

On Semicontinuous Polymerization of Vinyl Acetate

P. BATAILLE, B. T. VAN, and Q. B. PHAM, *Chemical Engineering Department, Ecole Polytechnique de Montreal, Case Postale 6079, Succursale A, Montreal, Quebec H3C-3A7, Canada*

Synopsis

A semicontinuous emulsion process was used to polymerize vinyl acetate. The parameters studied were the rate of addition of the various ingredients. The polymerization evolution was followed as samples were taken at regular intervals. These emulsion samples were analyzed for monomer conversion, rate of polymerization as well as for the size and the size distribution of the particles. The molecular weight and molecular weight distribution were obtained by gel permeation chromatography (GPC). Our study showed that the total surface of the particles is an important factor, that the reaction mechanism follows Krackeler's and Wessling's theory, and that the Smith-Ewart ideal case does not apply here.

INTRODUCTION

In industrial emulsion polymerization, two limiting cases can be distinguished: batch polymerization, in which all ingredients of the batch are put into the reaction vessel before starting the polymerization, and continuous polymerization. In many applications, for example, paint manufacture semicontinuous operation can be used to lengthen the particle generation period and slow the growth rate of the particle by regulating the rate of addition of reactants to the reactor. Such operations can be used to obtain high solids concentration and small particle size in highly exothermic polymerizations. Small particle size and high polymer concentration, are used to increase the viscosity of emulsions. Many commercial products usually sold as polymer latexes are produced in two semicontinuous processes. In the monomer feed process, water, emulsifier, initiator and part of the monomer are charged into the reaction vessel and polymerization is started. The remaining monomer is fed into the reaction vessel at a constant rate. In emulsion feed, part of the whole batch is put into the reaction vessel, the rest is fed generally as a monomer emulsion after which the polymerization is started. Both processes are often cited in literature and were used very early in copolymerization in order to obtain more homogeneous copolymers.

Fram et al.,¹ pioneers in semicontinuous polymerization, determined the feasibility of semicontinuous production of butyl acrylate-acrylonitrile copolymer. They also found that this technique offered versatility and was advantageous in preparing high solid latexes. The work unfortunately did not report on the kinetics and was inconclusive as to which technique (batch or semicontinuous) give the better copolymer. Finkentscher et al.² briefly discussed both monomer addition (M add) and emulsion addition (E add) techniques. They studied particle-size distribution curves comparing the two techniques using an acrylic ester as monomer. Elgood et al.³ published data on E add and M add

techniques used in vinyl acetate polymerization. Samples of the polymer were removed during the reaction to determine the rate of polymerization and average particle size during the course of the reaction. They concluded that the surface area of a particle is an important factor with respect to the rate of polymerization. Although the results were not analyzed kinetically, they showed that the number of particles per milliliter of latex decreased as the reaction progressed. Yeliseyeva et al.⁴ compared reaction rates and average molecular weight variation for E add and M add polymerizations. They were interested in evaluating the stability of carboxyl containing acrylate latexes. They showed that rates, average molecular weight values (\bar{M}), as well as stability, differed according to the method of adding monomer to the system. The M add technique resulted in a reduced rate of reaction, a lower \bar{M} and an improved latex stability. Recently, Wessling⁵ presented an analysis of the kinetics of continuous addition emulsion polymerization: for systems that follow the Smith-Ewart mechanism, the analysis predicted that the reaction approaches a steady state, the rate of polymerization (R_P) depends on R_z according to a reciprocal relationship; above a critical value of R_z , the particles become saturated with monomer and R_P will be constant and independent of R_z . The steady-state behavior predicted by this theory was tested against the Gerrens data on styrene, a monomer known to follow Smith-Ewart kinetics. The correlation however is somewhat ambiguous. In 1969, Gerrens,⁶ working on the semicontinuous polymerization of styrene and methyl acrylate with a feed of either monomer or monomer emulsion, found that the polymerization rate R_P and degree of polymerization \bar{P}_n are independent of R_z as long as R_z is large enough to maintain the saturation value of monomer concentration $[M]$ in the latex particle. If $[M]$ falls below this value, a steady state is reached with monomer feed as well as with emulsion feed. The Smith-Ewart theory is taken as basis for the calculation. In the same year, Krackeler et al.⁷ (1969) introduced the monomer starvation concept which was related to the lower monomer concentration presented in the M add and E add systems compared to the batch system. Molecular weight and molecular weight distribution were compared on products made by these techniques. The comparable values of $\bar{M}_w/\bar{M}_n = 3.1$ obtained indicate a similar molecular growth phenomena which appears to stem from polymerization occurring near the particle surface for the addition system.

With the exception of Elgood et al.,³ all authors cited worked with systems that were known to follow the Smith-Ewart theory, i.e., systems with monomer having a very low solubility in water (styrene is a good example). In the present paper, the authors will discuss some qualitative and quantitative information about the characteristic behavior of the semicontinuous polymerization of vinyl acetate, a monomer more soluble in water than styrene, using the redox reaction of tert butyl hydroperoxide and sodium bisulfite as a source of initiators, and Pluronic F 68 and L 62 as surfactants. The reactions are carried out at 40°C. The results are analyzed kinetically using both the ideal case where $\bar{n} = 0.5$ of Smith-Ewart and the nonideal case where \bar{n} is much greater than 0.5. Due to the much higher solubility of vinyl acetate in water as compared to styrene, the reaction is more like solution polymerization than an emulsion polymerization.

EXPERIMENTAL PROCEDURE

Reactor Design and Analysis

The reactor is a glass 2-l reaction kettle with an overflow product outlet line at the side. All other connections are made through a glasscover with $\bar{\text{S}}$ joints. During the polymerization reaction, the reactor is fed by two metering pump heads. The feed pump is a F. A. Hughes, Series 2 Micropump, rated capacity of 750 ml/hr. The product is withdrawn for analysis first by pipet and then by overflowing. The pump has positive displacement heads with a flow rate that can be adjusted from 10% to 100% of capacity and with a metering accuracy of $\pm 1\%$ of the set values. The reactor temperature is maintained at 40°C by circulating water and by a system of thermoregulator and relay.

