is sensitive to polydispersity. The present lower limit of this method is 2200 Å .

(iv) Forward Angle Ratio. In this method the intensity of scattered light at various angles is measured and the ratio of intensities at five degree intervals computed. It is not very sensitive to the refractive index, and the concentration of the sample need not be known. The range covered is 500-5000 Å. An expensive spectrophotometer must be used.

(v) Flow Ultramicroscope. In this technique a highly diluted suspension is pumped through a glass tube, where the tube is illuminated by an intense narrow band of light. As a particle passes through, it appears as a flash of light through a microscope. This method is rapid, accurate, and reproducible. No calibration by means of a standard is required. Only particles of diameter larger than 500 Å can be measured. This method is not available commercially and the total solids must be known with high precision. Agglomerates will be counted as one large particle.

(vi) Photon Correlation Spectroscopy. This method depends on analysis of the constantly changing pattern of laser light scattered by particles or molecules while in Brownian Motion. There are two optical arrangements which can be used to detect the rate of change of the scattered light, the heterodyne and homodyne method. The former uses a reference beam, taken by splitting the laser beam before the sample, from which the power spectrum of the diffracted light can be analysed to obtain average particle size. It is much more convenient, however to use the latter, single beam, method and to analyse the time dependent changes against time, by so-called "auto-correlation spectroscopy". The homodyne method was the one used mostly in the present study. This method is simple, fast, and only the refractive index of the suspending medium needs to be known. The range depends on the power of the laser and the angle of measurement of the scattered light. The main disadvantage, like all light scattering experiments, is the need for dust free samples. The method is less accurate for sizes of larger than 1μ.

In the case of polydispersed samples the form of the correlation function, in theory, could give the distribution of diffusion coefficients which could be used to calculate a distribution for the particle sizes. However in practice only the hydrodynamic radius can be calculated with a measure of the degree of polydispersity of the sample.

(vii) Soap Titration.[108] This technique is based upon the concept that in the presence of sufficient soap, the surface of the particles would become saturated with a monolayer of soap molecules, each of which would occupy a specific area. If the soap concentration in the latex is less than that required to saturate the surface of the particles, it is possible to titrate the latex until the C.M.C. is reached. This point may be recognised by measuring the conductivity or the surface tension of the latex. The difference between the C.M.C. in the presence and absence of the particles is thus recorded as the amount of soap adsorbed onto the surface of the polymer particles Knowledge of the specific surface area of the soap molecule and the total volume of polymer would allow calculation of the mean particle diameter. One of the disadvantages of this method is the difficulty in determining the end point of the titration. There has also been some discrepancy in reported values of cross-sectional areas of adsorbed soap molecules.

### *5.3.2 Molecular Weight*

The molecular weight of a polymer is of fundamental importance. The study of molecular weights takes on two aspects: the determination of an average molecular weight, and the determination of the distribution. The measurements of greatest practical importance when determining an average molecular weight are osmotic pressure, light scattering, and intrinsic viscosity.

Osmometry is concerned with measurements of colligative properties and hence yield absolute values of the molecular weight. However the inherent experimental errors are such as to prohibit the use of this method for molecules with molecular weight greater than 500,000. In principle, one measures the difference in pressure between a dilute solution of the polymer and the pure solvent, separated by a membrane which is permeable to the solvent but not the polymer. Measurement of osmotic pressure is a tedious and time-consuming operation, and requires considerable care in preparing the solutions and handling the osmometers. However, it is still the simplest "absolute" method of determining molecular weights, particularly of fairly low molecular weight polymers.

Determination of the intrinsic viscosity (135) is the most widely used technique for measuring average molecular weight of a polymer. The intrinsic viscosity, or the limiting viscosity number as recommended by IUPAC, can be regarded as the fractional increase in viscosity of unit volume of solvent due to the addition of 1g of noninteracting polymer molecules.

The ratio of viscosity of a polymer solution to viscosity of the solvent is related to the molecular weight M by the expression

$$\frac{(\eta/\eta_o) - 1}{C} = K'M^\alpha \qquad (5.5)$$

where K' is constant for a given type of polymer, solvent and temperature, $\alpha$ is a function of the geometry of the molecule and C is the concentration of polymer solution in g/100 ml. Equation (5.5) is only valid for very dilute solutions. The intrinsic viscosity is found by extrapolating either $((\eta/\eta_o)-1)/C$ or $\ell n((\eta/\eta)/C)$ to zero concentration.

$$|\eta| = \lim_{c \to o} \frac{(\eta/\eta_o)-1}{C} \approx \lim_{c \to o} \frac{1}{C} \ell n\, (\eta/\eta_o) \qquad (5.6)$$

hence

$$|\eta| = K'M^\alpha \qquad (5.7)$$

## *5.4 Design and Operation of the Continuous Reactor*

Reactor design can have a significant influence on reactor performance in a number of ways. Some aspects of reactor design such as heat transfer, structural design are reasonably well-understood. Other phenomena such as mixing details, latex floculation, and the formation of wall polymer are not completely understood.

In designing the continuous reactor for this study certain factors had to be considered:

(i) Liquid Level: The reactor should be operated full. A vapour space always causes problems. The latex can dry on the wall and present a site for growth, sometimes accelerating the rate, of more deposits. The aeration of the latex increases, and thus oxygen contamination increases.

(ii) Nozzle Location: The location of the feed and effluent nozzle should insure rapid mixing of the feed streams and prevent short circuiting between feed and effluent. Electrolyte streams should be as dilute as feasible to prevent electrolyte flocculation of the latex. The mixing of the soap and monomer before introduction to the reactor is preferable.

(iii) Reactor Surface: The internal surface of the reactor should be smooth. Rough places provide sites for polymer nucleation and/or deposition. Glass and polished stainless steel surfaces are preferable.

(iv) Heat Transfer: The surface to volume ratio of the reactor for a given volume should be as large as feasible to increase the heat transfer through the walls.

(v) Agitation: The agitation needs to be designed to provide adequate mixing of the feed streams and adequate heat transfer. Since high Shear can sometimes cause coagulation a balance should be drawn between flow and turbulence. The baffles in a reactor represent potential sites for wall polymer and thus should be eliminated if possible.

(vi) Wall Temperatures: Non-uniform wall temperatures can play a role in wall polymer formation. The reaction in any deposit could be faster if the temperature is higher.

(vii) Reactor Volume: The volume of the reactor should be as small as feasible for the ease of control and flexibility. However, it should be large enough for sampling. The change of the latex volume inside the reactor due to agitation and surface tension oscillation, should be negligibly small.

(viii) Cleaning: the reactor should be cleaned very well and during cleaning care should be taken to avoid damaging the surface.

As will be seen later in the next chapter, the design of the continuous reactor for this study tries to compromise between the different factors. It is important to note here that the glass was found to be the most suitable material for minimum formation of wall polymer. Also it was found that plastics which are chemically inert might not be physically inert as a site for wall polymer and coagulation. The most striking example for such plastics is PTFE.

It was also noticed that non-polar plastics, like polypropylene, can come into contact with the latex in the reactor as long as they are chemically compatible.

It was found necessary to design the reacor in such a way that it was possible to vary the reactor capacity, in order to vary the holding time of the reactor , without changing the pump settings.

This was achieved by the introduction of inserts of different sizes, or by the use of different size reactors of the same shape. A more comprehensive discussion of these techniques can be found later in the next chapter.

## *5.5 On Line Techniques and Measurements*

To be able to control a continuous emulsion polymerisation reactor, it is essential to have on line measurements of the different variables which are involved in the reaction. The on line techniques should be simple, accurate and fast enough to be used as control measurements. From all the techniques available for the measurement of particle size, the photon correlation spectroscopy appears to be the most practical and quickest for on line control studies. Analysis time can be less than two minutes.

Measurements of the change in density of the latex and then relating this to the conversion is another example of the on line techniques. A brief discussion of available density meters follows.

The use of precision density measurements for monitoring polymerisation reactions can be done rapidly and automatically. The method is independent of the reactor size and design but suffers from sampling difficulties.

There are three classes of density meters which are considered suitable for automatic, continuous operation with sufficient precision for calculation of polymerisation conversion. The classes are based on the mode of operation: $\gamma$-ray absorption, oscillatory frequency of a sample filled tube, and mass measurement at fixed volume.

In the present study an attempt was made to use the oscillatory type density meter with five digits precision. The main limitations are: 1. The polymer scale formation and monomer separation (if the conversion is below 50%) in the cell which results in lower apparent density. 2. The long time to achieve temperature equilibrium of the samples, caused by the difference in the sample charge temperature and that of the thermostated cell. 3. The error introduced by continuing reaction in the density cell both in achieving a stable temperature and in estimating the actual density in the reactor which is not exactly that in the density cell.

There are several other techniques which can be used as on line methods. Gas chromatography analysis can be used for measuring conversion and conductivity or pH measurements can be related to the free soap concentration or the total interfacial area of polymer particles. Conductivity could be high during the early stages of polymerisation because soap is present in ionic form (as free soap or in micelles) producing better electrical transport than after it has become primarily attached to more bulky latex particles. Conductivity remains high in these systems, because of the salts other than soap which are present. However, the soap is by far the largest concentration of ionizable salt present. Surface tension measurement can also be used to follow and detect the critical micelle concentration and free soap.

# CHAPTER 6

## EXPERIMENTAL WORK

- 6.1 Description of Materials
- 6.2 Description of Apparatus
    - 6.2.1 Polymerisation Equipments
        - 6.2.1.1 Batch Reactor
        - 6.2.1.2 Continuous Reactor
    - 6.2.2 Vacuum Drier
    - 6.2.3 Refrigerator - Centrifuge
    - 6.2.4 Semimicro-Burette
    - 6.2.5 Other Equipments
- 6.3 Procedures
    - 6.3.1 Start-Up Procedures
    - 6.3.2 Polymerisation
    - 6.3.3 Sampling
    - 6.3.4 Conversion
    - 6.3.5 Molecular Weight
    - 6.3.6 Particle Size
    - 6.3.7 Preparation of Seed Latex

## 6.1 Description of Materials

### Monomer:

Styrene was the monomer used. It was obtained from "Aldrich Chemical Company" in 4 kg metal containers. The styrene contained t-butylcatechol as an inhibitor. Before use styrene was freed from inhibitor by washing with 10% aqueous solution of sodium hydroxide and later distilled under reduced pressure. The prepared styrene was used immediately or stored in a refrigerator at -35°C before use.

### Emulsifier:

The emulsifier used was sodium dodecyl sulphate, an anionic soap, obtained from "Fisons Scientific Apparatus". The soap was dissolved in hot water which contained sodium hydroxide. The soap was of reagent grade quality and was used directly as received.

### Initiator

The two types of initiators used were analytical grade ammonium persulphate and potassium persulphate. Because of the better water solubility of ammonium persulphate it was used for most of the experimental work. Both initiators were obtained from "Fisons Scientific Apparatus" and were used without further purification.

### Inhibitor:

Hydroquinol, which was part of the precipitant for polymer coagulation, served as an inhibitor. It was used without further purification.

### Methanol, Isopropanol, and Toluene:

They were of analytical grade and were used as received.

The other chemicals used were the following:

Ammonium ceric sulphate, ferrous ammonium sulphate, potassium certic nitrate, sodium bromide, sodium hydroxide, and sodium thiosulphate.

They were all of analytical grades and were used as received.

*Water:*

Distilled water was used for all the experiments and high purity filtered water was used for the particle size experiments.

*Dialysis Bags:*

Visking tubing made of cellulose acetate material was used. It was obtained from "Griffin and George Limited".

## *6.2 Description of Apparatus*

### *6.2.1 Polymerisation Equipments*

Polymerisation experiments were carried out in a single stage continuous reactor, while the seeds, which were used in some experiments, were prepared in a batch reactor. A description of the batch reactor follows.

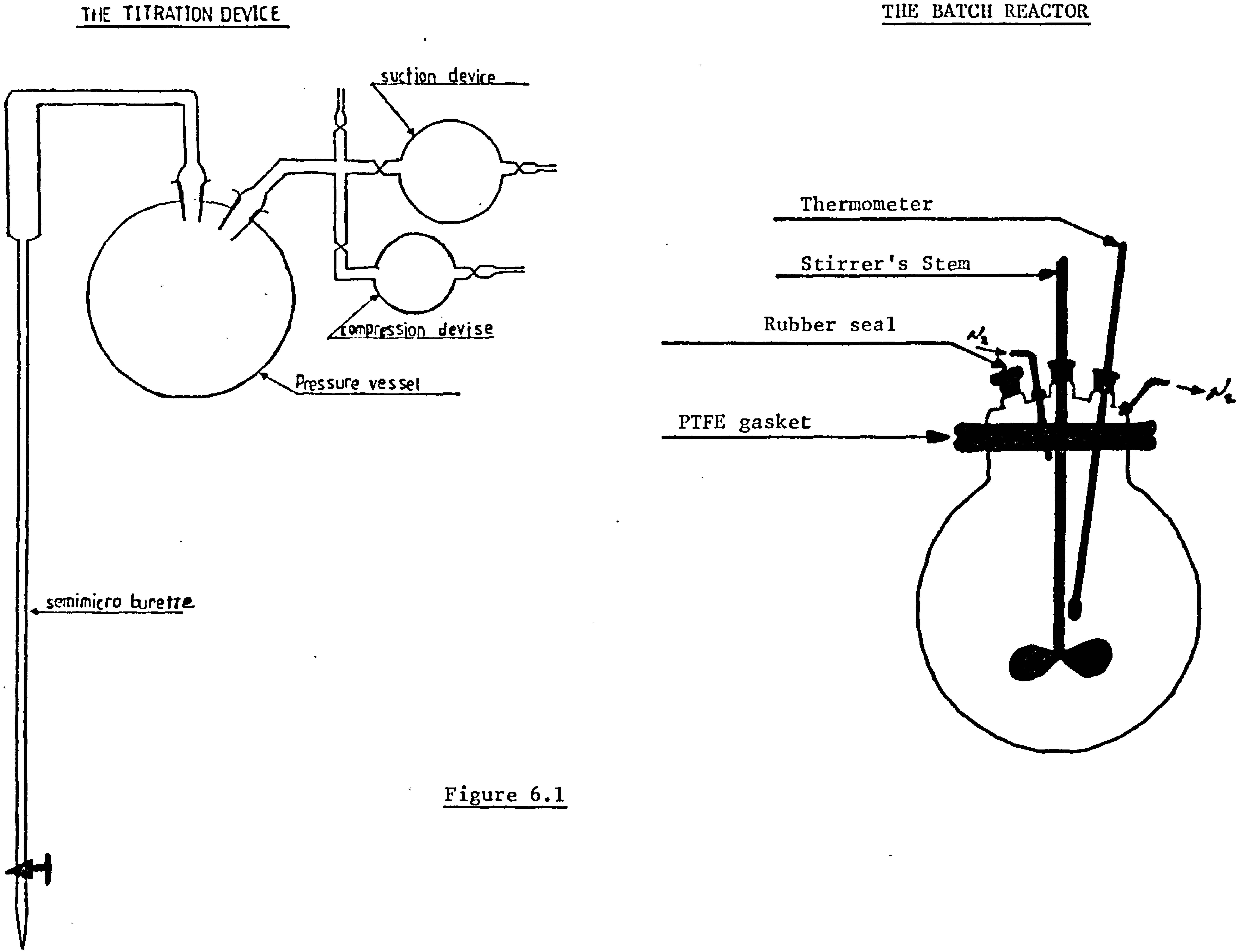
#### *6.2.1.1 Batch Reactor*

A schematic diagram of the batch reactor is shown in Figure 6.1 The reactor was a round bottomed glass vessel which had a detachable top. Two reactor sizes were used. The first had a full capacity of 700 ml, while the other had a full capacity of 3-litres but in no experiments were they completely filled with emulsion. The necessary nitrogen atmosphere required for the reactions was created in the space at the top of the emulsion. The detachable top had five protruded openings which served different purposes.

Through the central opening was passed the stirrer which was in turn connected to an electric motor. The leg of the stirrer passed through PTFE (Polytetrafluorethylene) gland which allowed for its free and steady motion. Through one of the side openings was passed a thermometer to monitor the temperature inside the reactor, while the third opening was covered with thin rubber bung. It was through this rubber bung that a long hypodermic needle was inserted periodically to withdraw samples from the emulsion inside the reactor. The syringe was also used to introduce some of the reactants into the reactor. The last two openings served as the inlet and outlet of the nitrogen gas during the experiments. The outlet-line for nitrogen was connected to a water bubbler to indicate the flow of nitrogen. In order to avoid evaporation of water from the reactor, the nitrogen gas was bubbled through distilled water of the same temperature as that of the reactor.

#### *6.2.1.2 Continous Reactor*

The reaction apparatus is shown in Figure 6.2. Three separate


THE TITRATION DEVICE

THE BATCH REACTOR

Figure 6.1

feed tanks were used for the raw materials. The feed tanks, which were made from glass, were blanketed with nitrogen to prevent oxygen retardation. The first tank containing the monomer had a 2-litre capacity. The second tank containing the soap solution which was kept at 25°C by means of a hot plate, had a 5 litre capacity. The third and final tank, containing the initiator solution, had a capacity of 2 litres. The separate feeds were fed to the reactor at constant rate by reciprocating metering pumps through high density polyethylene tubing.

### *The Reactor*

The reactor consists mainly of three parts. The upper Y-shaped glass adaptor contained four ground joint connectors. The joint in the centre contained the stirrer rod. The other two joints contained the nitrogen purge line, and a glass enclosed thermocouple to record the temperature of the latex inside the reactor. The emulsified product left the reactor via a horizontal overflow pipe attached to the adaptor about 5 mm above the bottom joint to the main reactor vessel. Negligible reaction took place in the overflow pipe because it had a small volume and was enclosed by a cooler.

The main glass body of the reactor had two thermometer wells in the upper section for controlling the reactor temperature. A circular plate was used to clamp the reactor vessel firmly to a stainless steel base plate with a PTFE gasket to seal the joint. Two holes in the base plate allowed the inflow of the reactants. These were fitted with nylon/glass junction pipes. One of these junctions served as an inlet to the initiator while the other served as an inlet to both the soap and the monomer.

The conical shape of the reactor vessel was chosen to reduce the effect of vortex caused by the agitation. The reactor was also designed so that it could be disassembled and reassembled very easily to facilitate cleaning.

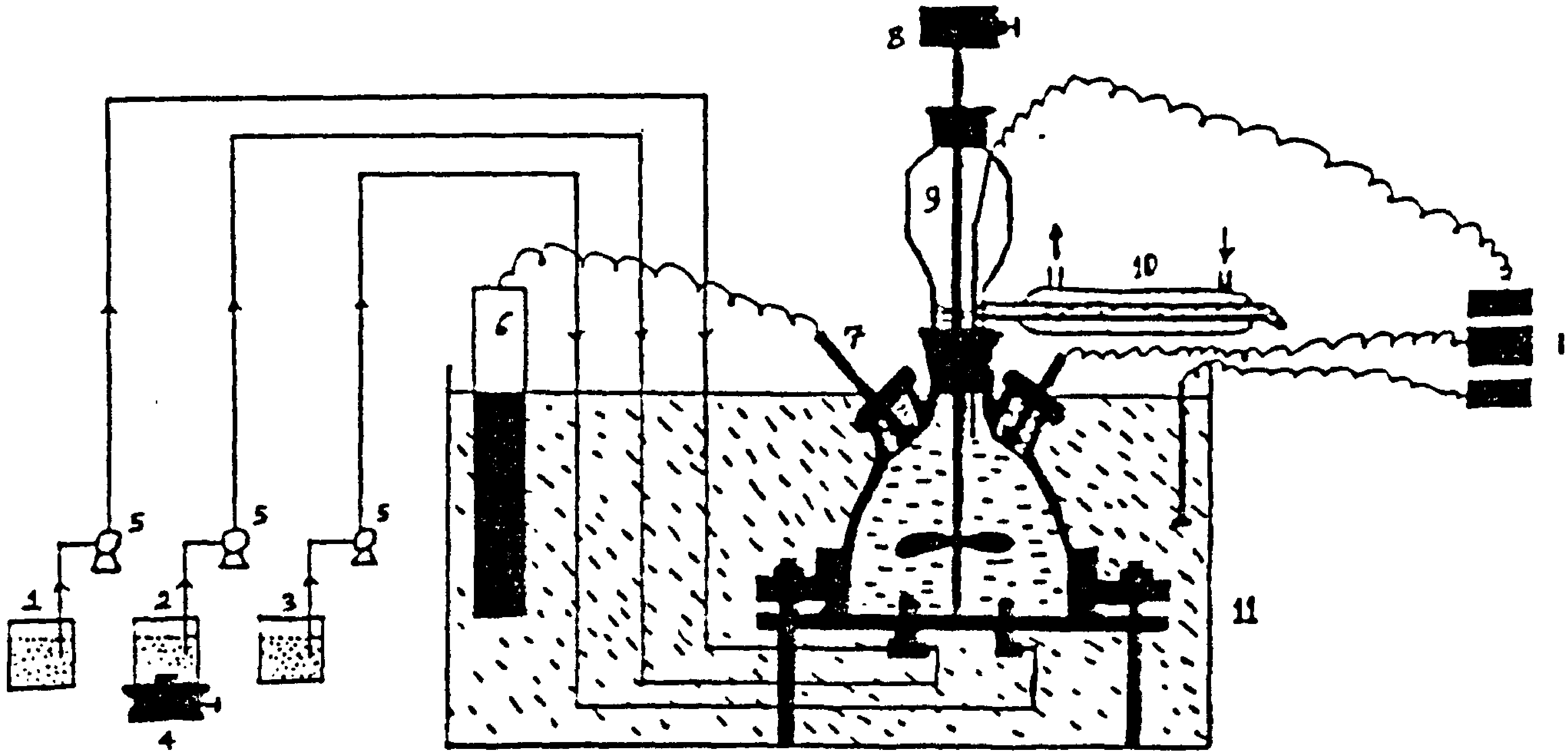
The effective capacity of the reactor was determined by the size of the "reducer". The "reducer" is a piece of P.T.F.E., glass or stainless steel which can be attached to the stirrer. The conical shape of the reducer gave minimum interference with the reactor configuration. The large and heavy "reducers" had a cylindrical shape

## FIGURE 6.2

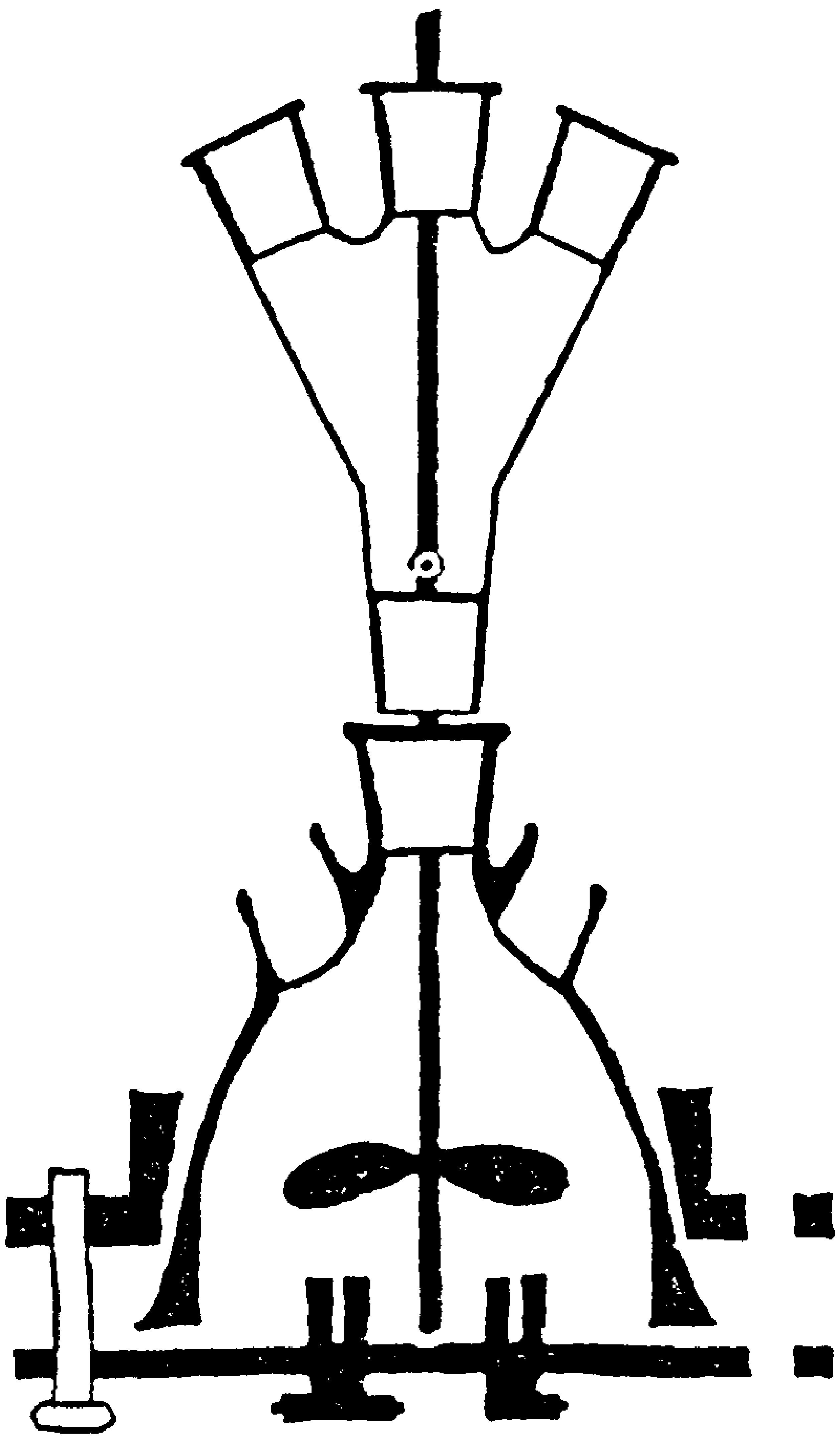
## SCHEMATIC DIAGRAM OF REACTION APPARATUS

1. Monomer storage tank
2. Soap storage tank
3. Initiator storage tank
4. Magnetic stirrer - hot plate
5. Pumps
6. Temperature controller
7. Contact thermometer
8. Stirring motor
9. Reactor
10. Cooler
11. Water bath
12. Temperature indicators

Figure 6.2



Polymerisation Apparatus



Disassembled Reactor

and rested on the bottom of the reactor. Whenever a larger change in the capacity of the reactor was required, a different size reactor, of similar shape, was used.

### *Agitation*

The reactants were stirred with RZR1 Heidolph variable speed motor. The long stainless steel stirrer was fixed with four slanted blades. The motor was operated at 600 r.p.m.

### *The Temperature Control System*

To keep a constant temperature in the reactor, the reactor was placed in a water bath which contained three heaters. The temperature setting of two of the heaters was 3°C lower than that required for the reaction. The third heater was controlled via a contact thermometer measuring the temperature inside the reactor. This setting gave a temperature stability of ± .2°C.

