SEEDED EMULSION POLYMERIZATION OF VINYL ACETATE

by

Jian Wang

A Master's Thesis
Submitted in partial fulfilment of the
requirements for the award of
MASTER OF PHILOSOPHY
of the
Loughborough University of Technology

February 1991

Supervisor: Professor B. W. Brooks
Director of Research: Professor B. A. Buffham

To my parents
To my motherland

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to my supervisor Professor B. W. Brooks for his much valued guidance, suggestions and encouragement throughout this work.

My thanks also to Professor B. A. Buffham, and Dr P. Rice for their encouragement and help in this study

I would also like to thank my friends and colleagues, especially Dr Y. Lü, Dr G. Subramanian, Dr M. Ronnier Luo, Mr G. Zhang, Mr B. Han, Mr R. Wang, Mr J. Zhang, and Mr X. Yan for their encouragement and help.

My special thanks to Mr A. Milne, Mr P. Jethwa, Mr. D. L. Smith, and Mr H. Clayton for their technical assistance. My thanks also to Mr J. S. Bates for his most valued assistance in all the photographic work.

I also wish to express my sincere thanks to Mr S. S. Dhillon, the British Council Regional Officer, for his help during my staying in Loughborough.

Finally, my grateful thanks to the Chinese Government and the British Council for their financial support during my study.

SYNOPSIS

The study of seeded emulsion polymerization of vinyl acetate in the absence of emulsifiers, with potassium persulfate as an initiator has been conducted in order to investigate the kinetics and mechanism of particle nucleation. Poly(vinyl acetate) latex particles are stabilized by the ionic end groups from decomposition of initiator. The polymerization behaviour of vinyl acetate in the water phase has been clarified.

The variation of the polymerization rate with changes in initiator concentration, monomer-polymer ratio, and stirring speed were determined. The polymerization rate of seeded emulsion polymerization of vinyl acetate is dependent on the initiator concentration to the 0.60 ± 0.05 power, however, it is independent of the monomer-polymer ratio. There was no significant change in polymerization rate when the stirring rate was changed from 50 to 150 rpm, but, the polymerization rate was considerably reduced when the stirring rate was increased to 300 rpm.

New small particles were formed in the system where the monomer-polymer ratio was substantial large (that is the system containing a small amount of seed particles).

The emulsifier-free emulsion polymerization of vinyl acetate in the absence of seed particles was also investigated. It was found that the polymerization rate is proportional to the 0.69 power of initial monomer concentration.

Keywords: Emulsion, Polymerization, Latex, Seed, Emulsifier-free, Vinyl acetate, Kinetics.

CONTENTS

NOMENCLATURE

a:	Radius of the sphere.
C:	Polymerization conversion (%).
D_p:	The diameter of latex particles (μm).
D_{seed}:	The diameter of seed particles (μm).
D_{theory}:	The theoretical diameter of latex particles (μm).
e:	The fundamental electronic charge.
I:	Ionic strength
[I]:	Initiator concentration (g-mole/l-H_2O).
M_o:	Monomer concentration (g-mole/l-H_2O).
N:	Particle number (/l-H_2O).
N_A:	Avogadro's number.
R_f:	The rate of coagulation.
R_i:	The rate of radical generation.
R_p:	Polymerization rate (g-mole/s·l-H_2O).
$W_{monomer}$:	The weight of monomer (g).
W_{seed}:	The weight of seed latex (g).
ε:	Dielectric constant of the medium.
Ψ_r:	Surface potential of a distance (r-a) from the surface of the sphere.
Ψ_s:	Electrostatic surface potential.

Chapter 1. Introduction

Kinetic and mechanism studies of the emulsion polymerization of vinyl acetate and vinyl acetate copolymers are of great interest due to the industrial importance of the latexes produced. It has been pointed out that the emulsion polymerization of vinyl acetate, which is a hydrophilic monomer, takes place mainly in the water phase[1-3]. Patsiga *et al*[1] have investigated this point from the rates of the seeded polymerization of vinyl acetate and styrene dilatometrically using the poly(vinyl acetate) particles as seed. It was concluded from their results that the initiation and most of the polymerization of vinyl acetate take place in the water phase, and that unstable microparticles and growing polymers are swept up by the larger particles. Several other research groups[4-6,9], however, have indicated that beyond the particle nucleation period of emulsion polymerization, most polymerization takes place in the monomer-swollen polymer particles.

The kinetics of the emulsion polymerization of vinyl acetate have been studied thoroughly by a number of researchers in recent years[1-20]. It is clear from these results that it does not follow the kinetics derived by Smith and Ewart for styrene[26]. In addition, the experimental results differ widely in different papers, and are contradictory in many respects; however, no group of researchers used exactly the same experimental conditions.

Chang *et al*[20] summarized features of the vinyl acetate emulsion polymerization.

(a) The rate of polymerization is approximately zero order with respect to monomer concentration at least from 20 to 85% conversion.

(b) In unseeded polymerization, the number of particles is roughly independent of conversion after 30% conversion.

(c) The polymerization rate depends on the particle concentration to about 0.2 power.

(d) The dependence of the polymerization rate on the emulsifier concentration is small with a maximum of 0.25 power.

(e) The molecular weights are independent of all variables and mainly depend on chain transfer to monomer.

The major disagreements in the emulsion polymerization of vinyl acetate are on the order of dependence of the rate on initiator concentration which ranges from 0.5 to 1.0 and, in unseeded polymerizations, the dependence of the particle concentration on the initiator concentration, which varies from zero to 1.2. These differences appear to be genuine since the induction periods are similar and the rates of comparable order of magnitude. Table 1 is a summary of different results reported by various researchers. Only those dealing with the potassium persulfate and sodium lauryl sulfate system are listed in the table. The polymerization conditions varied significantly for different studies. The first significant variable was temperature. The second variable was the monomer-water phase ratio.

Table 1. Results of Previous Investigations of Vinyl Acetate Emulsion Polymerization

Investigators	$K_2S_2O_8$ range ($\times 10^3$M)	Temp (^{0}C)	Reaction rate order on initiator	Particle Number order on initiator
Priest[50]	0.12-0.16	50	--	0.0
Patsiga *et al*[2]	0.8	60	0.8-1.0[a]	--
Dunn *et al*[6]	0.185-1.48	60	0.64	0.35
Gershberg[59]	1.0-30.0	50	0.6	--
Dunn *et al*[60]	0.1-0.8	60	0.6-0.9	0.6-0.9
Litt *et al*[7]	0.25-2.0	60	1.0	1.2
Nomura *et al*[12]	4.62	50	0.5	0.0
Friis *et al*[16]	0.5-4.0	50	0.5	0.0
Chang *et al*[20]	0.10-1.0	60	0.6[a]	--

a) Seeded polymerization

A number of models have also been proposed to interpret the kinetics and other features of vinyl acetate emulsion polymerization.

Litt *et al*[7] and Stannett *et al*[8] postulated that much of the polymerization took place in the aqueous-phase.

Harriott[9], based on the assumption of equilibrium distribution of free radicals in the heterogeneous system, derived a very simple rate expression. His model, which was tested by Trivedi *et al*[10], predicts a first-order dependency of the polymerization rate on the monomer concentration in the latex particle. Harriott stated that polymerization takes place in the polymer-phase (monomer-polymer particles).

Harada *et al*[11], Nomura *et al*[12-14] and Chern *et al*[15] considered the transport of monomer-unit free radicals out of the latex particles into the aqueous phase. Kinetic models have been developed. Reasonable agreement between the model predictions and experimental data were observed.

Friis *et al*[16,17] studied the emulsion polymerization of vinyl acetate using Ugelstad's model[18]. They indicated that the linearity of the conversion-versus-time curve is due to the decrease of the desorption rate constant and the termination rate constant with increasing monomer conversion.

Zollars[19] studied the reaction kinetics of vinyl acetate emulsion polymerization and developed an empirical model for particle number and polymerization rate under various reaction conditions.

Chang *et al*[20] investigated the kinetics of the seeded emulsion polymerization of vinyl acetate thoroughly and derived the most comprehensive kinetic model for the seeded emulsion polymerization of vinyl acetate considering a sequence of elementary reactions involved in the polymerization. The unique feature of their model is that the chain transfer to monomer reaction generates a rather stable monomer-unit free radicle. This monomer-unit free radical can then diffuse easily out of the latex particles into the aqueous phase.

Although these publications have dealt with the kinetics of vinyl acetate emulsion polymerization, none of them are perfect, most researchers have neglected formation of new particles beyond interval I (the particle nucleation period) and during seeded emulsion polymerization. The formation of new particles during the seeded emulsion polymerization of vinyl acetate in the presence of a small amount of seed particles have been identified by Hayshi *et al*[3]. The purpose of this study is to examine the formation of new particles during the seeded emulsion polymerization of vinyl acetate in the absence of emulsifier, and clarify the polymerization behaviour of vinyl acetate.

Chapter 2. Literature Survey

2-1. Introduction

The aim of this literature survey is to review the progressing history of emulsion polymerization.

The systematical study of emulsion polymerization is originated in 1940s. The most important qualitative theory of emulsion polymerization which has appeared in the literature is undoubtedly that of Harkins. He[21-24] interpreted the reaction mechanism and physical concept of emulsion polymerization for insoluble monomers in water (such as styrene) qualitatively. Based on Harkins theory, Smith-Ewart[25-27] proposed a quantitatively theory for emulsion polymerization. Their theory is called as classical theory of emulsion polymerization.

Since the establishment of Harkins, Smith-Ewart classical theory of emulsion polymerization, it becomes very active to study emulsion polymerization, and a lot of papers have been published, and then the classical theory of emulsion polymerization has been revised and developed. Gardon[28], Harada *et al*[29], Parts *et al*[30], and Sundberg *et al*[31] derived different mathematical equation for the emulsion polymerization stage I, respectively. Stockmayer[32] and O'Toole[33] have given a general solution to the Smith-Ewart recurrence equation for emulsion polymerization stage II using mathematical method. A mathematical treatment for stage II was also given by Ugelstad *et al*[34], which based on the stationary assumption, and Gardon[35], which based on the non-stationary assumption. Hui *et al*[37], and Friis *et al*[37,38] emphatically studied the Trommsdorff-effect[39], i.e. "gel-effect" during their investigation of stage III of emulsion polymerization.

Roe[40], Fitch *et al*[41], Friis *et al*[16], and Goodall *et al*[42] studied the emulsion polymerization of more water-soluble monomers, and proposed a oligomer mechanism of particle formation during the emulsion polymerization of more water-soluble monomers.

Min and Ray[43-46] have done a lot of work on the aspect of establishment of mathematical models of emulsion polymerization since 1974. A comprehensive mathematical model of emulsion polymerization has been proposed. Reasonable agreement between the model predictions and experimental data is observed for some monomers.

2-2. Description of Polymerization Process

Emulsion polymerization is one of several methods producing polymers used in industry. Emulsion polymerization which is a form of addition polymerization reaction is a process which involves the combination of several small molecules (monomers) to form a large molecule without the elimination of any molecules in the process. At present many monomers (e.g. styrene, acrylonitrile, vinyl acetate, vinyl chloride, methyl methacrylate, etc.) are polymerized by emulsion polymerization.

Emulsion polymerization is one of the four commonly used polymerization techniques: bulk (mass), solution, suspension, and emulsion[70,71].

2-2-1. Bulk Polymerization

Bulk or mass polymerization is a process in which the monomer is polymerized in bulk form (usually liquid, but occasionally gaseous). This polymerization, which involves only the pure monomer and catalyst, if it is required, offers the simplest process with a minimum of contamination of the product. However, bulk polymerization is difficult to control due to the characteristics radical chain polymerization. Their highly exothermic nature, the high activation energies involved, and the tendency toward the gel effect combine to make heat dissipation difficult. Bulk polymerization requires careful temperature control. Further, there is also the need for strong and elaborate stirring equipment since the viscosity of the reaction system increases rapidly at relatively low conversion.

2-2-2. Solution Polymerization

Solution polymerization is a polymerization carried out in the presence of a solvent for the monomer. This process overcomes many of the disadvantages of the bulk process. The solvent acts as diluent and aids in the transfer of the heat of polymerization easily. The solvent also make it easier for stirring, because the viscosity of the reaction system is decreased. Thermal control is much easier in the process of solution polymerization compared to bulk polymerization. However, the separation of solvent molecule and polymer will sometimes become difficult, if pure polymer is required after the polymerization process. Further, unless the solvent is chosen with appropriate consideration, chain transfer to solvent can also become a problem.

2-2-3. Suspension Polymerization

Suspension polymerization is a procedure whereby the monomer is dispersed in a medium (usually aqueous) in which it is insoluble, and the polymerization allowed to proceed within the individual monomers droplets. Suspensions maintained by mechanical agitation and the addition of stabilizers. Monomer-soluble initiators are used, and the reaction is best regarded as a "micro-bulk" polymerization. The kinetics and the mechanism of polymerization within each droplet are the same as those of the corresponding bulk polymerization. Heat and viscosity control in suspension polymerization is relatively easy compared to bulk polymerization. The main practical problem in the suspension polymerization is the prevention of droplet coalescence in the intermediate stages of the reaction when the droplets consist of what is essentially monomer-plasticised polymer, and are therefore very tacky. In the early stages, the droplets are sufficiently fluid to breakup continuously as they coalesce; in the latter stages, they are too hard to coalesce; but in the intermediate, semi-solid tacky condition they coalesce readily but re-disperse with difficulty. Careful attention to stirring is necessary if the reaction is to be successfully carried through to completion.

2-2-4. Emulsion Polymerization

Emulsion polymerization involves polymerization of monomers which are in the form of emulsions. This technique is used extensively in the polymerization of vinyl monomers (such as styrene, methyl methacrylate, vinyl acetate), the basic emulsion is usually formed by the mixing of monomer, emulsifier, and water together. Initiator is used to start the polymerization. The system remains perfectly fluid over the entire extent of the reaction. Heat dissipation is no problem. Polymer particles formed in the emulsion polymerization are usually smaller than those produced in suspension polymerization. Compared to the other polymerization process, the main advantage of emulsion polymerization is that high molecular weight polymers can be produced while a high polymerization rate is simultaneously maintained. Though the presence of emulsifier and other additives in the final emulsion limits its usefulness, the emulsion can, in some instances, be employed directly without further separation or purification.

2-3. Particle Nucleation Mechanisms of Emulsion Polymerization

The mechanisms proposed for the particle nucleation in emulsion polymerization have been discussed by Hansen *et al*[47], and Vanderhoff[48], respectively. Particle nucleation mechanisms can be divided into four main categories according to the locus of particle nucleation: monomer-swollen micelles[23,25,26,27], adsorbed emulsifier layer[49], aqueous phase[1,40,41,50,51,52,53], and monomer droplets[54,55,56].

According to the initiation-in-micelles mechanism, radicals generated in the aqueous phase enter monomer-swollen micelles and initiate polymerization, to form a monomer-swollen polymer particle. Only one of every 100-1000 micelles captures a radical and becomes a polymer particle; the others give up their monomer and emulsifier to neighbouring micelles which have captured a radical. The particle nucleation stage ends with the disappearance of the micelles. The monomer droplets act as reservoirs, feeding monomer to the micelles and polymer particles by diffusion through the aqueous phase. Radical entry into monomer droplets does not occur to any significant extent because of their relatively small surface area.

According to the initiation-in-the-adsorbed-emulsifier-layer mechanism, the particle nucleation occurs in the adsorbed monomer layer whether it is in the micelles, polymer particles, or emulsion droplets. Conceptually, this mechanism is similar to the initiation-in-micelles mechanism. A radical which is generated in the aqueous phase and diffuses to an adsorbed emulsifier layer is likely to initiate polymerization equally well in a micelle, polymer particle, or monomer droplet; however, the probability that a radical enters any of these depends upon their relative surface area. At the beginning of the reaction, the surface area of the micelles is orders of magnitude greater than that of the emulsion droplets, and therefore radicals are likely to enter micelles to the exclusion of the monomer droplets. The polymer particles, once formed, complete with the micelles for the radicals according to their surface area. Therefore, since this initiation-in-the-adsorbed-emulsifier-layer mechanism is conceptually similar to the initiation-in-micelles mechanism, it will not be considered further in this discussion.

According to the initiation-in-the-aqueous-phase mechanism, radicals generated in the aqueous phase add monomer units until the oligomeric radicals exceed their solubility and precipitate. The precipitated oligomeric radicals from spherical particles which adsorb emulsifier and adsorb monomer to become primary particles. These primary particles persist or flocculate with already-existing particles or other primary particles. In this system, the function of the emulsifier is to stabilize the particles precipitating from the aqueous phase. This mechanism is generally applied to those monomers which have significant solubilities in water.