Reactants Preparation

Vinyl acetate was distilled at $60^\circ \pm 1^\circ\text{C}$ to remove the inhibitor. *Tert* butyl hydroperoxide, sodium bisulfite and pluronic surfactants are used as provided by the suppliers.

Formulations

For the purpose of this research, it was most desirable to select one formulation for all the polymerizations. Table I presents the overall formulation that was used.

TABLE I
Overall Formulation for All Polymerizations

Monomer parameters	
dm :	density of monomer = 0.934 g/cm^3 (ref. 8)
dp :	density of polymer = 1.190 g/cm^3 (ref. 8)
ϕm :	the monomer volume fraction in the particle = 0.85 (ref. 8)
k_p :	at 40°C : constant of propagation = $19.7 \times 10^{15} \text{ cm}^3/\text{mole sec}$ (ref. 8)
k_t :	constant of termination at 50°C = $116.8 \times 10^9 \text{ cm}^3/\text{mole sec}$ (ref. 9)
R :	rate of initiation reaction = $1.98 \times 10^{-8} \text{ mole/cm}^3 \text{ sec}$
Formulation of the reaction: run A	
Initial charge: 100 g H_2O	
Solution 1: 900 cm^3 vinyl acetate	
4 cm^3 <i>tert</i> butyl hydroperoxide	
L62: 16 g	
F68: 16 g	
Rate of feeding solution 1: 300 cm^3/hr	
Solution 2: 810 g H_2O	
6 g Na_2HPO_4	
6 g NaHSO_3	
Rate of feeding of solution 2: 290 cm^3/hr	
Monomer to water ratio = 1.037	

Procedure

(a) In all the reactions, 100 g of water was added initially in the reactor. When the vessel was at the required temperature, the solutions I and II which contain water, vinyl acetate, surfactant, and initiators (Table I) were pumped, simultaneously into the reactor. This was considered the start of the reaction.

(b) Starting at 15 min after the pumping action, the products were withdrawn using a pipet at intervals of 15 min. The reaction of polymerization in the withdrawn sample was stopped by using hydroquinone.

(c) All reactions were run for 4 hr. All showed >98% conversion at this point.

Surfactants Parameters

F68 and L62 are commercial names for the pluronic series of nonionic surfactants. These are made by the addition of ethylene oxide to polymers of propylene oxide, the latter being hydrophobic, while the poly oxyethylene ends of the resulting molecule are hydrophylic. Their characteristics are given in Table II.¹¹

ANALYSIS OF THE REACTION

Conversion and Rate of the Reaction

Samples of the reaction mixture were taken at various intervals. These samples were relatively small so that the overall composition in the reactor was not seriously affected. Once a sample was removed, it was short stopped with 7 ppm hydroquinone. The purification and precipitation of the polymer in the latex samples were done using Grassie's method.¹² The accurately weighed latex samples were diluted in equal amount of acetone. The resulting solution was then precipitated with 10–20 times its volume in a 4–1 water-methanol solution. The precipitated polymer was filtered, washed with distilled water and dried to constant weight under vacuum. Since the composition of the materials in the reactor at sampling time is known, the percent conversion of the total monomer is easily calculated.

Electron Microscopy

In order to obtain particle size and particle size distributions of the latexes, each sample was submitted to examination by a scanning electron microscope. The latexes were diluted to 250 times prior to measurements.

TABLE II
Pluronic Polyols

	F68	L62
Molecular weight	8000	2000
Hydrophylic group	80	20
Hydrophyle lypophyle balance	29	7
a_s (surface area)	920×10^{-16} cm ² /molecule	230×10^{-16} cm ² /molecule

Average Size of Particle by Spectrophotometry

A technique for comparing the average particle size between different emulsions was devised.¹³ It involved the measurement of the light transmitted through an emulsion diluted down to 0.03% by weight of solid with a B & L Spectronic 20 instrument. For a given system of emulsion, a direct relationship between the percent transmittance and the average particle size, obtained from the electron microscope pictures were possible.

Gel Permeation Chromatography (GPC)

GPC was obtained for all the polymer samples. The solvent was tetrahydrofuran and the polymer concentration of the injected sample was from 0.2% to 0.25%.

DISCUSSIONS OF THE RESULTS

Polymerizations were run at different feed rates R_z , all other variables being held constant. Conversion versus time curves (Fig. 1) for vinyl acetate were very similar to those of methyl acrylate given in literature.⁶ Experimental rates of polymerization R_p _{expt}, calculated with respect to the dried weight of the polymer sample were plotted versus time of the reaction in Figure 2. The volume expressed in the rates is the total volume of emulsion in the reactor at the specified time. For all the runs, the conversion-time curves in Figure 1 were linear, and dependent on the feed rates. These observations show that our runs were in the controlled region, as defined by Wessling et al.¹⁴; these authors suggested that in the controlled region, the unreacted monomer in the reactor builds up during the run, may exceed the level of solubility of monomer in polymer and is absorbed on the polymer particles. At higher feed rates, the conversion-time curve becomes nonlinear, independent at feed rate, and the reaction is in the flooded region which is essentially equivalent to region II in a batch emulsion polymer-

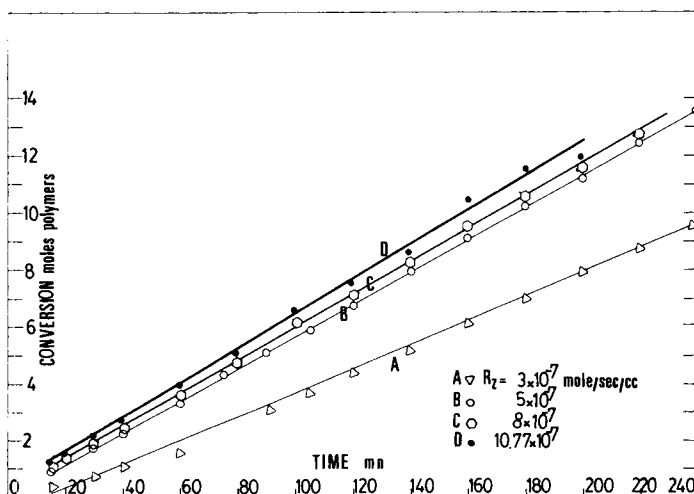


Fig. 1. Conversion vs time at different feed rates. (A) $R_z = 3 \times 10^{-7}$ mole/sec/cm³, Δ ; (B) $R_z = 5 \times 10^{-7}$ mole/sec/cm³, \circ ; (C) $R_z = 8 \times 10^{-7}$ mole/sec/cm³, \circ ; (D) $R_z = 10.77 \times 10^{-7}$ mole/sec/cm³, \bullet .