### *6.2.2 Vacuum Drier*

The conversion was determined gravimetrically. The samples were dried under reduced pressure in a vacuum drier at a temperature of less than 65°C.

### *6.2.3 Refrigerator - Centrifuge*

Four cylindrical P.V.C. inserts were machined to fit an existing refrigerator - Centrifuge. Each of these inserts can hold up to five heavy wall, 25 ml glass tubes. These tubes were used to collect the samples for gravimetrical analysis. The operating speed of the centrifuge was 2000 r.p.m.

### *6.2.4 Semimicro Burette*

For the volumetric analysis of the persulphate ion a semimicro burette with some special features was used. It had a suction device which allowed it to be filled from the tip, and a compression device to control the outflow of the solution during the titration.

### *6.2.5. Other Equipment*

Rotary evaporator, electron microscope MZ6, Malvern K7025 multibit correlator and its accessories, electronic and mechanical balances, viscometer, pressure vessel, filters, water pumps, and a variety of glass ware.

## *6.3 Procedures*

### *6.3.1 Start-Up Procedures*

One of the aims of the present work was to study the effect of feasible start-up procedures on the transients and the steady state levels. A summary of the start-up procedures are presented in Table 6.1.

In procedure 1,the reactor was filled to its operating capacity with water. Pumping of the styrene, soap, and persulphate solutions was started as soon as the required steady temperature of the reactor contents was reached. The reactor was purged by nitrogen gas for half an hour before the pumps were started.

Procedure 2, is similar to 1 except the reactor was started with a soap solution. The concentration of soap in the reactor differed from one run to another as indicated later on each appropriate run.

In procedure 3 the initial charge was a mixture of soap and styrene. The ratio of soap to styrene was varied. However, in most of the runs the ratio was similar to the incoming flow where the initiator was replaced by water.

Procedure 4, was the same as 3 except the inititator replaces the monomer.

Procedure 5 and 6 are similar, where the reactor is initially charged with all the ingredients in the required ratios and the reactor runs as a batch reactor for a certain set time before the start of the pumps. In 5 the pumps were started as soon as the initiator was injected, i.e. a batch reactor for 0.0 mins.

Procedure 8 was the same as 5 except the initial temperature of the reactor was different from the final reaction temperature. A set time was allowed to elapse before the initial temperature was changed to the reaction temperature.

In procedure 7, the reactor was charged with a seeded latex with certain characteristics. Soap, monomer and initiator were added to simulate a batch reactor at a specific conversion. The pumps were started as soon as the initiator was injected.

In Table 6.1 the temperatures used are for guidance only. The same applies to the seed and the batch duration columns.

| Procedure | Initial Charge | Initial Temperature (°C) | Reaction Temperature (°C) | Batch Duration (min) | Seed to simulate conversion | Comment |
|---|---|---|---|---|---|---|
| 1 | $H_2O$ | 50 | 50 | - | - | |
| 2 | Soap | 50 | 50 | - | - | |
| 3 | Soap & Monomer | 50 | 50 | - | - | Temperature may be different |
| 4 | Soap & Initiator | 50 | 50 | - | - | |
| 5 | Soap,Monomer & Initiator | 50 | 50 | 0.0 | - | Temperature may be different |
| 6 | Soap, Monomer & Initiator | 50 | 50 | 40 | - | Batch duration may be different |
| 7 | Seed, Soap, Monomer & Initiator | 50 | 50 | 0.0 | 80% | Seed to simulate conversion and Temperature may be different. |
| 8 | Soap, Monomer & Initiator | 40 | 50 | 0.0 | - | Both temperatures may be different |

<u>Table 6.1</u> Start-Up Procedures

### *6.3.2 Polymerisation*

Different recipes were used in the present study and a list of them is given in Appendix III. As an illustration, a detailed description of start-up procedure number 6 is given. The initiator was predissolved and the solution was purged with nitrogen for 30 minutes before the reaction was started, as well as, during the experiment. To the emulsifier solution, which was prepared and purged in the same way as the initiator, 15g of NaOH was added to every 4.5 ℓ of the solution. The soap solution was kept at 25°C during the experiment. The monomer was also purged with nitrogen for the entire time of the experiment. The reactor start-up (procedure 6) consisted of charging the reactor with soap and monomer in the required proportions and the nitrogen purge system was turned on. The reactor was brought up to the required temperature, and the stirrer was switched on. The speed of the stirrer was less than 600 r.p.m. to avoid the formation of foam in the reactor. After 30 minutes a purged solution of the required initiator concentration, at the same temperature as that of the reactor, was injected and the stirrer speed was adjusted to 600 r.p.m. The reaction was allowed to run for a preset time as a batch reactor before the pumps were switched on. This was considered the start of the continuous reactor and samples taken for the determination of conversion, particle size, and molecular weight were started from this time. Since a decrease in the volume of the emulsion accompanies the reaction, the initial charge was larger than the normal capacity of the continuous reactor. This was achieved by blocking the overflow arm in the side of the reactor. Immediately after the completion of a run, the reactor contents were discarded and the reactor was washed carefully. The monomer pump was cleaned by passing toluene through it, while both the soap and initiator pumps were cleaned by hot distilled water.

### *6.3.3 Sampling*

The conversion samples were obtained at frequent intervals by collecting about 1-3 grams of latex in a preweighed glass tube. The tube was weighed immediately, after the collection of the sample, and then about 20 ml of acidic methanol - hydroquinol solution was added to it to avoid any further reaction.

The particle size samples were obtained by collecting a drop of the latex in a clean specimen tube, where high purity filtered water was added to dilute the sample. The resultant sample was about 0.1% solids. This was stored for further particle size analysis.

### *6.3.4 Conversion:*

Due to the unpracticality of the filtration method (filtration requires a long time, and at least 1g of solids is needed for the analysis), an alternative method was used. The sample tubes were inserted in the P.V.C. holders, described earlier, and then centrifuged at a speed of 2000 r.p.m. for at least 30 minutes. The liquid at the top was removed by the use of a pipette connected to a vacuum water pump. The solid was then washed twice with pure methanol and centrifuged as before. This action cleaned the coagulated polystyrene from the unreacted monomer, inhibitor, and soap.

The samples were dried under reduced pressure at a temperature of less than 65°C overnight and then weighed the next day.

### *6.3.5 Molecular Weight*

The same samples which were used to determine the conversion were also used for molecular weight analysis. The attempt to use Gel Permeatation Chromatography to determine the molecular weight of the polymer failed to give satisfactory results.

The intrinsic viscosity of each polymer solution in toluene was determined in an Ubberlohde dilution viscometer. A plot of $(\eta/\eta_o-1)$ versus C gave the intrinsic viscosity when extrapolated to zero concentration. All viscosities were determined at 30°C. From the intrinsic viscosity values, the viscosity average molecular weight was calculated. The intrinsic viscosity and molecular weight of selected samples are given in Appendix IV.

### *6.3.6 Particle Size*

Two methods were used to determine the average particle size and the particle size distribution. These are transmission electron microscopy and photon correlation spectroscopy.

Electron Microscope. From the latex of interest, a small drop was transferred onto a carbon support (grid) which was earlier prepared. The grid was allowed to dry under reduced pressure in the microscope From different parts of the grid various photographic shots were taken with the aid of the camera inside the electron microscope. Special care had to be taken to obtain a representative photograph due to the wide particle size distribution of most of the samples. From the enlarged photographs of the particles the average particle was determined. Hand counting was necessary because satisfactory automatic methods were unavailable. The use of the electron microscope to determine the particle size is time consuming, tedious, and could lead to unrepresentative distributions.

Photon correlation spectroscopy

The movement of a particle or a macro-molecule in a fluid undergoing Brownian motion is a three dimensional random walk. The rate and the way the particles move under the effect of thermal motion is a direct function of their size.

When particles in suspension are illuminated with a laser,they will scatter light, and because the particles are constantly in motion, the scattered light will fluctuate as the phases of scattering contributions from various particles change relative to each other. Observation of these fluctuations, with a photon detector, and relating it to time will yield a correlation function, $g(\tau)$. This may be used to compute the characteristic movement rate (diffusion coefficients) of the particles and hence the particles size.

$$g(\tau) = 1 + \exp\left(-2D \frac{4\pi}{\lambda} \sin\left(\frac{\theta}{2}\right) \tau\right) \qquad (6.1)$$

and the hydrodynamic average diameter

$$D_w = \frac{2kT}{3\pi\eta D} \qquad (6.2)$$

where D = the diffusion coefficient

$\lambda$ = laser wavelength

k = Boltzman constant

$\eta$ = solvent viscosity

T = absolute temperature

In the present study a 15 mW laser was used in conjunction with a Malvern Matibit Correlator and a Commodor Micro-processer to analyse the resultant correlation. For each sample at least 10 runs were performed and with the aid of the computer it was possible to obtain reliable results. A sample of the output of the computer is available in Appendix V.

### *6.3.7 Preparation of Seed Latex*

The seed latex was prepared in a batch reactor. The main recipe for the seeded latex is presented in Table 6.2. The reaction was carried out to high conversion at a steady temperature of 50 ± 0.5°C.

Table 6.2

| | Weight(g) |
|---|---|
| Styrene | 458 |
| Sodium dodecyl sulphate | 12.45 |
| Ammonium persulphate | 8.04 |
| Sodium hydroxide | 3.00 |
| Water | 1542 |

At the start of an experiment, a predetermined amount of emulsifier and sodium hydroxide were weighed accuately and transferred into the reactor. Next the required amount of distilled water was added. The reactor's detachable top along with the stirrer was next positioned in place, after which the whole equipment was transferred into the thermostatically controlled water bath. Finally all the connecting accessories to the reactor were put in place. The electric motor was switched on at the same time as the supplied purified nitrogen purge system. The reactor was usually purged over a period of about 30 minutes. Before transfer into the reactor the monomer was freed of oxygen by bubbling nitrogen through it for about 15 minutes. After the transfer of monomer to the reactor, about 20 minutes of mixing was allowed to get the monomer well emulsified before the start of the polymerisation.

The required amount of initiator was weighed out accurately and dissolved in 50 ml of distilled water and the solution was purged of oxygen and finally transferred into the reactor to start the reaction. Immediately after the initiator was introduced into the reactor the stop-clock was started. Samples were withdrawn by the aid of the syringe from the reactor at intervals to monitor the progress of the reaction. The samples were treated in the same way as mentioned in section 6.3.4.

After the preparation of the seed, it was usually necessary to dialyse it to remove the persulphate and its products from the seed. Before the dialysis a soap titration was carried out to determine the average surface area of the latex particles.

Dialysis is defined as the transfer of solute molecules across a membrane by diffusion from a concentrated solution to a dilute solution (93) . There is also a simultaneous diffusion of solvent molecules through the membrane in the opposite direction. In the present system the remaining initiator, its products, and the sodium hydroxide behaved as the solute. A tiny amount of the soap also left the surface of the particles and diffused out of the bag.

The dialysis bag (containing the latex) was suspended in a glass water bath of distilled water which was stirred continuously. The water was maintained at room temperature of about 20°C. The water in the bath was replaced once daily for a week.

The solid content of the dialysed latex was determined in the same way as before, and the soap titration method was applied again to determine the amount of soap left on the particles surfaces. It was found that a negligible amount of soap had actually left the surface of the particles which meant that the soap titration method was no longer required.

Before the seeded experiments were carried out, the required amounts of soap, NaOH and persulphate were added to the latex in the usual way, to simulate a batch reactor with a certain conversion.

# CHAPTER 7

# CALCULATIONS AND EXPERIMENTAL RESULTS

# CHAPTER 7

# CALCULATIONS AND EXPERIMENTAL RESULTS

## *7.1 Calculations*

### *7.1.1 Conversion and Fraction Solids*

In the batch reactor, the conversion is defined as the weight of polymer formed per weight of initial monomer present. In a match flow CFSR, that is when the feed and the initial reactor recipes are identical, the conversion can be defined in a similar manner to a batch reactor. However, if the feed and initial reactor concentrations are not identical another type of conversion definition must be formulated.

Generally the conversion can be defined as the fractional weight of polymer per fractional weight of monomer in all forms in the reactor at any moment in time. The fractional weight of polymer can be determined from the dried samples as described in chapter 6, while the fractional monomer can be calculated as follows

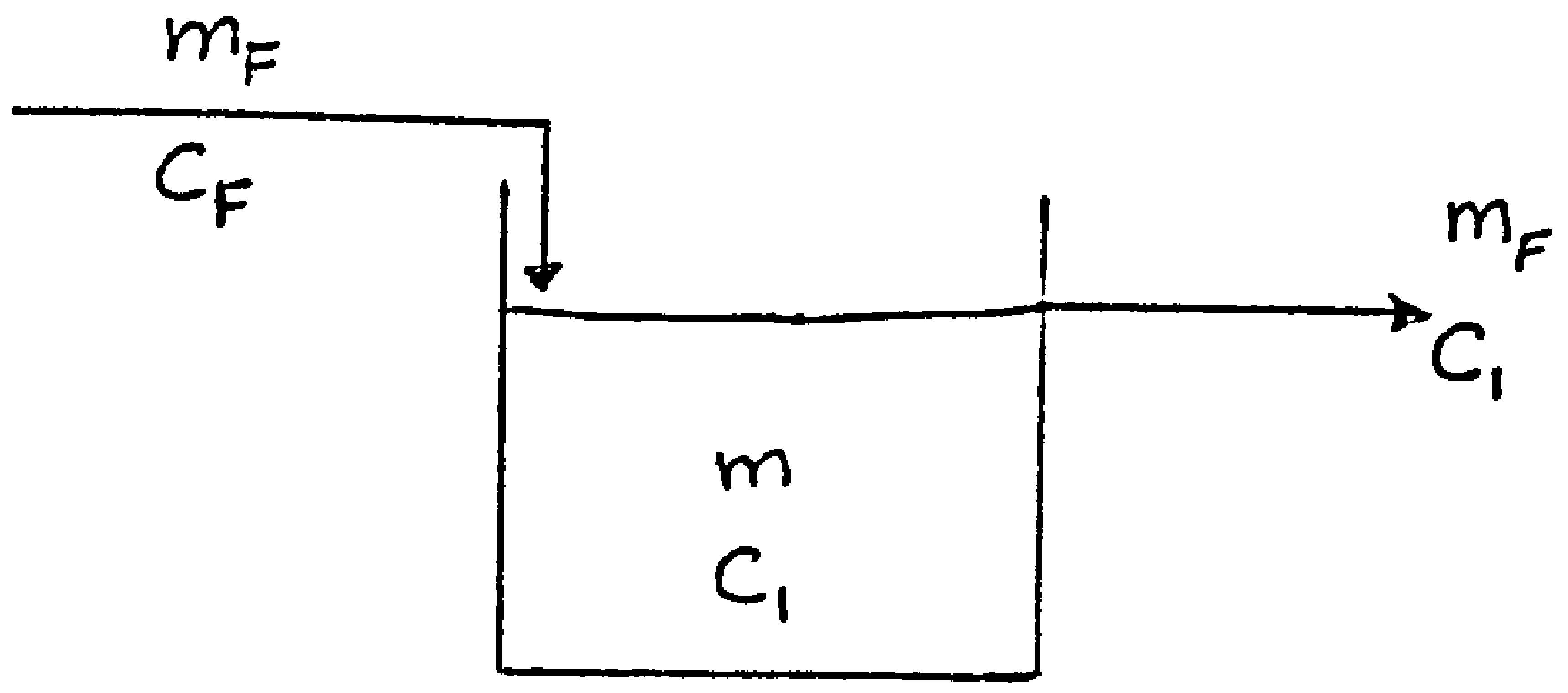


Figure 7.1

A mass balance around the CFSR will yield the following equation, assuming no chemical reaction is taking place

$$m_F\, C_F = m_F\, C_1 + m\,\frac{dC_1}{dt} \tag{7.2}$$

where $C_F$, $C_1$ are the monomer feed and reactor concentrations in (g/g) of solution. And $m_F$, m are the feed mass flow rate and mass capacity of the reactor.

For a constant monomer feed concentration, $C_F$, the Laplace transformation of equation (7.2) gives:

$$\frac{C_F}{S} = \bar{C}_1 + \frac{m}{m_F}\left(S\,\bar{C}_1 - C_o\right) \qquad (7.3)$$

where $C_o$ is the initial monomer concentration in the reactor.

Rearranging equation (7.3)

$$\bar{C}_1 = C_F\left(\frac{1}{S} - \frac{1}{S+\frac{m_F}{m}}\right) + \frac{C_o}{\left(S+\frac{m_F}{m}\right)} \qquad (7.4)$$

Hence

$$C_1 = C_F\,(1 - \mathrm{EXP}(-t/\Theta) + C_o\,\mathrm{EXP}\,(-t/\Theta) \qquad (7.5)$$

$$= C_F + (C_o - C_F) * e^{-t/\Theta} \qquad (7.6)$$

where $\Theta = m/m_F$ is the average residence time in the reactor. Now the conversion, x, can be calculated.

$$x = \frac{\text{Fractional Solids - Fractional Dissolved Solids}}{C_1}$$

$$x = \frac{F_s - F_d}{C_1} \qquad (7.7)$$

The dissolved solid represent the non volatile materials in the recipe which is left with the polymer after washing with methanol, i.e. NaOH, $S_2O_8^{--}$, and the products of the decomposition of the persulphate. These are usually present in small amounts and can be ignored.

### *7.1.2 Average Number of Radicals Per Particle ($\bar{q}$)*

The steps and assumptions involved in the calculation which led to the values of $\bar{q}$ follow:

By the electron microscope or the photon correlation spectroscopy the average diameter of the particles, $\bar{D}$, ($\overset{o}{A}$), was determined.

The total volume of the particles per litre of emulsion, V was determined from the conversion and the density of the swollen polymer particles, assuming the maximum ratio of monomer to polymer in the particles is 1.08, i.e. $M_p = 5$ molar as described later.

$$V = \frac{\text{weight of particles per litre of emulsion}}{\text{Density of swollen particles}} \qquad (7.8)$$

$$\therefore\ V = C_1/d_p \qquad x \geqslant 0.48 \qquad (7.9a)$$

$$V = C_1\ (1+1.083)\ x/d_p \qquad x < 0.48\ . \qquad (7.9b)$$

$$d_p = 0.975\ (g/cm^3) \qquad x < 0.48 \qquad (7.10a)$$

$$d_p = (1.047 - 0.909) * x + 0.909 \quad x \geqslant 0.48 \qquad (7.10b)$$

$$N = \frac{V}{5.24 \times 10^{-28} * (\bar{D})^3} = 1.91 * 10^{27} * \frac{V}{(\bar{D})^3} \qquad (7.11)$$

where $5.24 * 10^{-28} * (\bar{D})^3$ is the average volume of particle in litres

The overall rate of polymerisation per litre of emulsion, $R_p$ is given by the expression:

$$R_p = k_p\, C_R\, M_p \qquad (7.12)$$

where

$C_R$ = concentration of radicals in swollen particles

$M_p$ = concentration of monomer in swollen particles

From the polymerisation experiment, $R_p$, can be calculated for CFSR, as follows:

$$R_p = \frac{x}{(\Theta*60)} * \frac{10^3 * C_F}{M_{MW}} \qquad (7.13)$$

where $M_{MW}$ is the molecular weight of monomer

To determine $M_p$ an assumption was made, that is the maximum concentration of monomer in the polymer particles is 5 molar.

$$M_p = 10^3 * (1-x)/M_{MW} \qquad x \geqslant 0.48 \qquad (7.14a)$$

$$M_p = 5 \text{ molar} \qquad x < 0.48 \qquad (7.14b)$$

The total number of radicals per litre of emulsion $N_R$, can be calculated from the expression

$$C_R = \frac{N_R}{N_A} \qquad (7.15)$$

where $N_A$ is Avogadro's number = $6.023 * 10^{23}$

After all the known values had been substituted into equation (7.12), the unknown value of $N_R$ can be obtained. Once the values of N and $N_R$ are known, the average number of radicals per particle, $\bar{q}$, for a given system can easily be calculated from the expression:

$$\bar{q} = \frac{N_R}{N} \qquad (7.16)$$

### *7.2 Errors in Experimental Work*

### *7.2.1 Reactor Size and Space Time*

The relatively small size reactor was chosen for the ease of control and to insure good mixing of the reactants. The small size facilitated the use of small quantities of reactants, which can be purified easily to reduce impurities. In addition, the smaller the reactor, the wider the range of space times achieved by the use of relatively small "reducers", without changing the pump settings.

A wide range of space times were used in the present study (30 - 189 minutes). The problem with a large space time is the long run time necessary to reach steady state, and the longer the run the greater the chance of accidents or mechanical failure in the equipment, especially the pumps. The difference between the temperature of the day and that of the night especially during the summer was appreciable and sometimes reaches 10°C. Since the pumps deliver constant volumes of the reactants, the temperature fluctuation will result in a fluctuation in the reactor's holding time. Another possibility of fluctuation of the reactor's holding time can result from the oscillation in the degree of conversion of monomer to polymer. In the present work the monomer to water ratio was made as small as feasible to reduce the effect of conversion oscillations.

### *7.2.2 Contaminants*

Contamination of the reaction mixture was possible from any of the feed reactants. To minimize the contaminant concentration of styrene, analytical grade styrene of 99+% purity was used. The styrene was washed with sodium hydroxide solution and distilled under reduced pressure. The impurities would be primarily ethyl benzene and t-butyl catachol. If the traces of ethyl benzene, left after purification of the styrene, did react during polymerisation it would act as a chain transfer agent and thus reduce the molecular weight. The t-butyl catachol acts as an inhibitor below temperatures of 40°C. The sodium dodecyl sulphate was high purity analytical reagent grade and special care was taken to choose a soap with very low divalent ions like $Cu^{++}$ because of their drastic effect on the polymerisation. The main impurity in the soap would have been the dodecyl alcohol. Even for the purest possible soap, the soap will hydrolize in the alkaline solution and produce dodecyl alcohol. The contaminants present with the soap are known to have a pronounced effect on the inhibition times and reaction rate during the polymerisation reactions. And in order to obtain reproducible results the soap in most of the experimental runs was taken from a single bottle. The ammonium persulphate initiator was reagent grade of 99+% pure. The bottle of the initiator was properly sealed between use. Care was taken to use the same tubing as long as possible to minimize contamination from the plasticizer which may have been used in the plastic tubing. When a new tube was used the reactant was passed through the tube for two hours before the start of the experiment.

The most serious contaminant in the reaction recipe was the presence of oxygen, which acts as an inhibitor by retarding the free radicals present. This problem can be overcome by proper purge of the reaction system with high purity nitrogen gas. The nitrogen was never allowed to bubble through the reaction mixture. Only a nitrogen atmosphere was maintained over the reaction mixture. The reason for this is to minimize contamination from the impurities in the nitrogen gas itself, and to avoid evaporation of water/styrene from the reaction mixture. A problem that arises when most of the oxygen has been removed and the reactor temperature is hot enough is pre-reaction before the addition of initiator. The pre-reaction is caused by thermal polymerisation in the reactor during the period of nitrogen addition to the reactor. In the present work, the styrene was purged separately and then added to the reactor in the initial charge, and then the mixture was purged together for a short time, while the temperature was being increased to the required one. This prevented pre-reaction.

### *7.2.3 Errors in Analysis*

Errors due to the method of sampling, for conversion, are the time required to obtain a sample and the uniformity of the product obtained. In the present study the sampling took from 30 seconds to 1 minute, and the results were recorded at the mean time. This was only possible because of the method used to analyse the conversion as described in Chapter 6. Experiments with sodium hydroxide solution showed that the reactor behaved as a "well-mixed" continuous reactor. However, the emulsion mixture was much more viscous than the hydroxide solution especially at higher conversions. Due to the high agitation speed it is possible that the reactor behaviour was still ideal under normal operating conditions.

Errors in the solids analysis can occur in three phases, sampling, weighing, or drying. The possibility of reaction occurring after the emulsion leaves the overflow arm is small, as the oxygen from the air acts as an inhibitor to the emulsion reaction. The overflow pipe was also enclosed by a cooler to reduce the emulsion product temperature, which resulted in a reduction in the rate of polymerisation in the pipe. Errors in weighing were possible due to the evaporation of water and styrene during and before weighing. Tests showed that the errors from evaporation were insignificantly small and the errors from handling the tubes by hand could be larger than that of the evaporation. Readings were accurate to ± 0.0005 grams.

For examples, assume that the sample latex was 3 g and the fraction monomer in all forms was 0.23. If the sample had the following conversions the errors would be as follows:

| Conversion % | maximum error % |
|---|---|
| 10 | ± 0.075 |
| 50 | ± 0.08 |
| 100 | ± 0.089 |

Run (C8) was performed to determine the maximum error in an experiment which exhibited oscillatory behaviour. The repeated samples were taken directly after each other. This means that some samples had a delay of up to 3 minutes before being weighed and others had up to 2 minutes before being taken. It can be seen that the two samples at 170 minutes have the maximum difference, which is about 0.7% conversion.

Errors in the molecular weight determinations could have occurred in sampling and in analysis. The samples for molecular weight were the same samples for the conversion, and the sampling errors discussed above applies to them. The major source of error in the analysis was the use of the empirical formula, equation (5.7) which may not apply for the entire range of molecular weights encountered in a run. The constants in equation (5.7) did not apply for the very high range of molecular weights being used. Due to unavailability of another method the errors in the molecular weight can not be estimated, but it is believed to be high for molecular weights of over $3 * 10^6$.

Errors in particle number measurement may have occurred in sampling and analysis procedures. The discussion about the sampling has been already pointed out earlier. The major source of error in the calculations in section (7.12) was in the estimation of the average volume of swollen particles in the emulsion. Two factors affected this estimation, the first was the estimated average size of the particles and the second was the calculated density of the swollen particles.

Comparison between the electron microscope and the photon correlation spectroscopy, for narrow distributions of particle size samples, showed that small particles appeared smaller in the photon spectroscopy, while large particles appeared smaller in the microscope. The fact that the particles observed with the electron microscope, would have been larger when they were in the reactor because they would then contain unreacted monomer, and that the contrast of the photographs of the small particles was poor, may explain the discrepancies.

With a minimal amount of soap around the particles in the diluted mixture, the possibility existed of several small polymer particles combining and forming an aggregate, and for the large ones to precipitate. This was observed for samples which are left for more than one week. Only the medium size particles can be seen in the micrograph. Thus samples should not be stored for too long a period before sampling. In case the above happens the distribution of particle sizes would seem to be very sharp. It was found possible to preserve a sample for up to a month with-out appreciable changes by diluting it with highly purified soap solution, provided no micelles are introduced.

The errors which could be encountered in the determination of persulphate ions are dealt with in Appendix II.

In all the calculations involved with the density of the latex, the density was assumed to be 1g/$cm^3$

FIGURE 7.2 shows results reproducibility.