The relatively large monomer droplets (generally 2-5μm in diameter) have too small a surface area to capture radicals from the aqueous phase and therefore serve as reservoirs for the diffusion of monomer through the aqueous phase to the polymerizing oligomeric radicals, micelles, or polymer particles. Despite the unfavourable statistical probabilities, however, some monomer droplets capture radicals and polymerize to form microscopic or near-microscopic particles[56], and some of these particles which are entirely separate from the main particle size distribution are formed in most batch polymerizations. Polymerization in monomer droplets becomes much more significant when the size of the emulsion droplet is decreased. The use of ionic emulsifier-fatty alcohol mixtures[54,55]allows the preparation of 0.1-0.2μm size styrene monomer droplets, which compete favourably with initiation-in-the-aqueous-phase as the mechanism of particle nucleation. The mechanism of formation these "miniemulsion" has been attributed to the very low solubility of the fatty alcohols in water[57] or to the formation of crystalline complexes between the ionic emulsifiers and fatty alcohols[58], the two mechanism are not mutually exclusive. Thus this mechanism pertains only to special systems.

Therefore, the two mechanisms to be discussed further and compared in this part are those of initiation-in-micelles and initiation-in-the-aqueous-phase. For initiation in micelles, the disappearance of the micelles marks the end of the particle nucleation stage, the particle growth stage begins with the formation of the first polymer particle and becomes the sole stage after the disappearance of micelles. For initiation in the aqueous phase, the rate of particle nucleation is initially the rate of radical generation $\mathbf{R}_i$, but shortly thereafter a steady stage is reached between the initiation and capture of the oligomeric radicals $\mathbf{R}_c$ and the flocculation of the latex particles $\mathbf{R}_f$[41]:

$$dN/dt = R_i - R_c - R_f$$

Thus the nucleation of particles continues throughout the course of the polymerization but is moderated by the capture of the precipitating oligomeric radicals and the flocculation of primary and mature particles. The duration of the particle nucleation stage is the most important point in distinguishing between the initiation-in-micelles and initiation-in-the-aqueous-phase mechanisms. The initiation-in-mecelles mechanism is generally applied to monomers which are only sparingly soluble in water and the initiation-in-the-aqueoue-phase mechanism to monomers with significantly higher solubilities in water. Table 2 lists the water solubilities of monomers which have been studied extensively. The particle nucleation of the monomers through butadiene is generally considered to proceed by initiation-in micelles if the emulsifier is present in concentrations above the critical micelle concentration (cmc) and that of the monomers from vinyl acetate onward, by initiation-in-the-aqueous-phase. For the intermediate ethyl acrylate, methyl methacrylate, and vinyl chloride, both mechanisms have been proposed in separate instances, but most consider initiation in the aqueous phase are more appropriate mechanism. Indeed, initiation in the aqueous phase has been proposed for sparingly soluble monomers such as styrene[40,51-53].

For initiation-in-micelles, the emulsifier concentration must exceed the cmc. The concept of the cmc is that it represents that concentration at which micelles form, at higher concentrations, more micelles form, and at lower concentrations, no micelles are present.

For initiation-in-the-aqueous-phase, the principal function of the emulsifier is to stabilize the oligomeric radicals as they precipitate from the aqueous phase. Therefore, the initiation and propagation of polymerization in the aqueous phase follows the general kinetic behaviour for bulk, solution, and suspension polymerization.

Table 2. Water Solubility of Vinyl Monomers[a]

Monomer	Water Solubility(25-50°C),mM
n-octyl acrylate	0.34
dimethylstyrene	0.45
vinyltoluene	1.0
n-hexyl acrylate	1.2
styrene	3.5
n-butyl acrylate	11
chloroprene	13
butadiene	15
vinylidene chloride	66
ethyl acrylate	150
methyl methacrylate	150
vinyl chloride	170
vinyl acetate	290
ethylene	200-600
methyl acrylate	650
acrylonitrile	1600
acrolein	3100

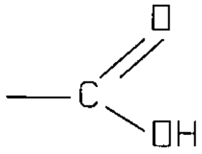
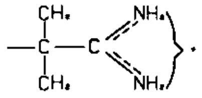
a) Data from literature 48

2-4. The Stability of Polymer Latices

A typical polymer latex particle will be composed of a large number of polymer chains, with the individual chains having molecular weights in the range of about 10^5 to 10^7. According to the arrangement of the polymer chains within the particle, the latter can be amorphous, crystalline, rubbery, or glassy. Moreover, in many cases monomer is retained by the particle and hence the particles can also be, in case where the polymer is soluble in the monomer, either extensively or minutely swollen. The physical state of the particle can be important in close-range interactions and in drying. For example, if the particles are soft, coalescence of the particles can occur to give continuous film formation, whereas with hard particles their individuality is retained in the dry state.

In determining the colloidal behaviour of a latex, the surface properties play a very important role, and these are directly related to the preparative method employed. They frequently depend on (i) groupings arising from the initiator used; (ii) adsorbed or grafted surfactants; and (iii) adsorbed or grafted polymers, particularly, those soluble in the dispersion medium.

In aqueous-based emulsion polymerization using water-soluble initiators, the surface groupings formed are frequently determined by the nature of the initiator used and the following have been reported[69]:

Weak acid		from hydrogen peroxide, persulfate, or bisazocyanopentanoic
Strong acid	$-\mathrm{O}-\mathrm{SO}_3$	from persulfate
Base		from azobisisobutyramidine
Nonionic	$-\mathrm{OH}$	from hydrogen peroxide or hydrolysis of sulfate groups

In addition, latex particles with mixed anionic and cationic groups on the surface can be prepared

In an ionizing medium of high relative permittivity (e.g., water) the acidic and basic groupings exist in the ionozed form, depending on their pK_a and pK_b values and pH, and consequently the surface of the particle becomes electrically charged. In addition the adsorption of other ionic species, such as surface-active ions, can also contribute to the surface charge. In physical terms the water is a good solvent for the ions and poor for the latex particle; that is, most of the polymers used for latex preparation are totally insoluble in water. A schematic illustration of this situation is shown in Figure 1 where the particle surface is shown to be that of a smooth sphere with the charges evenly distributed over the spherical surface. The condition of electroneutrality is maintained by balancing the charge on the latex surface by the charges on small ions of opposite sign in the solution phase (counterions). This forms the so-called electrical double layer in which an equilibrium is set up between electrostatic forces and diffusion forces. As a consequence of its surface charge, the latex particle surface has an electrostatic surface potential Ψ_s which can be either positive or negative, depending on the nature of the surface groupings, relative to earth. This potential falls off exponentially with distance from the surface of sphere according to the equation:

$$\Psi_r = \Psi_s(a/r)\exp[-\kappa(r-a)]$$

where Ψ_r is the surface potential at a distance (r-a) from the surface of the sphere where a is the radius of the sphere. κ is defined by:

$$\kappa^2 = (8\pi e^2 N_A/1000\varepsilon kT)I$$

and is dependent on the ionic strength I of the solution phase, e the fundamental electronic charge, N_A Avogadro's number, and ε the dielectric constant of the medium. It is κ that determines how rapidly the electrostatic potential falls off with distance from the particle

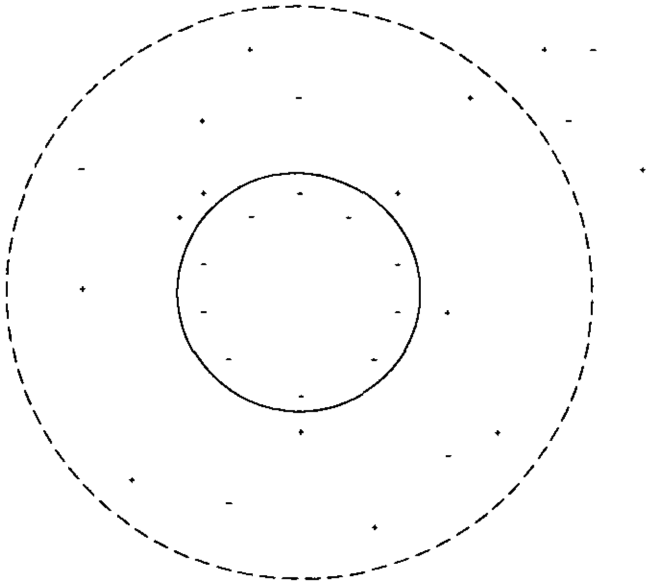


Fig. 1. Schematic illustration of a negatively charged spherical polymer latex particle with an electrical double layer. ---represents the range of influence of electrostatic forces.

surface and consequently the range of electrostatic interaction forces. The dished line in Figure 1 indicates that the range of electrostatic forces can extend well beyond the physical size of the particle.

When latices are prepared in nonaqueous media such as hydrocarbons then charged-surface groups no longer provide a practical means of stabilizating the particles formed. Under these conditions polymer chains, soluble in the dispersion medium, can be grafted to the core polymer particle which remains insoluble in the dispersion medium. A typical example is the use of poly(12-hydroxystearic acid) chains to stabilize particles of poly(methyl methacrylate) in dodecane. This leads to what might be termed a "hairy particle" with the noncharged "hairs" extending into the solvent medium as shown in Figure 2. Again the range to which the chains extend is important as it determines the distance at which one particle of this sort can start to interact sterically with another, giving the so-called sterically stabilised systems.

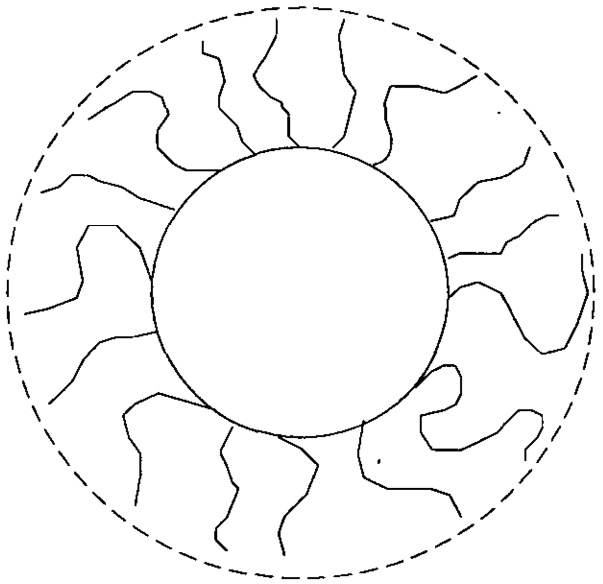


Fig. 2. Schematic illustration of a noncharged polymer latex particle with adsorbed or grafted nonionic polymer chains. ---represents the range of influence of steric forces.

Returning again to ionizing media, a combination of these two effects can be employed by grafting to a polymer core particle polyelectrolyte chains. This is illustrated schematically in Figure 3. It provides a combinatorial effect of electrostatic and steric interactions. These will have different interactive ranges as illustrated in Figure 3 by the dotted line for the electrostatic range and the dished line for steric effects.

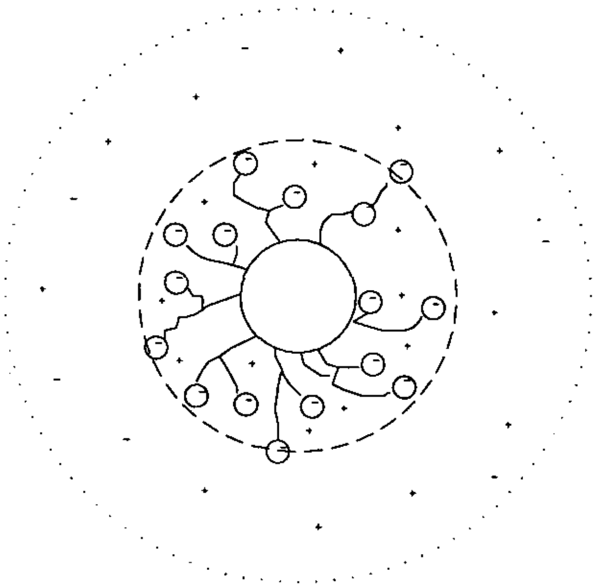


Fig. 3. Schematic illustration of a polymer latex core with grafted polyelectrolyte chains attached to the core surface. ···represents the range of electrostatic forces, and ---represents the range of steric forces.

The chains shown in Figure 3 are those of long poly(ions) deliberately added. However, there is some evidence to indicate that even in conventional emulsion polymerizations the particles formed may not be as smooth as those shown in Figure 1, and the charged groups may be floating a short distance in the medium as "microhairs". In practice one should not be misled by the convenience of the smooth sphere model for theoretical modeling of colloidal phenomena.

From this qualitative description of latex particles we can immediately recognize the origins of three basic forces that have to be considered in understanding the behaviour of dispersions in both aqueous and nonaqueous media. These can be summarized as:

1. *Electrostatic effects*: usually repulsive but opposite charges on particles can lead to attraction.

2. *Steric effects*: arising from the geometry and conformation of adsorbed or grafted molecules.

3. *Solvation Effects*: arising from the organization of solvent molecules near an interface or between the chains of adsorbed macromolecules.

Chapter 3. Experimental Work

3-1. Introduction

The experimental work was designed to investigate the emulsifier-free emulsion polymerization of vinyl acetate using potassium persulfate as initiator. Polymerization rate during un-seeded and seeded polymerization was determined with changing reaction parameters (initial monomer concentration, initiator concentration, monomer-polymer ratio, stirring speed).

In order to seek evidence for new particle formation during seeded polymerization of vinyl acetate, the polymerization was conducted in a higher monomer content. In this study, monodispersed poly(vinyl acetate) latex particles which were used as seed were prepared.

3-2. Materials

Monomer

Vinyl acetate (VAc) was obtained from Aldrich Chemical Co. Ltd. and purified by distillation under reduced pressure. It was then stored at 7°C.

Initiator

The initiator, potassium persulfate (KPS), was technical-grade chemical obtained from BDH chemicals Ltd. and was used without further purification.

Distilled Water

Distilled water supplied in the laboratory was used without further treatment.

Nitrogen

The nitrogen used is oxygen-free grade, supplied in the laboratory.

Dialysis Bag

$2\frac{1}{2}$ " cellophane tube, supplied by Medicell International Ltd. (London), was used.

Others

Potassium sulfate, to be used to adjust ionic strength, was analytical-grade chemical obtained from Fisons Scientific Apparatus Ltd. and was used without further purification. Quinone, which was used to stop reaction, was technical-grade chemicals obtained also Fisons Scientific Apparatus Ltd. and was used directly from the bottle.

3-3. Experimental Apparatus

A schematic diagram of the experimental apparatus is illustrated in Figure 4.

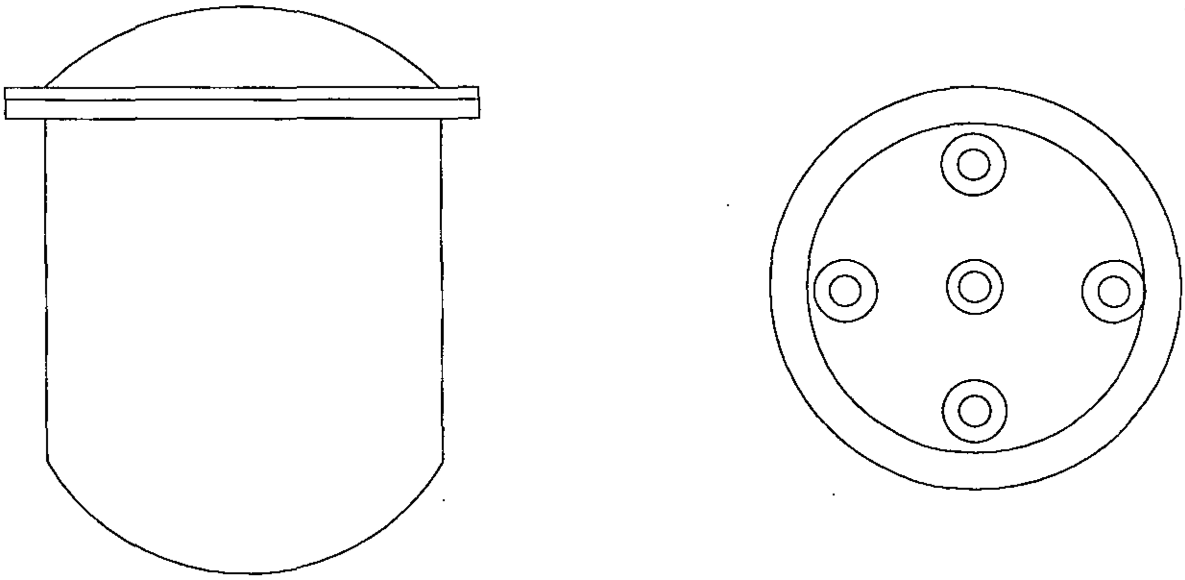


Fig.4. Schematic Diagram of the Reactor

The reactor, a 1 litre five-necked separable flask, was fitted with a stainless steel stirrer, a long glass-bulb mercury thermometer, a reflux condenser, a nitrogen inlet, and a glass stopper. The reactor was placed in a thermostatted water bath.