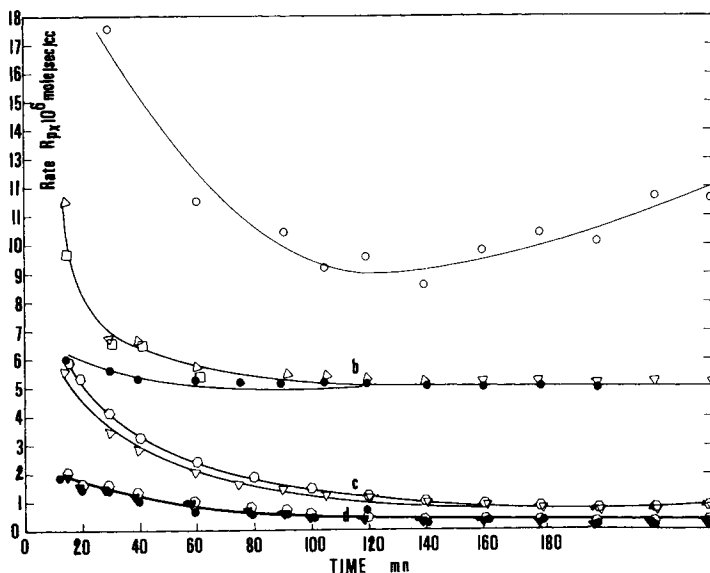


Fig. 2. Rate of polymerization vs. time. (a) Smith and Ewart, \circ ; (b) Stockmayer, Δ \bullet \square ; (c) experiments, Δ \circ ; (d) solution, \circ \blacktriangle \bullet .

ization.¹⁴ Also shown in Figure 2 is the rate of polymerization calculated by using Smith-Ewart's theory with $\bar{n} = 0.5$ and the rate according to Stockmayer with the average number of radicals per particle calculated by Bessel's function of first and second order. It is observed in Figure 2 that the experimental points are more represented by points calculated based on the theory of solution polymerization. With feed rate R_z ranging from 3×10^{-7} mole/sec cm^3 to 10.77×10^{-7} mole/sec cm^3 , the $R_{p \text{ expt}}$ attained an equilibrium after about 120 min. After this time, the $R_{p \text{ expt}}$ was changed linearly with time. A good explanation for this phenomena of the rate of reaction is given by Krackeler et al.⁷ Instead of proposing an uniform monomer concentration $[M]$ within the monomer-polymer M-P particle in an M add, the authors suggested that a situation exists within the monomer-polymer particle where much of the polymerization occurs in a zone which maintains an essentially constant $[M]$ throughout the reaction. This is visualized as a concentration gradient through the particle with a greater $[M]$ in the outer zone of the particle. Figures 3(a) and 3(b) (ref. 7) show a schematic representation of the effective $[M]$ for M add during the reaction. If the monomer is located mainly in the outer zone of the M-P particle, the thickness of this zone would depend on the amount of the monomer present and the reaction would be localized primarily in this outer zone. The $[M]$ at the reaction sites would tend, therefore, to have a more uniform value throughout the entire reaction. A reaction occurring in an outer zone of the particle would closely approximate Medvedev's proposed mechanism.¹⁵ It was noted by Funderburk¹⁶ that the Medvedev's model predicts very large particle. As it will be seen later, this condition of large particles fitted well here. Elgood et al.³ also noted that the rate of polymerization appeared to be most closely related to particle surface area per ml of emulsion. It is interesting to observe Figures 4 and 5 which show a linear relationship between the experimental rate of polymerization $R_{p \text{ expt}}$ with the total surface area and number of particles per cm^3 of latex. This special characteristic of vinyl acetate polymerization seemed not to be caused by the

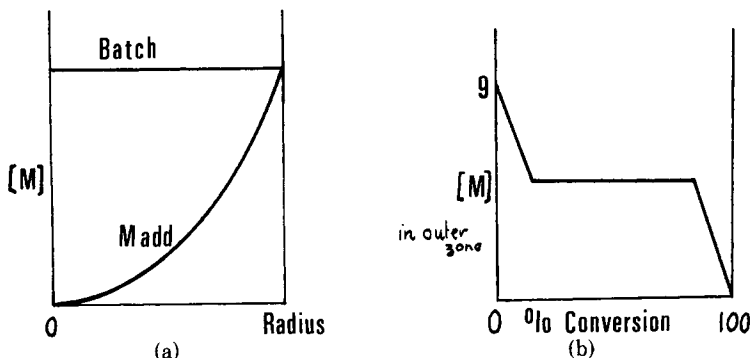


Fig. 3. (a) Schematic: distribution of $[M]$ in the monomer-polymer particle. (b) Schematic: change of $[M]$ with conversion for monomer "add" technique.

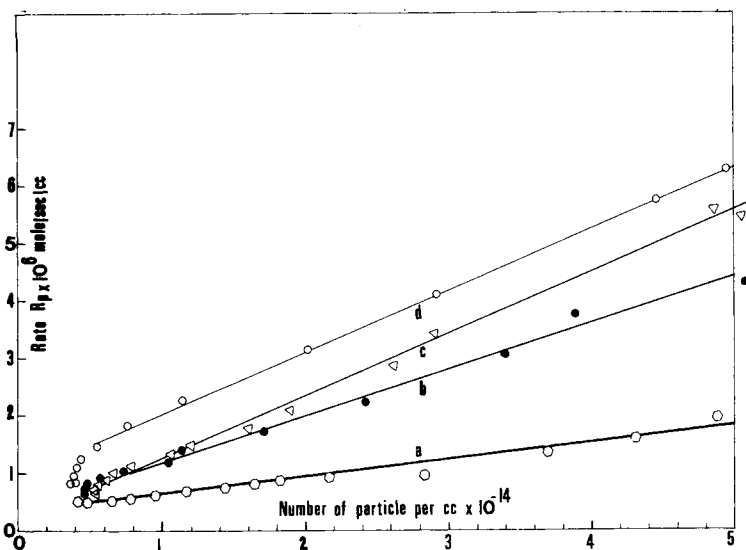


Fig. 4. Rate of polymerization vs number of particle/cm³. Experimental values. (a) $R_z = 3 \times 10^{-7}$ mole/sec/cm³, \circ ; (b) $R_z = 5 \times 10^{-7}$ mole/sec/cm³, \bullet ; (c) $R_z = 8 \times 10^{-7}$ mole/sec/cm³, Δ ; (d) $R_z = 10.77 \times 10^{-7}$ mole/sec/cm³, \circ .