## *7.3 Experimental Results*

A total of 39 successful continous and 10 batch runs were completed during the course of this study. The effects of initiator, emulsifier concentration, residence time, initial reactor contents, and seeds were studied in conjunction with different start-up procedures. Some of the results in a comparative way are presented in graphical forms in this chapter and the discussion of these results and others will be dealt with in the next chapter. The raw data and some processed ones can be found in the appendix. Particle size measurements were taken for almost all the samples in each run, while a selective molecular weight determination were performed. It should be kept in mind, however, that the emulsion polymerisation is an extremely complex heterogeneous process. A large numberof researchers had done work to elucidate the effect of several variables on the rate of polymerisation. However, the experimental results are very often contradictory.

A qualitative description of some of the results will be given in the following pages.

Soon after the start-up , the conversion of polymer reached a relatively high value. In some experiments, the polymerisation rate declined subsequently and in a few cases a steady rate was then observed. In other experiments the polymerisation rate stayed high and was not observed to decline to the low polymerisation rate observed by other workers. In both the high and low conversions, the polymerisation rate may oscillate with time around a mean value.

Soon after start-up a large number of small particles were present, they were then reduced in number, but grew in size. It is believed that particle nucleation almost ceased just before the "peak" conversion. This is indicated by the absence of very small particles at this stage. The size distribution of the particles continued to narrow down and no new particles were observed until just before the steady state conversion was observed in the case of the low conversion steady states. On the other hand the high conversion steady states were accompanied by very wide distribution of particle sizes just after the maximum conversion was observed.

The average particle size for the high conversion levels were much larger than that of the lower levels even though the recipe and the reaction conditions were the same except for the start-up procedures. The average particle size and the molecular weight never attained a steady state but oscillated with time even though the conversion reached a steady state in some cases. In the case of the high level conversion, in the early stages the average particle size oscillation was in phase with the conversion, while in the later stages, it oscillated out of phase.

In almost all the experimental runs, the viscosity-average molecular weight started very high and then declined to comparatively low values by the end of the runs in both the high and low level conversions.

## FIGURE 7.2

## RESULTS REPRODUCIBILITY

| Run Number | BC 3 | BC4 |
|---|---|---|
| Symbol | X | ● |
| Temp ($^{o}C$) | 50 | 50 |
| $\Theta$(min) | 85 | 85 |
| Procedure | 6 | 6 |
| Batch Duration (min) | 50 | 50 |
| Seed (conv.%) | - | - |
| Reactor Volume (ml) | 260 | 260 |
| **FEED COMPOSITION %** | | |
| Water | 77 | 77 |
| Styrene | 22.9 | 22.9 |
| Soap | 0.638 | 0.63 |
| Initiator | 0.384 | 0.39 |
| **INITIAL CHARGE %** | | |
| Water | 80 | 80 |
| Styrene | 20 | 20 |
| Soap | 0.79 | 0.79 |
| Initiator | 0.43 | 0.43 |

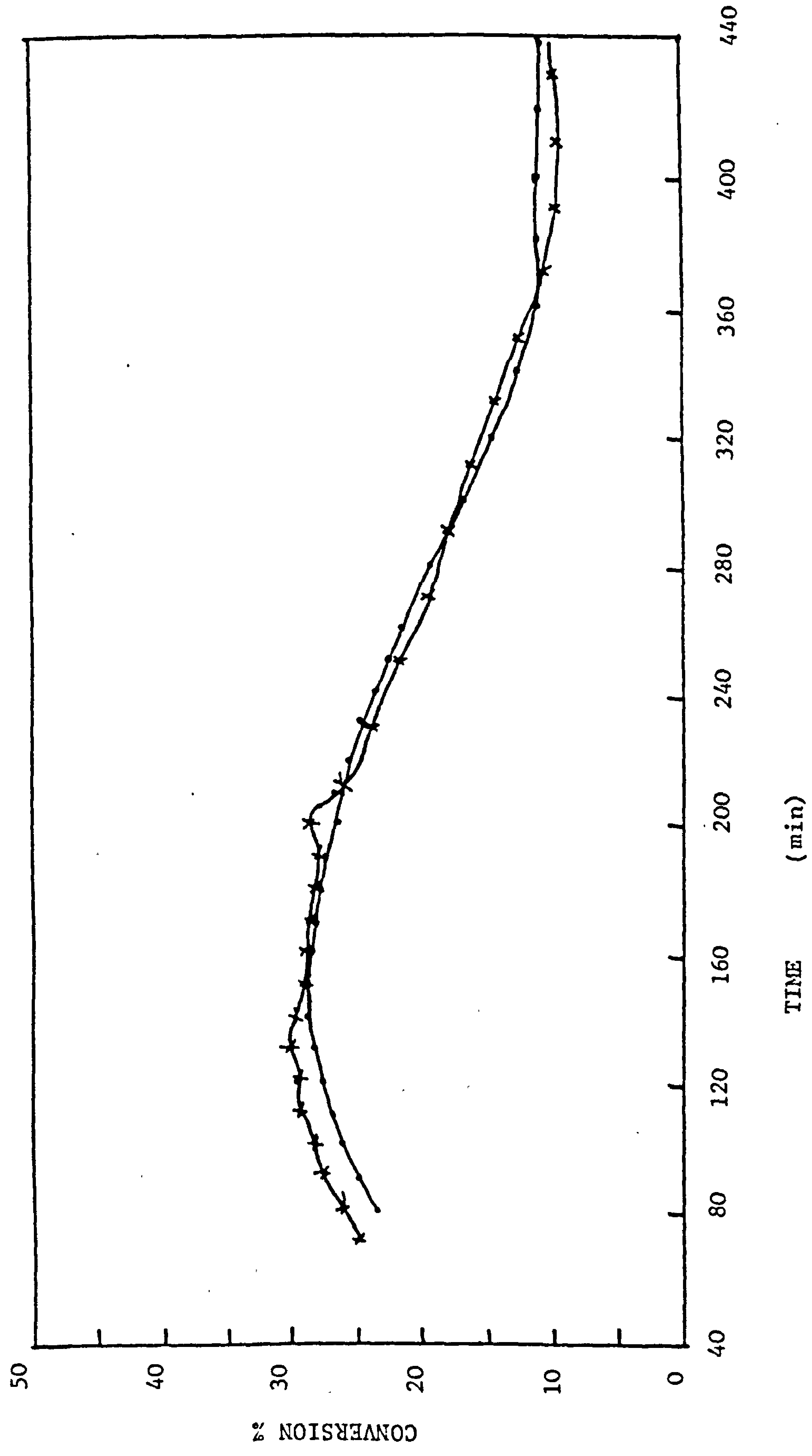

CONVERSION %
0
10
20
30
40
50
TIME (min)
40
80
120
160
200
240
280
320
360
400
440

FIGURE: (7.3): General View of Some of The Experimental Results

## FIGURE 7.4

## EFFECT OF START-UP PROCEDURES ON CONVERSION

| Run Number | SC1 | BC6 | C21 | C23 | C24 |
|---|---|---|---|---|---|
| Symbol | X | ■ | ▲ | O | ● |
| Temp ($^oC$) | 50 | 50 | 50 | 50 | 50 |
| $\Theta$(min) | 116 | 116 | 116 | 121 | 116 |
| Procedure | ⑦ | ⑥ | ③ | ④ | ② |
| Batch Duration Min) | - | 20 | - | - | - |
| Seed (conv.%) | 80 | - | - | - | - |
| Reactor Volume (ml) | 360 | 360 | 360 | 355 | 355 |
| **FEED COMPOSITION %** | | | | | |
| Water | 77 | 77 | 77 | 78 | 78 |
| Styrene | 22.8 | 22.5 | 22.8 | 22 | 22 |
| Soap | 0.635 | 0.65 | 0.635 | 0.69 | 0.67 |
| Initiator | 0.39 | 0.37 | 0.39 | 0.34 | 0.37 |
| **INITIAL CHARGE %** | | | | | |
| Water | S | 77 | 77 | 77 | 77 |
| Styrene | E | 22.4 | 22.9 | - | - |
| Soap | E | 0.65 | 0.63 | 0.635 | 0.635 |
| Initiator | D | 0.39 | - | 0.39 | - |

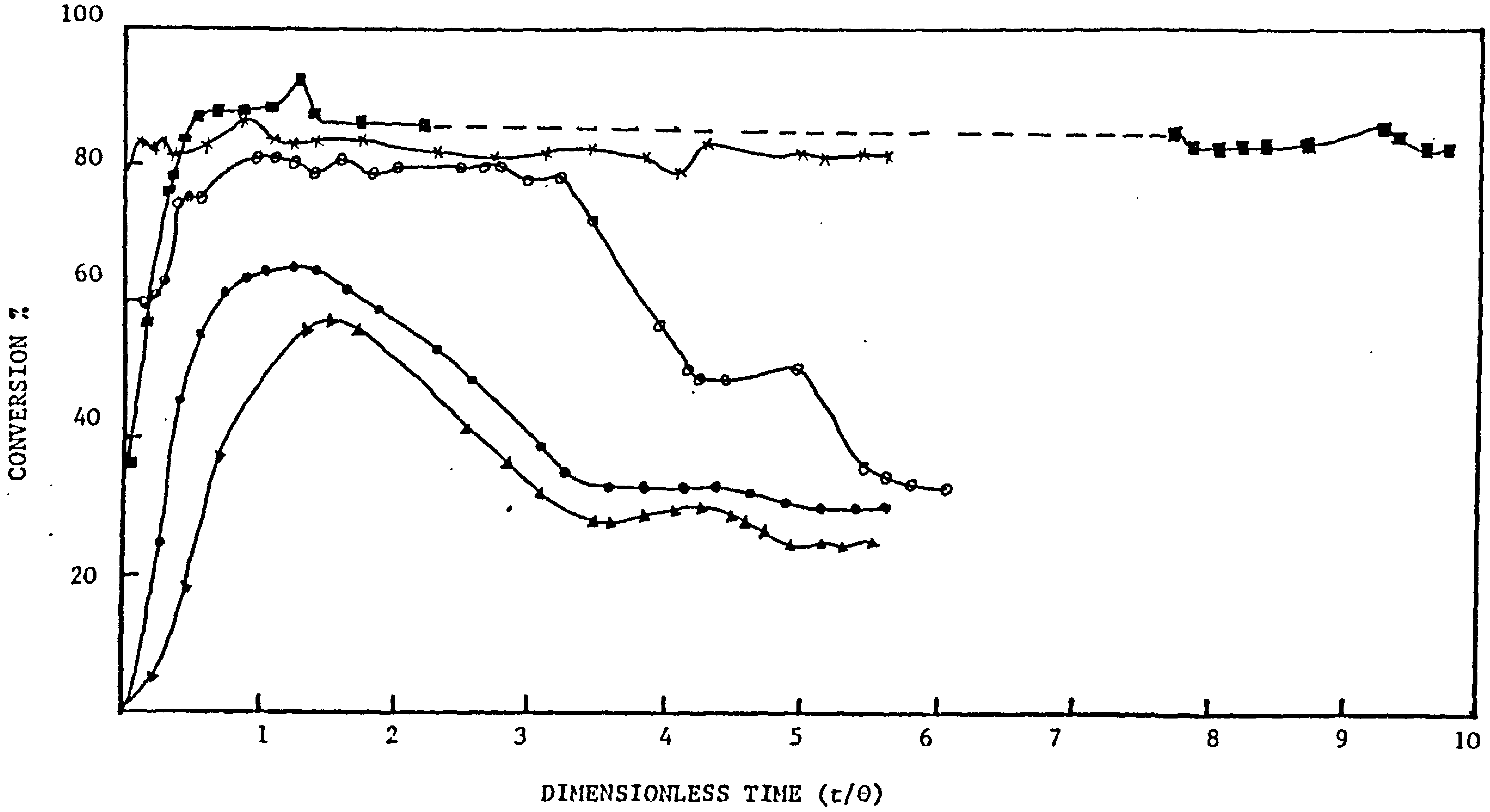

100
80
60
40
20
CONVERSION %
1
2
3
4
5
6
7
8
9
10
DIMENSIONLESS TIME (t/θ)

FIGURE: 7.4

## FIGURE 7.5

## EFFECT OF START-UP PROCEDURES ON CONVERSION

| Run Number | C3 | C4 |
|---|---|---|
| Symbol | ● | X |
| Temp ($^{o}C$) | 50 | 50 |
| $\Theta$(min) | 34 | 34 |
| Procedure | ③ | ① |
| Batch Duration (min) | - | - |
| Seed (conv.%) | - | - |
| Reactor Volume (ml) | 190 | 190 |

### FEED COMPOSITION %

| | | |
|---|---|---|
| Water | 82 | 82 |
| Styrene | 15.9 | 15.9 |
| Soap | 0.71 | 0.71 |
| Initiator | 1.1 | 1.1 |

### INITIAL CHARGE %

| | | |
|---|---|---|
| Water | 80 | 100 |
| Styrene | 20 | - |
| Soap | 0.95 | - |
| Initiator | - | - |

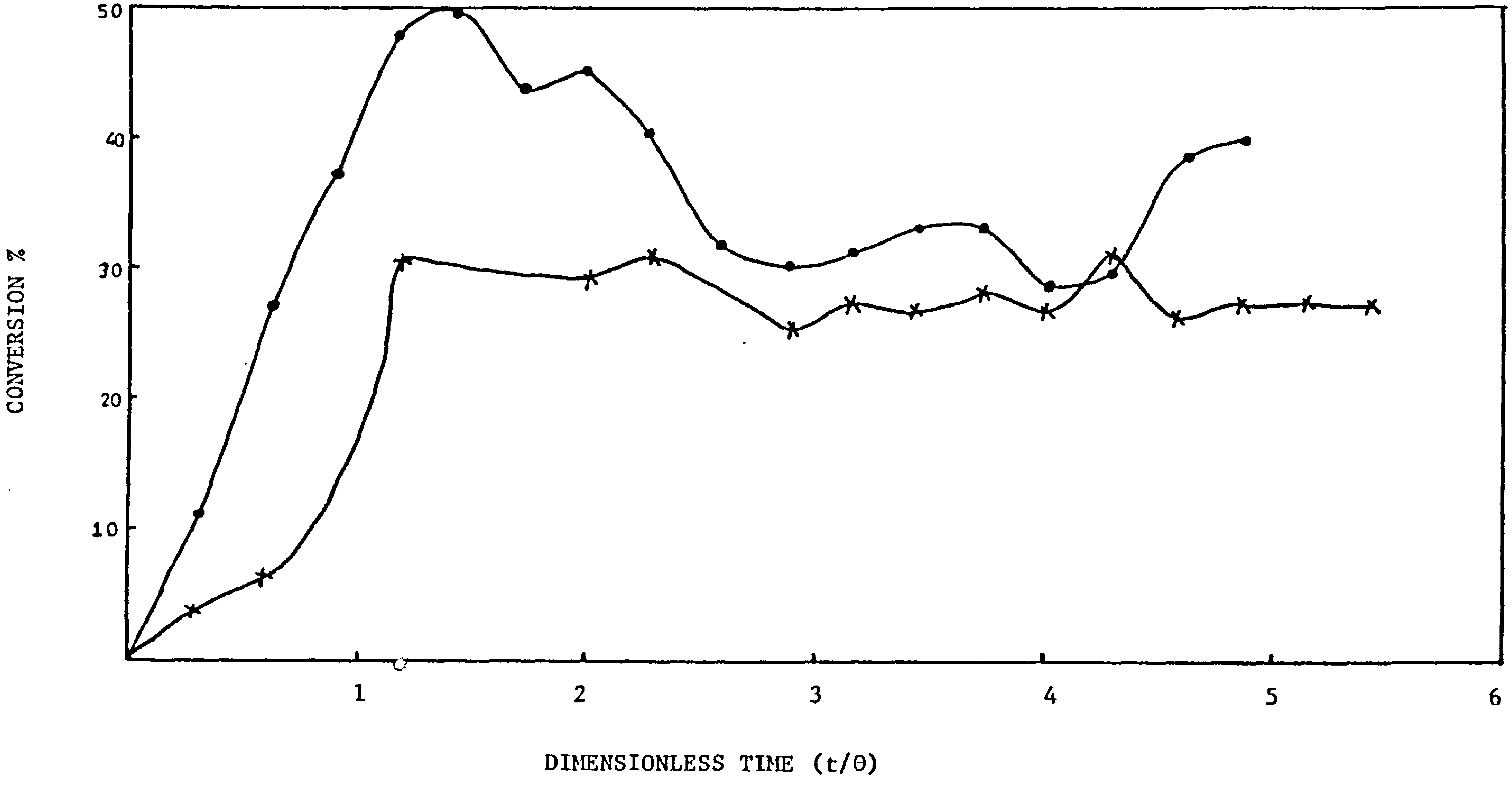


FIGURE: 7.5

## FIGURE 7.6

### EFFECT OF START-UP PROCEDURES ON CONVERSION

| | | |
|---|---|---|
| Run Number | BCT1 | BC11 |
| Symbol | X | ● |
| Initial Temp.($^{o}$C) | 50 | 40 |
| Duration of Initial Temp (min) | 30 | - |
| Final Temp. ($^{o}$C) | 40 | 40 |
| Procedure | ⑧ | ⑤ |
| Batch Duration(min) | 0.0 | 0.0 |
| Reactor Volume (ml) | 355 | 355 |
| **FEED COMPOSITION (wt. %)** | | |
| Water | 77 | 77 |
| Styrene | 22.8 | 22.8 |
| Soap | 1.165 | 1.165 |
| Initiator | 1.34 | 1.34 |
| **INITIAL CHAR (wt. %)** | | |
| Water | 77 | 77 |
| Styrene | 22.8 | 22.8 |
| Soap | 1.165 | 1.165 |
| Initiator | 1.34 | 1.34 |

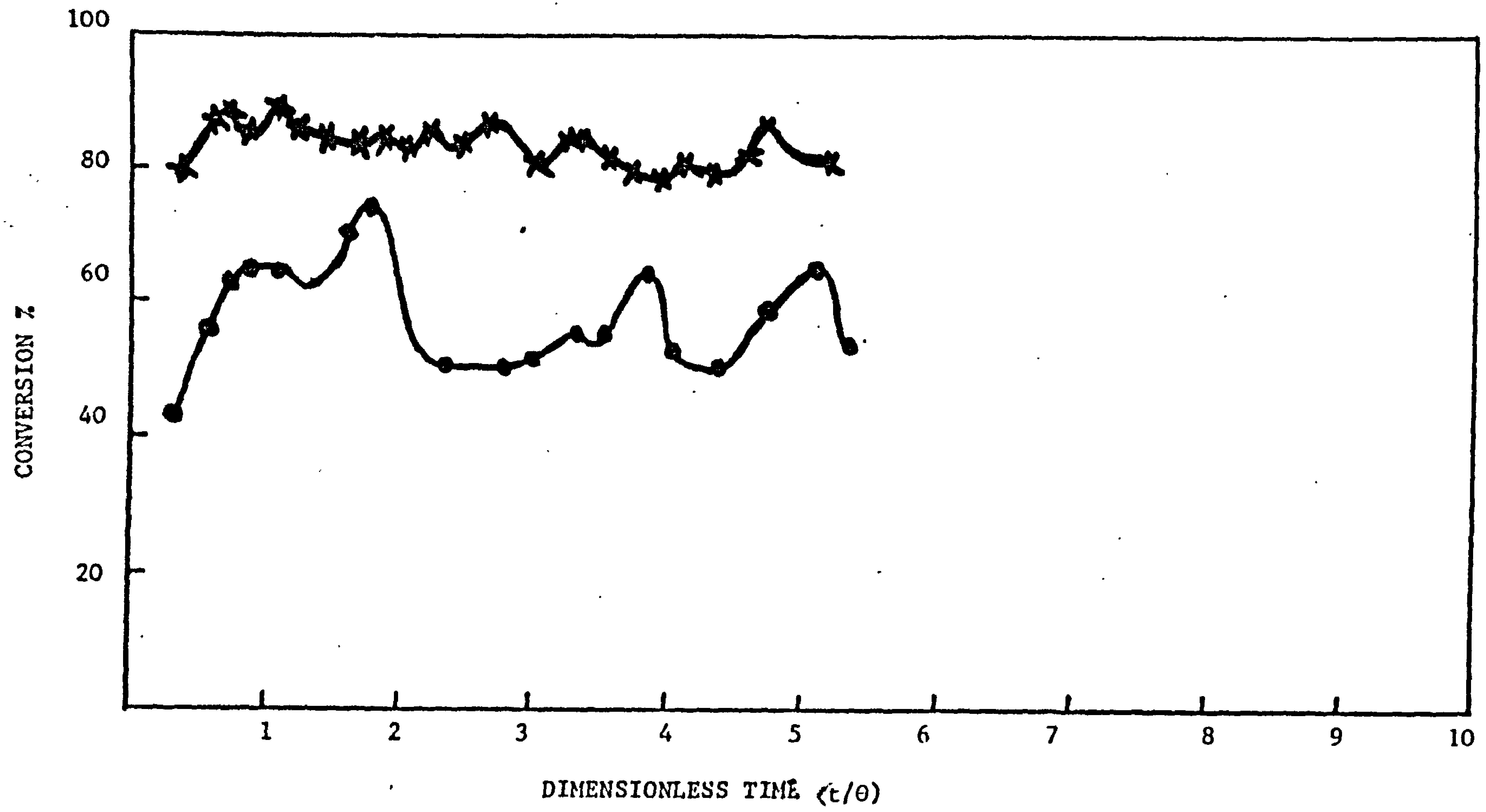

100
80
60
40
20
CONVERSION %
1
2
3
4
5
6
7
8
9
10
DIMENSIONLESS TIME (t/θ)

FIGURE: 7.6

## FIGURE 7.7

## EFFECT OF DURATION OF BATCH ON CONVERSION

| Run Number | BC5 | BC6 | BC7 |
|---|---|---|---|
| Symbol | ▲ | X | ● |
| Temp ($^{o}$C) | 50 | 50 | 50 |
| $\Theta$(min) | 116 | 116 | 116 |
| Procedure | 6 | 6 | 6 |
| Batch Duration (min) | 50 | 20 | 0.0 |
| Seed (conv.%) | - | - | - |
| Reactor Volume (ml) | 360 | 360 | 360 |
| FEED COMPOSITION % | | | |
| Water | 77 | 77 | 77 |
| Styrene | 22.6 | 22.5 | 22.9 |
| Soap | 0.63 | 0.65 | 0.63 |
| Initiator | 0.39 | 0.37 | 0.39 |
| INITIAL CHARGE % | | | |
| Water | 77 | 77 | 77 |
| Styrene | 22.5 | 22.4 | 22 |
| Soap | 0.65 | 0.65 | 0.65 |
| Initiator | 0.39 | 0.39 | 0.39 |

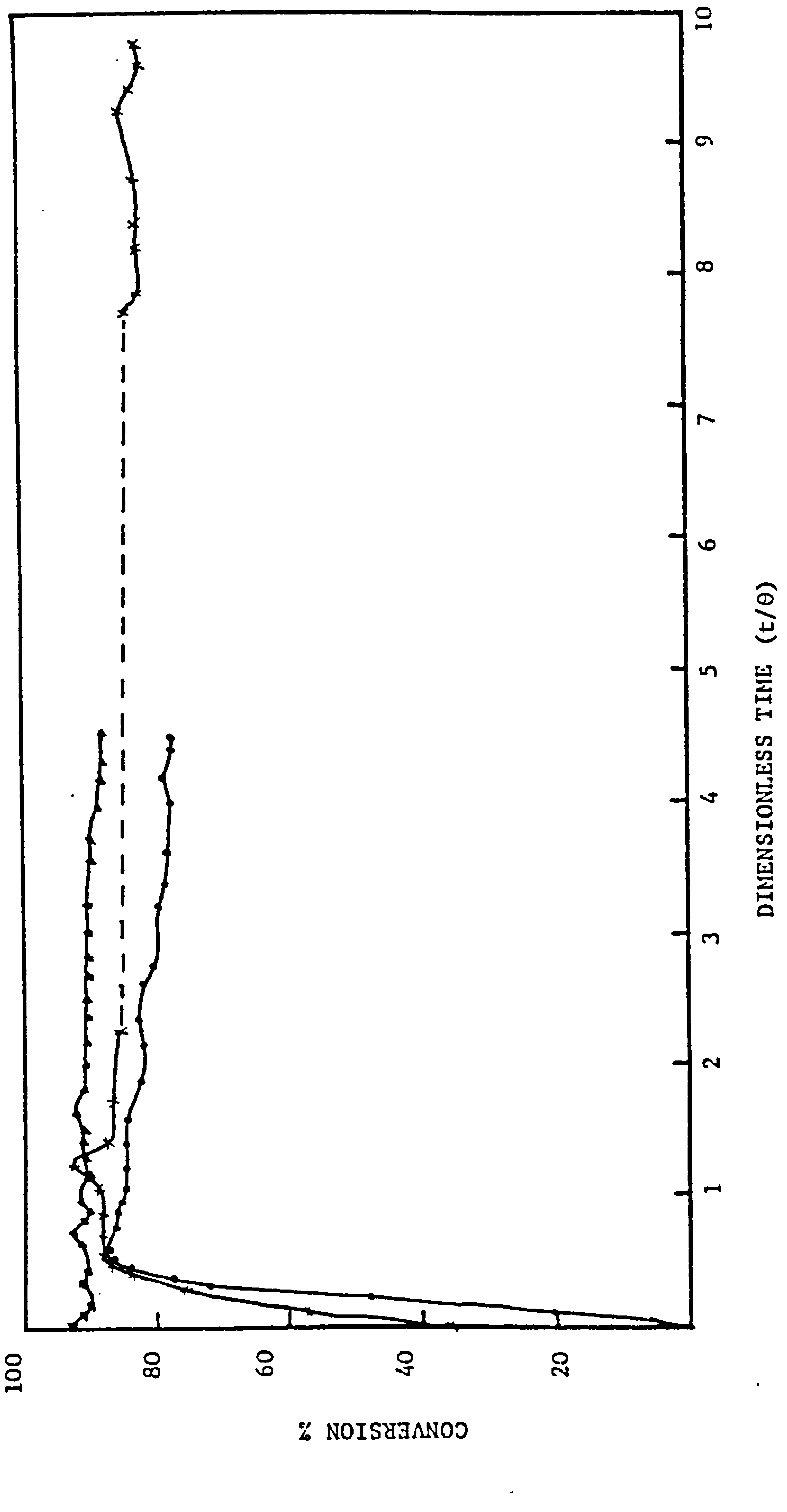

CONVERSION %
100
80
60
40
20
DIMENSIONLESS TIME (t/θ)
1
2
3
4
5
6
7
8
9
10

FIGURE: 7.7

## FIGURE 7.8

## EFFECT OF INITIAL MONOMER CONCENTRATION ON CONVERSION

| Run Number | C17 | C18 |
|---|---|---|
| Symbol | ● | X |
| Temp ($^{o}C$) | 50 | 50 |
| $\Theta$(min) | 188 | 189 |
| Procedure | 3 | 3 |
| Batch Duration (min) | - | - |
| Seed (conv.%) | - | - |
| Reactor Volume(ml) | 580 | 580 |