5 ml syringe was used for withdrawing samples from the reactor. A needle which was long enough to reach almost the bottom of the reactor was fixed. Sometimes, pipette pump fixed with long pipette was used instead of syringe, because the long needle was blocked easily by latex particles when withdrawing samples.

3-4. Polymerization Procedure

All the polymerization were conducted in the reactor showed in Figure 4.

Before the start of any experiment the stirrer, reactor and all glassware needed for the experiment were thoroughly cleaned by the use of detergent and tap water. Each item was then rinsed with distilled water, and was finally dried in an oven.

3-4-1. Preparation of Seed Particles

At the start of an experiment, a predetermined amount of distilled water and vinyl acetate (according to the recipe) was weighed and transferred into the reactor which was placed in a thermostated controlled water bath. After that, the reactor was purged over a period of about 20 minutes using oxygen-free nitrogen.

The polymerization was started by the addition of potassium persulfate solution which was purged for 20 minutes, which was the initiator. The polymerization was run until the conversion reached nearly 100%. Poly(vinyl acetate) latex prepared in this way was dialyzed, and was used as seed.

For the determination of polymerization rate during the batch emulsion polymerization of vinyl acetate (there were no seed latex in the system), the procedure involved was identical with that of seed preparation with the only exception that samples were withdrawn from the reactor at different intervals. Polymerization conversion was determined gravimetrically.

3-4-2. Seeded Emulsion Polymerization

Before the experiment the distilled water, vinyl acetate, and seed latex were flushed for 20 minutes at room temperature with oxygen-free nitrogen, respectively. After flushing, accurately weighed distilled water, vinyl acetate, and seed latex were transferred to the reactor, which was also flushed for 20 minutes with oxygen-free nitrogen. In the case of the recipes which contained potassium sulfate, the specified amount was accurately weighed and introduced into the reactor before addition of other ingredient.

The mixture of distilled water, vinyl acetate, and seed latex were stirred for 20 minutes at experimental temperature. And then the polymerization could be started by addition of solution of potassium persulfate, which was flushed for 15 minutes with oxygen-free nitrogen. The polymerization was run until desired conversion of monomer to polymer was achieved.

3-5. Dialysis of Seed Latex

After the preparation of a seed, it was necessary to dialyse it to remove any excess initiator, its byproducts, and unreacted monomer. The seed latex was put in a dialysis bag, and then was dialyzed in distilled water for 20 days, in which the distilled water was changed every day. Dialyzed latex was stored at 7°C.

3-6. Determination of Average Particle Diameter

A diluted latex sample was dropped onto a carbon-plating copper grid which was earlier prepared. After the grid was dried, electron micrographs of particles were taken with a JEOL-JEM type 100cx transmission electron microscope.

The diameter of about 100 particles was measured on each sample using a ruler, and was indicated as the number-average diameter.

3-7. Determination of Conversion

Polymerization conversion was determined gravimetrically.

To stop further reaction, the samples withdrawn from reactor were cooled down, and a small quantity of solid hydroquinone was added. Approximately 2 *g* this sample was weighed using a dried aluminium plate (which weight was weighed in advance), and dried *in vacuo* at 70°C for 24 hours. The dried samples were weighed again, and the polymerization conversion (C) can be calculated using these data.

For the standard polymerization system, expression for conversion (C) is:

$$C = 100 \times \frac{\mathit{totalweightofemulsion}}{\mathit{totalweightofmonomer}} \times \frac{\mathit{weightofpolymerinsample}}{\mathit{weightoflatexsample}}$$

For the seeded polymerization system, expression for conversion (C) is:

$$C = 100 \times \frac{\left[\mathit{totalweightofemulsion} \times \frac{\mathit{weightofpolymerinsample}}{\mathit{weightoflatexsample}} - \mathit{weightofinitialpolymer}\right]}{\mathit{weightofinitialmonomer}}$$

Chapter 4. Results and Discussion

All the results in this study are concerned only the polymerization of vinyl acetate in the absence of emulsifier. Unless otherwise indicated, micrographs shown in this thesis are taken at the end of polymerization.

4-1. Latex Stability

The stability of a latex particle is determined by the balance between the electrostatic and steric repulsion forces and the London-van der Waals attraction forces. The electrostatic repulsion forces arise from adsorbed or chemically bound surface ions; these forces are affected strongly by the concentration and valence of the counterions. The steric repulsion forces arise from adsorbed or chemically bound hydrated uncharged surface groups; these forces are not affected significantly by other parameters of the system. The London-van der Waals attraction forces arise from the difference in dielectric constant between the particles and the medium; these forces are not affected significantly by other parameters of the system.

Latex particles can be stabilized by three different mechanisms: (i) adsorbed groups; (ii) chemically bound groups; (iii) polar-but-uncharged groups of monomer molecules.

The adsorbed groups may be conventional emulsifiers (e.g., sodium lauryl sulfate) or polymeric emulsifiers (e.g., methylcelluose). These adsorbed groups may desorb from the surface when the composition of the latex serum is changed, when the latex flocculates, or when the latex is dried to form a continuous film. Thus the adsorption of these conventional and polymeric surfactants is governed by an adsorption-desorption equilibrium. These equilibria are easy to recognize for the conventional surfactants, but are more difficult to recognize for polymeric emulsifiers, which desorb only difficult; however, the addition of fresh absorbing surface usually results in the desorption of the polymeric emulsifier and its readsorption, to meet a new adsorption-desorption equilibrium. It should be emphasized that any polymeric emulsifier, ionic or nonionic, which adsorbs on the latex particles to increase their stability may also cause flocculation of the latex by "bridging". Generally, very low concentrations of the polymeric emulsifier give flocculation whereas higher concentrations give stability. Such polymeric emulsifiers may be prepared *in situ* when a monomer containing a functional group (e.g., acrylic acid, 2-sulfoethyl methacrylate, or 2-hydroxyethyl acrylate) is used in the polymerization; in this case, the polymeric emulsifier may flocculate the latex or improve its stability, according to its concentration and molecular weight.

The chemically bound groups may be polymer end groups (e.g., sulfate end groups arising from the persulfate initiator), reaction products of these end groups (e.g., hydroxyl or carboxyl groups), reaction products of the polymer (e.g., oxidation to form carboxyl groups), and incorporatied monomers containing functional groups (e.g., acrylic acid, 2-sulfoethyl methacrylate, or 2-hydroxyethyl acrylate). These chemically bound groups cannot desorb without removing the surface layer of the particles and therefore remain fixed on the particle surface despite changes in composition of the latex serum or drying to form a continuous film.

The polar-but-uncharged functional groups of the monomer units orient themselves in the polymer-water interface so as to improve the stability of the latex. Acrylate esters are cited as examples of this type, e.g., the methyl ester gives a higher degree of orientation in the interface and a lesser adsorption of conventional emulsifier than the *n*-butyl ester. This concept has not yet been demonstrated for a wide variety of monomers, but offers a means of explaining hitherto unexplained latex stability data.

According to the above mechanism, some emulsion polymerization can be conducted without addition of any emulsifier (surfactant). Emulsifier-free emulsion polymerization of styrene has received much attention because of both practical and academic interests[63,64,42,51,65]. In the present studies, poly(vinyl acetate) latex particles were prepared using potassium persulfate as initiator in the absence of emulsifier. In such system, latex particles are stabilized by ionic end groups from the decomposition of initiator. Letting M denote a monomer (vinyl acetate) molecule, the following sequence of reaction can be envisaged:

$$S_2O_8^{2-} \rightarrow 2 \cdot SO_4^-$$

$$M + \cdot SO_4^- \rightarrow \cdot MOSO_3^-$$

$$M + \cdot MOSO_3^- \rightarrow \cdot M_2OSO_3^-$$

$$\cdot$$
$$\cdot$$
$$\cdot$$

$$M + \cdot M_nOSO_3^- \rightarrow \cdot M_{n+1}OSO_3^-$$

So, sulphate end groups ($-SO_4^-$) become chemically combined with polymer chains. This conclusion has been confirmed by the work of Van den Hul and Vanderhoff[66] using S^{35}-labelled potassium persulfate as initiator.

4-2. Batch Emulsion Polymerization of Vinyl Acetate

The emulsifier-free polymerization of vinyl acetate using potassium persulfate as an initiator proceeded smoothly in the batch process. The typical recipe used in this study is shown in Table 3. Figure 5 is a typical curve of conversion of monomer to polymer against polymerization time obtained from Run SEF-2. It has been shown from the curves that polymerization rates remained constant until very high conversions. This behaviour is very similar to that observed by Brooks *et al*[67] where the seeded emulsion polymerization of vinyl acetate were conducted in the presence of emulsifier (sodium dodecyl sulphate). Figure 6 shows typical transmission electron micrographs (TEM) of poly(vinyl acetate) particles prepared by the emulsifier-free polymerization. It can be seen from this picture that the particles had a uniform size. The monodispersity of latex particles produced by emulsifier-free emulsion polymerization probably results from the domination of heterocogulation between mature latex particles and small particle nuclei, or oligomer radicals in the aqueous phase[68]. When the production rate of particle nuclei is fairly high with high initiator concentration, mature latex particles absorb small particle nuclei and grow at about the same rate to give a narrower particle size distribution.

Table 3. A typical recipe for the emulsifier-free polymerization of vinyl acetate

Vinyl Acetate	24.0 g
Distiled Water	240.0 g
KPS	2.40 g
Temperature	70°C
Stirring Speed	100 rpm

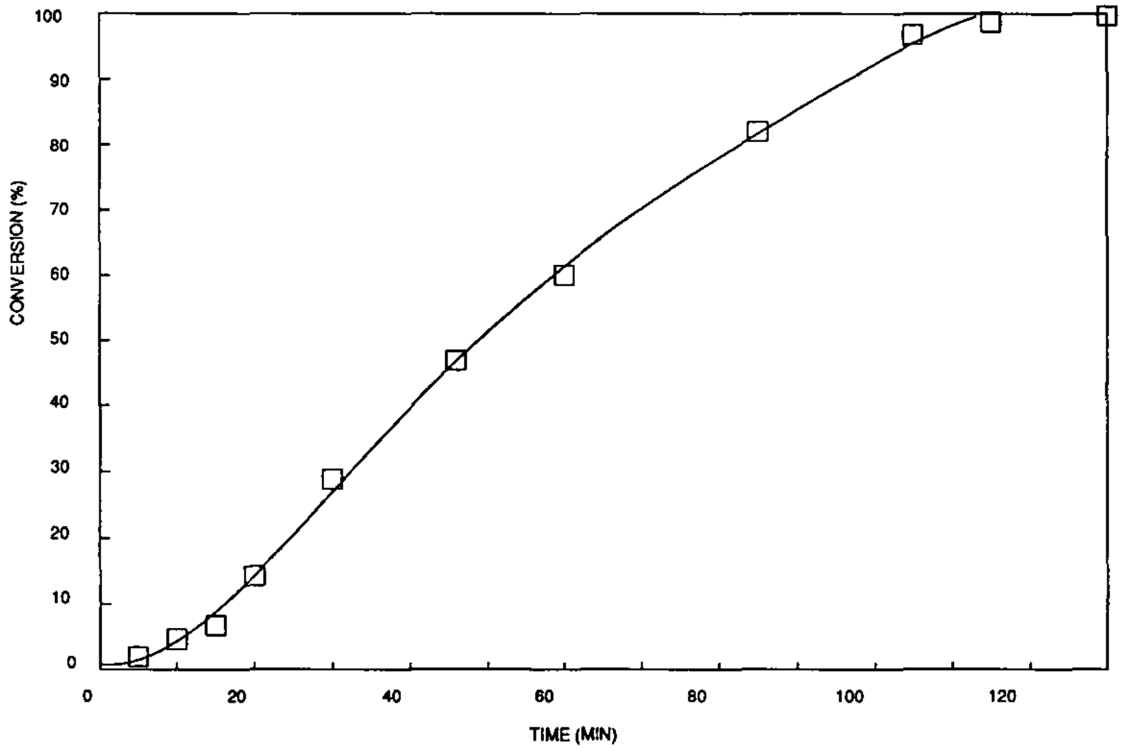
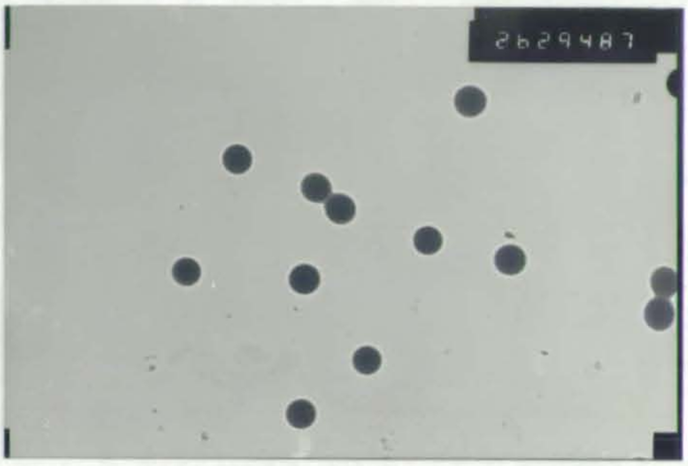


Fig.5. Polymerization curve of VAc emulsion polymerization



Magnification: 26,000

Fig.6. Electron micrograph of PVAc latex particles(SEF-2)

The effect of initial monomer concentration on polymerization rate and average particle diameter was investigated. Figure 7 shows the relationship between the conversion of monomer to polymer and reaction time. Figure 8 to Figure 11 are their electron micrographs. Polymerization rate (R_p) is calculated from the slope of the linear portion of the conversion versus time plot. The results were summarized in Table 4.

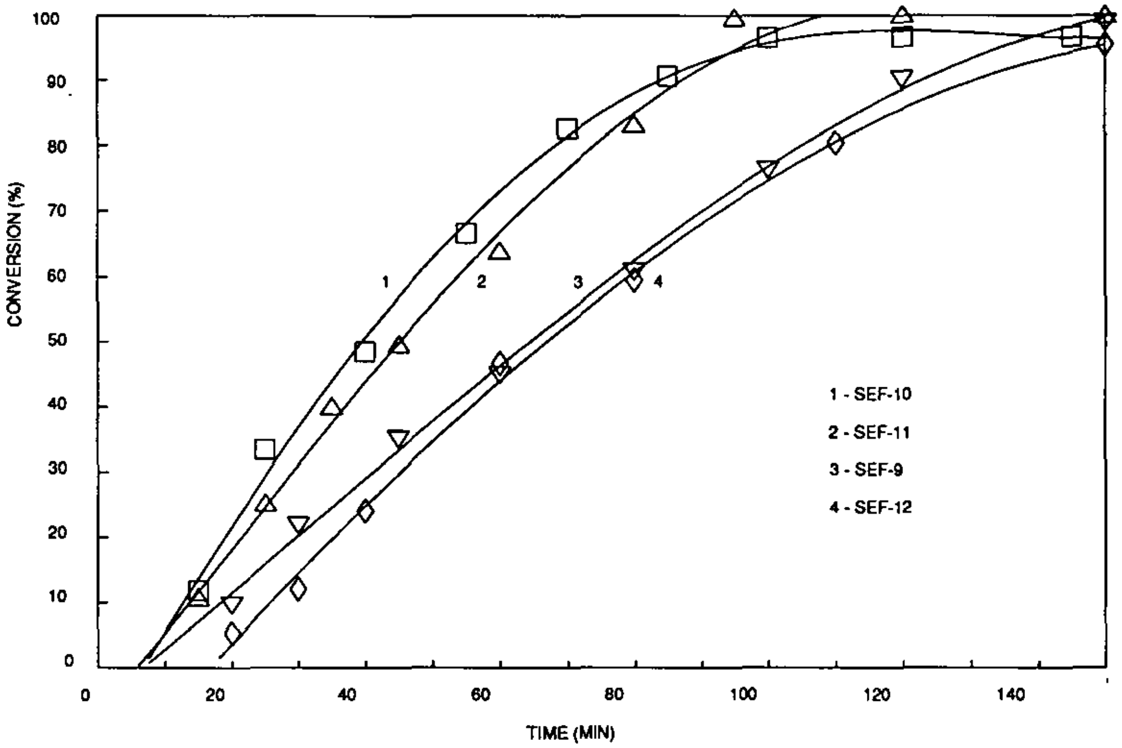
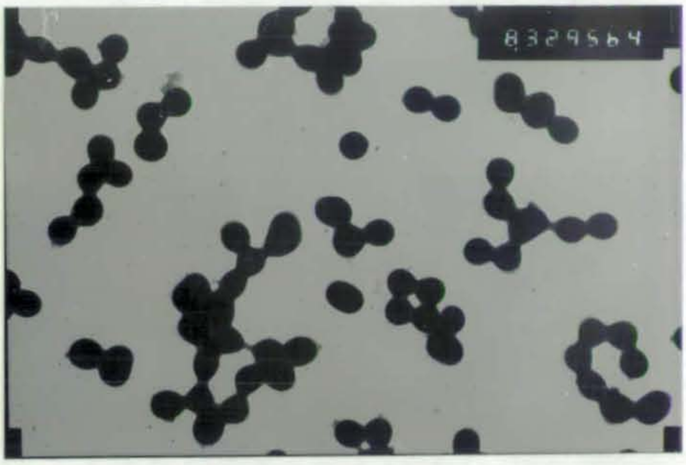
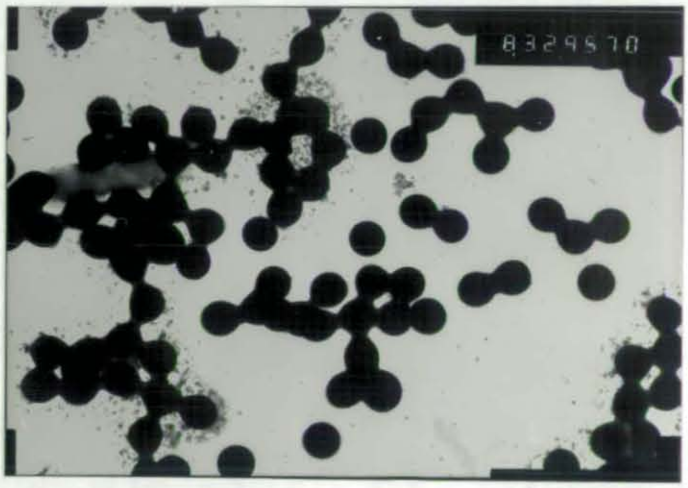