technique of polymerization which was continuous addition, but by the chemical characteristic of the monomer (mostly the solubility of vinyl acetate in water) since other authors¹⁷ obtained the same results when studying the polymerization of vinyl acetate by dilatometry.

Figure 6 shows deviation of vinyl acetate system (line 2) from the mechanism proposed by Gerrens⁶ (line 1), where $R_p = R_z$ for methyl acrylate and styrene. The deviation was probably caused by the different degree of solubility of vinyl acetate in water as compared with styrene and methyl-acrylate and also by the fact that Gerrens calculated the rates of polymerization from the linear portion of the conversion versus time curves, whereas here, the rates of polymerization were calculated from the steady-state condition. Line 3 in Figure 6 shows the linear relationship between $1/R_p$ versus $1/R_z$ as proposed by Wessling,⁵ thus, confirmed the experimental fact that in the steady state, conversion changed linearly with time.

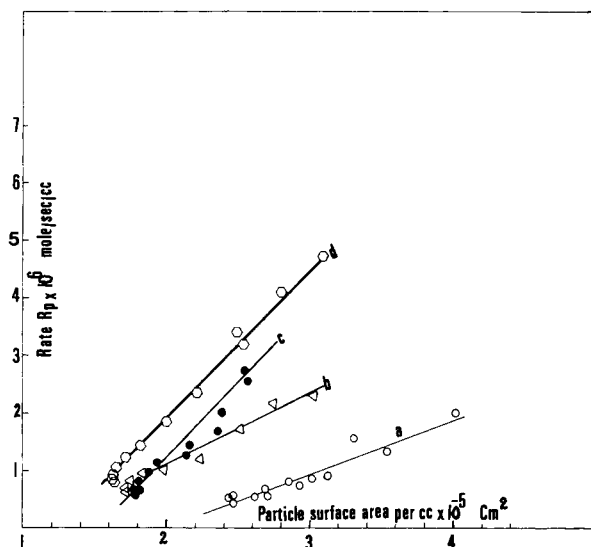


Fig. 5. Dependence of rate on the surface area of particle. (a) $R_z = 3 \times 10^{-3}$ mole/sec/cm³, \circ ; (b) $R_z = 5 \times 10^{-7}$ mole/sec/cm³, Δ ; (c) $R_z = 8 \times 10^{-7}$ mole/sec/cm³, \bullet ; (d) $R_z = 10.7 \times 10^{-7}$ mole/sec/cm³, \circ .

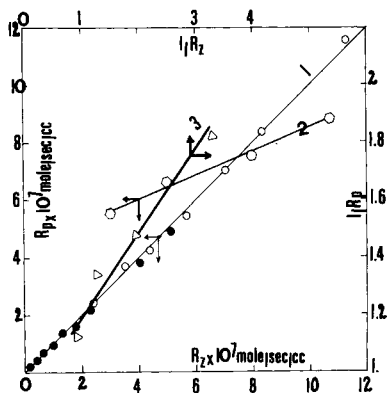


Fig. 6. Polymerization rate R_p vs feed rate R_z . 1: Methyl acrylate and styrene, \bullet ; 2, 3: vinyl acetate, present paper, \circ , Δ .

Figure 7 shows the rate plots for the four runs. Straight lines indicate that the conversion of monomer to polymer is a first order reaction and that auto acceleration is not present, unlike the situation in other polymers.¹⁸ The initiator concentration remains fairly constant through the run. The nonzero intercept on the time axis shows the existence of an inhibition period in each run, a common occurrence in vinyl acetate polymerization.

Particle Size, Particle Number per Unit Volume of Latex, and Size Distribution

Table III shows the average diameter and number of particles as function of time of the reaction. The average diameters of the particles were obtained by spectronic B and SL 20 by the technique mentioned earlier in the subsection,

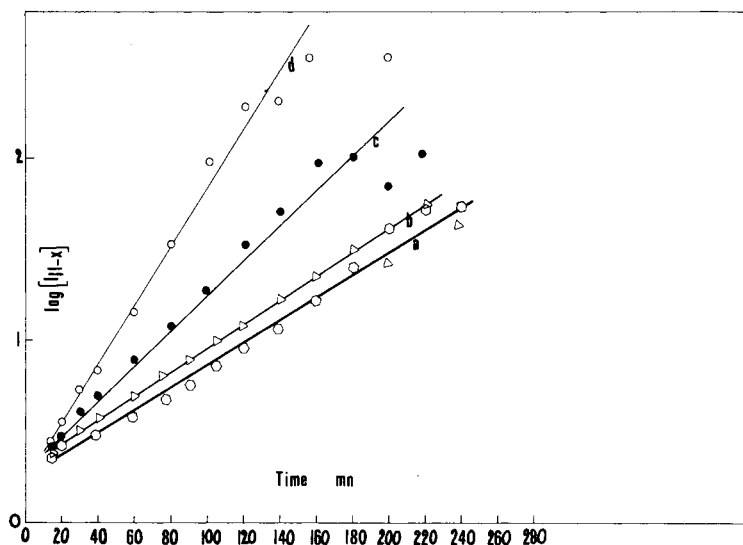


Fig. 7. First-order rate plot. (a) $R_z = 3 \times 10^{-7}$ mole/sec/cm³, ○; (b) $R_z = 5 \times 10^{-7}$ mole/sec/cm³, ●; (c) $R_z = 8 \times 10^{-7}$ mole/sec/cm³, ▽; (d) $R_z = 10.77 \times 10^{-7}$ mole/sec/cm³, ○.