**FEED COMPOSITION %**

| | | |
|---|---|---|
| Water | 77 | 77 |
| Styrene | 22.8 | 22.8 |
| Soap | 0.635 | 0.635 |
| Initiator | 0.39 | 0.39 |

**INITIAL CHARGE %**

| | | |
|---|---|---|
| Water | 68 | 77 |
| Styrene | 31.2 | 22.8 |
| Soap | 0.8 | 0.63 |
| Initiator | - | - |

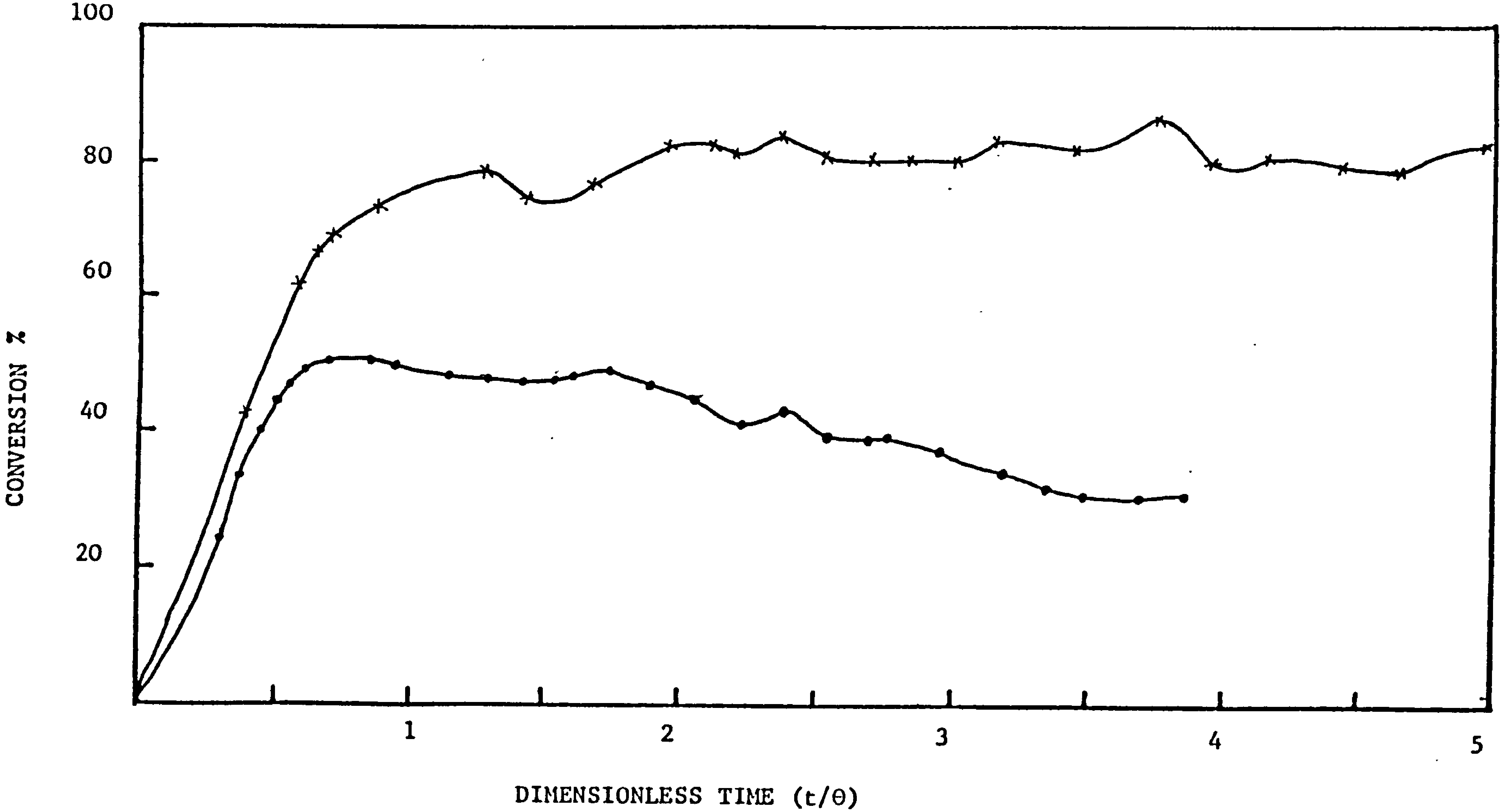


FIGURE: 7.8

## FIGURE 7.9

### EFFECT OF INITIAL SOAP CONCENTRATION ON CONVERSION

| Run Number | C15 | C21 |
|---|---|---|
| Symbol | ● | X |
| Temp ($^{o}$C) | 50 | 50 |
| Θ(min) | 113 | 116 |
| Procedure | 3 | 3 |
| Batch Duration (min) | - | - |
| Seed (conv.%) | - | - |
| Reactor Volume (ml) | 345 | 360 |
| **FEED COMPOSITION %** | | |
| Water | 78 | 77 |
| Styrene | 21.6 | 22.9 |
| Soap | 0.64 | 0.635 |
| Initiator | 0.39 | 0.39 |
| **INITIAL CHARGE %** | | |
| Water | 77 | 77 |
| Styrene | 22 | 22.9 |
| Soap | 1.1 | 0.63 |
| Initiator | - | - |

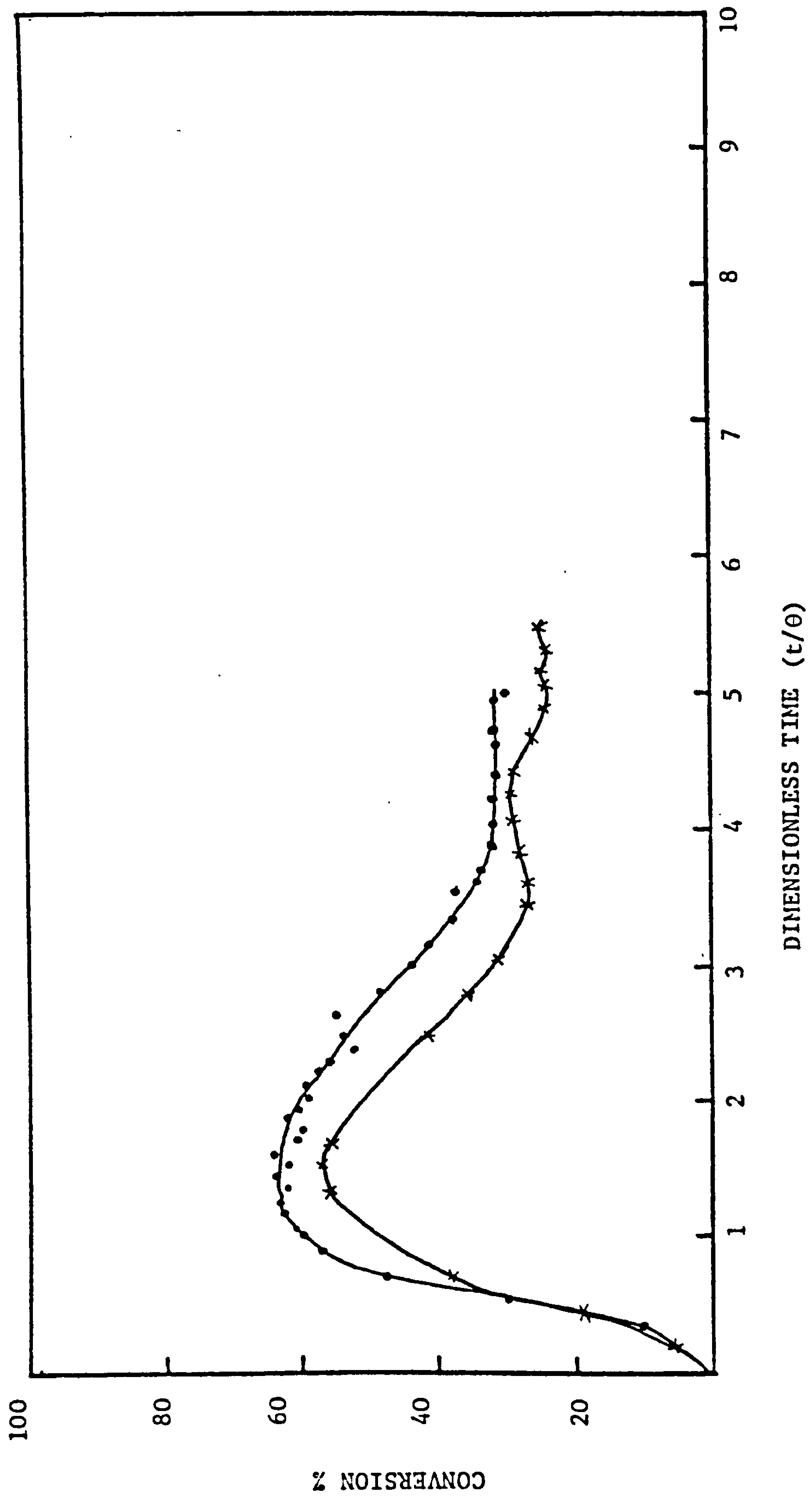

CONVERSION %
100
80
60
40
20
DIMENSIONLESS TIME (t/θ)
1
2
3
4
5
6
7
8
9
10

FIGURE: 7.9

## FIGURE 7.10

## EFFECT OF INITIATOR CONCENTRATION ON CONVERSION

| Run Number | C5 | C6 | C7 |
|---|---|---|---|
| Symbol | ▲ | ● | X |
| Temp ($^{o}$C) | 50 | 50 | 50 |
| Θ(min) | 30 | 30 | 30 |
| Procedure | 3 | 3 | 3 |
| Batch Duration (min) | - | - | - |
| Seed (conv.%) | - | - | - |
| Reactor Volume (ml) | 190 | 190 | 190 |
| **FEED COMPOSITION %** | | | |
| Water | 73 | 74 | 73 |
| Styrene | 26.7 | 26 | 26.6 |
| Soap | 0.71 | 0.68 | 0.71 |
| Initiator | 0.75 | 0.83 | 0.46 |
| **INITIAL CHARGE %** | | | |
| Water | 69 | 69 | 68 |
| Styrene | 30.5 | 30 | 31.7 |
| Soap | 0.8 | 0.8 | 0.8 |
| Initiator | - | - | - |

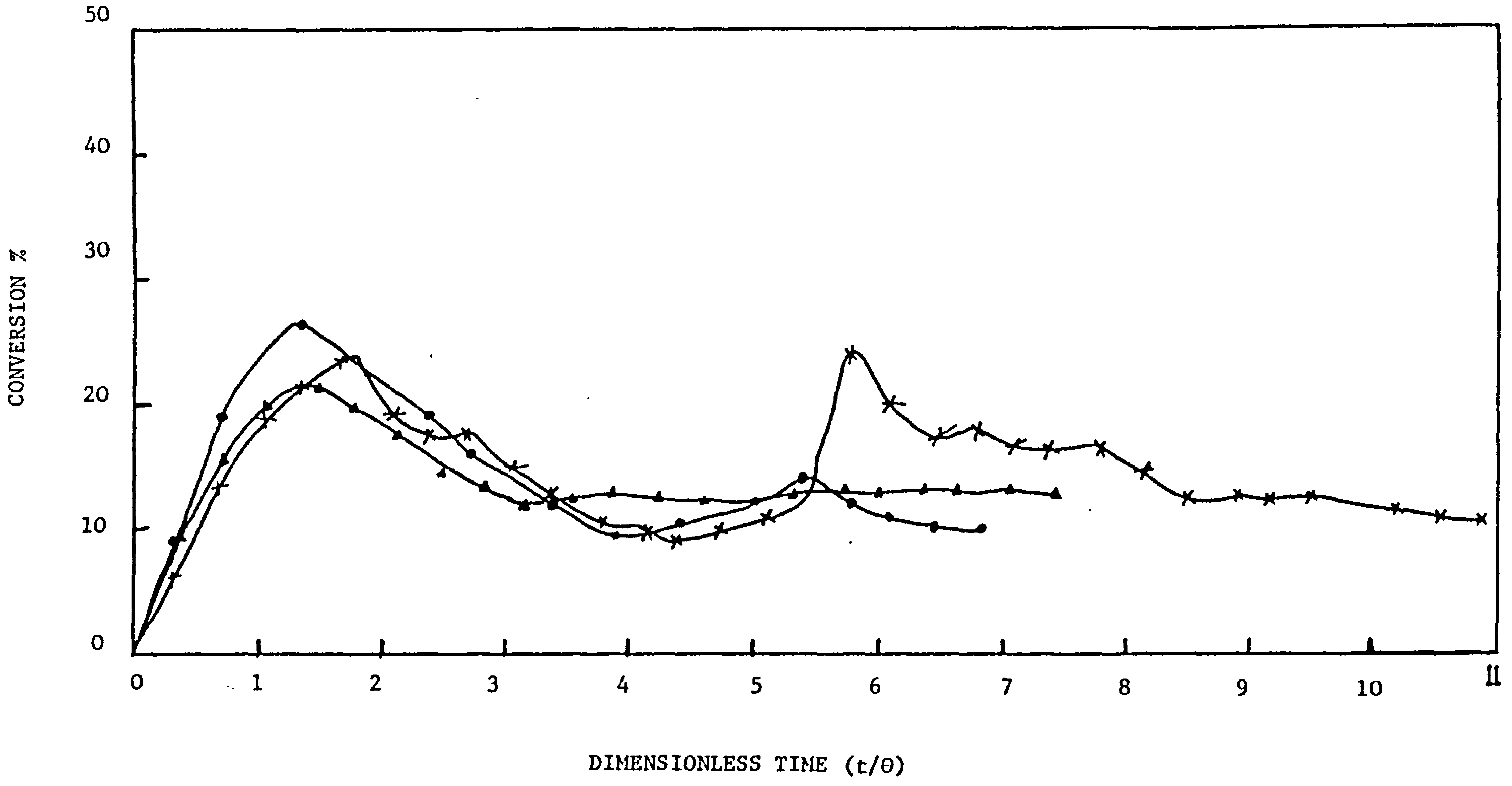

CONVERSION %
50
40
30
20
10
0
0
1
2
3
4
5
6
7
8
9
10
11
DIMENSIONLESS TIME (t/θ)

FIGURE: 7.10

## FIGURE 7.11

## EFFECT OF INITIATOR CONCENTRATION ON CONVERSION

| Run Number | BC9 | BC10 |
|---|---|---|
| Symbol | X | ● |
| Temp ($^{o}$C) | 50 | 50 |
| $\Theta$(min) | 116 | 116 |
| Procedure | 6 | 6 |
| Batch Duration (min) | 30 | 30 |
| Seed (conv.%) | - | - |
| Reactor Volume(ml) | 360 | 360 |
| **FEED COMPOSITION %** | | |
| Water | 77 | 77 |
| Styrene | 22.8 | 22.8 |
| Soap | 0.635 | 0.635 |
| Initiator | 0.78 | 1.56 |
| **INITIAL CHARGE %** | | |
| Water | 77 | 77 |
| Styrene | 22.9 | 22.9 |
| Soap | 0.63 | 0.63 |
| Initiator | 0.78 | 1.56 |

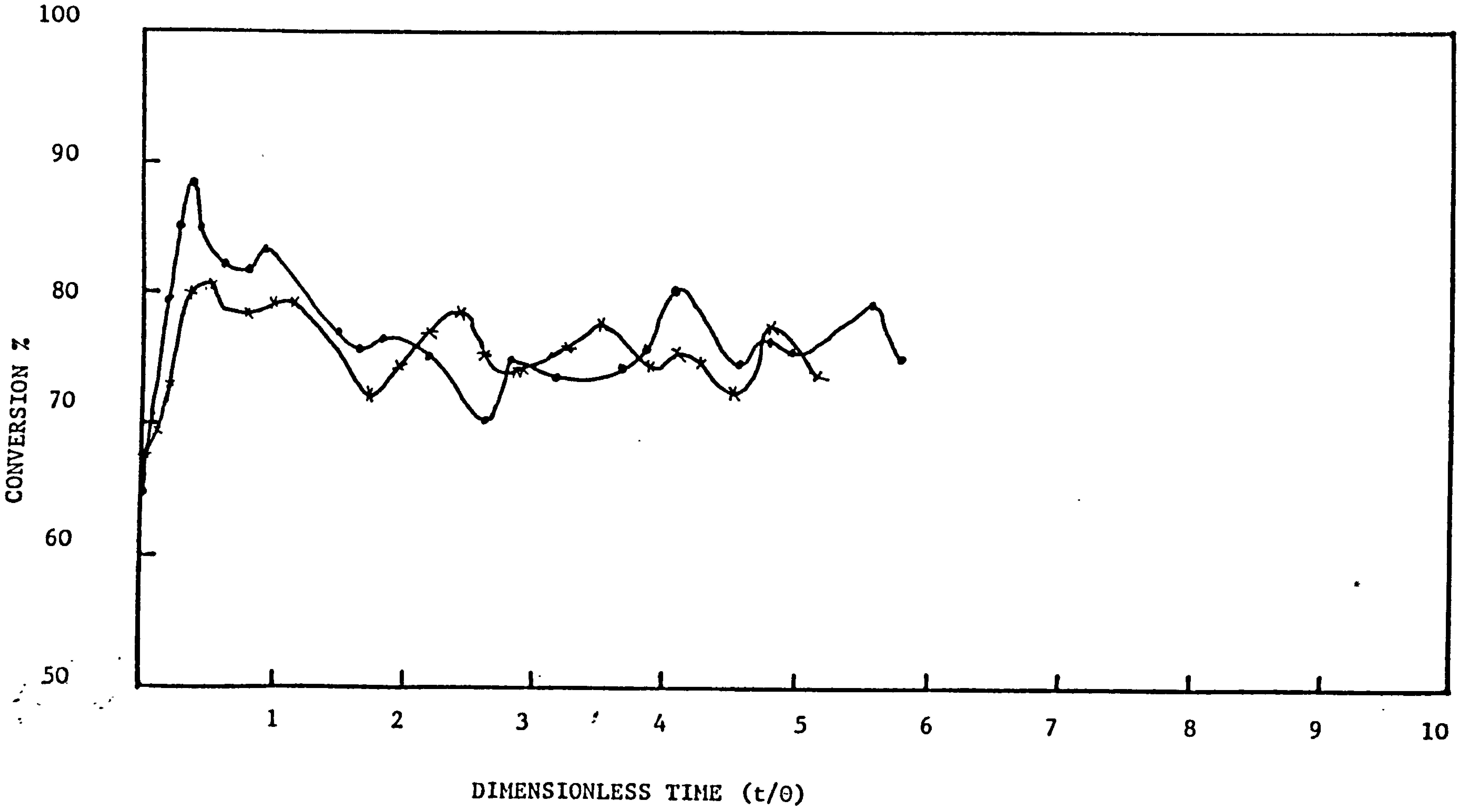

100
90
80
70
60
50
CONVERSION %
1
2
3
4
5
6
7
8
9
10
DIMENSIONLESS TIME (t/Θ)

FIGURE: 7.11

## FIGURE 7.12

## EFFECT OF INITIATOR CONCENTRATION ON CONVERSION

| Run Number | C21 | C22 |
|---|---|---|
| Symbol | ● | X |
| Temp ($^{o}$C) | 50 | 50 |
| θ(min) | 116 | 116 |
| Procedure | 3 | 3 |
| Batch Duration (min) | - | - |
| Seed (conv.%) | - | - |
| Reactor Volume (ml) | 360 | 360 |

### FEED COMPOSITION %

| | | |
|---|---|---|
| Water | 77 | 77 |
| Styrene | 22.8 | 22.8 |
| Soap | 0.635 | 0.635 |
| Initiator | 0.39 | 0.78 |

### INITIAL CHARGE %

| | | |
|---|---|---|
| Water | 77 | 77 |
| Styrene | 22.9 | 22.9 |
| Soap | 0.63 | 0.63 |
| Initiator | - | - |

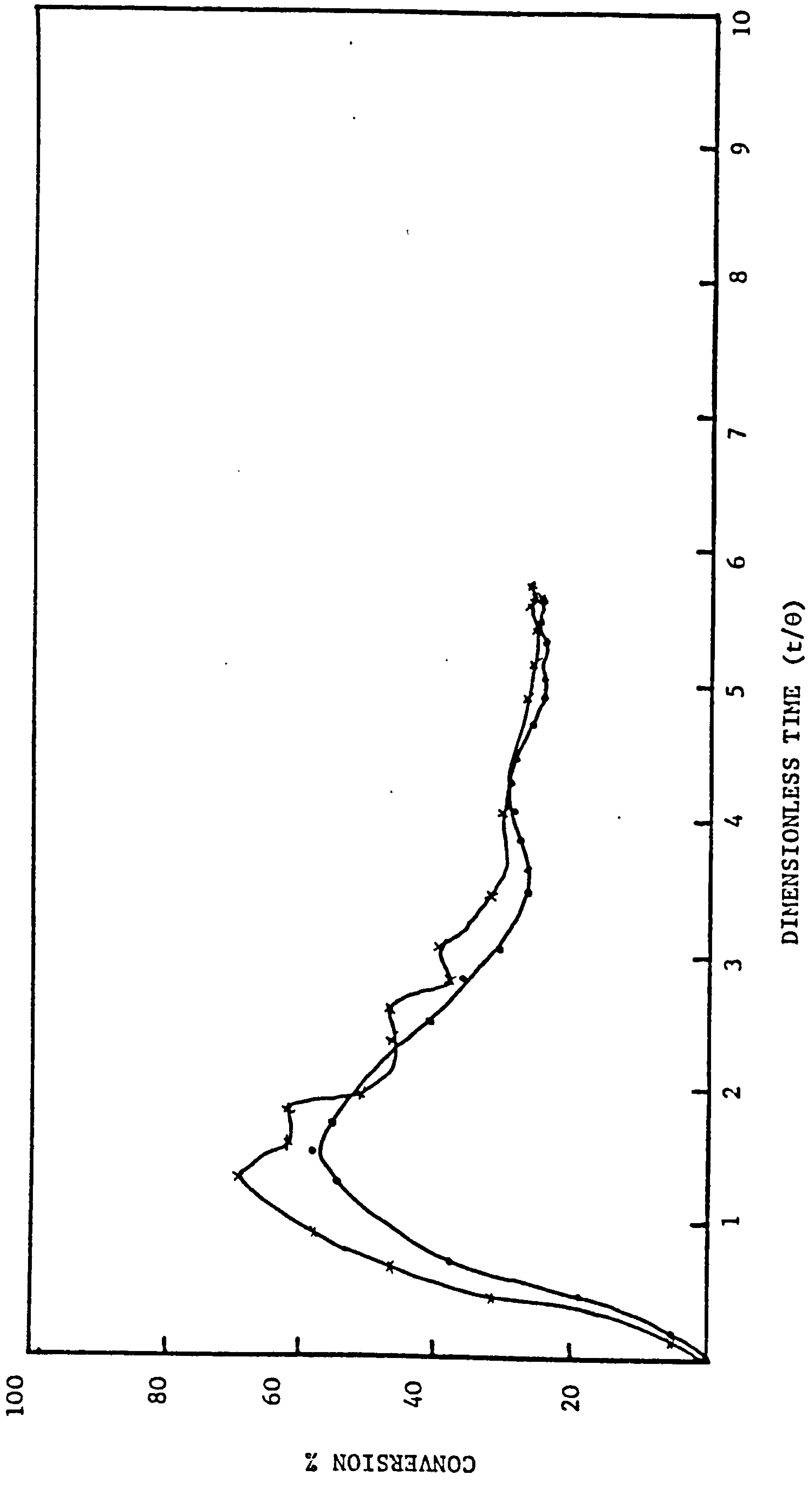

CONVERSION %
100
80
60
40
20
DIMENSIONLESS TIME (t/θ)
1
2
3
4
5
6
7
8
9
10

FIGURE: 7.12

## FIGURE 7.13

## EFFECT OF SPACE TIME ON CONVERSION

| Run Number | BC1 | BC2 |
|---|---|---|
| Symbol | ● | X |
| Temp ($^{o}$C) | 50 | 50 |
| Θ(min) | 73 | 84 |
| Procedure | 6 | 6 |
| Batch Duration (min) | 40 | 30 |
| Seed (conv.%) | - | - |
| Reactor Volume(ml) | 260 | 260 |

### FEED COMPOSITION %

| | | |
|---|---|---|
| Water | 76 | 77 |
| Styrene | 23.7 | 22.5 |
| Soap | 0.69 | 0.64 |
| Initiator | 0.3 | 0.39 |

### INITIAL CHARGE %

| | | |
|---|---|---|
| Water | 78 | 78 |
| Styrene | 21.6 | 20 |
| Soap | 0.69 | 0.69 |
| Initiator | 0.3 | 0.3 |

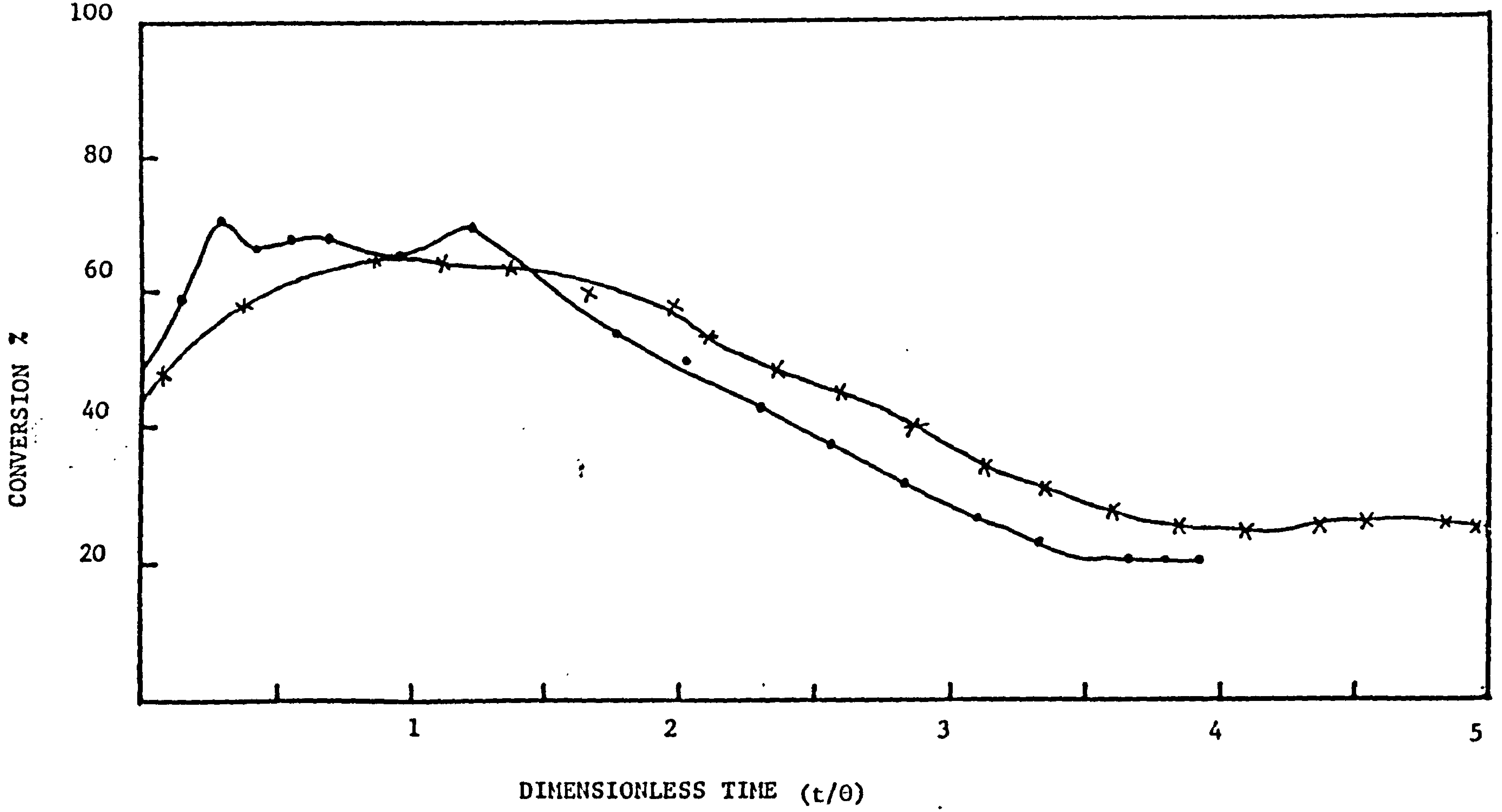


FIGURE: 7.13

## FIGURE 7.14

## EFFECT OF SPACE TIME ON CONVERSION

| Run Number | BC2 | BC6 |
|---|---|---|
| Symbol | ● | X |
| Temp (°C) | 50 | 50 |
| Θ(min) | 85 | 116 |
| Procedure | 6 | 6 |
| Batch Duration (min) | 30 | 20 |
| Seed (conv.%) | - | - |
| Reactor Volume (ml) | 260 | 360 |
| **FEED COMPOSITION %** | | |
| Water | 77 | 77 |
| Styrene | 22.5 | 22.5 |
| Soap | 0.64 | 0.65 |
| Initiator | 0.39 | 0.37 |
| **INITIAL CHARGE %** | | |
| Water | 77 | 77 |
| Styrene | 22.4 | 22.4 |
| Soap | 0.64 | 0.65 |
| Initiator | 0.39 | 0.39 |