Fig.7. Effect of initial monomer concentration on conversion



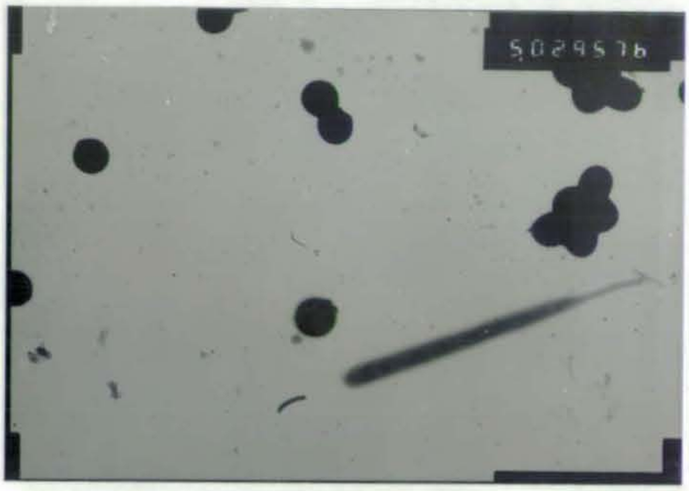
Magnification: 6,600

Fig.8. Electron micrograph of PVAc particles (SEF-10)

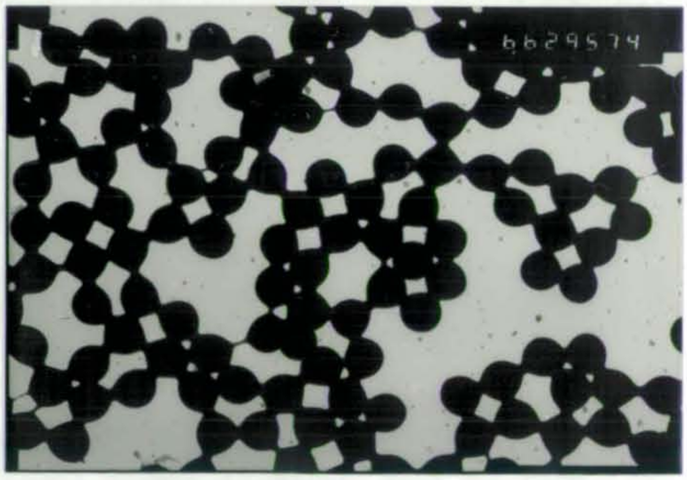


Magnification: 8,300

Fig.9. Electron micrograph of PVAc particles (SEF-11)



Magnification: 5,000
Fig.10. Electron micrograph of PVAc particles (SEF-12)



Magnification: 6,600
Fig.11. Electron micrograph of PVAc particles (SEF-9)

Table 4. Effect of initial monomer concentration on R_p and D_p

Expt. no.[a]	SEF-10	SEF-11	SEF-9	SEF-12
M_0 (g-mole/l-H_2O)	1.1649	1.4466	2.9076	4.3567
D_p (μm)	0.48	0.58	0.78	0.88
Particle Number(N)($\times 10^{14}$/l-H_2O)	14.54	10.24	8.47	8.37
R_p ($\times 10^4$[g-mole]/[s][l-H_2O])	2.4001	2.6355	3.8131	6.2226

(a) Reaction condition: Initiator concentration 0.037 mole/l-H_2O; Temperature 45 °C; Stirring speed 150 rpm.

Figure 12 shows the relationship between polymerization rate (R_p) and initial monomer concentration (M_0). It is found from log-log plot of R_p to M_0 that the rate of polymerization is proportional to the 0.69 power of initial monomer concentration. This result is different from that obtained by Litt *et al*[62] in which no significant change in rate was observed. However, Litt's result were obtained from their early experiments, and were not repeated, and also the change of initial monomer concentration in their experiment was very small.

Figure 13 shows variation of final particle diameter with change of initial monomer concentration (M_0). As initial monomer concentration increases, final particle diameter increases. From Table 4, it has been shown that higher monomer concentration results in fewer particles. This can be explained using the mechanism of latex particles stability.

Polymer particles in emulsifier-free emulsion polymerization in which ionic initiator is used are stabilized by ionic end groups from the initiator as described above. Low initiator concentration provides less ionic end groups to stabilize polymer particles. In this study, initiator concentration (g-mole/l-H_2O) was kept constant with increasing monomer concentration, therefore the concentration of ionic end groups at particle surface decreased at same monomer conversion. So, the particle stability decreased with increasing monomer concentration, more particles tend to coalescence to form a new big particle. This results in fewer particles with increasing monomer concentration.

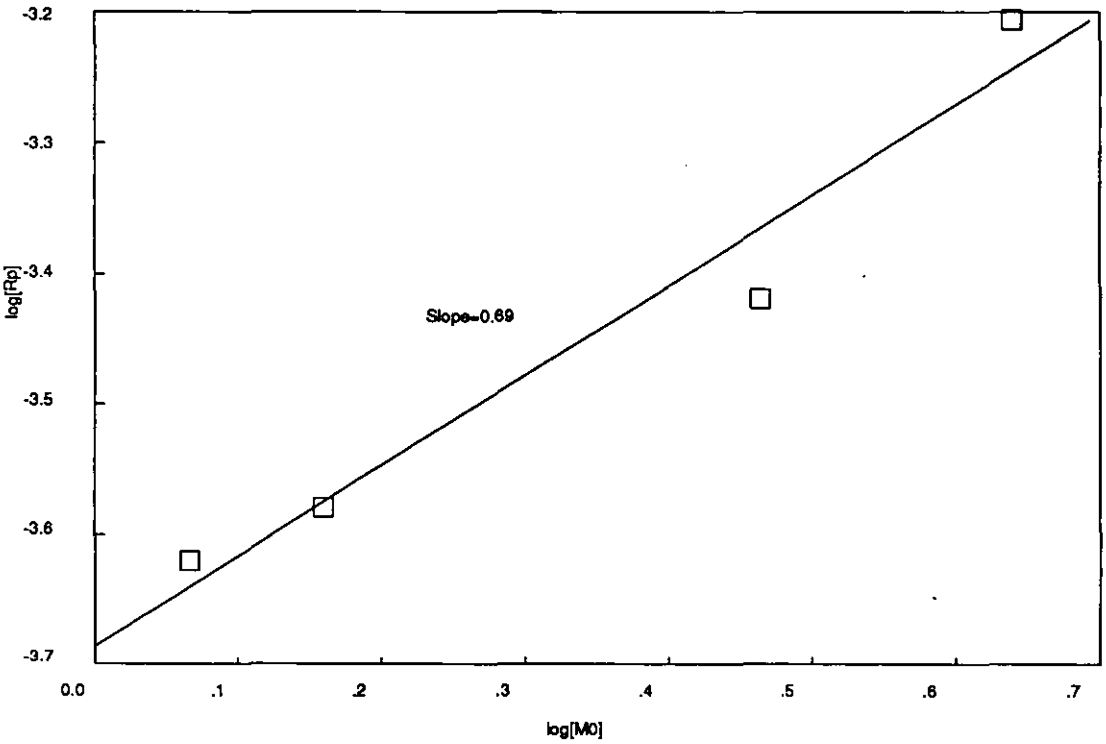


Fig.12. log[R_p]-log[M_0]

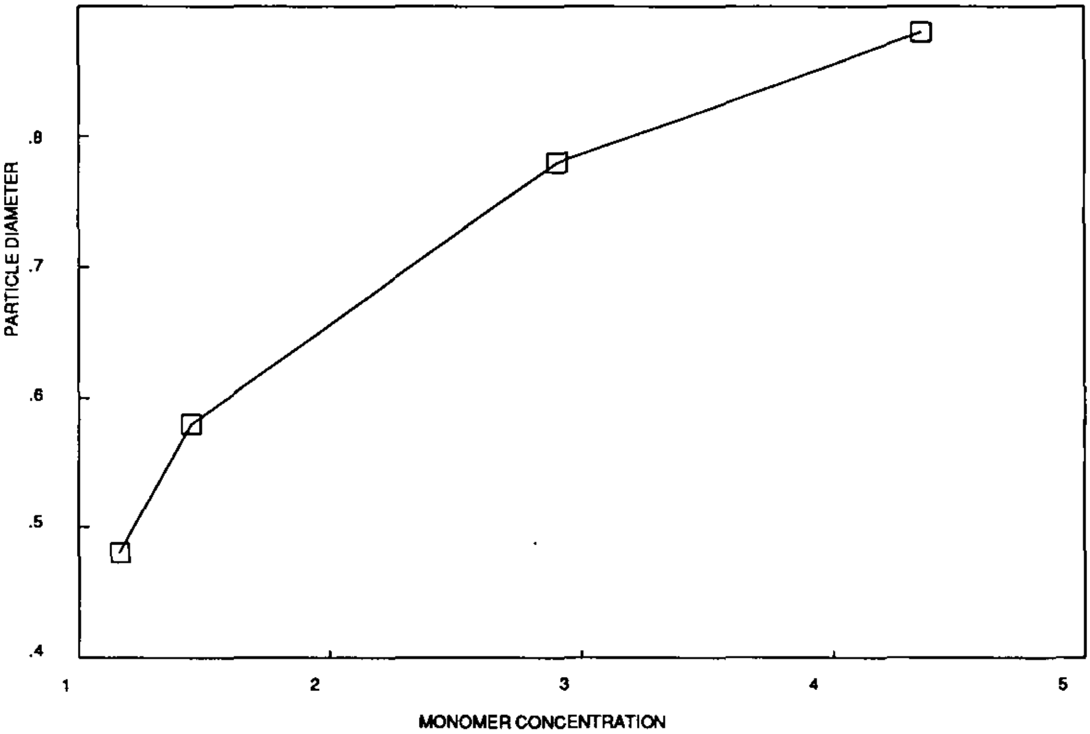


Fig.13. Variation of particle diameter with monomer concentration

4-3. Effect of Initiator Concentration

The effect of initiator concentration on the polymerization rate of seeded emulsion polymerization of vinyl acetate at 50 °C was determined over a wide range of potassium persulfate concentrations and monomer-polymer ratio. The initial persulfate concentration was varied from 1.9×10^{-3}M to 17×10^{-3}M, and monomer-polymer ratio was varied from 10 to 40. Potassium sulfate was added as needed to keep the ionic strength constant in each experiment.

Plots of polymerization conversion versus time as a function of initiator concentration are shown in Figure 14 to Figure 16. As is expected polymerization rate increases with increasing initiator concentration. The polymerization rates were measured from the slope of the linear portion of the curves. A plot of log rate versus log initiator concentration for several monomer-polymer ratio is shown in Figure 17. There is some scatter of points; however, a slope of 0.60±0.05 is strongly indicated. This result is similar to that obtained by Chang *et al*[20] (where $R_p \propto [I]^{0.60\pm0.03}$), but is different from that obtained by Brooks *et al*[67] (where $R_p \propto [I]^{0.70\pm0.05}$). This difference arises because the experimental conditions varied significantly for different studies. The first significant variable was that Chang *et al* and Brooks *et al* used sodium lauryl sulfate as emulsifier during their studies, while there was no any addition of emulsifier in our studies. The second variable, monomer-polymer ratio, was significant different. The monomer-polymer ratio was changed from 0.52 to 1.70, and 7 to 50 for Brooks' and Chang's study, respectively. While it varied from 10 to 40 in the present study. The third variable was temperature, 60°C for Brooks *et al* and Chang *et al*, and 50°C for the present study.

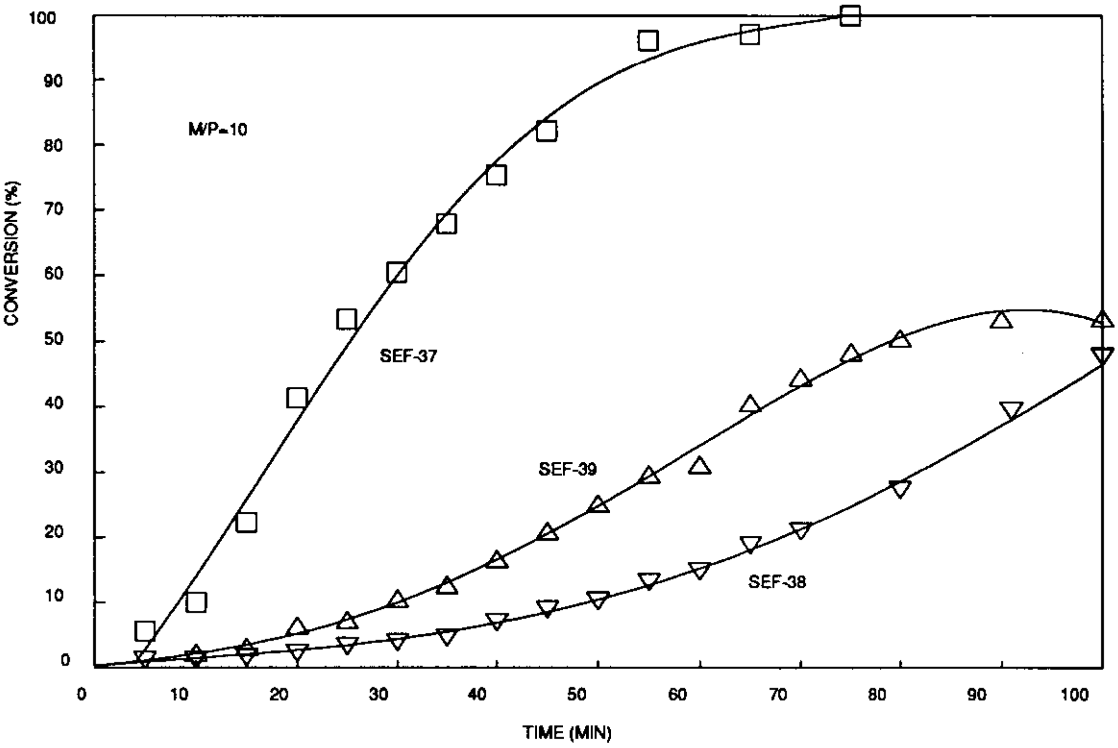


Fig.14. Effect of initiator concentration

Ionic strength: 0.05, Stirring speed: 100 rpm, Solid content: 10%, Temperature: 50 °C, The diameter of seed particles: 0.25 μm,

Initiator concentration:

SEF-37: 0.01669 M; SEF-39: 3.2794×10^{-3} M; SEF-38: 1.7278×10^{-3} M

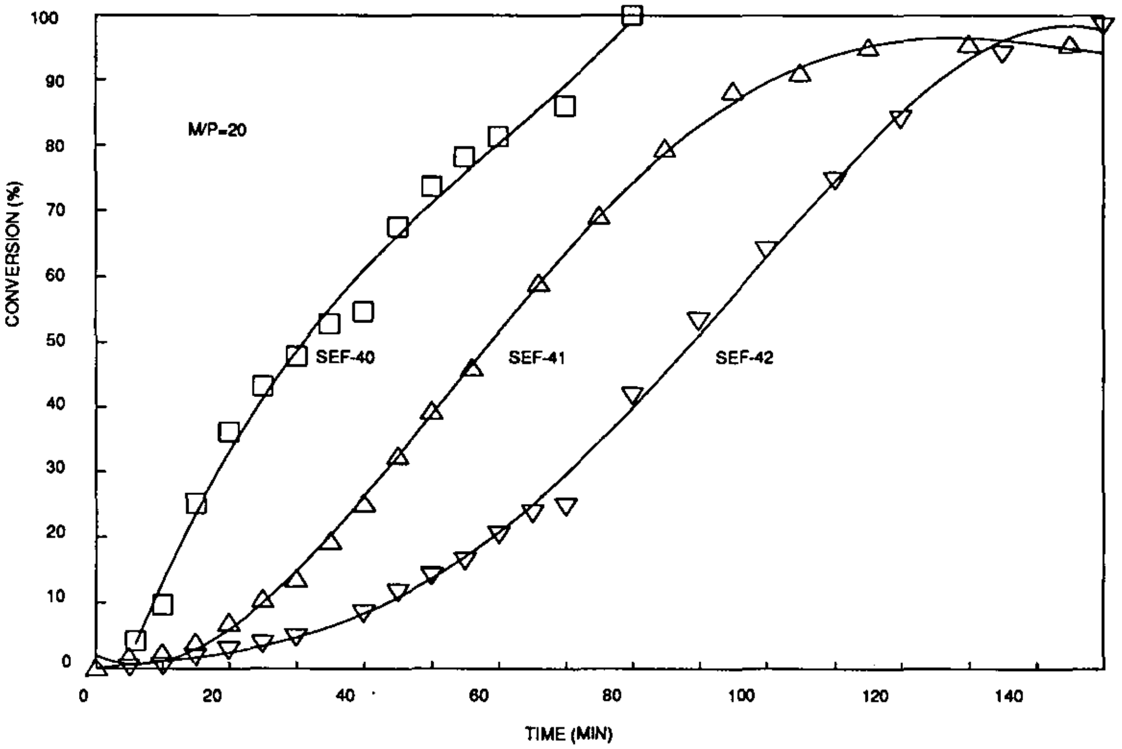


Fig.15. Effect of initiator concentration

Ionic strength: 0.05, Stirring speed: 150 rpm, Solid content: 10%, Temperature: 50 °C, The diameter of seed particles: 0.25 μm,

Initiator concentration:

SEF-40: 0.01675 M; SEF-41: 3.6982×10^{-3} M; SEF-42: 1.8996×10^{-3} M

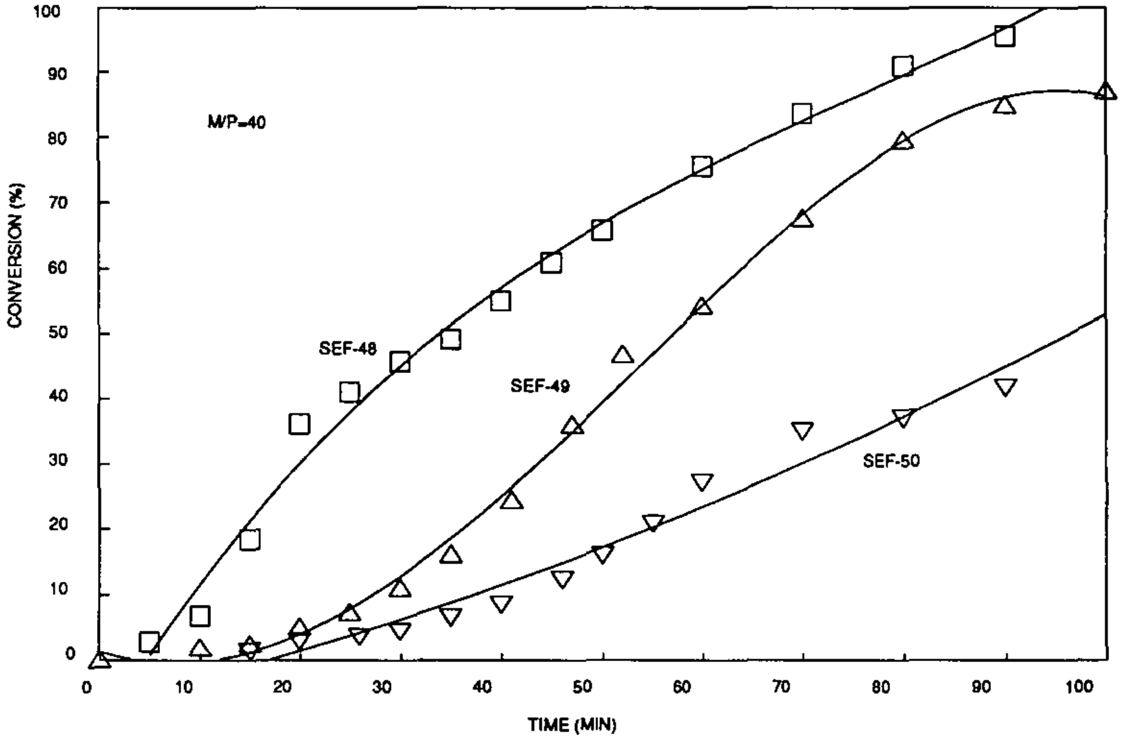


Fig.16. Effect of initiator concentration

Ionic strength: 0.05, Stirring speed: 150 rpm, Solid content: 10%, Temperature: 50 °C, The diameter of seed particles: 0.34 μm,

Initiator concentration:

SEF-48: 0.01678 M; SEF-49: 3.7935×10^{-3} M; SEF-50: 1.9157×10^{-3} M

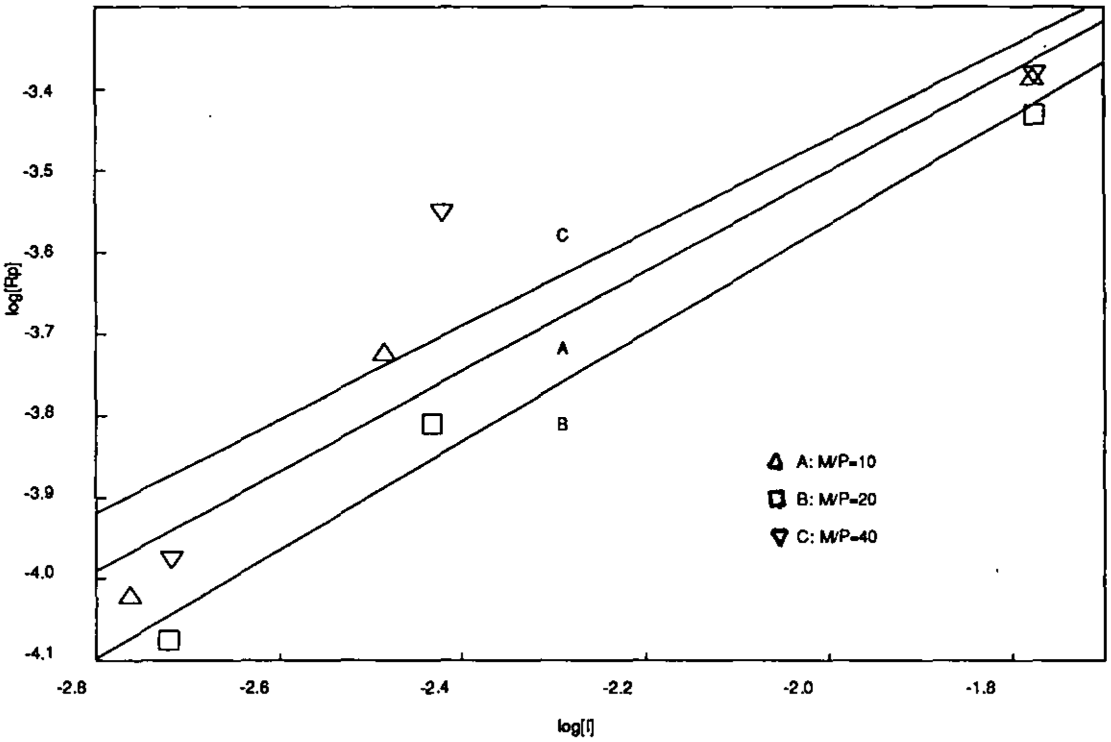


Fig.17. Effect of initiator concentration on polymerization rate

4-4. Effect of Monomer-Polymer Ratio

The effect of monomer-polymer ratio on polymerization rate and change of particle size during seeded emulsion polymerization of vinyl acetate in the absence of emulsifier was studied. The conversion-versus-time at different experimental condition were plotted in Figure 18 to Figure 20. Electron micrographs of latex particles are shown in Figure 21 to Figure 32. Polymerization rate was calculated from the slope of the linear portion of the plot.

The effects of the monomer-polymer ratio on the polymerization rate and the change of latex particle size in the seeded polymerization of vinyl acetate are summarized in Table 5 to Table 7. It has been shown that there is no significant change in polymerization rate in the seeded emulsion polymerization of vinyl acetate in the absence of emulsifier when monomer-polymer ratio were changed. As shown in Figure 24, 25,and 41, we can see that the existence of the large and small particles when the monomer-polymer ratio are quite big, in other words, there are small amount of seed particles in the system. However, there are only large uniform particles when the monomer-polymer ratio are small, i.e., there are large amount of seed particles in the system. It is considered from these results that, the large particles are those that arose from the increase in the volume of seed particles, and the small particles are those newly formed in the water phase during the seeded emulsion polymerization.

In the range where only big uniformed particles are formed in the system, the diameter of the particles agreed with the theoretical value calculated on the assumption that all of charged vinyl acetate was polymerized within seed particles:

$$D_{theory} = \sqrt[3]{\frac{W_{seed} + W_{monomer} \times C}{W_{seed}}} \times D_{seed}$$

Where, D_{theory} is the theoretical diameter of latex particles, D_{seed} is the diameter of seed particles measured from electron microscope, C is polymerization conversion, and $W_{monomer}$, W_{seed} are charged amount of monomer and polymer, respectively.

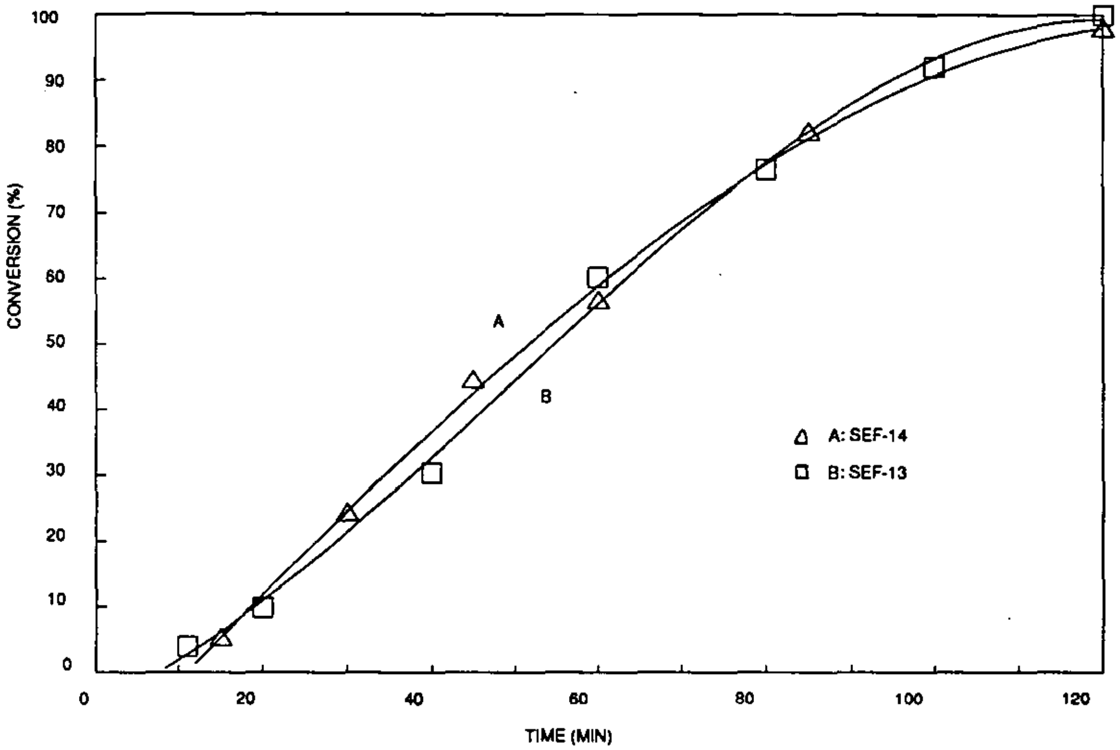


Fig. 18. Effect of monomer-polymer ratio

1) Experimental condition: Temperature 45 °C, Stirring speed 150 rpm. [I]=0.017 mole/l-H_2O.

2) The diameter of the seed particle was 0.42 μm.

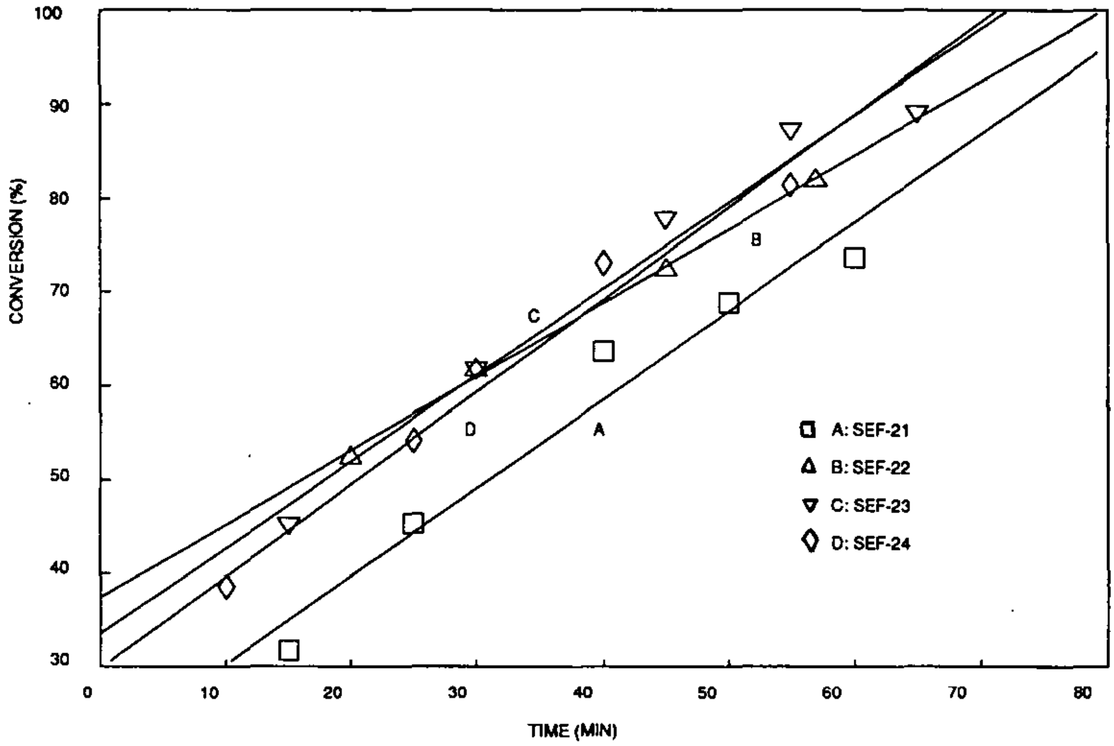


Fig. 19. Effect of monomer-polymer ratio

1) Experimental condition: Temperature 70°C, Stirring speed 80 rpm. [I]=0.028 mole/l-H_2O.
2) The diameter of seed particle was 0.32 μm.