TABLE III
Run B

Time (min)	Conversion (%)	Diameter of particle (μm)	Number of particle/cm ³ of latex × 10 ⁻¹⁴
15	56.0	0.130	4.8681
30	68.5	0.165	2.9123
40	74.0	0.175	2.6371
60	80.0	0.200	1.9098
75	84.5	0.215	1.6238
90	87.0	0.240	1.2019
105	90.0	0.252	1.0741
120	91.5	0.282	0.7792
140	94.0	0.300	0.6649
160	95.5	0.310	0.6122
180	97.0	0.320	0.5653
200	96.0	0.325	0.5341
220	98.0	0.325	0.5452
240	97.5	0.325	0.5424

Average Size of Particle by Spectrophotometry. The number of particles per cm³ of emulsion were calculated from the percent of conversion and the diameter of the particle.

As can be seen in Table III, in all runs the number of particles per ml diminishes as polymerization proceeds in all runs. It is well known in emulsion polymerization that the vast majority of the micelles which are formed initially do not result in particles. A conclusion to this is that many of the micelles originally formed will break down and migrate to M-P particles now in their growth stages where the emulsifier molecules are needed to stabilize these new particles.

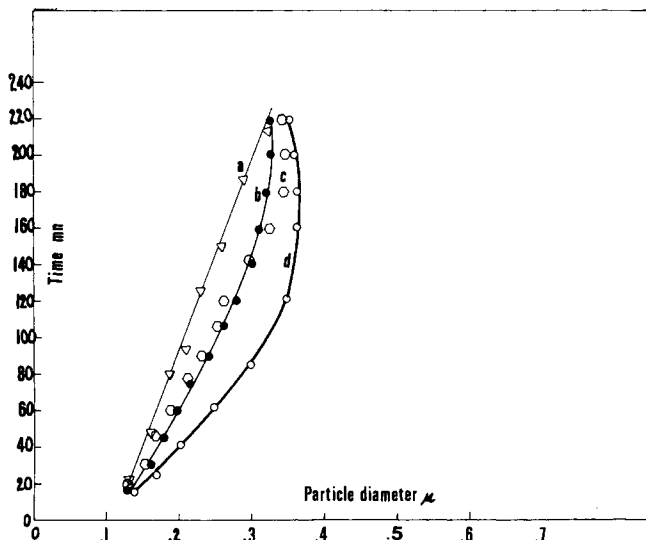


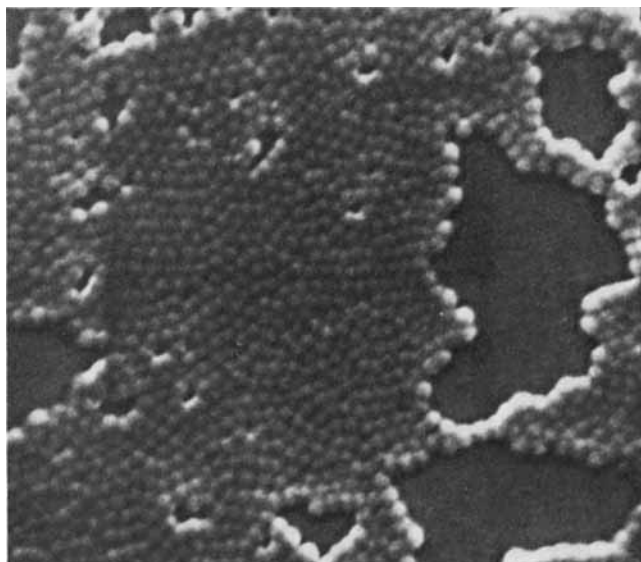
Fig. 8. Particle size by Spectronic 20. (a) $R_z = 3 \times 10^{-7}$ mole/sec/cm³, Δ ; (b) $R_z = 5 \times 10^{-7}$ mole/sec/cm³, \bullet ; (c) $R_z = 8 \times 10^{-7}$ mole/sec/cm³, \circ ; (d) $R_z = 10.77 \times 10^{-7}$ mole/sec/cm³, \circ .

Volumetric Growth Rate of Particles

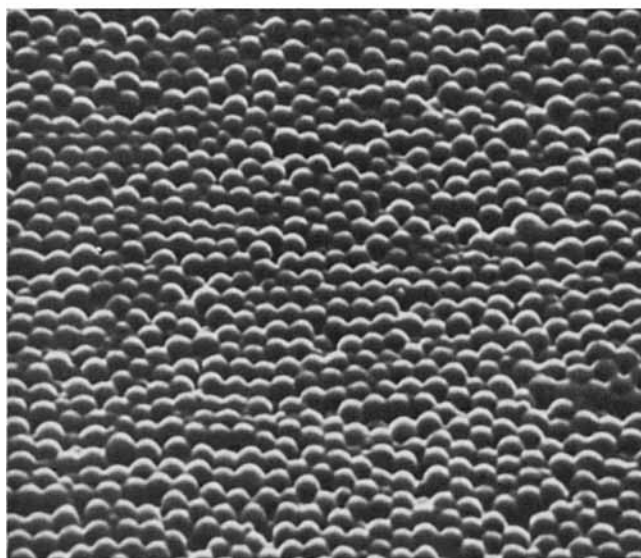
The growth mechanism of an emulsion polymer particle can be represented by $dV/dt = K_p D^m$ in which V is the volume of particle, t is the time, D is the diameter of particle, K_p is the proportionality constant, and m is an exponent which depends on the growth process. For Smith and Ewart, ideal cases of the average number of radical per particle $\bar{n} = 0.5$, $m = 0$, thus dV/dt is constant. For large particles m varies from $2.5 \rightarrow 3$.¹⁹ The time of growth for an individual particle must also be considered, i.e., those particles formed early in the reaction have a longer growth period compared to particles which formed later in the reaction. It follows that the "older" particles will then be larger than the "younger" particles. When the period of particle formation is extended as in the semibatch technique, this would tend to have a broadening effect on the particle size distribution.