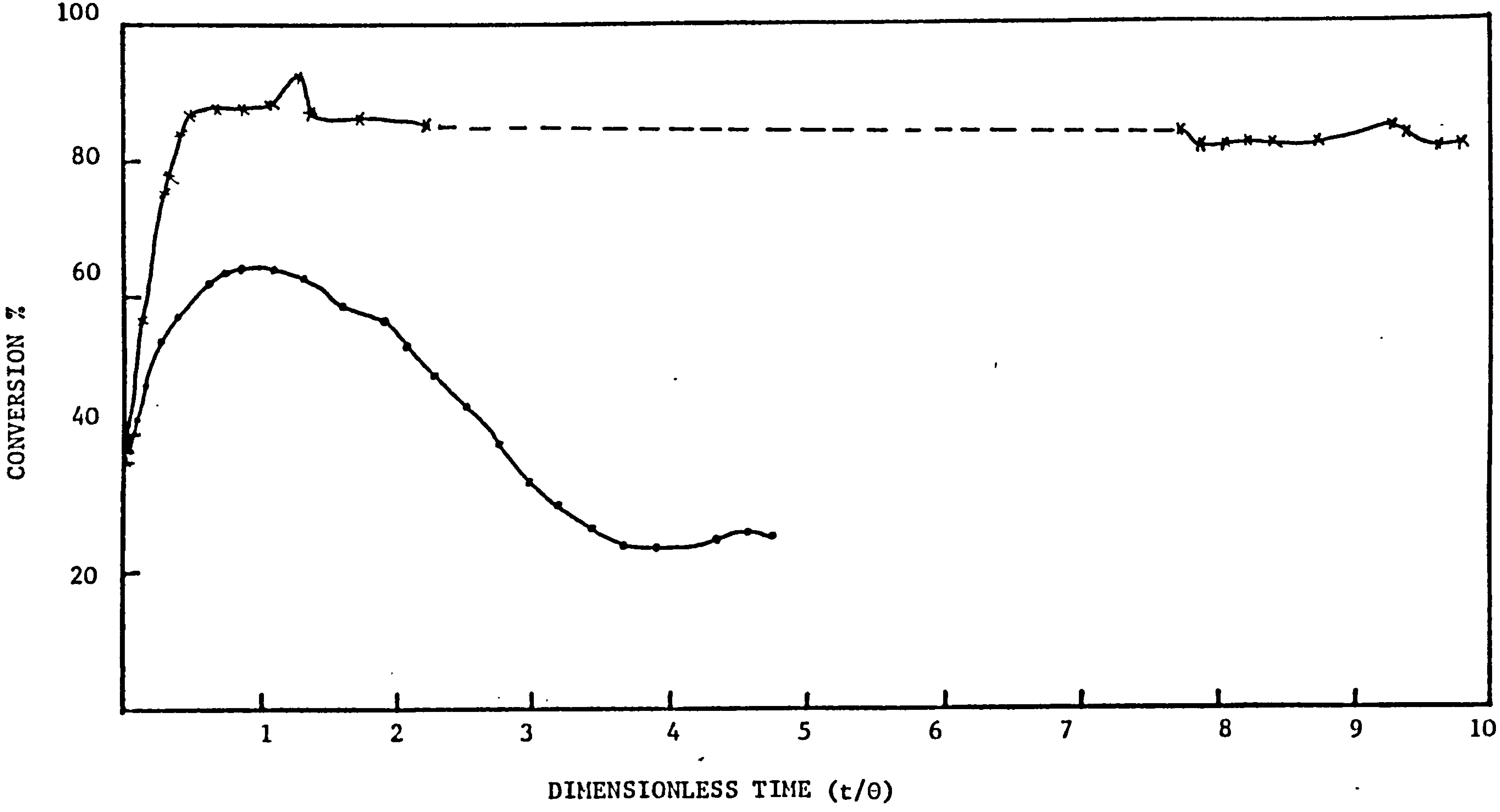

100
80
60
40
20
CONVERSION %
1
2
3
4
5
6
7
8
9
10
DIMENSIONLESS TIME (t/Θ)

FIGURE: 7.14

## FIGURE 7.15

## EFFECT OF SPACE TIME ON CONVERSION

| Run Number | C16 | C18 |
|---|---|---|
| Symbol | ● | X |
| Temp ($^oC$) | 50 | 50 |
| $\Theta$(min) | 129 | 189 |
| Procedure | 3 | 3 |
| Batch Duration (min) | - | - |
| Seed (conv.%) | - | - |
| Reactor Volume (ml) | 400 | 585 |

### FEED COMPOSITION %

| | | |
|---|---|---|
| Water | 77 | 77 |
| Styrene | 22.8 | 22.8 |
| Soap | 0.635 | 0.635 |
| Initiator | 0.39 | 0.39 |

### INITIAL CHARGE %

| | | |
|---|---|---|
| Water | 77 | 77 |
| Styrene | 22.8 | 22.8 |
| Soap | 0.63 | 0.63 |
| Initiator | - | - |

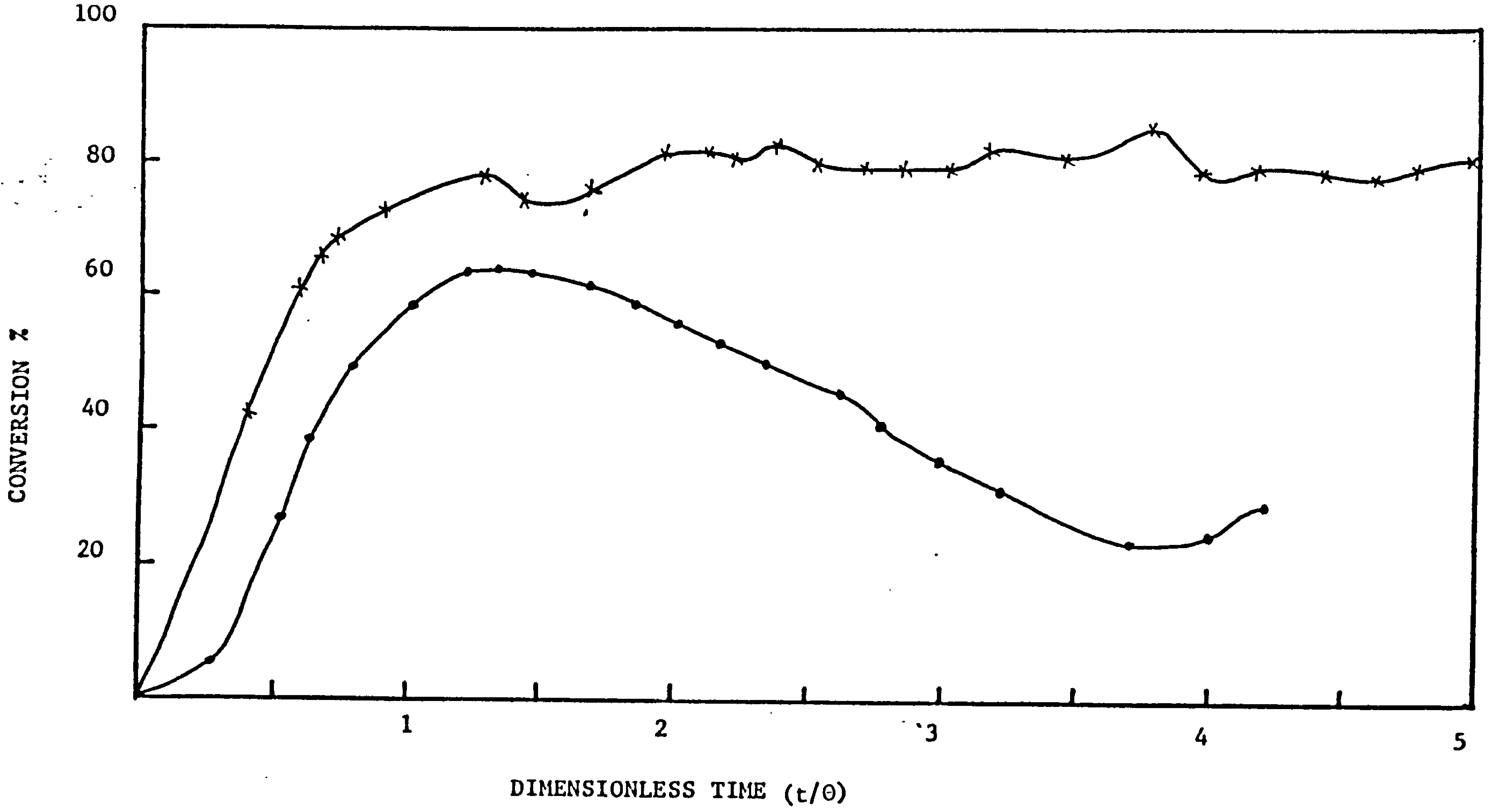


FIGURE: 7.15

## FIGURE 7.16

## EFFECT OF TEMPERATURE ON CONVERSION

| Run Number | SC1 | SC2 |
|---|---|---|
| Symbol | O | ● |
| Temp (°C) | 50 | 40 |
| Θ(min) | 116 | 116 |
| Procedure | 7 | 7 |
| Batch Duration (min) | - | - |
| Seed (conv.%) | 80 | 80 |
| Reactor Volume (ml) | 360 | 360 |

### FEED COMPOSITION %

| | | |
|---|---|---|
| Water | 77 | 77 |
| Styrene | 22.8 | 22.8 |
| Soap | 0.635 | 0.635 |
| Initiator | 0.39 | 0.39 |

### INITIAL CHARGE %

| | | |
|---|---|---|
| Water | S | S |
| Styrene | E | E |
| Soap | E | E |
| Initiator | D | D |

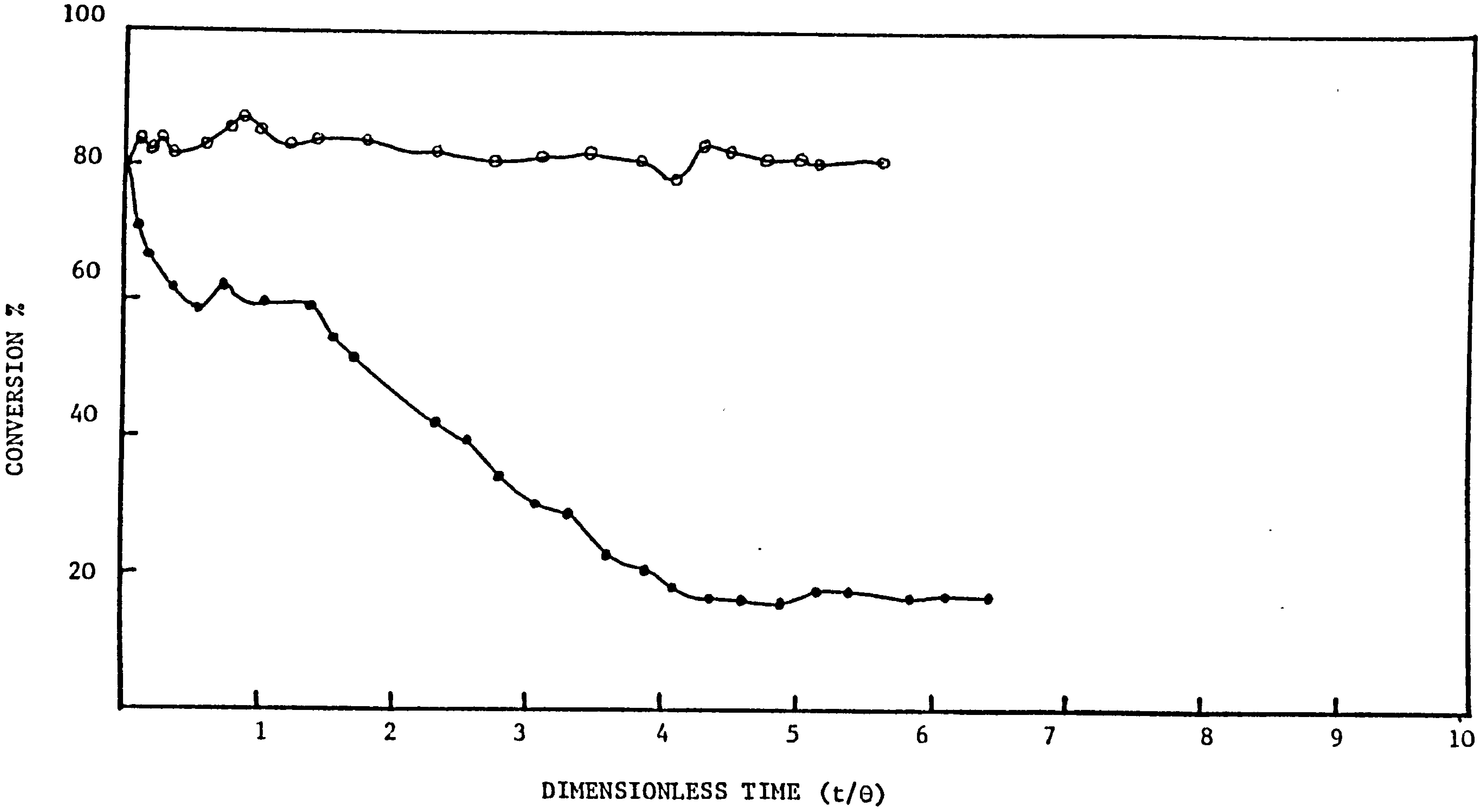

CONVERSION %
100
80
60
40
20
1
2
3
4
5
6
7
8
9
10
DIMENSIONLESS TIME (t/θ)

FIGURE: 7.16

## FIGURE 7.17

## EFFECT OF TEMPERATURE ON CONVERSION

| Run Number | C19 | C20 | C21 |
|---|---|---|---|
| Symbol | ● | X | ▲ |
| Temp ($^oC$) | 40 | 60 | 50 |
| $\theta$(min) | 116 | 116 | 116 |
| Procedure | 3 | 3 | 3 |
| Batch Duration (min) | - | - | - |
| Seed (conv.%) | - | - | - |
| Reactor Volume (ml) | 360 | 360 | 360 |
| **FEED COMPOSITION %** | | | |
| Water | 77 | 77 | 77 |
| Styrene | 22.8 | 22.8 | 22.8 |
| Soap | 0.635 | 0.635 | 0.635 |
| Initiator | 0.39 | 0.39 | 0.39 |
| **INITIAL CHARGE %** | | | |
| Water | 77 | 77 | 77 |
| Styrene | 22.9 | 22.9 | 22.9 |
| Soap | 0.63 | 0.63 | 0.63 |
| Initiator | - | - | - |

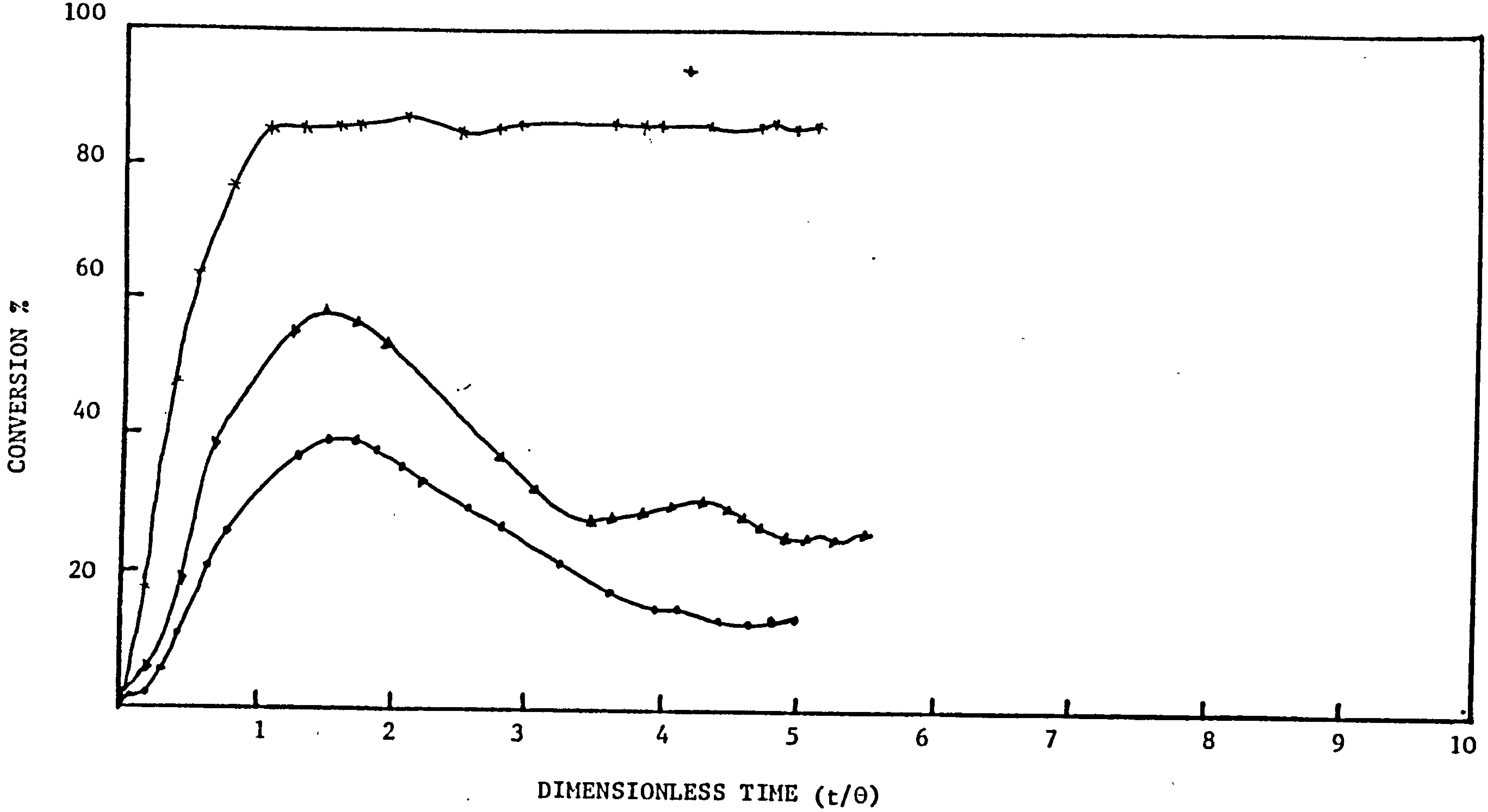

100
80
60
40
20
CONVERSION %
1
2
3
4
5
6
7
8
9
10
DIMENSIONLESS TIME (t/θ)

FIGURE: 7.17

# CHAPTER 8

## DISCUSSION OF RESULTS AND FINAL CONCLUSION

# CHAPTER 8

# DISCUSSION OF RESULTS AND FINAL CONCLUSION

## *8.1 Discussion of Results*

### *8.1.1 Introductory Discussion*

The main aim of the present work was to study the effect of the start-up procedures of the continuous flow stirred reactor on its behaviour in both the transient 不稳态 and steady states. It has been known for some time ( 27, 28 ) that the way in which the continuous emulsion polymerisation reactors are started-up can have a significant influence, not only on the transients before steady state is achieved, but also on the nature and level of the ultimate state obtained. The present study showed that it is not only the rate of polymerisation and hence conversion, which is affected by the start-up procedures but also the particle size, particle size distribution, average molecular weight, and probably the mechanism of particle nucleation and growth. A general picture of some of the experimental results, showing the high and low level conversion as a result of the start up procedures, is given in Figure 7.2.

As pointed out in section (3.33) several dynamic phenomena in continuous emulsion polymerisation reactors have been reported in the literature. These are mainly overshoot and transient oscillations, sustained oscillations, and multiple steady states. The overshoot, especially in conversion, has been reported by many workers and the reasons for this behaviour is more or less agreed on. The sustained oscillations and the steady state multiplicity have been investigated by very few researchers. As a result, the reasons for the above behaviour are not fully understood.

In the present study, conversion overshooting was detected in most of the experiments in which the level of conversion attained a low value. The only exception was when the reactor was started filled with distilled water, i.e. procedure 1, and the inhibition period was short. In this start-up procedure comparatively large particles were observed just after the start of the run. Smaller particles started to appear later. The size increased slightly after 3 residence times and reached what could be considered as a steady state. The size distribution was fairly narrow in comparison with other start-up procedures for runs with the sam experimental conditions. Figure (7.5) shows a comparison between run (C3) and (C4). The start-up procedure for run (C4) was procedure 1, and that of (C3) was procedure 3.

The experimental results of run (C4) can be explained as follows. At the beginning of the run only water was present, and the amount of monomer was by far the largest in the incoming feed. Before there was enough soap to start the nucleation in the common way, the monomer droplets started to polymerize. Since the surface area of the droplets and their number were small the polymerisation rate was low at the start. This also could explain the larger than normal size particles soon after the start of the run. As a result of the growth of these particles, a high absorption surface would then be presented to the incoming soap, and the nucleation of new particles would be expected to be small. This condition would not result in conversion overshooting as explained later. Nucleation would have re-commenced when a sufficient number of the initial particles had left the reactor. It is important to note at this stage that if the inhibition period is very long, procedure 1 will be virtually the same as procedure 5 due to the exponential nature of the dilution effect.

The initial overshoot and subsequent damped oscillations observed in some of the experiments can be attributed to the particle formation mechanism. At the beginning of the reaction, particle nucleation would have been very high in the presence of large quantities of excess free soap. The subsequent growth of these particles accounts for the larger overshoot of conversion. The above behaviour existed in all the start-up procedures where soap and preferably soap and initiator were present in the initial reactor contents. The growth of the surface area of the large number of particles led to an emulsifier starved system and under these conditions, the production rate of new particles would have decreased. As fresh soap was being added continuously and the particles formed previously were being washed out, an excess soap condition was again reached and new particles would have started to nucleate again. The repetition of the above process accounts for the observed damped oscillations to the ultimate steady state values. This sequence of events is supported by the observations and analysis of the particle size data in the present study. In the early stages of the polymerisation the particle sizes were small. However,just before the "peak" conversion occurred the small particles usually disappear and the average particle size seems to increase. The absence of small particles at this stage indicated that the generation of new particles had almost ceased. This can be attributed to the absence of free soap either to create new particles, as the micelle theory suggests, or to help in stabilizing the growing oligomers, in line with the homogeneous nucleation theories. The re-appearance of small particles and the apparent reduction in the average particle size after the conversion "peak" had passed showed that particle nucleation had started again. The above process had been observed to repeat it—self, with less severity, until the steady state was approached. A steady state could only be obtained if the rate at which the particles grow and that at which they leave the reactor, by wash out, are equal. There should be enough soap to nucleate new particles to replace the leaving ones. Small particles always existed at the steady state and this could be an indication of the presence of free soap in the system. The above mechanism explaining the oscillation, implies the formation of discrete particle populations and fluctuations in polymerisation rate and conversion, and it is clear, that under many operation conditions oscillations will prevail and the steady state may be impossible to obtain.

The level of the "peak" conversion will be determined by the initial concentration of soap, initiator, impurities, temperature and the average residence time of the reactor, i.e. the start-up procedure.

If the conversion overshoots to a very high level, it either decays back in an oscillatory form in the normal way or it may be "trapped" at the high level. To "trap" a conversion certain conditions are believed to be necessary and these will be discussed later. If this high level overshoot is not "trapped" and a steady state is attained, the steady state is usually, but not always, lower than that of a smaller "peak" in conversion, under similar experimental conditions and different start-up procedure.

The "trapped" conversion for styrene which was also reported by Ley and Gerrens ( 103) cannot be explained by the Trommsdorff effect only. Figure 7.7 shows that even at the "trapped" conversion the start-up procedure of the reactor had an effect on the "trapped" state in conversion and average particle size. Runs (BC5), (BC6) and (BC7) were started in the following way. The reactor was originally filled to its operating capacity with the emulsion recipe right from the beginning, and then run as a batch reactor for a period of time prior to introducing the feed stream. This period of time was different for the three runs. Run (BC5) was started after 50 minutes, (BC6) after 20 minutes, and (BC7) immediately, i.e. 0.0 minutes. It is observed from the conversion VS time plots, that the higher the batch duration was the higher the level of the "trapped" conversion. Run (BC6) was allowed to continue for about 20 hours, but the steady high conversion was maintained. It was found that the higher the level of the "trapped" conversion was, the marginally larger the average particle size provided the same start-up procedures were used.

### *8.1.2 The Effect of Initiator on the Rate of Polymerisation*

The effect of increasing the concentration of the initiator for the case of "trapped" conversion using procedure 6, was to increase the oscillatory behaviour of this high level conversion, Figure (7.11) in comparison with runs (BC5), (BC6) and (BC7) in Figure 7.7.