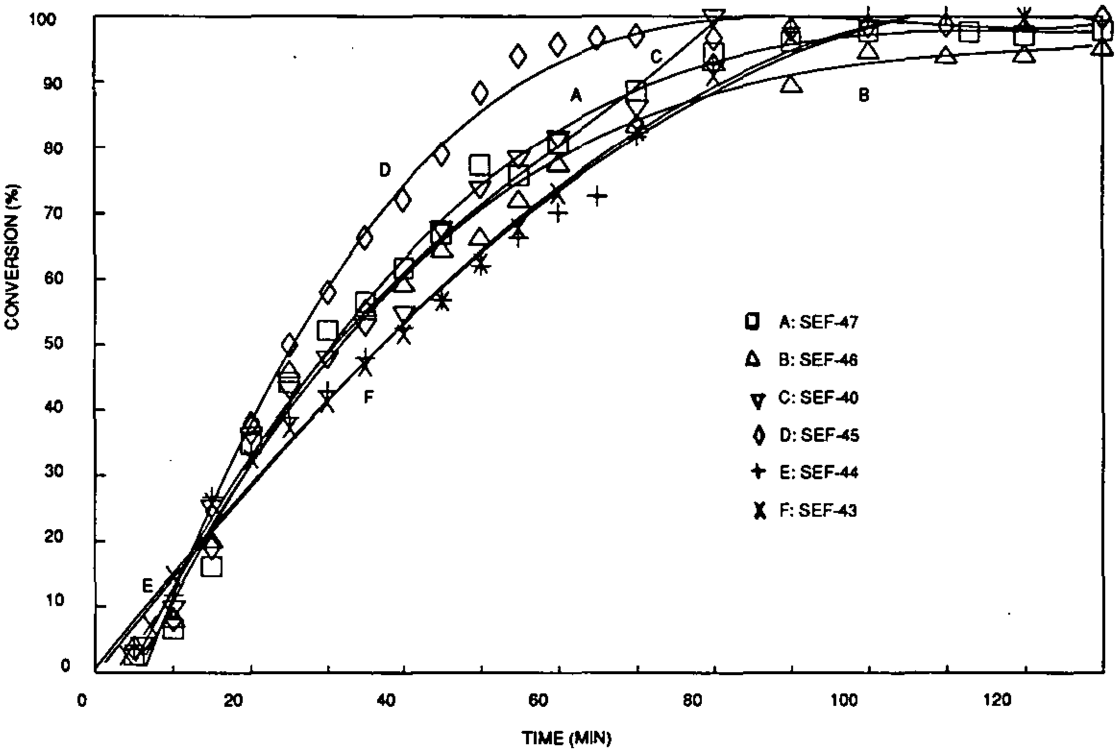
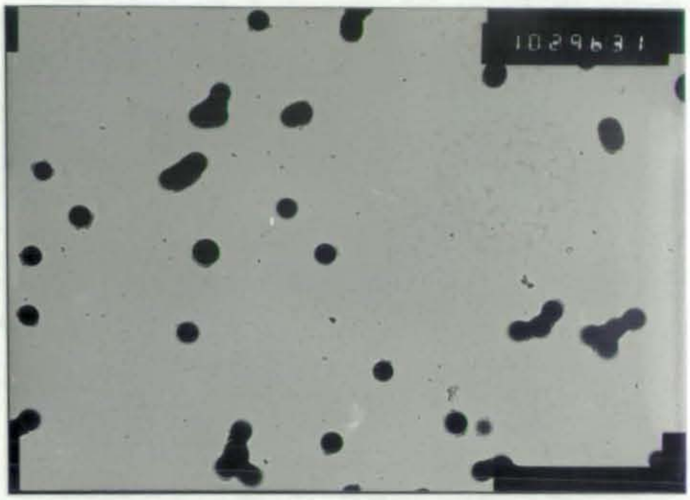


Fig. 20. Effect of monomer-polymer ratio

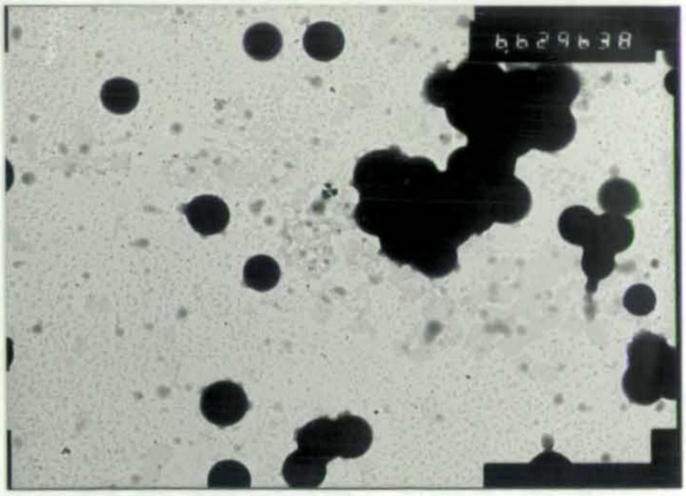
1) Experimental condition: Temperature 50 °C, Stirring speed 150 rpm. [I]=0.017 mole/l-H_2O.

2) The diameter of seed particle was 0.25 μm.



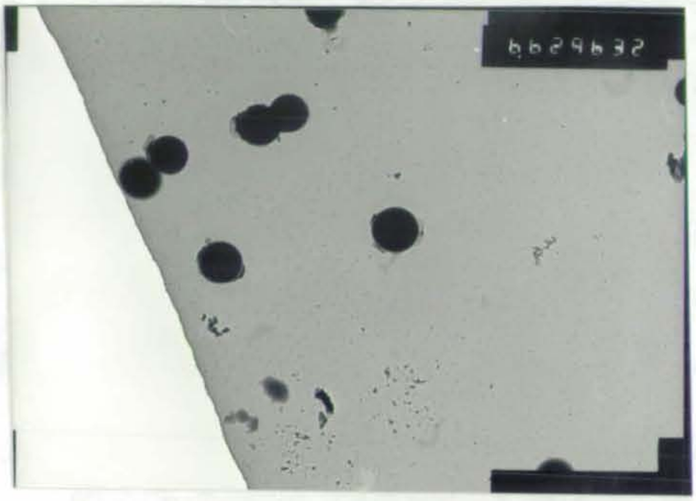
Magnification: 10,000

Fig. 21. Electron Micrograph of Seed Latex Particles(SEF-19)



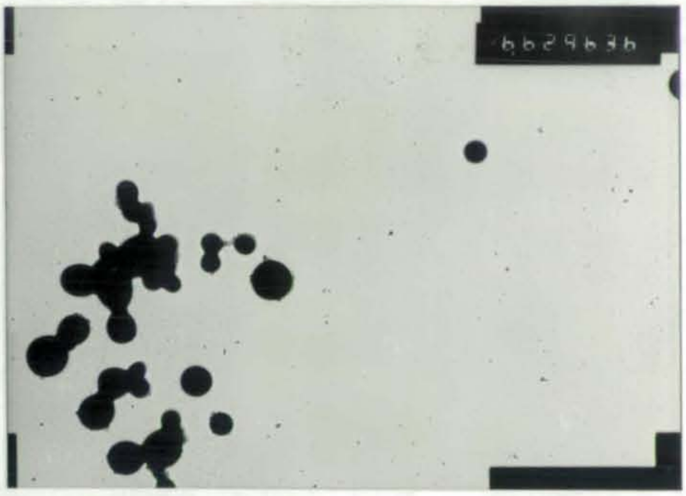
Magnification: 6,600

Fig. 22. Electron Micrograph of Latex Particles(SEF-24)



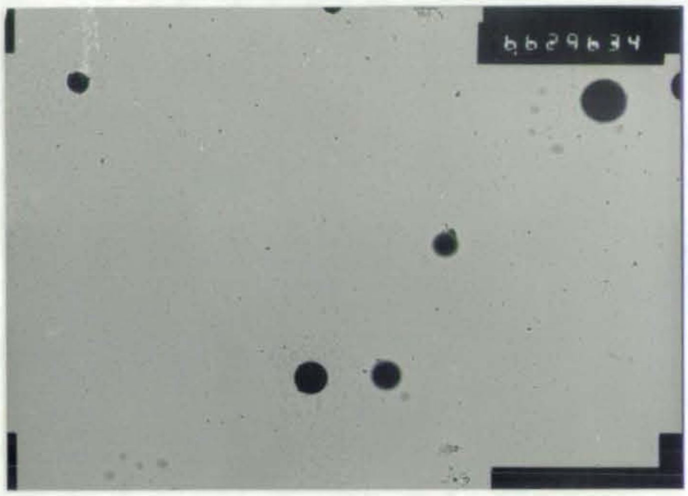
Magnification: 6,600

Fig. 23. Electron Micrograph of Latex Particles(SEF-21)



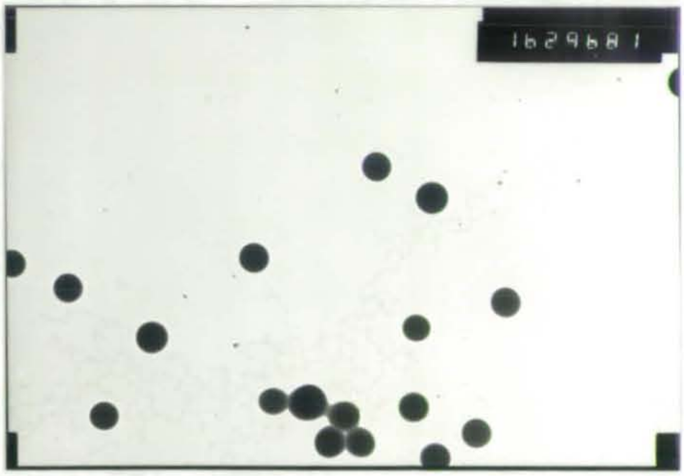
Magnification: 6,600

Fig. 24. Electron Micrograph of Latex Particles(SEF-23)



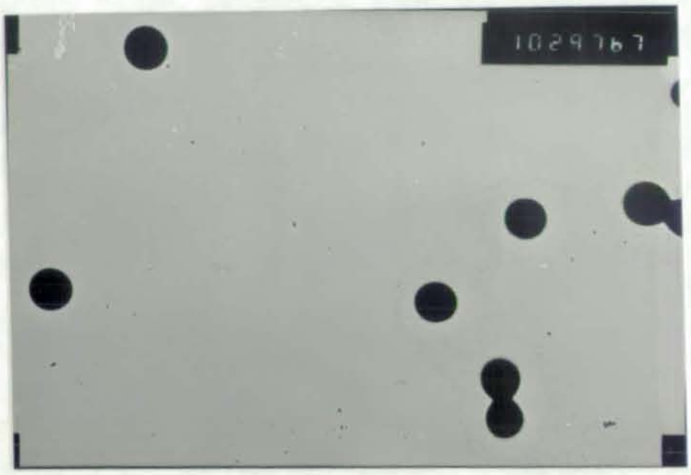
Magnification: 6,600

Fig. 25. Electron Micrograph of Latex Particles(SEF-22)



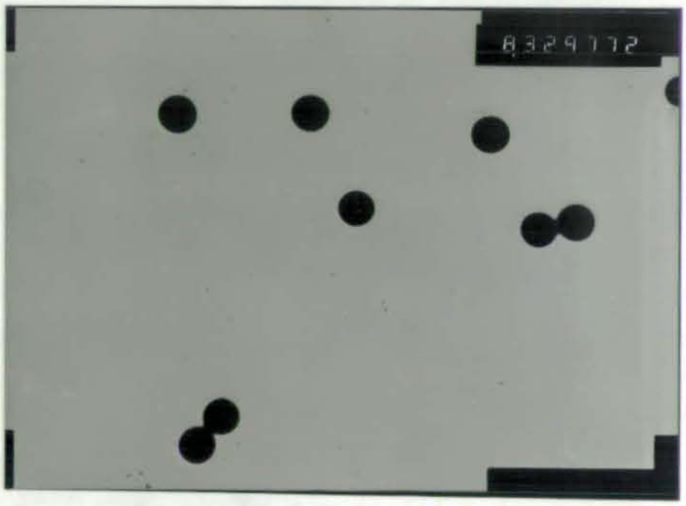
Magnification: 16,000

Fig. 26. Electron Micrograph of Seed Latex Particles(SEF-25)



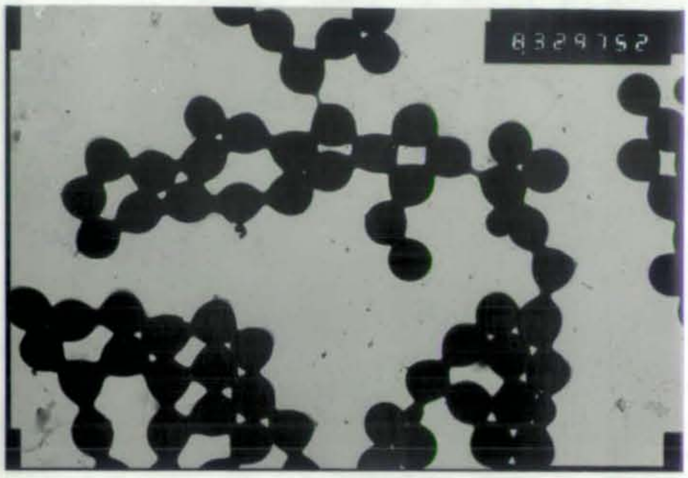
Magnification: 10,000

Fig. 27. Electron Micrograph of Latex Particles(SEF-47)



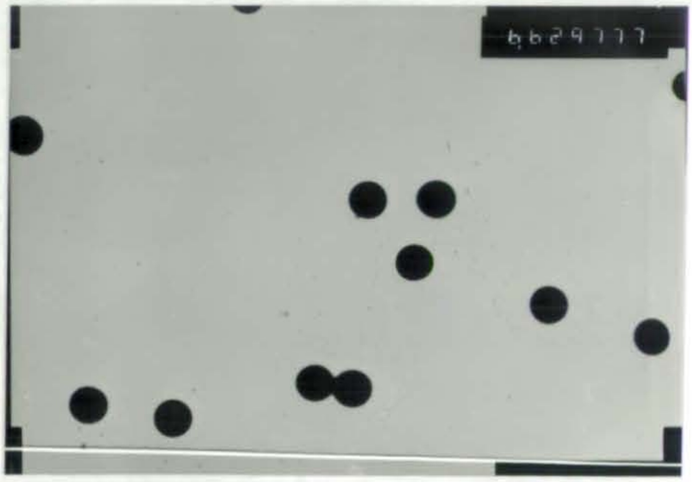
Magnification: 8,300

Fig. 28. Electron Micrograph of Latex Particles(SEF-46)



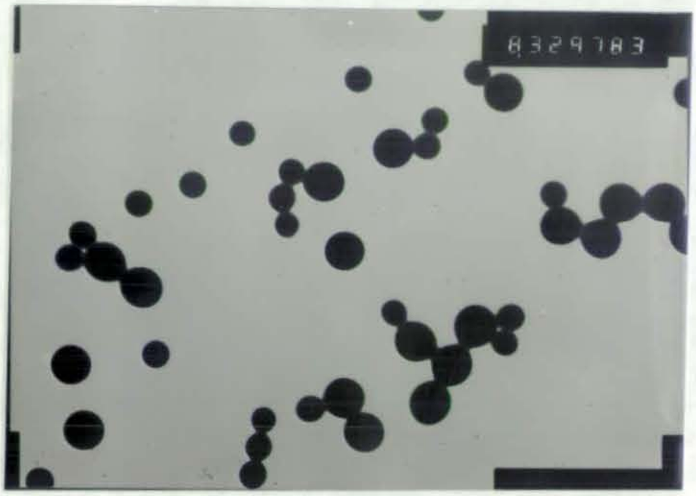
Magnification: 8,300

Fig. 29. Electron Micrograph of Latex Particles(SEF-40)



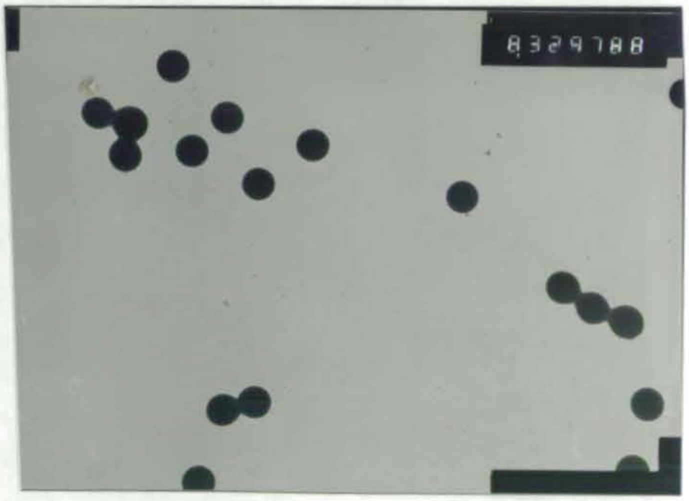
Magnification: 6,600

Fig. 30. Electron Micrograph of Latex Particles(SEF-45)



Magnification: 8,300

Fig. 31. Electron Micrograph of Latex Particles(SEF-44)



Magnification: 8,300

Fig. 32. Electron Micrograph of Latex Particles(SEF-43)

Table 5. Effect of monomer-polymer ratio

Expt. No.	Monomer-polymer ratio	Diameter after polymerization (μm)	Theoretical diameter (μm)	Newly Formed Small Particles Diameter (μm)	Polymerization Rate $(\times 10^4 \frac{[g-mole]}{[s]\,[l-H_2O]})$
SEF-13	4.22	0.84	0.79	--	1.9663
SEF-14	12.97	1.17	1.05	0.62	2.3909