Figure 9 shows the electron micrograph of the latex samples. It was observed from the figure that the particle size distribution is quite uniform and there is evidence of fresh nucleation. From the technique of polymerization it is obvious that particles are formed continuously as monomer, initiator and soap are fed into the reactor. It was discussed in the Conversion and Rate of the Reaction subsection that the total surface area of particle is an important factor in the polymerization, also, due to the high solubility of vinyl acetate in water; it is proposed that the locus of polymerization was both in the aqueous phase and in the micelles. Once particles are formed, they continue to grow in the aqueous phase by consuming monomer from the micelles and monomer droplets.

The oligomers thus formed, attained a certain size and are precipitated from the aqueous phase. By this process of precipitation, the oligomeric particles released the surfactant that kept them in equilibrium in the aqueous phase. The surfactant release will form micelles to generate new particles and to help keep them in equilibrium in the aqueous phase. This theory accounts for the decrease in the number of particles during the course of reaction and the fresh nucleation



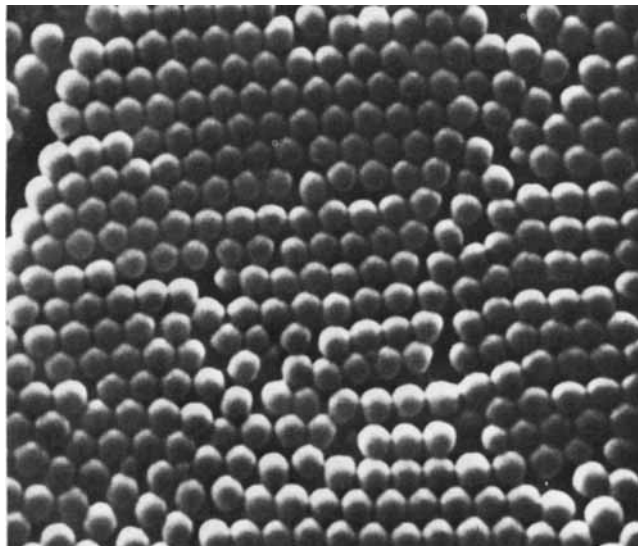
(a)



(b)

Fig. 9. Electron micrographs of the latex sample. (a) Sample at 15 min after starting of the reaction; magnification 27,800. Particles are not yet clearly defined and are covered by monomer. (b) Sample at 60 min after starting; magnification 26,000. Evidence of the fresh nucleation is observed. (c) Near the end of the reaction; particles are clearly defined and the particle size is uniform; magnification 27,800.

of particles even at high conversion. The same effect was also observed earlier in our laboratory²⁰ while analyzing the particle size distribution of emulsion polymerization of styrene. It is interesting to note in Figure 8 that in all runs, the particle size reached an equilibrium at steady state.



(c)

Fig. 9. (continued from previous page)

The Average Number of Radicals per Particle: Deviation from Ideal Case of Smith and Ewart

In a series of papers,²¹⁻²⁴ Gardon modified the theory of Smith and Ewart while retaining the essential features. By dividing the reaction of polymerization into three intervals: all particles are formed in interval I; the number of particles is constant in intervals II and III. Our working conditions, however, were more or less than in interval II. The variation of conversion with time during interval II is predicted to fit the equation $P = At^2 + Bt$, where P is the conversion in term of the volume of polymer present per unit volume of water and t is unit of time. The experimental values of P and t were regressed linearly using the least square method to find the values of A and B . The variation of the average number of radicals per particle \bar{q} , with conversion during interval II is given by

$$\bar{q}_1 = 0.5[1 + (4A/B^2)P]^{0.5} \quad (1)$$

With the aid of parameters A and B , defined by Gardon,²³ one can predict the variation of molecular weight with conversion during interval II:

$$\bar{M}_n = (4AN_A dp/BR)P / ([1 + (4A/B^2)P]^{0.5} - 1.0) \quad (2)$$

$$\bar{M}_v = (B^3 N_A dp/3AR)([A + (4A/B^2)P]^{1.5} - 1)/P \quad (3)$$

Values of d_p , R for the system were found in Table I and N_A is Avogadro's number.

Equation (1) measures the deviation from Smith and Ewart's model, if $1 \gg (4A/B^2)P$, the Smith-Ewart model is not valid and the number average molecular weight \bar{M}_n is given by

$$\bar{M}_n = (2dp/Na)R(P/t) \quad (4)$$

With systems that deviate from Smith and Ewart's theory, Stockmayer²⁵ and O'Toole²⁶ provided the general solution for the recursion formula proposed by Smith and Ewart; Stockmayer's solution was

$$\bar{q}_2 = \left(\frac{a}{4}\right) \frac{I_0(a)}{I_1(a)} \quad (5)$$

$$a^2 = 8\alpha, \quad \alpha = \left(\frac{R}{N}\right) \left(\frac{N_A \bar{V}}{k_t}\right) \quad (6)$$

where \bar{q}_2 is the average number of radical per particle according to Stockmayer, \bar{V} is the average volume of monomer swollen particle, k_t is the termination constant, and I_0 and I_1 are the Bessel functions of the first kind of zero and first order, respectively.

Van der Hoff²⁷ rearranged eq. (5) to obtain an expression for the Z factor:

$$Z = \frac{q_2}{(a/4)} = \frac{I_0(a)}{I_1(a)}$$

and the rate of polymerization in batch free radical polymerization is

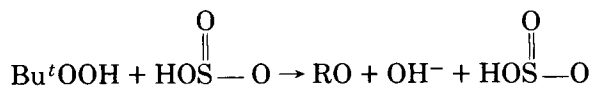
$$R_p = Zk_p(R/2kt)^{1/2}[M] \quad (7)$$

The Z factor allows eq. (7) to be applicable to solution, bulk, suspension, and emulsion polymerization systems. For bulk and solution, the "particle volume" is in effect the whole reactor and $Z = 1$.

From Table IV, it was observed that as a varies from 1 to 85, Z factors vary from 2 to 1, according to a graphic by van der Hoff,²⁷ which presented the factor Z as a function of parameter a , it is concluded that the reaction of polymerization in the system studied here was on the bulk side. This conclusion was further strengthened by Figure 2 where the experimental points of conversion versus time are more represented by calculation based on the theory of bulk polymerization.