The effect of initiator was also investigated for five runs, three of which had an average residence time of 30 minutes while the other two had an average residence time of 116 minutes. Runs (C5), (C6), and (C7) had the same recipe and reaction conditions Figure (7.10). Runs (C21) and (C22) had the same recipe and reaction conditions which were different from the first three runs Figure (7.12). Both sets of runs were started using procedure 3. It is observed that an increase in the initiator concentration resulted in a higher level of oscillation in the second set, while in the first set more pronounced oscillation was observed for run (C7) with the lowest initiator concentration. In both sets the runs with the highest initiator concentrations exhibited higher conversion "peaks". Although the major difference between the two sets was the average residence time of the reactor, yet the observed effect of the initiator cannot be predicted by the simplistic models which are currently available (39,64,66,117). It should be noted however, that the space time of both runs in Figure (7.11) and those in Figure (7.12), which exhibited similar behaviour, had an average value of 116 minutes. The observation of Brooks et al (27), Poehlein(125), and others, that the rate of polymerisation of styrene, at the steady state, in a continuous flow stirred reactor is independent of the initiator concentration seems to be valid provided the start-up procedures are the same. This conclusion can be drawn for any of the sets mentioned above where the runs in each set were either approaching the same steady state or oscillating about a mean value.

### *8.1.3 The Effect of Initial Soap Concentration on Rate of Polymerisation*

Several workers have studied the effect of the emulsifier concentration in the feed on the rate of polymerisation of styrene Brooks et al (27) found that when the initiator concentration was constant the steady state polymerisation rate varied linearly with the emulsifier concentration. De Graff and Poehlien (39) also observed the same dependency and their model was able to predict this dependency, for large residence times, with some accuracy.

The effect of the emulsifier concentration in the initial charge of the continuous emulsion polymerisation reactors which has been ignored previously was investigated in the present study. In Figure (7.9), both run (C15) and (C21) had almost the same experimental conditions except the concentration of soap in the initial recipe. Run (C15) had about twice the amount of soap in the initial reactor contents while the concentration of soap in the incoming feed was the same for both runs. The conversion overshoot for run (C15) was larger than that of run (C21), and the steady state value for run (C15) was also higher than that of run (C21). Run (C21) exhibited larger oscillations around the steady state than run (C15),which had the higher initial soap concentration. Run (C15) was characterised by oscillation in the "peak" area. Two other unsuccessful runs due to mechanical failure in the pumps indicated similar behaviour.

The conclusion from the above discussion is that it is not only the emulsifier concentration in the feed, i.e. the ultimate concentration in the reactor, but also the emulsifier condition at the start of the continuous reactor which can affect the behaviour of the reactor.

### *8.1.4 The Effect of Initial Monomer Concentration on Polymerisation Rate*

Usually in experimental studies of emulsion polymerisation, it is customary to ignore the monomer to water ratio. Since most of the studies on the kinetics and mechanism of emulsion polymerisation are normally carried out in batch reactors, several workers, investigated the surface area of the monomer droplets. The reason for this is the ability of the droplets to share the available emulsifier which means less soap to nucleate new particles. Hence the interest in the degree of emulsification of the soap-monomer mixture and also the ratio of monomer to polymer. Several workers have studied the effect of stirring on the course of the polymerisation and put forward different reasons for the observed decrease in the rate of polymerisation when the agitation was increased. (44, 118 ). Coa et al (32) developed a model for the emulsion polymerisation in a batch reactor where the amount of soap adsorbed onto monomer droplets was accounted for. In a continuous reactor the ratio of monomer to water could have a more far reaching effect on the reaction rate and other behaviour of the reactor. Figure (7.8) gives an example of the ultimate steady state which can be obtained by varying the concentration of monomer in the initial charge of the reactor. Run (C17), which had a larger charge of monomer, attained a much lower steady state conversion than that of run (C18). Both runs used start-up procedure 3 and the space time for both runs was 189 minutes. The monomer/soap ratio in run (C17) was the same as that of (C18). This eliminated the variations of the factors encountered in the early stages of a batch reactor i.e. the sharing of emulsifier by the excess monomer in the system. It was observed that the average particle size of run (C18) was much larger than that of (C17) at the final stages.

The observation from various runs in the present study showed that the rate of polymerisation was affected by the ratio of monomer to water. The rate was usually lower for higher concentrations of monomer. The increase of the monomer concentration in the reaction recipe does not always increase the number of particles in the systems in the same proportion.

The conclusion from the above discussion is that the effect of monomer/water ratios on the rate of polymerisation in a continuous emulsion polymerisation reactor is too complex to be related to the particle number in a rigorous manner.

## *8.1.5 Effect of Space Time on the Rate of Polymerisation*

The space time of several runs was varied to study its effect on the polymerisatiion rate under different start-up procedures. Figure (7.13) shows conversion versus the dimensionless (t/Θ) for run (BC1) and (BC2). The space time for run (BC1) was 73 minutes and that of (BC2) was 84 minutes. The start-up procedure was number (6). Both runs seem to approach the same steady state. Figure (7.14) compares run (BC2) with run (BC6). The average residence time for run (BC6) was 116 minutes. Run (BC6) attained a high level conversion while run (BC2) attained a low level conversion. The average particle size for run (BC6) at the final stage was larger than that of BC2. Figure (7.15) shows the effect of large space time on the rate of polymerisation using start-up procedure (3). Run (C18) with a space time of 189 minutes exhibited a "trapped" conversion whereas run (C16) did not). The likely explanation which could be advanced at this stage is that both runs (C18) and (BC6) had an overshoot conversion where the conditions for the "trapped" conversion mechanism were operative.

## *8.1.6 The Effect of Temperature on the Polymerisation Rate*

Figure (7.17) shows the effect of three different temperatures on the rate of polymerisation. The space time of the three runs was 116 minutes, and the start-up procedure was number (3). Run (C19) at 40°C had a small "peak" and a longer inhibition period at the start. Run (C20) had an overshoot to the "trapped" conversion level, in addition to a very small inhibition period at the start. The level of the "peak" and steady state conversion for run (C21) was higher than those of run (C19), and the inhibition period was shorter. Both run (BC8) and run (BC7) used procedure (5) for start-up. The reaction temperature for run (BC8) was 40°C while that of run (BC7) was 50°C. The space time for both runs was 116 minutes and all other experimental conditions were the same. The conversion level of run (BC7) was in the "trapped" region while the conversion for run (BC8) decayed to a low value.

To investigate the effect of starting the reactor with a seed, a batch reactor was used to prepare a seed at 50°C with the same recipe used in a matched flow continuous reactor. The seed was charged to the reactor, and then the soap monomer, initiator, and water were added to the reactor to simulate a batch reactor at 80% conversion. Two runs were carried out with the above recipe at two different temperatures. The temperature of run (SC1) was 50°C while that of (SC2) was 40°C. The space time of both experiments was 116 minutes. The run at 50°C exhibited a "trapped" conversion of about 82% while run (SC2) decayed to a low level conversion similar to other runs at 40°C which were started using procedure (5). The average particle size of run (SC1) was much larger than the similar "trapped" runs at the same temperature but with different start-up procedures.

### 8.1.7 The Effect of Start-Up Procedures on the Polymerisation Rate

As mentioned earlier, the main aim of the present study was to investigate the effect of different start-up procedures on the behaviour of the continuous emulsion polymerisation reactor. Excursions into very high conversion regions because of the conversion overshooting are usually unacceptable in an industrial reactor. The stability of the latex in this region is usually poor and this could lead to the reactor fouling. In studying the effect of start-up procedures, it therefore, becomes necessary to investigate the causes and mechanism of the "trapped" conversion region. Before proceeding to analyse the reasons behind the "trapped" conversion, a few things have to be pointed out to simplify the understanding of the discussion.

First a general look at the effect of different start-up procedures on the rate of polymerisation of styrene in both the transient and steady state.

Figure (7.4) shows the effect of a wide variety of possible start-up procedures. Run (SC1) starting with the initial charge containing seed to simulate 80% conversion, while run (BC6) started as a batch reactor for 20 minutes before introducing the feed. Run (C21) started up with a mixture of soap and styrene in the usual way, while run (C23) started with a mixture of soap and initiator solutions in the absence of any monomer. Finally in run (C24), the reactor was filled with soap only at the start of the run. All other experimental conditions were almost the same. From Figure (7.4) it can be seen that two runs attained a "trapped" conversion. These are runs (SC1) and (BC6). The level of the "trapped" conversion for run (BC6) was higher than that of (SC1), while the average particle size of run (SC1) was larger. The conversion of both run (C21) and (C24) decayed to a low steady conversion after the "peak", with run (C24) having slightly higher level conversion in the "peak" and the steady state. Run (C23) had three levels of conversion, the first at the early stages where the conversion was "trapped", which lasted for 3 residence times. The second which was slightly lower than the first lasted for one and a half residence times, while the third was the lowest and lasted to the end of the run. It is interesting to note here that the analysis of the particle size for this run showed that there was a slight drop in the average particle size just before the first dropin conversion.

It was also observed that there was a slight increase followed by a drop in the average particle size just before the drop in conversion after four and a half residence times. The average particle size was found to be in the same range as those of other runs exhibiting "trapped" conversion.

A rather interesting observation on the start-up procedure of run (BCT1) in Figure (7.6) is that the higher initial temperature of this experiment resulted in a subsequent conversion level which was higher than run (BC11) with the lower initial temperature. The oscillation of run (BC11) about an average conversion of 60% was larger in amplitude than that of (BCT1) about a conversion of 85%. The sustained oscillation of these two runs could be a result of the higher level of the initiator used in these experiments. The oscillatory behaviour was observed for all high level concentrations of initiator as indicated before.

In Chapter 2 the initiation and initiator efficiency was discussed and in section 2.3 in particular the inhibitor effect in the continuous emulsion polymerisation reactor was discussed. In the following section the effect of the inhibition period on the start-up of the reactor is discussed.

A rather undesirable feature that a person working in the field of polymerisation in general and in emulsion polymerisation reaction in particular faces, is the existence of a delay period before the polymerisation starts called the induction period. In other words in a continuous emulsion polymerisation reaction, the reaction cannot start as soon as the feed streams are introduced to the emulsion system. The length of the inhibition period can vary with different experimental conditions, and the rate of agitation can be a decisive factor in an impure system as discussed in chapter 1. A long induction period can alter certain start-up procedures and this could lead to unpredictable reactor performance as shown earlier in this chapter. This is particularly undesirable in an industrial plant where the contaminants might vary from batch of raw materials to another, especially the emulsifiers.

The observation of several workers that the persulphate concentration has no effect on the rate of reaction except at low concentrations could be explained as follows:

In a CFSR impurities enter the reactor continuously with the feed. At low initiator concentrations, a large proportion of the free radicals produced from the decomposition of the initiator were consumed by the impurities. In this case the reaction would be sensitive to changes in the initiator concentration. On the other hand at higher initiator concentrations, more radicals were produced and the total consumption of radicals by the impurities would have been insignificant.

### *8.1.8 The "Trapped" Conversion*

Until now the reasons for sustained high level conversion which was observed for several start-up procedures and which was referred to as "trapped" conversion, were not given. Later in this section an attempt will be made to give possible reasons for this phenomenon and how it can be obtained or avoided.

Examination of the "trapped" conversion experimental results reveals the following significant points:

1) small and large particles co-exist in the entire period of the reaction, i.e. new particles were generated despite the fact that "all" monomer is ostensibly contained within existing particles.

2) It was also noticed that the number of small and large particles was relatively equal, unlike in the low conversion steady state case where the small particles existed in far greater numbers.
3) The extremely small particle sizes do not exist anywhere in the entire region.
4) very large particles do exist in most of this region.
5) As the particles grow in size at the constant conversion the system may pass from emulsifier starved system to excess emulsifier, without changing the relative number of small and large particles, i.e. excess emulsifier in this case did not create a large number of new particles. Such phenomena do not normally occur in a batch reactor since the reaction proceeds successively through interval I, where both monomer drops and free soap coexist. And in interval II where only monomer drops exist. In interval III, the monomer droplets disappear and what little monomer is dissolved in the aqueous phase is soon consumed. However in a continuous reactor, there is always a fresh supply of monomer and emulsifier entering the reactor in the feed stream. In the region of the "trapped" conversion the system could be a monomer starved system even in the presence of excess soap.

The mass transfer of monomer to the particles and the effect of surfactant on it has been discussed by Brooks (21). He showed that the average initial transfer rate of toluene to the particles is about $6 * 10^3$ molecule $sec^{-1}$ $particle^{-1}$ at 25°C, (Toluene molecules and styrene molecules are almost equal in size). He pointed out that at 60% saturation the transfer rate decreases and the rate of saturation then varies linearly with percentage saturation. Even at the later stages of the polymerisation of styrene in a batch reactor, the transfer rate of monomer to the particles would still be higher than the polymerisation rate. This is also the case in the "trapped" conversion region. In the systems where the equilibrium concentration of monomer in the swollen particles are about 60% it was found experimentally by several workers that the monomer droplets disappeared at conversion of more than 60%. This means that the average concentration of monomer in the particles was less than 40%, which is less than the equilibrium concentration, even though the monomer droplets were still present. However as the monomer droplets become smaller and the polymer particles become larger a situation might be realised in which the aqueous phase is no longer saturated with monomer.

This case can arise if the diffusion rate of monomer to the particles exceed the diffusion rate from the droplets. Brooks (21) pointed out that any resistance to monomer transfer will have the greatest effect when the polymer particles are still very small and their monomer capacity is low. He concluded that if this happens, the particles will become highly viscous owing to the high percentage of polymer within them, and any particle (or micelle) coalesence which may occur during this period will therefore be hindered. This was for a batch reactor. For a continuous reactor in the "trapped" conversion region, the amount of the monomer in the system is much less than the saturation equilibrium of the particles.

Since the average particle size is large in this region the average surface area of the particles in most cases will be less than the total covering power of the soap, i.e. excess soap. Thus the incoming monomer droplets should have their surfaces saturated with soap, and this will reduce the mass transfer rate of monomers from the droplets to the aqeuous phase. And since the transfer rate of monomer to the particles is still high, the aqueous phase will become monomer starved. The micelles, if present, will also be monomer starved, and this could explain the absence of extremely small particles in this system, because the micelles are not capable of polymerisation. This situation will leave only the polymer particles and the monomer droplets as sites for polymerisation. The monomer droplets will be small, because of the existence of excess soap and because they exist in small number, which reduce the likelihood of collision and subsequent coalescence. The absence of the very small particles but the coexistence of small and large particles can be considered as an evidence for the above mechanism. The relatively small number of the small particles could be attributed to the small number of monomer droplets which exist in such a system

To explain the high polymerisation rate one has to assume that the large particles are growing at an unusually fast rate. At this stage two different approaches can be discussed. The first is that the polymerisation takes place within the particles, and the second is that the polymerisation process takes place on the surface of these large particles. If the first assumption is true given the state of the particles and their high viscosity, one has to assume that the temperature inside the particle will be much higher than that on the surface, i.e. the polymerisation rate constant in the large particles is much higher than that of the small particles. On the other hand if the second assumption is the operative one , then the free radicals will be far from each other and the mutual termination of two growing radicals will be minimized. In both cases the reaction rate in the large particles will be much faster than that of the small particles. These two mechanisms can only operate for fairly large particles which was encountered in these experiments. The second mechanism is similar in the result to the reduction of the termination rate due to the gel effect except that the gel effect works at higher conversion than the one encountered in the present study. The "trapped" conversion in this study varied between 50% and 90% conversion depending on the start-up procedures and other experimental conditions.

In order that a "trapped" conversion can be observed there should be an overshoot to a high conversion. For this task several start-up procedures and experimental conditions can be useful.

1 - To run the reactor as a batch reactor until the required conversion is reached.
2 - To run the reactor at a higher temperature
3 - To increase the space time to higher value
4 - To start with a seed simulating high conversion in a batch reactor.
5 - To start the reactor under conditions of high initiation rate.

The previous five points may take the conversion to high values but other conditions should be present when the overshoot takes place. The main factor is that the rate of growth of the particles should balance the rate of washout. This means a dependence on the rate of polymerisation and the space time combined. This is observed in Eigure (7.14) and (7.15).

Very few workers encountered the "trapped" conversion because of the way they started their reactors and the absence of the critical minimum space time to balance the rate of growth to that of the washout. In particular many of the workers fed their reactors with a mixture of initiator and soap, which as pointed out in chapter 2, will mean a decreasing amount of initiator in the feed with time. This is due to the high rate of decompositions of persulphate in the presence of emulsifiers. Other workers who run a train of reactors at temperatures as high as 90°C would have actually fed their second reactor with no initiator at all since the half life of the persulphate at these conditions would have been a few minutes.

The start-up procedures of a CFSR has received very little attention in the literature. The few reported studies on the start-up procedures are usually incomplete and too general to be accurate.

## *8.2 Final Conclusion*

A comprehensive study has been undertaken to determine the effect of different start-up procedures on the behaviour of a continuous flow stirred emulsion polymerisation reactor. From this study the following conclusions can be drawn.

1. The way in which a continuous flow stirred emulsion polymerisation reactor is started-up can have a significant effect on the nature of both the transient and steady states.
2. Two distinct levels of conversion can be obtained by varying the start-up procedures in suitable experimental conditions
3. Both particle size and molecular weight data for the high level conversion oscillate with time even if the conversion attains a steady state.
4. The steady state rate of polymerisation in a CFSR is independent of the initiator concentration provided that the same start-up procedure has been used.
5. An increase in the concentration of the persulphate initiator leads to an increase in the amplitude of oscillation of the rate of polymerisation.
6. At the start of the continuous reactor the presence of a long inhibition period can vary the start-up procedure.
7. The emulsifier concentration in the initial reactor content can affect the behaviour of the reactor.
8. The monomer/water ratio in the initial reactor content can have a significant effect on the ultimate steady state conversion.
9. For each of the reaction conditions there exists a space time under which a high level steady state conversion is not possible
10. The average particle size for the high level conversion is always larger than the corresponding low level conversion.
11. To explain the high level steady state conversion a mechanism for monomer droplet polymerisation and probable mechanisms for particle growth are suggested.

## *8.3 Suggestions for Further Work*

The present study showed that the performance of a continuous flow stirred emulsion polymerisation reactor depends on many factors. One of which is the start-up procedure. It is recommended that the following tasks should be undertaken to widen the scope of understanding of the emulsion polymerisation process.

1. The study should be widened to include other monomers in addition to styrene especially the more soluble monomers such as methyl methacrylate and vinyl acetate.
2. To further explain the mechanism of nucleation and growth of polymer particles at high level conversion, a complete analysis of the particle size distribution of several reactor runs is required.
3. In view of the results obtained in the present study, a detailed analysis of the monomer concentration in droplet form should be carried out not only at low but also at high level conversions.
4. The oscillatory behaviour and the constant decline of the average molecular weight observed in the study means that more accurate measurement of molecular weight and if possible molecular weight distribution would be an invaluable tool in the investigation of the kinetics of emulsion polymerisation.
5. In the seeded polymerisation reactions carried out in the study, the average particle size of the polymer was very large compared to the non-seeded reactions.

   The use of well-characterised seed both in the initial reactor charge and feed could be a useful means of determining the morphology of the polymer particles.
6. In the study, the start-up procedures were carried out at 40°C, 50°C and 60°C.

   It is recommended that a wider range of temperatures should be used to enable complete characterisation of possible reactor behaviour at different reaction temperatures.

7. It has been reported in the literature that fully fluorinated soap had no effect on the rate of decomposition of the persulphate initiator.

The use of a fully fluorinated soap to study the effect of the initiator on the reactor behaviour under different start-up procedures is, therefore recommended.

8. Since consistent results were obtained in the above study, the development of the experimental techniques described and especially the use of the Photon Correlation Spectroscopy for both molecular weight measurement and particle size distribution is highly recommended.

## APPENDIX I

## STEADY STATE ANALYSIS OF THE MECHANISM FOR THE FIRST ORDER UNCATALYSED PERSULPHATE DECOMPOSITION.

Let $R^{\cdot}$ be a radical and P the product from an oxidizable substrate, $\overline{S}$. The proposed steps for the general case are:

$$S_2O_8^{2-} \xrightarrow{k_1} 2\ SO_4^{\cdot\,-} \tag{1-I}$$

$$SO_4^{\cdot\,-} + H_2O \xrightarrow{k_2} OH^{\cdot} + SO_4^{-} \tag{2-I}$$

$$OH^{\cdot} + \overline{S} \xrightarrow{k_3} OH^{-} + R^{\cdot} \tag{3-I}$$

$$R^{\cdot} + S_2O_8^{2-} \xrightarrow{k_4} P + SO_4^{2-} + SO_4^{\cdot\,-} \tag{4-I}$$

$$R^{\cdot} + SO_4^{\cdot\,-} \xrightarrow{k_5} P + SO_4^{2-} \tag{5-I}$$

Several differential equations can be set up from this scheme.

$$-d\ |S_2O_8^{2-}|/dt = k_1\ |S_2O_8^{2-}| + k_4\ |R^{\cdot}|\ |S_2O_8^{2-}| \tag{6-I}$$

$$-\ d\ |\overline{S}|/dt = k_3\ |OH^{\cdot}|\ |\overline{S}| \tag{7-I}$$

$$d|SO_4^{\cdot\,-}|\ dt = 2\ k_1|S_2O_8^{2-}| - k_2|SO_4^{\cdot\,-}| + k_4\ |R^{\cdot}||S_2O_8^{2-}| - k_5|R^{\cdot}||SO_4^{\cdot\,-}| \tag{8-I}$$

$$d|R^{\cdot}|/dt = k_3|OH^{\cdot}|\ |\overline{S}| - k_4|R^{\cdot}||S_2O_8^{2-}| - k_5|R^{\cdot}||SO_4^{\cdot\,-}| \tag{9-I}$$

$$d|OH^{\cdot}|/dt = k_2|\ SO_4^{\cdot}| - k_3\ |OH^{\cdot}||\overline{S}| \tag{10-I}$$

By the steady state hypothesis $|SO_4^{\cdot\,-}|$, $|R^{\cdot}|$ and $|OH^{\cdot}|$ are constant, therefore

$$d|SO_4^{\cdot\,-}|/dt = d|R^{\cdot}|/dt = d|OH^{\cdot}|/dt = 0 \tag{11-I}$$

Thus, from (10-I) and 11-1)

$$k_2|SO_4^{\bullet -}| = k_3\ |OH^{\bullet}||\overline{S}\ | \qquad (12\text{-I})$$

Substitution of (12-I) in 7-I) gives

$$-d\ |\overline{S}\ |/dt = k_2|SO_4^{\bullet -}| \qquad (13\text{-I})$$

and substitution of (12-I) in (9-I) gives

$$d|R^{\bullet}|\ /dt = k_2|SO_4^{\bullet -}| - k_4|R^{\bullet}||S_2O_8^{2-}| - k_5|R^{\bullet}||SO_4^{\bullet -}| = 0 \quad (14\text{-I})$$

Adding equation (8-I) and (14-I)

$$k_1\ |S_2O_8^{2-}|\ = k_5\ |R^{\bullet}||SO_4^{\bullet -}| \qquad (15\text{-I})$$

and subtracting equations (8-I) and (14-I)

$$k_2|SO_4^{\bullet -}| = k_1|S_2O_8^{2-}|\ + k_4\ |R^{\bullet}||S_2O_8^{2-}| \qquad (16\text{-I})$$

Thus from equations (6-I), (13-I) and (16-I)

$$-d|S_2O_8^{2-}\ |/dt = -d|\ \overline{S}|/dt$$

Now from equation (15-I)

$$|SO_4^{\bullet -}| = k_1\ |S_2O_8^{2-}|\ /k_5|R^{\bullet}| \qquad (17\text{-I})$$

and substitution for (17-I) in (16-I) gives

$$k_1 + k_4\ |R^{\bullet}| = k_1k_2/k_5|R^{\bullet}| \qquad (18\text{-I})$$

Therefore

$$k_4|R^{\bullet}|^2 + k_1|R^{\bullet}| - k_1k_2/k_5 = 0 \qquad (19\text{-I})$$

Solving for this quadratic gives

$$|R^{\cdot}| = |-k_1 \pm (k_1^2 + 4\ k_1k_2k_4/k_5)^{\frac{1}{2}}|\ /2\ k_4 \qquad (20\text{-I})$$

and substitution for $|R^{\cdot}|$ in equation (6-I) gives

$$\text{Rate} = \tfrac{1}{2}\ |k_1 \pm (k_1^2 + 4\ k_1k_2k_4/k_5)^{\frac{1}{2}}||\ S_2O_8^{2-}| \qquad (21\text{-I})$$

If $k_1$ is very small and since the rate is positive equation (21-I) simplifies to

$$\text{Rate} = (k_1k_2k_4/k_5)^{\frac{1}{2}}\ |S_2O_8^{2-}| \qquad (22\text{-I})$$

$$= k_0'\ |S_2O_8^{2-}| \qquad (23\text{-I})$$

Where $k_0'$ = the observed rate constant.

# APPENDIX II

## ESTIMATION OF UNDISSOCIATED PERSULPHATE IN SOLUTION

### II.1 *Theory and Practical Consideration*

The quantity of unreacted persulphate in a sample can be estimated through the liberation of iodine. The stoichiometric equation for the reaction is:

$$S_2O_8^{2-} + 2I^- \rightarrow I_2 + 2\ SO_4^{2-} \qquad (1\text{-II})$$

The slow oxidation of iodide ion by persulphate is known to be increased by an increase of ionic strength of the medium The value of the rate constant of equation (1-II) decreases as the reaction proceeds, the decrease being attributed to the formation of the tri-iodide ion according to equation (2-II)

$$I^- + I_2 \rightleftharpoons I_3^- \qquad (2\text{-II})$$

The quantity of liberated iodine was determined volumetrically by using sodium thiosulphate solution. Thiosulphate is oxidized rapidly, in acid or neutral solution, to tetrathionate by iodine according to the following reaction:

$$2\ S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2\ I^- \qquad (3\text{-II})$$

A weakly alkaline iodine solution gives a partial oxidation to tetrathionate and a partial oxidation to sulphate:

$$S_2O_3^{2-} + 4\ I_2 + 10\ OH^- \rightarrow 2\ SO_4^{2-} + 8I^- + 5\ H_2O \qquad (4\text{-II})$$

According to the normal reaction (oxidation to tetrathionate), 1 mole of thiosulphate corresponds to 1 equivalent ($\frac{1}{2}\ I_2$), whereas in the oxidation to sulphate 1 mole of thiosulphate consumes 8 equivalents of iodine. Therefore, one will find less thiosulphate required for the titration of iodine in weakly alkaline medium than in neutral or acid medium (Eq. (3-II) ). More of the thiosulphate will be oxidised to sulphate (Eq. (4-II) ), the higher the hydroxyl-ion concentration. The iodine and iodide concentrations, the temperature and the presence of foreign substances also affect the extent to which reaction (4-II) takes place.

The two important sources of errors in iodimetric titrations are the air oxidation of an acid iodide solution and the loss of iodine by volatilization.

Iodide in acid medium is slowly oxidised by oxygen:

$$4\ I^- + 4\ H^+ + O_2 \rightarrow 2\ I_2 + 2\ H_2O \qquad (5\text{-II})$$

This reaction is extremely slow in neutral medium, but the velocity increases with increasing hydrogen-ion concentration and is greatly accelerated by direct sunlight.