Table 6. Effect of monomer-polymer ratio

Expt. No.	Monomer-polymer ratio	Diameter after polymerization (μm)	Theoretical diameter (μm)	Newly Formed Small Particles Diameter (μm)	Polymerization Rate ($\times 10^4 \frac{[g-mole]}{[s]\,[l-H_2O]}$)
SEF-24	6.81	0.71	0.56	--	1.9413
SEF-21	7.04	0.76	0.64	--	2.1092
SEF-23	10.77	0.64	0.73	0.35	1.9017
SEF-22	21.84	0.68	0.91	0.38	2.0211

Table 7. Effect of monomer-polymer ratio

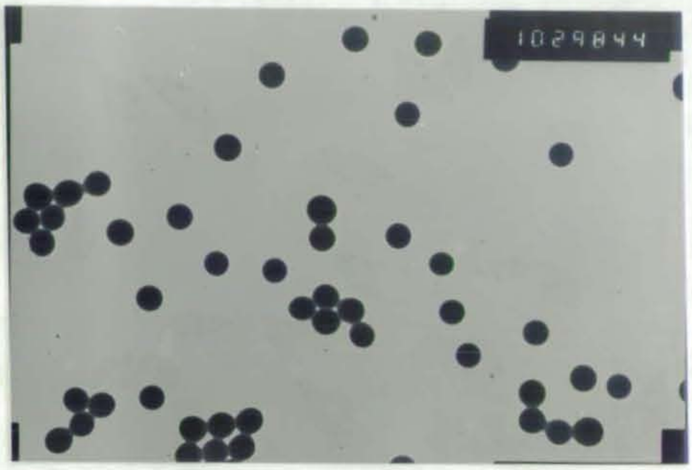
Expt. No.	Monomer-polymer ratio	Diameter after polymerization (μm)	Theoretical diameter (μm)	Newly Formed Small Particles Diameter (μm)	Polymerization Rate $(\times 10^4 \frac{[g-mole]}{[s]\,[l-H_2O]})$
SEF-47	8.65	0.55	0.54	--	4.8433
SEF-46	14.38	0.58	0.62	--	5.6047
SEF-40	19.80	0.69	0.70	--	3.7095
SEF-45	25.00	0.74	0.74	--	5.1752
SEF-44	39.00	0.62	0.87	0.42	4.4232
SEF-43	∞	0.51	--	--	4.1622

4-5. Effect of Stirring Speed

The seeded polymerizations were investigated using varying the stirring speed. The reaction conditions used in experiment were shown in Table 8. Both the electron micrographs of monomer-swollen particles and final particles are taken, see Figure 33 to Figure 37. It can be seen from these pictures that the particles have a uniform size after the seeded polymerization.

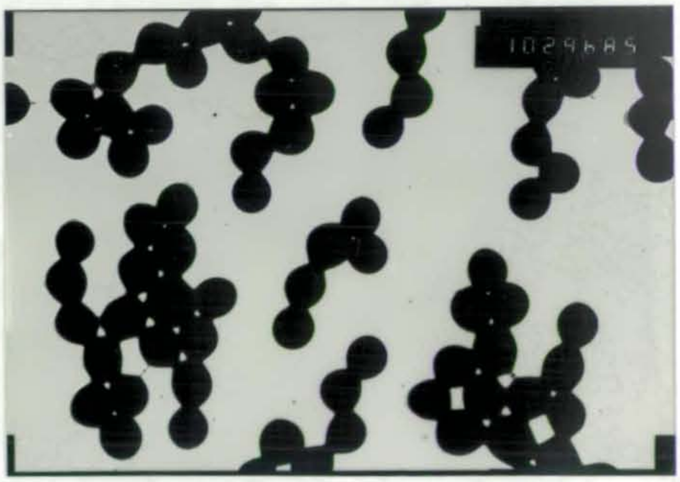
Table 8. Experimental conditions for the studying on the effect of stirring

Initiator concentration	0.017 mole/l-H_2O
Monomer-Polymer ratio	10
Solid content	0.10
Ionic strength	0.05
Reaction temperature	50 °C
Seed particle diameter	0.25 μm



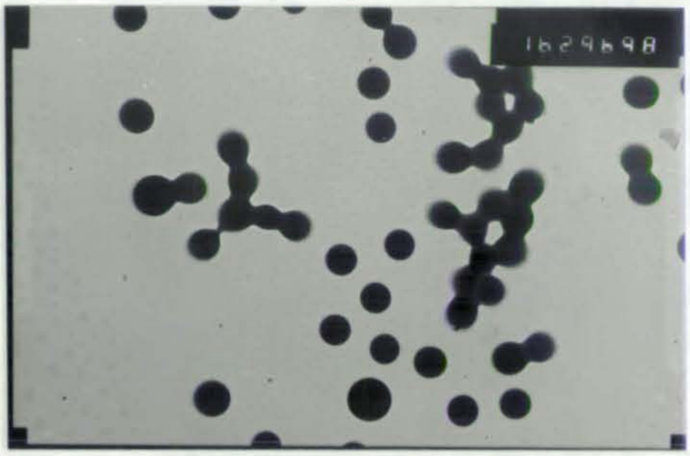
Magnification: 10,000

Fig. 33. Electron Micrograph of Seed Latex Particles(SEF-33)

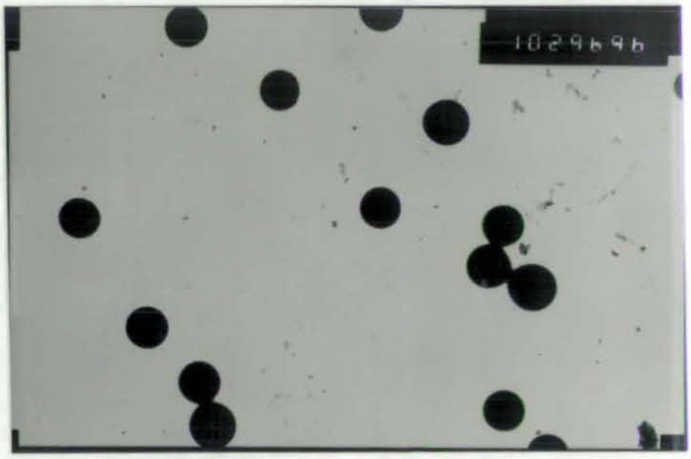


Magnification: 10,000

Fig. 34. Electron Micrograph of Latex Particles(SEF-34)



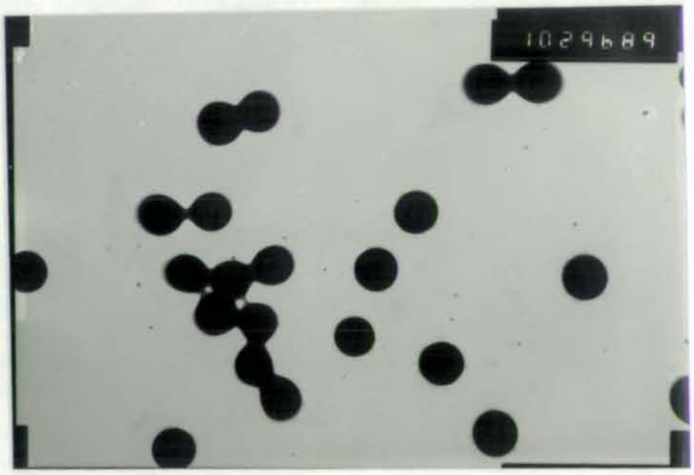
Magnification: 16,000
monomer-swollen particles



Magnification: 10,000
particles after polymerization

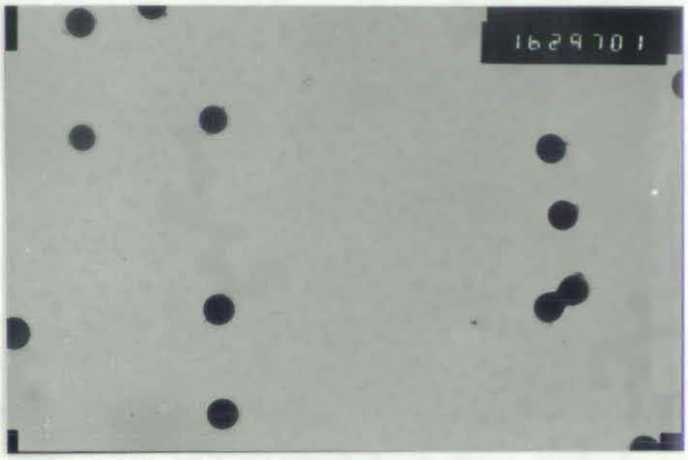
Fig. 35. Electron Micrograph of Latex Particles(SEF-37)

Magnification: 16,000
monomer-swollen particles

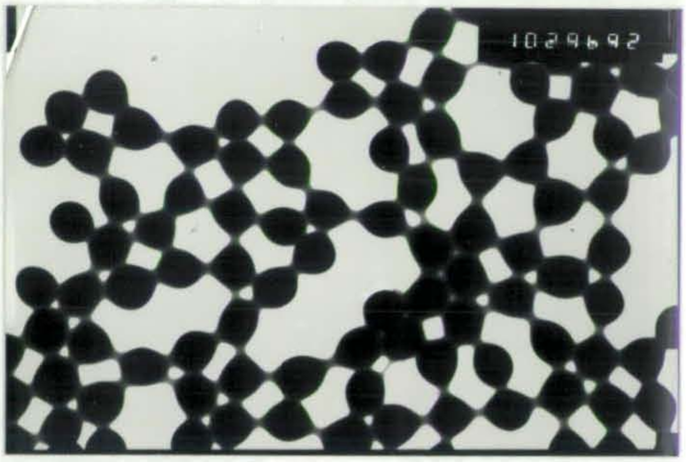


Magnification: 10,000
particles after polymerization

Fig. 36. Electron Micrograph of Latex Particles(SEF-35)



Magnification: 16,000
monomer-swollen particles



Magnification: 10,000
particles after polymerization

Fig. 37. Electron Micrograph of Latex Particles(SEF-36)

The effects of the stirring speed on the increase in the diameter of seed particles and polymerization rate are summarized in Table 9. The results have shown that the diameter of the grown seed particles, agreed with the theoretical value (see section 4-4) calculated on the assumption that all of the charged vinyl acetate was polymerized within seed particles. This result is compatible with that found by Netschey *et al*[61] and Hayashi *et al*[3].

In Run SEF-36 the particle diameter could not be measured because the particles stuck together as shown in Figure 36.

Table 9. Effect of Stirring

Expt.no.	SEF-34	SEF-37	SEF-35	SEF-36
Agitation Speed (rpm)	50	100	150	300
Conversion (%)	86.17	100	81.99	95.01
Particle Diameter (µm)	0.52	0.56	0.56	---
D_{theory}(µm)	0.57	0.57	0.57	0.57
$R_p(\times 10^4 \frac{[g-mole]}{[s]\,[l-H_2O]}$	4.2457	4.1154	4.2894	1.1643

The result of polymerization rate shows that there was no significant change in rate when the stirring speed changed from 50 rpm to 150 rpm. However, the rate was considerably reduced when the stirring speed was increased to 300 rpm. Similar results were obtained by Chiu *et al*[64] and Song *et al*[68] for the study of the emulsifier-free polymerization of styrene. This result may be attributed to an increased extent of particle coagulation with increasing stirring speed. Evidence for this is shown in Figure 36.

Figure 36 is the electron micrograph of latex particle obtained at high stirring speed. It has shown that the particles stick together. In such case, we think the particles diameter becomes bigger. So, the particle number decreased. The decrease in the number of latex particles results in the decrease in polymerization rate.

Chapter 5. CONCLUSIONS

1. The emulsifier-free polymerization of vinyl acetate can be conducted using potassium persulfate as initiator. Poly(vinyl acetate) latex particles prepared in such system are stabilized by ionic end groups ($-OSO_3^-$) from decomposition of initiator. And the polymerization behaviour of vinyl acetate in the water phase has been clarified.
2. Monodispersed poly(vinyl acetate) latex particles are easily obtained by the emulsifier-free polymerization of vinyl acetate using potassium persulfate as initiator.
3. In the batch emulsifier-free polymerization of vinyl acetate, the polymerization rate is proportional to the 0.69 power of initial monomer concentration.
4. In the seeded emulsifier-free polymerization of vinyl acetate using monodispersed poly(vinyl acetate), the polymerization rate is proportional to the 0.60 ± 0.05 power of the initiator concentration, but independent of the monomer-polymer ratio. There was no significant change in polymerization rate when the stirring speed was changed from 50 to 150 rpm, however, the rate was considerably reduced when the stirring speed was increased to 300 rpm.
5. New small particles were observed in the system containing a small amount of seed particles in the seeded emulsion polymerization of vinyl acetate, and it is believed that these small particles are those newly formed in the water phase during the seeded polymerization.

Chapter 6. Suggestions for Further Work

1. Exploring an accurate and fast method for measuring the particle size distribution during the course of seeded emulsion polymerization of vinyl acetate. From that, the mechanism of particle formation could be understood clearly.
2. Limited coalescence has been shown to determine the number of latex particles formed in the emulsion polymerization. So, the kinetic model for describing the polymerization behaviour of vinyl acetate should be derived, where coalescence of latex particles will be included.

LITERATURE

1. R. Patsiga, M. Litt, and V. Stannett, *J. Phys. Chem.*, **64**, 801(1960)

2. S. Okamura, and T. Motoyama, *J. Polym. Sci.*, **58**, 221(1962)

3. S. Hayashi, A. Komatsu, and T. Hirai, *J. Polym. Sci., Part A: Polym. Chem.*, **27**, 157(1989)

4. D. H. Napper, and A. G. Parts, *J. Polym. Sci.*, **61**, 113(1962)

5. D. H. Napper, and A. E. Alexander, *J. Polym. Sci.*, **61**, 127(1962)

6. A. S. Dunn, and P. A. Taylor, *Makromol. Chem.*, **53**, 207(1965)

7. M. Litt, R, Patsiga, And V. Stannett, *J. Polym. Sci., Part A-1*, **8**, 3607(1970)

8. V. Stannett, A. Klein, and M. Litt, *Br. Polym. J.*, **7**, 139(1975)

9. P. Harriott, *J. Polym. Sci., Part A-1*, **9**, 1153(1971)

10. M. K. Trivedi, K. R. Rajagopal, and S. N. Joshi, *J. Polym. Sci., Polym. Chem. Ed.*, **21**, 2011(1983)

11. M. Harada, M. Nomura, W. Eguchi, and S. Nagata, *J. Chem. Eng. Jpn.*, **4**, 54(1971)

12. M. Nomura, M. Harada, K. Nakagawara, W. Eguchi, and S. Nagata, *J. Chem. Eng. Jpn.*, **4**, 160(1971)

13. M. Nomura, M. Harada, W. Eguchi, and S. Nagata, in **EMULSION POLYMERIZATION**, I. Piirma, and J. L. Gardon, Eds., ACS Symposium Series 24, Washington, DC, 1976

14. M. Nomura, S. Sasaki, M. Harada, and W. Eguchi, *J. Appl. Polym. Sci.*, **22**, 1043(1987)

15. C. S. Chern, and G. W. Poehlein, *J. Appl. Polym. Sci.*, **33**, 2117(1987)

16. N. Friis, and L. Nyhagen, *J. Appl. Polym. Sci.*, **17**, 2311(1973)

17. N. Friis, and A. E. Hamielec, *J. Appl. Polym. Sci.*, **19**, 97(1975)

18. J. Ugelstad, P. C. Mork, P. Dahl, and P. Ragnes, *J. Polym. Sci., Part-C*, **27**, 49(1969)

19. R. L. Zollars, *J. Appl. Polym. Sci.*, **24**, 1353(1979)

20. K. H. S. Chang, M. H. Litt, and M. Nomura, in **EMULSION POLYMERIZATION OF VINYL ACETATE**, M. S. El-Aasser, and J. W. Vanderhoff, Eds., Applied Science, London, 1981, P89