Molecular Weight and Molecular Weight Distribution by GPC

Table V showed the number average molecular weight calculated by eq. (2) and the viscosity average molecular weight by eq. (3). These two equations represented the system as in interval II of Gardon.²³ An increase in the polydispersity with conversion observed in this table showed an increase in the density of chain-branching.¹⁸ Figure 10 showed the GPC of one sample of run A. In addition to the main peak which appeared in the low molecular weight region, there was another peak, very sharp, in the high molecular weight region. A possible explanation for this anomaly was due to the reaction of initiation of radicals: Kharasch and collaborators²⁸ proposed that the mechanism of the redox system of Bu^tOOH and sodium bisulfite would appear to be analogous to the ion decomposition of hydroperoxides: the hydrogen sulfite ion donates one electron giving a hydrogen sulfite radicals and an alkoxy radical:



For a polarizable radical, like $\text{OH}\cdot$, both the presence of an electrical double layer on the particle surface and solvation after transfer by the water favor the escape of the radical to the aqueous phase.²⁷ In similar case of hydroperoxides,²⁷ pairs of radicals are produced in such a way that only the organic radicals $\text{RO}\cdot$ enters the particle while the inorganic fragments $\text{OH}\cdot$ remains in the aqueous phase

TABLE IV
Results for Run A

Rate of Polymerization		\bar{q}_1^a	\bar{q}_2^b	Z	a^c	R_p , (SE) ^d × 10 ⁶	R_p (Stockmayer) ^e × 10 ⁶	R_p (bulk) ^f × 10 ⁶	R_p (expt) ^g × 10 ⁶
Time (min)	Conversion (%)								
15	56.0	0.6773	0.5610	2.2262	1.0080	37.0478	11.4913	1.9329	2.0006
30	62.0	0.7194	0.8275	1.2982	2.5497	17.6117	6.7011	1.7074	1.5586
40	66.0	0.7539	0.8334	1.2934	2.5774	19.9167	6.6763	1.5652	1.3176
60	73.0	0.8327	1.4701	1.1115	5.2905	11.4501	5.7374	1.3624	0.8854
92	82.0	0.9985	2.5908	1.0553	9.8201	10.6055	5.4473	1.0218	0.8537
105	86.0	1.1213	3.8062	1.0359	14.6792	9.2409	5.3472	0.8799	0.7996
120	89.0	1.2527	4.3279	1.0312	16.7878	10.3977	5.3229	0.7667	0.7367
140	91.0	1.3814	6.4311	1.0204	25.2101	8.5155	5.2671	0.6859	0.6671
160	94.0	1.6791	8.4021	1.0155	33.0954	9.8136	5.2418	0.5509	0.6019
180	96.0	2.0459	11.9126	1.0108	47.1413	10.3902	5.2176	0.4452	0.5222
200	97.5	2.5779	19.5153	1.0065	77.5741	10.1444	5.1954	0.3492	0.5091
220	98.0	2.8785	21.0774	1.0060	83.8068	11.7500	5.1928	0.3115	0.4684
240	98.0	2.8785	21.4137	1.0059	85.1524	11.5644	5.1923	0.3115	0.4319

^a Average number of radicals per particle, calculated by eq. (1).^b Average number of radicals per particle, calculated by eq. (5).^c Parameter defined by Stockmayer and O'Toole [eqs. (5) and (6)].^d Rate of polymerization calculated based on the theory of Smith and Ewart with the average number of radicals per particle = 0.5.^e Rate of polymerization on the assumption $\bar{n} \gg 1$; $R_p = k_p[M](R_i/2k_t)^{1/2}$, where k_p is a function of time.^f $R_p = k_p(M)(R_i/2k_t)^{1/2}$.^g Rate of polymerization based on the dried weight of the polymer sample.

TABLE V
 Molecular Weights and Polydispersities of the Resulted Polymer

Time (min)	Conversion (%)	\bar{M}_n [eq. (2)]	\bar{M}_v [eq. (3)]	Second peak		First peak		PD
				\bar{M}_n (expt)	\bar{M}_w (expt)	\bar{M}_n (expt) $\times 10^7$	\bar{M}_w (expt) $\times 10^7$	
15	56	19,405	19,522	28,371	171,496	5,4028	11,8039	2.18
30	62	20,099	20,317	36,724	211,429	14,1620	4,4669	3.15
40	66	20,677	20,950	38,764	333,786	62,1670	15,0671	2.42
60	73	21,966	22,408	40,094	313,390	39,775	11,3439	2.85
78	78	23,271	23,932	43,381	276,823	76,014	18,1796	2.39
92	82	24,700	29,289	30,414	227,609	61,846	19,2371	3.11
105	86	26,724	30,759	33,013	258,873	120,130	27,973	2.74
120	89	28,940	32,797	32,696	233,790	233,790	—	—
140	91	31,010	34,935	29,847	241,452	—	—	—
160	94	35,917	40,492	42,070	325,224	—	—	—
180	96	41,965	47,820	52,712	542,682	—	—	—
200	97.5	50,733	58,871	57,260	716,090	—	—	—
220	98	55,688	65,229	93,674	1,152,642	—	—	—
240	98	55,688	65,229	—	—	—	—	—