The other source of error lies in the comparative ease with which iodine is volatilized from its solutions. This volatility is materially decreased by the presence of a large excess of iodide, which reacts with iodine to form triiodide ions (Eq. (2-II)). In titration at room temperature (< 25°C) losses are negligibly small if the solution contains at least 4% of potassium iodide.

In the present study it was found that both source of errors could be eliminated if the oxidation of iodine ions by persulphate, was carried out in the presence of hydroxyl-ion which removes the iodine according to the equations:

$$S_2O_8^{2-} + 2I^- \rightarrow I_2 + 2\ SO_4^{2-} \qquad (1\text{-II}$$

$$3\ I_2 + 6\ OH^- \rightarrow 5\ I^- + I\ O_3^- + 3\ H_2O \qquad (6\text{-II})$$

and overall

$$3S_2O_8^{2-} + I^- + 6\ OH^- \rightarrow 6\ SO_4^{2-} + IO_3^- + 3\ H_2O \qquad (7\text{-II})$$

Since the solution is alkaline, the oxidation of iodide by oxygen is prevented. Also in this case the iodine will be converted into iodate and triiodide ions leaving a negligible amount of free iodine in solution which minimise the losses by volatilization.

The titration with thiosulphate can be carried out as normal by the addition of acetic or sulphuric acid, just before the titration is started, to shift the pH to below 7. Even with only a slight excess of hydrogen ions the following reaction rapidly goes to completion:

$$IO_3^- + 5\,I^- + 6\,H^+ \rightarrow 3\,I_2 + 3\,H_2O \qquad (8\text{-}II)$$

## II.2 *Calculation of Residual Persulphate*

In order to estimate the persulphate undissociated in a sample, the following definitions are necessary:

$Y$ = weight of sample, g

$W$ = weight of undissociated persulphate in the sample, g

$W_o$ = weight of undissociated persulphate per gram of latex at time zero

$\bar{V}$ = volume of standardised $Na_2S_2O_3$ needed to react with liberated iodine, mls

$\bar{N}$ = normality of thiosulphate solution

$Rt$ = percentage residual persulphate at time t, %

W, was simply determined from the equations below:

$$\frac{W}{228.2/2} = \frac{\bar{N}\,\bar{V}}{1000}$$

$$\therefore \quad W = \frac{114.1\,\bar{N}\,\bar{V}}{1000}\ , \text{g}$$

If the quantity of persulphate at time zero is known, the residual persulphate at any time can be calculated:

$$Rt = \frac{W}{W_o Y} * 100, \quad \%$$

where the molecular weight of sodium persulphate equals 228.2

## APPENDIX III

### Recipes

The following table shows the concentration of soap and initiator which were used later in the feed to the reactor.

| Recipe | Soap (g/ℓ) | Initiator (g/ℓ) |
|---|---|---|
| 1 | 11.17 | 116 |
| 2 | 11.17 | 60 |
| 3 | 12.4 | 30 |
| 4 | 12.4 | 15 |
| 5 | 24.8 | 60 |

## APPENDIX IV

### Intrensic Viscosity and Molecular Weight

Run BC7

| Time (min) | $[\eta]$ | Mol. Wt. |
|---|---|---|
| 35 | 6.25 | 6,594,515 |
| 65 | 0.537 | 125,763 |
| 421 | 2.54 | 1,543,318 |
| 510 | 1.13 | 420,314 |

## C8

| Holding Time (Min) | Temp. (°C) | Procedure | Batch Duration (Min) | Seed Conv. (%) |
|---|---|---|---|---|
| 30 | 50 | 3 | --- | --- |

| TIME | LATEX | POLYMER | FR MONOMER | CONVERSION% |
|---|---|---|---|---|
| 10 | 3. 6598 | 0218964 | .260271 | 2. 29674 |
| 20 | 3. 61121 | .0874024 | .252209 | 9. 55544 |
| 30 | 3 654 | .145203 | .246319 | 16. 1125 |
| 40 | 3 7709 | .191895 | 242015 | 21. 6175 |
| 50 | 3 7356 | .207903 | .23887 | 22 5508 |
| 50 | 3. 813 | .201202 | 23887 | 22 6965 |
| 50 | 3. 6565 | .190201 | .23887 | 21. 7753 |
| 60 | 3. 6839 | .198799 | .236573 | 22. 8183 |
| 70 | 3. 9276 | .195 | .234994 | 21. 1166 |
| 80 | 3. 8782 | .1772 | .233667 | 19. 5541 |
| 90 | 3. 9203 | .162499 | .232771 | 17. 8074 |
| 100 | 4. 0774 | .147804 | .232116 | 15. 617 |
| 110 | 4. 4973 | .142296 | .231638 | 13 6594 |
| 110 | 3. 4659 | .108299 | .231638 | 13. 4997 |
| 120 | 3. 7889 | .1073 | .231288 | 12. 2443 |
| 120 | 4. 158 | .113899 | .231288 | 11. 8426 |
| 130 | 3. 8602 | .097702 | .231033 | 10. 9552 |
| 130 | 3. 6566 | .0923004 | .231033 | 10. 5258 |
| 140 | 4. 2057 | .108299 | .230846 | 11. 1549 |
| 150 | 3. 4958 | .103798 | 23071 | 12. 87 |
| 160 | 4. 17931 | 128006 | .23061 | 13 2815 |
| 160 | 4. 5649 | .153801 | 23061 | 14 61 |
| 160 | 3. 96951 | .135903 | .23061 | 14. 8461 |
| 170 | 2. 9022 | 0984039 | .230537 | 14. 7077 |
| 170 | 4. 2412 | .150704 | .230537 | 15. 4132 |
| 180 | 5. 0353 | 177101 | .230484 | 15. 26 |
| 190 | 4. 0729 | .141899 | .230445 | 15. 1185 |
| 200 | 2. 8776 | .0919952 | .230417 | 13. 8746 |
| 200 | 3. 9849 | .132195 | .230417 | 14. 3973 |
| 210 | 4. 3286 | .139198 | .230396 | 13. 9575 |
| 220 | 4. 1921 | .122101 | .230381 | 12. 6427 |
| 230 | 3. 8937 | .111603 | .23037 | 12. 4419 |
| 250 | 3. 4498 | .109001 | .230356 | 13. 7164 |
| 260 | 4. 2361 | .134003 | .230351 | 13. 7327 |
| 270 | 4. 3373 | .141296 | .230348 | 14. 1425 |
| 280 | 4. 2843 | .128998 | .230346 | 13. 0714 |
| 290 | 4. 00481 | 128105 | .230344 | 13 887 |
| 300 | 4 0345 | 137901 | .230343 | 14. 619 |
| 310 | 3 6992 | .122299 | .230342 | 14. 353 |
| 310 | 4. 0849 | .141701 | .230342 | 15. 0597 |
| 330 | 3. 8624 | 138001 | .230341 | 15. 5115 |
| 330 | 5. 96249 | .212898 | .230341 | 15 5015 |
| 340 | 4. 0458 | .144898 | .230341 | 15. 5484 |

## C11

| Holding Time (Min) | Temp. o ( C) | Procedure | Batch Duration (Min) | Seed Conv. (%) |
|---|---|---|---|---|
| 125 | 50 | 3 | --- | --- |

```
P1= .333          P3= .95           P4= .236          GRAM / MIN.
VOLUM OF REACTR = 190 ML

T               L               P               C1              CONVERSION%
20              2. 64781        .0213013        .316472         2. 54206
40              2. 3442         .0821991         302102         11. 607
60              2. 72431        .193306          289855         24. 4799
80              2. 6182         .257996         .279418         35. 266
100.            4, 1541         .515503         .270523         45. 8723
120             2. 5382         .328896         .262943         49. 28
140             2. 9143         .4207           .256483         56. 2835
160             3. 0332          463204         .250977         60. 8467
180             3. 0082         .473            .246285         63. 6435
200             3. 0043         .475996         .242286         65. 3935
220             2. 9959         .468903         .238878         65. 5207
240             2. 69991        .427307         .235974         67. 07
260             3. 2159         .509796         .233499         67. 8907
280             3. 0242         ,4394           .231389         62 7923
300             3. 446          .482002         .229591         60. 9226
320             3 2351          .436104         .228059         59 1091
340             4. 0846          513397         .226754         55. 4307
360             1. 6912         .205101         .225641         53. 7471
380             1. 7133         .189705         .224693         49. 2783
```

# C12

| Holding Time (Min) | Temp. o ( C) | Procedure | Batch Duration (Min) | Seed Conv. (%) |
|---|---|---|---|---|
| 109 | 50 | 3 | --- | --- |

```
P1= .73          P2= 1.56        P3= .78806     GRAM / MIN
VOLUM OF REACTR = 336 ML

T               L               P               C1              CONVERSION
20              2.9449          .0242004        .258674         3.17687
40              3.2027          .178299         .255073         21.8257
60              3.5408          .399605         .252075         44.7713
80              3.0562          .424599         .249578         55 6661
100             3.0684          .470398         .2475           61.9412
120             2.9773          .466698          245769         63 7802
140             3.3261          .523201         .244328         64.3813
160             3.0677          .451401         .243126         60 522
180             3.09641         .470604         .24213          62.7697
220             3.0053          .406098         .240606         56.1613
240             3.057           .387497         .240029         52.8091
260             3.08469         .366997         .239549         49.6656
280             3.13281         .343704         .23915          45.8756
300             3.07201         .310005         .238817         42.2554
320             3.1568          .289902         .23854          38.4984
340             3.0729          .264298         .238309         36.6914
360             3.063           .254105         .238117         34.8397
380             3.0912          .255203         .237958         34.6944
400             3.0028          .247002         .237824         34.5873

BOTTOM
```

# C14

| Holding Time (Min) | Temp. o ( C) | Procedure | Batch Duration (Min) | Seed Conv. (%) |
|---|---|---|---|---|
| 106.5 | 50 | 3 | --- | --- |

```
P1= . 679          P2= 1. 566        P3= . 479        GRAM / MIN
VOLUM OF REACTR = 290 ML

T                   L                 P                C1                 CONVERSION.
20                  2. 1329           . 00370026       . 260648           . 665592
60                  3. 07671          . 00050354       . 257083           . 0636612
80                  2. 7741           . 0582962         255744            8. 21699
100                 2. 6353            1446             254634            21. 5487
120                 2. 2936           . 199402         . 253715           34. 2661
140                 2. 6321           . 305901         . 252953           45 9451
160                 2. 3816           . 302994         . 252322           50. 4209
180                 2. 96111          . 3871           . 251798           51. 9179
200                 2. 8336           . 376            . 251364           52 7893
220                 2. 8951           . 372696         . 251005           51. 2873
240                 3. 0145           . 376602         . 250707           49. 8312
260                 2. 909            . 341797         . 25046            46. 9122
280                 2. 7941           . 305405         . 250256           43. 6767
300                 2. 2486           . 222099         . 250086           39. 4954
320                 2. 9596           . 276497         . 249946           37. 3777
340                 2. 686            . 228302         . 249829           34. 0221
360                 2. 5987           . 207199         . 249733           31. 9269
380                 2. 56361          . 186302         . 249653           29. 1092
400                 2. 4299           . 167305         . 249587           27 5867
420                 2. 4859            1632            . 249532           26. 3095
440                 2. 6141           . 169296         . 249486           25. 9585
460                 2. 7081           . 179001         . 249448           26. 4978
480                 2. 996            . 194298         . 249417           26 0016
500                 3. 01              193199          . 249391           25. 737
520                 2. 5934           . 1689           . 24937            26. 1165
```

# C15

| Holding Time (Min) | Temp. o ( C) | Procedure | Batch Duration (Min) | Seed Conv. (%) |
|---|---|---|---|---|
| 112.7 | 50 | 3 | --- | --- |

```
P1=  66           P2= 1. 6          P3= . 8          GRAM / MIN
VOLUM OF REACTR = 345 ML


T               L               P              C1             CONVERSION%
20              2. 9313         . 00549317     . 210924       . 888456
40              2. 9535         . 0656967      . 211698       10. 5073
60              2. 8882         . 186302       . 212347       30. 3771
80              2. 9274         . 302895       . 21289        48 6022
100             2. 9663         . 368698       . 213344       58. 2606
110             3. 0403         . 395798       . 213543       60. 9638
120             3. 1083         . 410004       . 213725       61. 7178
130             3. 2279         . 443695       . 213891       64. 2646
140             3. 4284         . 472694       . 214044       64 415
153             3. 34029        . 451401       . 214223       63 083
161             3. 3861         . 471901       . 214323       65. 0253
170             3. 1808         . 431503       . 214427       63. 2556
180             3. 18549          449898       . 214534       65. 8325
193             2. 9652         . 3927         . 21466        61. 6959
200             3. 0318         . 396202       . 214722       60. 8612
210             3. 2657         . 4468         . 214803       63. 6936
220             3. 0883         . 410301       . 214878       61. 8287
230             3. 0593         . 394104       . 214947       59. 9318
240             3. 0617         . 398506       . 21501        60. 5361
250             3. 0037         . 379799       . 215067       58. 7927
260             3. 11051        . 379601       . 21512        56. 7304
270             3. 113          . 358498       . 215168       53. 5217
280             2. 9654         . 350494       . 215212       54. 9202
290             2. 9606         . 341301       . 215252       53. 5563
300             3. 10671        . 376801       . 215289       56. 3365
320             3. 1548         . 337097       . 215354       49. 6171
340             3. 1283         . 301201       . 215408       44. 6978
360             3. 1207         . 2836         . 215453       42. 1796
380             3. 1016         . 257103       . 215491       38. 4674
400             3. 1057         . 259102       . 215523       38. 7096
410             3. 09721        . 234001       . 215537       35. 0532
420             2. 9737         . 220902       . 215549       34. 4632
440             3. 1426         . 222099       . 215572       32. 7844
460             3. 04041        . 221001       . 21559        33. 7158
480             3. 0311         . 217796       . 215606       33. 3265
500             3. 08991        . 2174         . 215619       32. 6307
520             3. 06841          211807       . 21563        32. 0125
540             3. 1759         . 226799       . 215639       33. 1168
460             3. 0873         . 218102       . 21559        32 768
560             3 0873          . 218102         215647       32. 7595
580             3 0985          . 207497       . 215653       31. 0531
600             2. 908            1866           215659       29 7542
BOTTOM
```

## C19

| Holding Time (Min) | Temp. o ( C) | Procedure | Batch Duration (Min) | Seed Conv. (%) |
|---|---|---|---|---|
| 116.5 | 40 | 8 | 0.0 | 80 |

P1= 1. 58 P2= 1. 58 P3= 0. 803 GRAM / MIN
VOLUM OF REACTR = 360 ML

| TIME | LATEX | POLY. | FR. MONOMER | CONVERSION% |
|---|---|---|---|---|
| 10 | 2. 7729 | 0. 00340271 | 0. 228943 | 0. 535998 |
| 20 | 3. 4052 | 0. 00679016 | 0. 22889 | 0. 871186 |
| 33 | 2. 39841 | 0. 0245972 | 0. 228828 | 4. 4818 |
| 50 | 2. 6915 | 0. 0665894 | 0. 228757 | 10. 8153 |
| 72 | 3. 80481 | 0. 180008 | 0. 228679 | 20. 6887 |
| 90 | 2. 772 | 0. 162399 | 0. 228625 | 25. 6152 |
| 150 | 2. 4754 | 0. 207504 | 0. 228496 | 36. 6863 |
| 200 | 1. 8526 | 0. 164902 | 0. 228428 | 38. 9667 |
| 220 | 2. 21901 | 0. 190613 | 0. 228409 | 37. 608 |
| 240 | 2. 8494 | 0. 229401 | 0. 228392 | 35. 2502 |
| 260 | 2. 4576 | 0. 188889 | 0. 228378 | 33. 6543 |
| 300 | 2. 12781 | 0. 143295 | 0. 228356 | 29. 4908 |
| 330 | 2. 1624 | 0. 131394 | 0. 228344 | 26. 6102 |
| 380 | 2. 5126 | 0. 121704 | 0. 22833 | 21. 2138 |
| 422 | 2. 95729 | 0. 114288 | 0. 228322 | 16. 9263 |
| 480 | 1. 89159 | 0. 0628967 | 0. 228314 | 14. 5636 |
| 518 | 1. 9521 | 0. 0578003 | 0. 228311 | 12. 9688 |
| 540 | 2. 90819 | 0. 085495 | 0. 22831 | 12. 8764 |
| 560 | 2. 5038 | 0. 078598 | 0. 228309 | 13. 7496 |
| 580 | 2. 2757 | 0. 072403 | 0. 228308 | 13. 9355 |

## C21

| Holding Time (Min) | Temp. o ( C) | Procedure | Batch Duration (Min) | Seed Conv. (%) |
|---|---|---|---|---|
| 116.5 | 50 | 3 | --- | -- |

P1= 0.705 P2= 1.58 P3= 0.803 GRAM / MIN
VOLUM OF REACTR = 360 ML TEMP. =50 C

| TIME | LATEX | POLY. | FR. MONOMER | CONVERSION% |
|---|---|---|---|---|
| 25 | 2.002 | 0.0231934 | 0.228866 | 5.06197 |
| 51 | 2.2944 | 0.101914 | 0.228753 | 19.4176 |
| 79 | 1.7175 | 0.151703 | 0.228657 | 38.629 |
| 152 | 2.12239 | 0.267197 | 0.228492 | 55.6978 |
| 175 | 2.037 | 0.278504 | 0.228458 | 59.8456 |
| 200 | 2.19231 | 0.275696 | 0.228428 | 55.0527 |
| 291 | 2.01871 | 0.193405 | 0.228361 | 41.954 |
| 330 | 1.37871 | 0.115509 | 0.228344 | 36.6905 |
| 355 | 1.68379 | 0.117004 | 0.228336 | 30.4326 |
| 406 | 2.15141 | 0.133606 | 0.228325 | 27.1988 |
| 425 | 2.0125 | 0.128204 | 0.228321 | 27.9011 |
| 450 | 2.4382 | 0.157501 | 0.228318 | 28.2927 |
| 475 | 1.51691 | 0.1008 | 0.228315 | 29.1049 |
| 500 | 2.0527 | 0.143097 | 0.228313 | 30.5333 |
| 525 | 2.7601 | 0.178192 | 0.228311 | 28.2773 |
| 550 | 2.84869 | 0.169296 | 0.228309 | 26.0302 |
| 575 | 1.9323 | 0.105698 | 0.228308 | 23.9591 |
| 600 | 1.6097 | 0.0899048 | 0.228307 | 24.4636 |
| 625 | 2.1528 | 0.119797 | 0.228306 | 24.3738 |
| 640 | 2.65691 | 0.1633 | 0.228306 | 26.921 |

## C22

| Holding Time (Min) | Temp. o ( C) | Procedure | Batch Duration (Min) | Seed Conv. (%) |
|---|---|---|---|---|
| 116.5 | 50 | 3 | --- | --- |

P1= 0.705 P2= 1.58 P3= 0.803 GRAM / MIN
VOLUM OF REACTR = 360 ML
TEMP. =50 C

| TIME | LATEX | POLY. | FR. MONOMER | CONVERSION% |
|---|---|---|---|---|
| 20 | 2.4863 | 0.0294952 | 0.22889 | 5.18289 |
| 50 | 2.3315 | 0.172699 | 0.22876 | 32.3803 |
| 75 | 2.3808 | 0.260498 | 0.228669 | 47.8491 |
| 100 | 2.75569 | 0.372498 | 0.228599 | 59.1316 |
| 150 | 3.54759 | 0.571198 | 0.228496 | 70.4653 |
| 175 | 1.711 | 0.242996 | 0.228458 | 62.1646 |
| 210 | 2.17209 | 0.316895 | 0.228418 | 63.8714 |
| 225 | 0.798706 | 0.0960999 | 0.228404 | 52.6783 |
| 250 | 2.30721 | 0.26010 | 0.228385 | 49.3616 |
| 290 | 2.27251 | 0.212799 | 0.228361 | 41.0056 |
| 300 | 3.2446 | 0.362396 | 0.228356 | 48.9114 |
| 325 | 2.2486 | 0.193207 | 0.228346 | 37.6286 |
| 360 | 2.52341 | 0 233109 | 0.228335 | 40.4575 |
| 400 | 2.15779 | 0 1586 | 0.228326 | 32.1913 |
| 425 | 2.08171 | 0.144409 | 0.228321 | 30.3828 |
| 475 | 2.3676 | 0.169708 | 0.228315 | 31.395 |
| 500 | 2.5069 | 0.173401 | 0.228313 | 30.296 |
| 525 | 2.47501 | 0.166306 | 0.228311 | 29.4309 |
| 575 | 1.95949 | 0.120789 | 0.228308 | 26.9999 |
| 600 | 2.2791 | 0.136795 | 0.228307 | 26.2898 |
| 630 | 2.49771 | 0.148209 | 0.228306 | 25.9904 |
| 650 | 3.00681 | 0.188492 | 0.228306 | 27.4581 |
| BOTTOM | | | | |

```
C23

PUMP #1= .641     PUMP #2= 1.63     PUMP #3= .65
VOL OF REACTOR = 355 ML
TEMP.= 50  C

 SPACE TIME = 121.533721   MIN

#TIME#CONV%# DIA(A) #  RATE  # NUMBER # N.R.P.P #
■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■
 20   61.563  400     1.78E-4  9.98E 17  2.36E-1
 30   63.717  465     1.84E-4  9.13E 17  2.83E-1
 43   75.656  530     2.18E-4  8.27E 17  5.53E-1
 51   76.009  690     2.19E-4  4.30E 17  1.08E 0
 60   75.806  620     2.19E-4  6.75E 17  6.83E-1
 72   78.1370 930     2.26E-4  2.28E 17  2.30E 0
 90   79.699  910     2.30E-4  2.85E 17  2.02E 0
 113  82.525  910     2.38E-4  3.28E 17  2.11E 0
 132  82.304  990     2.38E-4  2.79E 17  2.45E 0
 150  81.621  1080    2.36E-4  2.30E 17  2.83E 0
 171  79.961  1200    2.31E-4  1.79E 17  3.27E 0
 191  82.211  1202    2.37E-4  1.86E 17  3.64E 0
 221  79.747  1260    2.30E-4  1.72E 17  3.37E 0
 241  80.7    1600    2.33E-4  8.64E 16  7.13E 0
 300  80.841  1600    2.33E-4  9.16E 16  6.78E 0
 321  81.33   2000    2.35E-4  4.76E 16  1.34E 1
 341  80.205  1900    2.32E-4  5.62E 16  1.06E 1
 511  33.733  1700    9.76E-5  6.04E 16  1.58E 0
 360  78.307  2500    2.26E-4  2.49E 16  2.12E 1
 570  31.57   1670    9.13E-5  6.00E 16  1.48E 0
 390  79.623  2000    2.30E-4  4.93E 16  1.16E 1
 420  73.049  2000    2.11E-4  5.02E 16  7.95E 0
 479  56.862  1860    1.64E-4  6.46E 16  3.00E 0
 515  49.623  1900    1.43E-4  6.15E 16  2.35E 0
 536  49.484  2300    1.43E-4  3.47E 16  4.14E 0
 600  51.586  2100    1.49E-4  4.58E 16  3.42E 0
```

```
C24

PUMP #1= .663     PUMP #2= 1.644     PUMP #3= .739
VOL OF REACTOR = 355 ML
TEMP.= 50  C

 SPACE TIME = 116.54629   MIN

#TIME#CONV%# DIA(A) #  RATE   # NUMBER # N.R.P.P # MOL.WT #
■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■
 30   27.185  540     8.13E-5  1.53E 18  5.17E-2   4459874
 45   46.795  680     1.40E-4  1.32E 18  1.03E-1   1613170
 61   56.701  650     1.69E-4  1.53E 18  1.29E-1   -
 80   62.472  800     1.86E-4  8.17E 17  3.10E-1   2476870
 101  64.247  970     1.92E-4  4.57E 17  5.98E-1   -
 121  65.128  990     1.94E-4  4.29E 17  6.62E-1   -
 140  65.79   1400    1.96E-4  1.51E 17  1.93E 0   4468949
 161  65.059  1200    1.94E-4  2.41E 17  1.17E 0   1462046
 188  62.858  990     1.89E-4  4.30E 17  5.99E-1   2898272
 221  59.789  1400    1.78E-4  1.52E 17  1.48E 0   -
 272  54.289  1400    1.62E-4  1.53E 17  1.17E 0   -
 300  49.724  1790    1.48E-4  7.41E 16  2.03E 0   -
 362  39.927  2330    1.19E-4  2.80E 16  4.17E 0   -
 380  37.21   2190    1.11E-4  3.14E 16  3.46E 0   744043
 420  33.717  1600    1.00E-4  7.30E 16  1.35E 0   536660
 450  33.797  2080    1.01E-4  3.33E 16  2.97E 0   710793
 480  33.763  1750    1.01E-4  5.58E 16  1.77E 0   -
 511  33.733  1700    1.00E-4  6.09E 16  1.62E 0   -
 540  32.534  1700    9.73E-5  5.87E 16  1.62E 0   -
 570  31.57   1670    9.44E-5  6.01E 16  1.53E 0   -
 601  30.391  1800    9.09E-5  4.62E 16  1.92E 0   -
 631  30.664  2110    9.17E-5  2.89E 16  3.10E 0   603336
 660  30.204  2400    9.03E-5  1.93E 16  4.56E 0   390000
```

## BC1

| Holding Time (Min) | Temp. o ( C) | Procedure | Batch Duration (Min) | Seed Conv. (%) |
|---|---|---|---|---|
| 73.4 | 50 | 6 | 40 | --- |

```
P1= 0.839       P2= 1.984       P3= 0.717       GRAM / MIN
VOLUM OF REACTR = 260 ML

T               L               P               C1              CONVERSION%
0               3.3165          0.334297        0.21            47.9992
10              3.3958          0.4282          0.213438        59.0791
20              3.6381          0.559403        0.216438        71.0423
30              3.5426          0.514298        0.219056        66.2733
40              3.6266          0.541702        0.221341        67.4838
50              3.91831         0.591904        0.223335        67.6389
70              3.92661         0 580399        0.226594        65.2321
90              3.8055          0.604698        0.229076        69.3663
112             2.89291         0.0480042       0.231128        7.17946
131             3.8065          0.471497        0.232468        53.2932
150             3.49821         0.4002          0.233502        48.9937
170             3.7979          0.378998        0.234337        42.5845
190             3.34731         0.287804        0.234974        36.5917
210             3.3859          0.249497        0.235458        31.2951
230             3.4427          0.216599        0.235827        26.6786
270             3.4081          0.160301        0.236322        19.9031
280             3.4297          0.159203        0.236469        19.635
290             3.4428          0.1586          0.236485        19.48
250             3.3757          0.182396        0.236108        22 8845
```