21. W. D. Harkins, *J. Chem. Phys.*, **13**, 381(1945)

22. W. D. Harkins, *J. Chem. Phys.*, **14**, 47(1946)

23. W. D. Harkins, *J. Am. Chem. Soc.*, **69**, 1428(1947)

24. W. D. Harkins, *J. Polym. Sci.*, **5**, 217(1950)

25. W. V. Smith, *J. Am. Chem. Soc.*, **70**, 3695(1948)

26. W. V. Smith, and R. H. Ewart, *J. Chem. Phys.*, **16**, 592(1948)

27. W. V. Smith, *J. Am. Chem. Soc.*, **71**, 4077(1949)

28. J. L. Gardon, *J. Polym. Sci., A-1*, **9**, 2763(1971)

29. M. Harada, M. Nomura, H. Kojima, W. Eguchi, and S. Nagata, *J. Appl. Polym. Sci.*, **16**, 811(1972)

30. A. G. Parts, D. E. Moore, and J. G. Watterson, *Macromol. Chem.*, **89**, 156(1965)

31. D. C. Sundberg, and J. D. Eliassen, in **POLYMER COLLOIDS**, Plenum, New York, 1971

32. W. H. Stockmayer, *J. Polym. Sci.*, **24**, 314(1957)

33. T. T. O'Toole, *J. Appl. Polym. Sci.,* **9**, 1291(1965)

34. J. Ugelstad, P. C. Mørk, and J. O. Aasen, *J. Polym. Sci., Part A. Polym. Chem.*, **5**, 2281(1967)

35. J. L. Gardon, *J. Polym. Sci., Part A. Polym. Chem.*, **6**, 665(1968)

36. A. W. Hui, and A. E. Hamielec, *J. Appl. Polym. Sci.*, **16**, 749(1972)

37. N. Friis, and A. E. Hamielec, *J. Polym. Sci., Part A. Polym. Chem.*, **11**, 3321(1973)

38. N. Friis, and A. E. Hamielec, *J. Appl. Polym. Sci.*, **12**, 251(1974)

39. E. Trommstdorff, H. Koble, and P. Leqully, *Makromol. Chem.*, **1**, 169(1947)

40. C. P. Roe, *Ind. Eng. Chem.*, **60**, 20(1968)

41. R. M. Fitch, and C. H. Tsai, in **POLYMER COLLOIDS**, R. M. Fitch, Ed., Plenum Press, New York, 1971, P73

42. A. R. Goodall, M. C. Wilkinson, and J. Hearn, *J. Polym. Sci., Polym. Chem. Ed.*, **15**, 2193(1977)

43. K. W. Min, and W. H. Ray, *J. Macromol. Sci., -Rew. Macromol. Chem.*, **C11**, 177(1974)

44. K. W. Min, and W. H. Ray, *ACS Symposium Series*, **24**, 369(1976)

45. K. W. Min, and W. H. Ray, *J. Appl. Polym. Sci.*, **22**, 89(1978)

46. K. W. Min, and H. I. Gostin, *Ind. Eng., Chem. Prod. Dev.*, V18, No4(1979)

47. F. K. Hansen, and J. Ugelstad, in **EMULSION POLYMERIZATION**, I. Piirma, Ed., Academic Press, New York, 1982. P51

48. J. W. Vanderhoff, *J. Polym., Polym. Symposium*, **72**, 161(1985)

49. S. S. Medvedev, in **INTERNATIONAL SYMPOSIUM ON MACROMOLECULAR CHEMISTRY**, Prague, Pergamon, New York, 1957, P174

50. W. J. Priest, *J. Phys. Chem.*, **56**, 1077(1952)

51. F. K. Hansen, and J. Ugelstad, *J. Polym. Sci., Polym. Chem. Ed.*, **16**, 1953(1978)

52. F. K. Hansen, and J. Ugelstad, *J. Polym. Sci., Polym. Chem. Ed.*, **17**, 3033(1979)

53. F. K. Hansen, and J. Ugelstad, *J. Polym. Sci., Polym. Chem. Ed.*, **17**, 3047(1979)

54. J. Ugelstad, M. S. El-Aasser, and J. W. Vanderhoff, *J. Polym. Sci., Polym. Lett.*, **11**, 505(1973)

55. J. Ugelstad, F. K. Hansen, and S. Lange, *Makromol. Chem.*, **175**, 507(1974)

56. D. P. Durbin, M. S. El-Aasser, G. W. Poehlein, and J. W. Vanderhoff, *J. Appl. Polym. Sci.*, **24**, 703(1979)

57. J. Ugelstad, and P. C. Mørk, *Adv. Colloid Interface Sci.*, **13**, 101(1980)

58. Y. J. Chou, M. S. El-Aasser, and J. W. Vanderhoff, in **POLYMER COLLOIDS II**, R. M. Fitch, Ed., Plenum, New York, 1980, P599

59. D. Gershberg, *AIChE Int. Chem. Symp. Ser.*, **3**, 4(1965)

60. A. S. Dunn, and C. H. Chong, *Br. Polym. J.*, **2**, 49(1970)

61. A. Netschey, and A. E. Alexander, *J. Polym. Sci., Part A-1*, **8**, 407(1970)

62. M. Litt, R. Patsiga, and V. Stannett, *J. Polym. Sci., Part A-1*, **8**, 3607(1970)

63. T. Matsumoto, and A. Ochi, *Kobunshi Kagaku*, 22, 4811(1965)

64. W. Y. Chiu, and C. C. Shih, *J. Appl. Polym. Sci.*, **31**, 2117(1986)

65. J. P. Feeney, D. H. Napper, and R. G. Gilbert, *Macromolecules*, **20**, 2922(1987)

66. H. J. van den Hul, and J. W. Vanderhoff, *Br. Polym. J.*, **2**, 121(1970)

67. B. W. Brooks, and B. O. Makanjuola, *Polymer*, **23**, 77(1982)

68. Z. Song, and G. W. Poehlein, *J. Polym. Sci., Polym. Chem. Ed.*, **28**, 2359(1990)

69. R. H. Ottewill, in **EMULSION POLYMERIZATION**, I. Piirma, Ed., Academic Press, 1982, P3

70. D. C. Blackley, **EMULSION POLYMERIZATION,** Applied Science Publishers LTD., London, 1975, P3

71. G. Odian, **PRINCIPLES OF POLYMERIZATION**, A Wiley-Interscience Publication, John Wiley & Sons, Second Edition, 1981, P319

APPENDIXES

Appendix I: Experimental Recipes and Conditions

The recipes and conditions used in this study are shown below:

Expt.no.	Vinyl Acetate (g)	KPS (g)	K_2SO_4 (g)	Distilled Water (g)	Seed (g)	Temp (°C)	Stirring Speed (rpm)	Conversion (%)
SEF-2	84.70	1.821	---	284.29	---	70	60	---
SEF-7	24.04	2.40	---	241.02	---	45	150	100
SEF-8	60.41	2.41	---	240.42	---	45	150	65
SEF-9	60.10	2.40	---	240.10	---	45	150	100
SEF-10	24.14	2.40	---	240.72	---	45	150	97
SEF-11	30.10	2.40	---	241.70	---	45	150	100
SEF-12	90.05	2.40	---	240.09	---	45	150	95
SEF-13	28.67	1.40	---	240.30	SEF-7 75.59	45	150	100
SEF-14	29.97	1.40	---	240.49	SEF-7 25.70	45	150	82
SEF-17	24.73	2.40	---	240.70	---	70	80	---
SEF-18	60.00	2.40	---	240.04	---	70	80	---

(Continued)

SEF-19	12.75	2.40	---	240.30	---	70	80	100
SEF-20	16.18	4.80	---	480.09	---	70	100	100
SEF-21	26.75	2.41	---	240.49	SEF-19 76.10	70	80	74
SEF-22	27.73	2.40	---	241.31	SEF-19 25.44	70	80	90
SEF-23	26.78	2.40	---	240.30	SEF-19 49.80	70	80	90
SEF-24	29.18	2.53	---	253.13	SEF-19 85.79	70	80	66
SEF-25	27.04	6.00	--	602.99	---	70	150	100
SEF-26	22.05	2.6635	---	140.23	SEF-20 59.97	70	100	51
SEF-27	20.32	0.8554	1.3520	140.83	SEF-20 60.24	70	100	40
SEF-28	21.69	0.2897	0.4188	140.86	SEF-20 61.64	70	100	31
SEF-29	20.00	0.0572	1.6956	140.21	SEF-20 60.52	70	100	69
SEF-30	20.58	0.2890	0.4574	140.70	SEF-20 59.88	70	100	90
SEF-31	19.77	1.3410	0.8436	141.21	SEF-20 60.78	70	100	75
SEF-32	16.95	2.1435	---	112.68	SEF-20 53.97	70	100	89

(Continued)

SEF-33	100.10	6.0885	---	604.11	---	70	130	100
SEF-34	20.11	0.8089	---	135.83	SEF-25 45.18	50	50	86
SEF-35	20.08	0.8117	---	135.53	SEF-25 45.01	50	150	82
SEF-36	19.87	0.8007	---	135.55	SEF-25 45.11	50	300	95
SEF-37	20.01	0.8099	---	135.85	SEF-25 45.63	50	100	100
SEF-38	19.16	0.0837	0.4780	135.74	SEF-25 45.40	50	100	88
SEF-39	20.36	0.1579	0.4110	134.86	SEF-25 45.18	50	100	54
SEF-40	29.43	1.2177	---	235.34	SEF-25 35.07	50	150	100
SEF-41	28.88	0.2690	0.6286	235.99	SEF-25 34.57	50	150	95
SEF-42	29.82	0.1374	0.7081	234.38	SEF-25 34.68	50	150	98
SEF-43	29.71	1.2217	---	270.21	---	50	150	100
SEF-44	29.21	1.2206	---	251.75	SEF-25 17.65	50	150	100
SEF-45	29.24	1.2193	---	240.97	SEF-25 27.62	50	150	98

(Continued)

SEF-46	29.60	1.2100	---	222.63	SEF-25 48.55	50	100	95
SEF-47	29.99	1.2274	---	188.13	SEF-25 81.80	50	100	98
SEF-48	30.21	1.2191	---	263.05	SEF-33 6.41	50	150	97
SEF-49	30.15	0.2759	0.6286	263.16	SEF-33 6.69	50	150	85
SEF-50	29.70	0.1393	0.7034	263.12	SEF-33 6.67	50	150	42

Appendix II: Experimental Data

The time-conversion data obtained from experiments at various conditions are given:

Table E-1. Emulsifier-free polymerization of vinyl acetate (SEF-2)

Time (min)	5	10	15	20	30	46	60	85	105	115	130
Conversion (%)	2.01	4.67	6.78	14.32	28.79	46.80	60.04	82.07	96.80	98.74	99.71

Table E-2. Effect of initial monomer concentration on conversion

Time (minutes)	Conversion (%)			
	SEF-10	SEF-11	SEF-9	SEF-12
	M_o= 1.1649	M_o= 1.4466	M_o= 2.9076	M_o= 4.3567
15	11.88	10.70	--	--
20	--	--	9.81	5.32
25	33.53	25.21	--	--
30	--	--	22.04	12.09
35	--	39.97	--	--
40	48.46	--	--	24.10
45	--	49.48	35.28	--
55	66.58	--	--	--
60	--	63.81	45.03	46.66
70	82.66	--	--	--
80	--	83.17	60.92	59.50
85	90.63	--	--	--
95	--	99.56	--	--
100	96.47	--	76.51	--
110	--	--	--	80.41
120	96.53	100	90.27	--
145	96.71	--	--	--
150	--	100	99.03	95.44

Table E-3. Effect of initiator concentration

Time (minutes)	Conversion (%)		
	SEF-37	SEF-39	SEF-38
	$[I]=$ 0.01669	$[I]=$ 3.2794×10^{-3}	$[I]=$ 1.7278×10^{-3}
5	5.57	--	1.37
10	9.98	2.11	1.39
15	22.32	2.96	1.82
20	41.34	6.25	2.47
25	53.39	7.15	3.49
30	60.44	10.39	4.15
35	67.83	12.52	4.80
40	75.41	16.48	7.17
45	82.20	20.78	9.10
50	--	25.04	10.41
55	96.18	29.53	13.30
60	--	30.95	14.96
65	97.12	40.34	18.97
70	--	44.32	21.08
75	99.95	48.17	--
80	--	50.28	27.50
90	--	53.17	39.53
100	--	53.39	47.81

Table E-4. Effect of initiator concentration

Time (minutes)	Conversion (%)		
	SEF-40	SEF-41	SEF-42
	[I]= 0.01675	[I]= 3.6982×10^{-3}	[I]= 1.8996×10^{-3}
5	4.21	1.72	0.31
10	9.75	2.30	0.55
15	26.16	3.93	1.98
20	36.20	6.94	3.00
25	43.19	10.47	3.88
30	47.87	13.52	4.91
35	52.90	19.29	--
40	54.74	25.09	8.62
45	67.64	32.40	11.77
50	73.69	39.29	14.25
55	78.26	45.93	16.54
60	81.40	--	20.58
65	--	59.02	23.84
70	86.07	--	24.86
75	--	69.15	--
80	100	--	41.90
85	--	79.48	--
90	--	--	53.50
95	--	88.27	--
100	--	--	64.24
105	--	91.03	--
110	--	--	74.80
115	--	94.98	--
120	--	--	84.22
130	--	95.41	--
135	--	--	94.13
145	--	95.42	--

Table E-5. Effect of initiator concentration

Time (minutes)	Conversion (%)		
	SEF-48	SEF-49	SEF-50
	[I]= 0.01678	[I]= 3.7935×10^{-3}	[I]= 1.9157×10^{-3}
5	2.87	--	--
10	6.86	1.90	--
15	18.43	2.38	1.57
20	36.11	5.02	3.08
25	41.04	7.29	3.85
30	45.71	10.99	4.62
35	49.12	16.07	6.76
40	55.05	24.31	8.72
46	60.94	35.96	12.50
50	65.80	--	16.15
52	--	46.65	--
55	--	--	20.98
60	75.62	54.18	27.32
70	83.67	67.56	35.16
80	90.86	79.45	37.15
90	95.62	84.82	41.81
100	--	85.78	--

Table E-6. Effect of monomer-polymer-ratio

Time (minutes)		11	15	20	30	40	45	60	80	85	100	120
Conversion (%)	SEF-13	3.93	--	9.84	--	30.34	--	60.22	76.65	--	92.03	100
	SEF-14	--	5.19	--	24.24	--	44.48	56.65	--	82.13	--	97.89

Table E-7. Effect of monomer-polymer ratio

Time (minutes)	Conversion (%)			
	SEF-24	SEF-21	SEF-23	SEF-22
	M/p=6.81	M/P=7.04	M/P=10.77	M/P=21.84
10	38.55	--	--	--
15	--	31.70	45.19	--
20	--	--	--	52.53
25	54.15	45.412	--	--
30	--	--	61.72	61.86
40	73.05	63.67	--	--
45	--	--	77.77	72.52
50	--	68.85	--	--
55	81.43	--	87.19	--
57	--	--	--	82.06
60	--	73.57	--	--
65	--	--	89.06	--

Table E-8. Effect of monomer-polymer ratio

Time (minutes)	Conversion (%)					
	SEF-47	SEF-46	SEF-40	SEF-45	SEF-44	SEF-43
	M/P=8.65	M/P=14.38	M/P=19.8	M/P=25	M/P=39	M/P=∞
4	--	--	--	--	--	2.59
5	2.65	--	--	3.74	3.49	--
6	--	--	4.21	--	--	--
7	--	--	--	--	--	7.17
10	6.64	8.02	9.75	8.06	11.76	14.76
15	16.15	20.18	26.16	19.03	26.77	25.91
20	34.80	37.76	36.20	37.98	33.51	32.54
25	44.14	46.03	43.19	49.90	38.83	37.19
30	52.19	--	47.87	57.98	42.82	41.15
35	56.54	55.54	52.90	66.35	48.00	46.73
40	61.72	59.25	54.74	72.14	52.60	51.66
45	66.87	64.48	67.64	78.93	56.83	56.65
50	77.31	66.40	73.69	88.33	62.02	62.45
55	75.69	72.06	78.26	93.95	66.33	67.73
60	80.63	77.54	81.40	95.74	70.16	73.02
65	--	--	--	96.68	72.61	--
70	88.64	83.53	86.07	97.00	81.71	82.56
80	94.47	92.97	100	96.69	92.71	90.98
90	96.17	89.56	--	98.05	98.20	97.13
100	97.75	94.75	--	98.57	100	--
110	--	93.98	--	98.65	100	--
120	97.18	94.28	--	--	100	99.87
130	97.86	95.26	--	--	--	--

Table E-9. Effect of stirring rate

Time (minutes)	Conversion (%)			
	SEF-34	SEF-37	SEF-35	SEF-36
	50 rpm	100 rpm	150 rpm	300 rpm
5	4.37	5.57	4.48	3.85
10	10.92	9.98	7.89	6.73
15	17.14	22.32	16.80	9.26
20	--	41.34	--	16.10
25	50.87	53.39	56.34	21.22
30	--	60.44	--	27.84
35	67.28	67.83	77.63	38.63
40	--	75.41	--	56.90
45	75.23	82.20	75.98	-
50	--	--	--	89.40
55	74.83	96.18	82.39	--
60	--	--	--	93.98
65	84.23	97.12	83.67	--
70	--	--	--	94.42
75	81.22	99.95	81.34	--
80	--	--	--	95.00
90	83.82	--	81.92	--
95	--	--	--	93.50
105	85.91	--	79.66	--
120	86.17	--	82.77	95.01