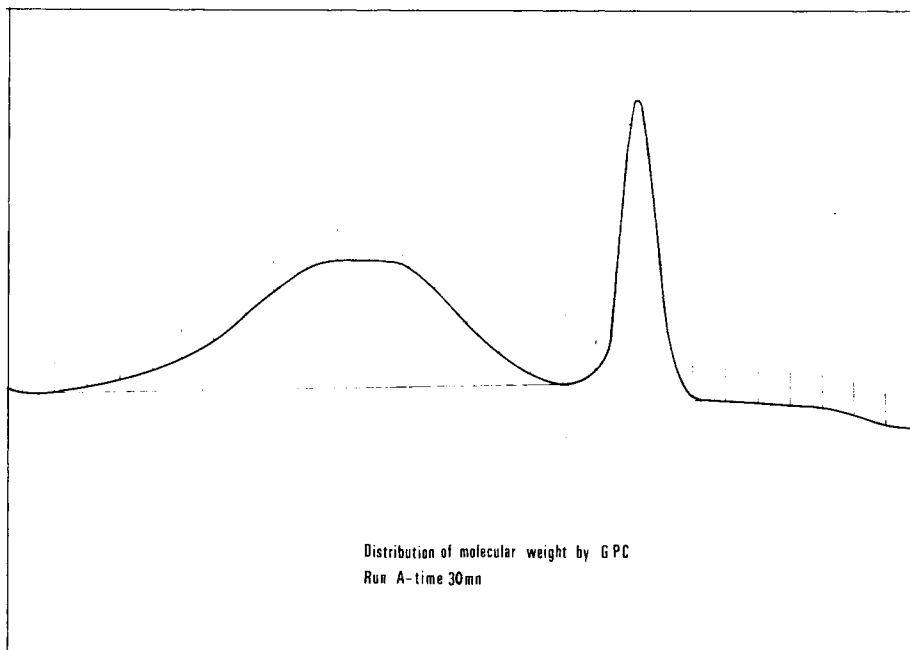


Fig. 10. Distribution of molecular weight by GPC.

where it can undergo further reaction. Since the solubility of vinyl acetate in water is high, the polymerization in the aqueous phase plays an important part. This explains the fact that the polymerization is more on the bulk side in the aqueous phase than in the emulsion side. Moreover, many authors¹⁸ suggested that the bulk polymerization gives polymers of higher molecular weight and very sharp distribution. By using the same system of initiation in the polymerization by batch and semicontinuous of vinyl acetate, Lanthier¹³ observed the same phenomena.

CONCLUSIONS

In conclusion we may say that more experimental data on the kinetics of the semicontinuous emulsion polymerization are badly needed if attempts to elucidate the system are to be made. In our view, the vital points are as follows: the solubility of monomers in water, since the medium of polymerization is mostly water, and the swellability of polymer particles. In one end of the scale, we have styrene that is almost insoluble in water and the polystyrene particle is non-swelling. In other end of the scale is vinyl acetate which is considerably more soluble in water and the polymer particle is swellable.

The reaction of polymerization by continuous addition of monomer in general follows the mechanisms and kinetics proposed by Krackeler et al., Wessling, Wessling et al., and other authors who discussed to some extent the subject. Within the framework of our experimental data, we observed that the polymerization of vinyl acetate by continuous addition of monomer, the total particle surface area per milliliter of latex is an important factor. The mechanism of the reaction follows in general the theory proposed by Krackeler et al. and of Wessling. The conversion of monomer to polymer is a first-order reaction and

that autoacceleration is not present. The polymerization reaction is in fact a solution polymerization. Due to the higher solubility of vinyl acetate in water, the locus of polymerization is both in the aqueous phase and in the micelles. Part of the monomer which is polymerized in the aqueous phase results in the fraction of polymer of higher average molecular weight and sharp distribution. In this technique of semicontinuous polymerization, the average number of radical per particle is much greater than one and hence the ideal case of Smith-Ewart is not applicable.

References

1. P. Fram, G. T. Stewart, and A. J. Szlochtum, *Ind. Eng. Chem.*, **47**, 1000 (1955).
2. F. Finkentscher, H. Gerrens, and H. Schuller, *Z. Angew. Chem., Int. Ed.*, **1**, 55 (1961).
3. B. G. Elgood, E. V. Gulbekian, and D. Kinsler, *J. Polym. Sci., Part B*, **2**, 257 (1964).
4. V. I. Yeliseyeva, N. G. Zharkova, A. V. Chubarova, and I. I. Zubov, *Polym. Sci. USSR*, **7**, 171 (1965).
5. R. A. Wessling, *J. Appl. Polym. Sci.*, **12**, 309 (1968).
6. H. Gerrens, *J. Polym. Sci., Part C*, **27**, 77 (1969).
7. J. J. Krackeler and H. Naidus, *J. Polym. Sci., Part C*, **27**, 207 (1969).
8. J. L. Gardon, *J. Polym. Sci., A-1*, **6**, 643 (1968).
9. J. Brandrup and E. H. Immergut, *Polymer Handbook*, 2nd ed., Interscience, New York, 1975, pp. II-63.
10. W. G. Barb, J. H. Baxendale, P. George, and K. R. Hargrave, *Trans. Faraday Soc.*, **47**, 493 (1951).
11. D. M. French, *J. Polym. Sci.*, **32**, 395 (1958).
12. N. Grassie, *Trans. Faraday Soc.*, **48**, 379 (1952).
13. R. Lanthier, unpublished data.
14. R. A. Wessling and D. S. Gibbs, *J. Macromol. Sci., Chem.*, **7**(3), 647 (1973).
15. S. S. Medvedev, *Collection Czech Chem. Common., Spec. Issue*, **22**, 174 (1957).
16. J. O. Funderburk, Ph.D. dissertation, Iowa State University, 1969.
17. R. Patsiga, M. Litt, and V. T. Stannett, *J. Phys. Chem.*, **64**, 801 (1960).
18. K. Nagasubramanian and W. W. Graessley, *Chem. Eng. Sci.*, **25**, 1559 (1970).
19. J. W. Vanderhoff, J. F. Vitkuske, E. B. Bradford, and T. Alfrey, Jr., *J. Polym. Sci.*, **20**, 225 (1956).
20. Q. B. Pham, Masters dissertation, Ecole Polytechnique, University of Montreal, 1976.
21. J. L. Gardon, *J. Polym. Sci., A-1*, **6**, 623 (1968).
22. J. L. Gardon, *J. Polym. Sci., A-1*, **6**, 643 (1968).
23. J. L. Gardon, *J. Polym. Sci., A-1*, **6**, 665 (1968).
24. J. L. Gardon, *J. Polym. Sci., A-1*, **6**, 687 (1968).
25. W. H. Stockmayer, *J. Polym. Sci.*, **24**, 314 (1957).
26. J. T. O'Toole, *J. Appl. Polym. Sci.*, **9**, 1291 (1965).
27. B. M. E. van der Hoff, *Adv. Chem. Ser.*, **34**, 6 (1962).
28. M. S. Kharasch, R. T. E. Schenck, and F. R. Mayo, *J. Am. Chem. Soc.*, **61**, 3092 (1939).

Received October 21, 1976

Revised July 29, 1977