## Bc2

| Holding Time (Min) | Temp. o ( C) | Procedure | Batch Duration (Min) | Seed Conv. (%) |
|---|---|---|---|---|
| 84.69 | 50 | 6 | 30 | --- |

```
P1= 0.69        P2= 1.58         P3= 0.8         GRAM / MIN
VOLUM OF REACTR = 260 ML

T                L                P                C1               CONVERSION%
10               2.8495           0.217003         0.202757         37.5596
20               3.04961          0.299904         0.205207         47.9232
30               3.7253           0.419396         0.207384         54.2959
40               2.8954           0.352806         0.209319         58.2128
60               3.17281          0.424004         0.212566         62.8684
80               3.0042           0.418305         0.21513          64.7235
100              3.0966           0.431198         0.217155         64.1242
120              2.9851           0.415199         0.218754         63.5233
145              3.0164           0.393501         0.220288         59.2199
170              3.2178           0.408707         0.22143          57.3609
180              3.63229          0.427399         0.2218           53.0506
200              3.0831           0.333901         0.222422         48.6914
220              3.1695           0.318199         0.222913         45.0374
240              3.1629           0.274201         0.2233           38.8234
262              3.1884           0.2379           0.223633         33.3645
280              3.2148           0.216293         0.223848         30.0563
300              3.207            0.190598         0.224039         26.5274
320              3.0379           0.165604         0.22419          24.3153
340              3.0273           0.160896         0.224309         23.6943
366              3.2187           0.175896         0.224427         24.3501
380              3.0975           0.180901         0.224477         26.0169
400              3.08             0.18             0.224536         26.0278
410              3.0754           0.1726           0.22456          24.9923
410              3.0754           0.1726           0.22456          24.9923
```

# BC3

| Holding Time (Min) | Temp. (°C) | Procedure | Batch Duration (Min) | Seed Conv. (%) |
|---|---|---|---|---|
| 85.2 | 50 | 6 | 50 | --- |

P1= 0.7        P2= 1.57        P3= 0.78        GRAM / MIN
VOLUM OF REACTR = 260 ML

| T | L | P | C1 | CONVERSION% |
|---|---|---|---|---|
| 0 | 2.5604 | 0.305 | 0.2 | 59.561 |
| 10 | 3.1904 | 0.332298 | 0.203266 | 51.241 |
| 20 | 2.5722 | 0.270203 | 0.206171 | 50.9516 |
| 30 | 2.4889 | 0.281502 | 0.208754 | 54.18 |
| 40 | 3.0926 | 0.370499 | 0.211051 | 56.7543 |
| 50 | 3.1759 | 0.391403 | 0.213094 | 57.6343 |
| 61 | 3.1743 | 0.410869 | 0.215081 | 60.1801 |
| 70 | 3.1951 | 0.413895 | 0.216527 | 59.8266 |
| 80 | 3.3473 | 0.451103 | 0.217964 | 61.8297 |
| 90 | 3.1809 | 0.424599 | 0.219242 | 60.8844 |
| 100 | 3.1351 | 0.411995 | 0.220378 | 59.631 |
| 110 | 3.1117 | 0.408005 | 0.221389 | 59.226 |
| 120 | 2.93971 | 0.380707 | 0.222287 | 58.2602 |
| 130 | 3.0226 | 0.387299 | 0.223087 | 57.4371 |
| 140 | 3.1768 | 0.406799 | 0.223797 | 57.2183 |
| 150 | 3.5555 | 0.469902 | 0.22443 | 58.888 |
| 160 | 2.8822 | 0.341301 | 0.224992 | 52.6317 |
| 180 | 3.4207 | 0.384102 | 0.225936 | 49.6988 |
| 200 | 2.9996 | 0.304398 | 0.226683 | 44.7671 |
| 220 | 3.1191 | 0.285896 | 0.227274 | 40.3301 |
| 240 | 3.3466 | 0.288696 | 0.227741 | 37.8787 |
| 260 | 3.1305 | 0.237702 | 0.228111 | 33.2869 |
| 280 | 3.06201 | 0.212105 | 0.228403 | 30.3279 |
| 300 | 3.0411 | 0.179596 | 0.228634 | 25.97 |
| 320 | 3.0929 | 0.160507 | 0.228817 | 22.6799 |
| 340 | 3.2976 | 0.160599 | 0.228962 | 21.2707 |
| 260 | 3.0559 | 0.147301 | 0.228111 | 21.131 |
| 380 | 2.5055 | 0.122307 | 0.229166 | 21.3013 |

# BE4

| Holding Time (Min) | Temp. o ( C) | Procedure | Batch Duration (Min) | Seed Conv. (%) |
|---|---|---|---|---|
| 85 | 50 | 6 | 50 | --- |

P1= 0. 698 P2= 1. 535 P3= 0. 819 GRAM / MIN
VOLUM OF REACTR = 260 ML

| T | L | P | C1 | CONVERSION |
|---|---|---|---|---|
| 0 | 2. 905 | 0. 242302 | 0. 2 | 41. 7043 |
| 0 | 3. 1315 | 0. 258995 | 0. 2 | 41. 3532 |
| 11 | 3. 5314 | 0. 294998 | 0. 203477 | 41. 0542 |
| 21 | 3. 1136 | 0. 2855 | 0. 206271 | 44. 4534 |
| 31 | 3. 03021 | 0. 299202 | 0. 208755 | 47. 2994 |
| 40 | 3. 0913 | 0. 323601 | 0. 210755 | 49. 6696 |
| 50 | 3. 1548 | 0. 351799 | 0. 212743 | 52. 4165 |
| 60 | 3. 0738 | 0. 353699 | 0. 214511 | 53. 6426 |
| 70 | 3. 0962 | 0. 367401 | 0. 216082 | 54. 9152 |
| 80 | 3. 0362 | 0. 372604 | 0. 21748 | 56. 4284 |
| 90 | 3. 0805 | 0. 387497 | 0. 218723 | 57. 5113 |
| 100 | 3. 1667 | 0. 401604 | 0. 219828 | 57. 6908 |
| 120 | 3. 063 | 0. 383705 | 0. 221685 | 56. 5085 |
| 130 | 3. 113 | 0. 389397 | 0. 222463 | 56. 2285 |
| 141 | 3. 0988 | 0. 3778 | 0. 223218 | 54. 6183 |
| 150 | 2. 6572 | 0. 315003 | 0. 223768 | 52. 9774 |
| 160 | 3. 14281 | 0. 380303 | 0. 224315 | 53. 9453 |
| 170 | 3. 1235 | 0. 461701 | 0. 224801 | 65. 7539 |
| 182 | 3. 1235 | 0. 347595 | 0. 225313 | 49. 3908 |
| 191 | 3. 1189 | 0. 334702 | 0. 225653 | 47. 5571 |
| 201 | 3. 2274 | 0. 329605 | 0. 225991 | 45. 1908 |
| 211 | 2. 6007 | 0. 255104 | 0. 226291 | 43. 3471 |
| 230 | 3. 2905 | 0. 287499 | 0. 226773 | 38. 5285 |
| 250 | 3. 1498 | 0. 241402 | 0. 227177 | 33. 7359 |
| 270 | 3. 848 | 0. 255699 | 0. 227496 | 29. 2092 |
| 290 | 3. 0106 | 0. 174301 | 0. 227749 | 25. 421 |
| 310 | 3. 1249 | 0. 1633 | 0. 227948 | 22. 9252 |
| 330 | 2. 9749 | 0. 155899 | 0. 228106 | 22. 9739 |
| 350 | 2. 9256 | 0. 155197 | 0. 228231 | 23. 2431 |
| 370 | 2. 3954 | 0. 124703 | 0. 22833 | 22. 8 |
| 390 | 3. 0199 | 0. 156899 | 0. 228408 | 22 7466 |
| 410 | 3 035 | 0. 176598 | 0. 228469 | 25. 4682 |
| 430 | 3. 0438 | 0. 204605 | 0. 228518 | 29 4158 |

## BC5

| Holding Time (Min) | Temp. (°C) | Procedure | Batch Duration (Min) | Seed Conv. (%) |
|---|---|---|---|---|
| 116.5 | 50 | 6 | 50 | --- |

```
P1= 0. 7          P2= 1. 57        P3= 0. 82        GRAM / MIN
VOLUM OF REACTP = 360 ML

T                 L                P                C1               CONVERSION%
0                 1. 07428         0. 259171        0. 255           94. 6081
10                2. 77051         0. 644211        0. 252659        92. 031
20                3. 4548          0. 788712        0. 25051         91. 1317
30                2. 74446         0. 621552        0. 248539        91. 1227
40                2. 91692         0. 664398        0. 246729        92. 3177
50                2. 9093          0. 652207        0. 245068        91. 4766
60                2. 9818          -0. 00991821     0. 243544        -1. 36577
70                2. 94556         0. 658997        0. 242145        92. 3933
80                2. 9554          0. 671097        0. 240861        94. 2763
90                2. 9122          0. 643005        0. 239683        92. 1205
100               3. 0054          0. 65329         0. 238602        91. 1024
110               2. 81911         0. 621109        0. 237609        92. 7242
130               2. 91808         0. 630783        0. 235863        91. 6482
150               2. 8802          0. 625702        0. 234392        92. 6834
170               3. 4991          0. 749603        0. 233153        91. 8829
190               3. 2088          0. 696396        0. 232109        93. 502
210               2. 7258          0. 579697        0. 23123         91. 9734
230               2. 9008          0. 614197        0. 23049         91. 8623
250               1. 99352         0. 418991        0. 229867        91. 4344
274               3. 28009         0. 689591        0. 229247        91. 707
290               2. 7856          0. 585907        0. 228899        91. 8896
310               3. 0564          0. 639206        0. 228527        91. 5155
330               2. 8535          0. 5961          0. 228213        91. 538
350               2. 87425         0. 598251        0. 227948        91. 3108
370               2. 8555          0. 595886        0. 227726        91. 6366
420               2. 8372          0. 584213        0. 227311        90. 5859
440               2. 96329         0. 612091        0. 227189        90. 9191
460               3. 15419         0. 640701        0. 227086        89. 4494
483               3. 1559          0. 637787        0. 226988        89. 0328
500               2. 94251         0. 593506        0. 226927        88. 8838
523               3. 0965          0. 602295        0. 226857        85. 7406
```

BC6

| Holding Time (Min) | Temp. o ( C) | Procedure | Batch Duration (Min) | Seed Conv. (%) |
|---|---|---|---|---|
| 116.5 | 50 | 6 | 20 | --- |

```
P1= 0.7          P2= 1.62          P3= 0.77          GRAM / MIN
VOLUM OF REACTR = 360 ML

T                L                 P                 C1                CONVERSION%
0                0.7827            0.0645905         0.229             36.0361
14               2.00969           0.26619           0.228721          57.9103
34               2.433             0.425995          0.228377          76.6674
45               2.20221           0.422608          0.228211          84.0896
60               2.043             0.412506          0.228009          88.5545
80               2.1593            0.437897          0.227777          89.0326
100              2.2704            0.455902          0.227581          88.2334
121              2.4565            0.584702          0.227409          104.667
141              2.04131           0.398605          0.227271          85.9192
180              1.9238            0.376297          0.227063          86.1442
240              1.97521           0.378601          0.226851          84.4946
880              1.96291           0.367004          0.226539          82.5334
900              1.96181           0.355606          0.226538          80.015
940              1.9594            0.358597          0.226538          80.7873
960              2.14681           0.39151           0.226538          80.5025
1000             1.8927            0.345505          0.226538          80.5809
1060             2.20361           0.410812          0.226538          82.294
1080             1.45221           0.262405          0.226538          79.7634
1102             1.8082            0.322296          0.226537          78.6809
1120             1.8055            0.326996          0.226537          79.9477
```

## BC7

| Holding Time (Min) | Temp. o ( C) | Procedure | Batch Duration (Min) | Seed Conv. (%) |
|---|---|---|---|---|
| 115.5 | 50 | 5 | 0.0 | --- |

```
P1= 0. 705       P2= 1. 562       P3= 0. 805       GRAM / MIN
VOLUM OF REACTR = 355 ML

-------------------------------------------------------------------

TIME          LATEX          POLY.           FR. MONOMER      CONVERSIONA
12            1. 1143        0. 0467987      0. 202909        20. 698
22            1. 83289       0. 183395       0. 205113        48. 7921
35            1. 7916        0. 270294       0. 207707        72. 6351
40            1. 66031       0. 272904       0. 208629        78. 7853
52            1. 7029        0. 310593       0. 210687        86. 5697
65            1. 6182        0. 305496       0. 212688        88. 7632
72            1. 63159       0. 307587       0. 213675        88. 227
85            1. 2011        0. 225494       0. 215358        87. 176
100           1. 6588        0. 314896       0. 217079        87. 4492
120           1. 50259       0. 286392       0. 219052        87. 0108
140           1. 8154        0. 343903       0. 220711        85. 8301
167           1. 81641       0. 346298       0. 222541        85. 6699
186           2. 0522        0. 392212       0. 223595        85. 4752
216           1. 31499       0. 247192       0. 224943        83. 5682
248           1. 3638        0. 255005       0. 226043        82. 7192
270           1. 8559        0. 345688       0. 226641        82. 1849
300           1. 44119       0. 266495       0. 227293        81. 3543
320           1. 93701       0. 355606       0. 227643        80. 6461
375            ----23         0------        0. 228343        80
397               ---             ----       0. 228542        79
421           1. 30669       0. 235901       0. 22872         78. 9321
470           1. 5622        0. 279801       0. 228987        78. 2172
486           2. 4057        0. 440201       0. 229052        79. 8867
486           2. 1263        0. 414          0. 229052        85. 0042
510           1. 57021       0. 281403       0. 229135        78. 2133
```

# BC8

| Holding Time (Min) | Temp. o ( C) | Procedure | Batch Duration (Min) | Seed Conv. (%) |
|---|---|---|---|---|
| 116.5 | 40 | 3 | --- | --- |

```
P1= 0. 705      P2= 1. 58       P3= 0. 803      GRAM / MIN
VOLUM OF REACTR = 360 ML

----------------------------------------------------------------

TIME            LATEX           POLY.           FR. MONOMER     CONVERSION%
20              2. 69071        0. 084198       0. 22889        13. 6713
30              2. 06479        0. 098999       0. 228842       20. 9517
40              2. 3044         0. 148407       0. 228798       28. 1479
60              3. 2719         0. 286301       0. 22872        38. 2578
82              2. 692          0. 3069         0. 228648       49. 8603
100             2. 81191        0. 342407       0. 228599       53. 2683
120             1. 97411        0. 278305       0. 228552       61. 683
142             1. 8392         0. 251999       0. 228509       59. 9605
160             2. 22701        0. 312103       0. 22848        61. 338
204             1. 91501        0. 264603       0. 228424       60. 4897
240             2. 03391        0. 255798       0. 228392       55. 0663
300             2. 89041        0. 30751        0. 228356       46. 5894
360             2. 3474         0. 204804       0. 228335       38. 2101
392             2. 03751        0. 154907       0. 228327       33 2978
430             2. 33749        0. 155106       0. 228321       29. 0624
462             3. 24199        0. 183701       0. 228316       24. 8177
490             2. 84059        0. 141892       0. 228314       21. 8784
563             2. 6776         0. 112198       0. 228309       18. 3534
600             2. 938          0. 123489       0. 228307       18. 4102
632             2. 15331        0. 0948944      0. 228306       19. 3027
660             2. 1525         0. 0921936      0. 228306       18. 7604
690             3. 2603         0. 133103       0. 228305       17. 8819
720             3. 53261        0. 139206       0. 228305       17 2603
```

```
BC8

PUMP [redacted]= .705     PUMP [redacted]= 1.58     PUMP [redacted]= .803
VOL OF REACTOR = 360 ML
TEMP.= 40  C

 SPACE TIME = 116.580311   MIN

#TIME#CONV%# DIA(A) #  RATE   # NUMBER # N.R.P.P #
■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■
 120  61.67    1650    1.93E-4   9.76E 16   3.23E 0
 142  59.96    1510    1.88E-4   1.27E 17   2.30E 0
 160  61.34    1600    1.92E-4   1.07E 17   2.91E 0
 204  60.49    1680    1.89E-4   9.26E 16   3.24E 0
 240  55.07    2200    1.72E-4   4.15E 16   5.79E 0
 300  46.59    2010    1.46E-4   5.34E 16   3.29E 0
 360  38.21    1600    1.19E-4   8.68E 16   1.66E 0
 392  33.3     1700    1.04E-4   6.30E 16   1.99E 0
 430  29.06    1850    9.12E-5   4.27E 16   2.57E 0
 462  24.82    1900    7.78E-5   3.36E 16   2.78E 0
 490  21.88    1850    6.86E-5   3.21E 16   2.57E 0
 563  18.35    2100    5.75E-5   1.84E 16   3.76E 0
 600  18.41    2050    5.77E-5   1.98E 16   3.49E 0
 632  19.3     2200    6.05E-5   1.68E 16   4.32E 0
 660  18.76    2400    5.88E-5   1.26E 16   5.61E 0
 690  17.88    2290    5.61E-5   1.38E 16   4.87E 0
 720  17.3     2300    5.42E-5   1.32E 16   4.94E 0
```

```
BC9

PUMP [redacted]1= .705     PUMP [redacted]2= 1.53     PUMP [redacted]3= .803
VOL OF REACTOR = 360 ML
TEMP.= 50  C

 SPACE TIME = 116.580311    MIN

#TIME#CONV%# DIA(A) #  RATE   # NUMBER # N.R.P.P #
###############################################
 0    66.68   1000    2.09E-4   4.36E 17   7.32E-1
 10   69.66   800     2.18E-4   8.48E 17   4.32E-1
 20   73.3    770     2.30E-4   9.47E 17   4.63E-1
 40   80.38   818     2.52E-4   7.82E 17   8.37E-1
 60   80.95   900     2.54E-4   5.86E 17   1.15E 0
 70   79.21   1250    2.48E-4   2.19E 17   2.77E 0
 90   78.49   1080    2.46E-4   3.40E 17   1.71E 0
 112  79.46   1100    2.49E-4   3.21E 17   1.92E 0
 131  79.88   1090    2.50E-4   3.30E 17   1.92E 0
 200  72.6    1550    2.27E-4   1.15E 17   3.65E 0
 225  74.8    1940    2.34E-4   5.89E 16   8.04E 0
 255  77.46   1550    2.43E-4   1.15E 17   4.76E 0
 280  78.82   2770    2.47E-4   2.01E 16   2.95E 1
 300  75.03   2000    2.35E-4   5.37E 16   8.92E 0
 331  74.88   1700    2.35E-4   8.76E 16   5.43E 0
 351  74.95   2400    2.35E-4   3.11E 16   1.53E 1
 375  75.69   2250    2.37E-4   3.77E 16   1.31E 1
 42   77.83   2250    2.44E-4   3.77E 16   1.48E 1
 450  74.78   2950    2.34E-4   1.67E 16   2.82E 1
 475  76.2    4000    2.39E-4   6.71E 15   7.62E 1
 500  75.12   3000    2.35E-4   1.59E 16   3.02E 1
 525  72.24   3200    2.26E-4   1.31E 16   3.15E 1
 553  77.5    3800    2.43E-4   7.81E 15   7.04E 1
 600  73.86   10000   2.31E-4   4.30E 14   1.04E 3
```

# BC 10

| Holding Time (Min) | Temp. o ( C) | Procedure | Batch Duration (Min) | Seed Conv. (%) |
|---|---|---|---|---|
| 116.5 | 50 | 6 | 30 | --- |

```
P1= 0.705        P2= 1.58         P3= 0.803        GRAM / MIN
VOLUM OF REACTR = 360 ML

-----------------------------------------------------------------

TIME          LATEX          POLY.          FR. MONOMER      CONVERSION
0             2.63649        0.390289       0.229            64.6435
21            2.40869        0.438995       0.228885         79.6272
31            2.2594         0.44101        0.228837         85.2959
41            2.17531        0.438599       0.228793         88.1258
50            2.45369        0.478897       0.228757         85.3195
70            2.8367         0.53479        0.228685         82.4388
90            2.24391        0.418701       0.228625         81.6159
110           2.62489        0.5009         0.228574         83.4857
150           3.04221        0.579407       0.228496         83.3522
170           2.60069        0.459396       0.228465         77.3176
180           2.6545         0.473602       0.228452         78.0975
190           2.78909        0.4841         0.22844          75.9803
210           3.31149        0.57869        0.228418         76.5053
255           3.1259         0.5383         0.228381         75.403
306           2.8598         0.456299       0.228354         69.8724
326           2.3649         0.405396       0.228346         75.0713
375           2.7188         0.457596       0.228331         73.7124
425           2.8056         0.478394       0.228321         74.6815
450           3.04241        0.526199       0.228318         75.7519
475           3.07141        0.564606       0.228315         80.5143
525           3.0632         0.524307       0.228311         74.9694
550           2.4531         0.429596       0.228309         76.7048
575           3.0807         0.533005       0.228308         75.7809
650           2.24201        0.406494       0.228306         79.4147
675           3.17589        0.544495       0.228305         75.0953
BOTTOM
```

```
BC18

PUMP ■1= .705     PUMP ■2= 1.58     PUMP ■3= .803
VOL OF REACTOR = 360 ML
TEMP.= 50  C

 SPACE TIME = 116.580311   MIN

#TIME#CONV%# DIA(A) #  RATE  # NUMBER # N.R.P.P #
■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■
 0     64.64    1400    2.02E-4   1.59E 17   1.83E 0
 21    79.63    1190    2.49E-4   2.54E 17   2.45E 0
 31    85.3     1090    2.67E-4   3.28E 17   2.82E 0
 41    88.13    760     2.76E-4   9.65E 17   1.22E 0
 50    85.32    850     2.67E-4   6.92E 17   1.34E 0
 70    82.44    1300    2.58E-4   1.94E 17   3.86E 0
 90    81.62    1450    2.56E-4   1.40E 17   5.06E 0
 110   83.49    1050    2.62E-4   3.67E 17   2.19E 0
 150   83.35    1200    2.61E-4   2.46E 17   3.24E 0
 170   77.32    1400    2.42E-4   1.56E 17   3.48E 0
 190   75.98    1600    2.38E-4   1.04E 17   4.81E 0
 210   76.51    1700    2.40E-4   8.74E 16   5.95E 0
 255   75.4     3000    2.36E-4   1.59E 16   3.07E 1
 306   69.87    1820    2.19E-4   7.18E 16   5.15E 0
 326   75.07    3080    2.35E-4   1.47E 16   3.26E 1
 375   73.71    2750    2.31E-4   2.07E 16   2.16E 1
 425   74.68    3200    2.34E-4   1.31E 16   3.58E 1
 450   75.75    3500    2.37E-4   1.00E 16   4.97E 1
 475   80.51    3600    2.52E-4   9.15E 15   7.21E 1
 525   74.67    3350    2.34E-4   1.14E 16   4.11E 1
 550   76.71    3550    2.40E-4   9.59E 15   5.48E 1
 575   75.78    3800    2.37E-4   7.83E 15   6.38E 1
 650   79.41    4800    2.49E-4   3.86E 15   1.59E 2
```

## SC1

| Holding Time (Min) | Temp. °C | Procedure | Batch Duration (Min) | Seed Conv. (%) |
|---|---|---|---|---|
| 116.5 | 50 | 8 | --- | 80 |

```
P1= 0. 705       P2= 1. 58        P3= 0. 803       GRAM / MIN
VOLUM OF REACTR = 360 ML

                                                   TIMP. =50 C
------------------------------------------------------------------

TIME          LATEX          POLY          FR. MONOMER     CONVERSION%
0             2. 42859       0. 5010       0. 229          90. 1
10            2. 72131       0. 525        0. 228943       84. 3
20            2. 3971        0. 457703     0. 22889        83. 4202
30            1. 85521       0. 357208     0. 228842       84. 1382
40            2. 0977        0. 397293     0. 228798       82. 7782
70            2. 4408        0. 467301     0. 228685       83. 7194
100           2. 12819       0. 427994     0. 228599       87. 9738
123           2. 25299       0. 4375       0. 228546       84. 9661
142           2. 4503        0. 471298     0. 228509       84. 1729
162           2. 2283        0. 430206     0. 228477       84. 5008
197           1. 9274        0. 372589     0. 228432       84. 6257
270           2. 204         0. 418396     0. 228372       83. 1255
320           2. 23039       0. 415695     0. 228348       81. 6201
360           2. 2442        0. 424103     0. 228335       82. 7632
400           2. 6534        0. 507401     0 228326        83. 7518
450           1. 728         0. 325897     0 228318        82. 6034
480           2. 73149       0. 491898     0. 228314       78. 8754
500           2. 4854        0. 480698     0. 228313       84. 7123
560           2. 2403        0. 4207       0. 228309       82. 2517
580           2. 19051       0. 414505     0. 228308       82. 8828
600           2. 7236        0. 509506     0. 228307       81. 9382
640           2. 7986        0. 527008     0. 228306       82. 482
660           2. 5126        0. 470703     0. 228306       82. 0553
```

```
SC2

PUMP ■1= .705     PUMP ■2= 1.58     PUMP ■3= .303
VOL OF REACTOR = 360 ML
TEMP.= 50  C

 SPACE TIME = 116.580311    MIN

#TIME#CONV%# DIA(A) #  RATE  # NUMBER # N.R.P.P #
■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■
 11   71.62   773    2.24E-4  9.38E 17  4.29E-1
 20   67.22   832    2.10E-4  7.57E 17  4.32E-1
 40   63.03   890    1.97E-4  6.21E 17  4.38E-1
 40   80.38   818    2.52E-4  7.82E 17  8.37E-1
 60   59.06   900    1.85E-4  6.04E 17  3.81E-1
 82   63.8    940    2.00E-4  5.26E 17  5.34E-1
 110  59.73   1000   1.87E-4  4.39E 17  5.38E-1
 120  60.33   1100   1.89E-4  3.30E 17  7.35E-1
 141  60.33   1130   1.89E-4  3.04E 17  7.97E-1
 163  59.89   1130   1.87E-4  3.04E 17  7.83E-1
 180  55.14   1150   1.73E-4  2.90E 17  6.75E-1
 201  52.53   1230   1.64E-4  2.38E 17  7.40E-1
 272  43.19   1560   1.35E-4  1.05E 17  1.25E 0
 300  40.28   1660   1.26E-4  8.19E 16  1.51E 0
 330  34.87   1900   1.09E-4  4.73E 16  2.26E 0
 360  30.54   2350   9.58E-5  2.19E 16  4.28E 0
 390  29.91   2040   9.38E-5  3.27E 16  2.80E 0
 420  23.35   2100   7.32E-5  2.34E 16  3.05E 0
 455  21.57   2350   6.76E-5  1.54E 16  4.28E 0
 540  16.91   2800   5.30E-5  7.16E 15  7.25E 0
 571  16.59   2080   5.20E-5  1.71E 16  2.97E 0
 600  18.47   2150   5.79E-5  1.72E 16  3.28E 0
 360  18.41   2410   5.77E-5  1.22E 16  4.62E 0
 695  16.97   2250   5.32E-5  1.38E 16  3.76E 0
 720  17.47   2260   5.48E-5  1.40E 16  3.81E 0
```

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