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The relationship between particle size and molecular weight in emulsion polymerization

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The relationship between particle size and molecular
weight in emulsion polymerization

by

David Victor Loebach

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
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NOMENCLATURE

a_s	area associated with a single molecule of surfactant, $\text{cm}^2/\text{molecule}$
D_a	area average particle diameter, \AA
D_n	number average particle diameter, \AA
D_v	volume average particle diameter, \AA
$f(t)$	exit age distribution
$[I]$	initiator concentration, moles/l
k_d	initiator decomposition rate constant, sec^{-1}
k_p	polymerization rate constant, l/mole-sec
k_t	termination rate constant, l/mole-sec
k_{tf}	chain transfer rate constant, l/mole-sec
K	growth constant for a latex particle, cm^3/sec
M	molecular weight, moles/l
M_o	molecular weight of monomer, moles/l
\bar{M}_n	number average molecular weight, gr/mole
\bar{M}_{np}	number average molecular weight of polymer in a particle, gr/mole
\bar{M}_v	viscosity average molecular weight, gr/mole
\bar{M}_{wp}	weight average molecular weight of polymer in a particle, gr/mole
$[M]$	monomer concentration in a particle, mole/l

n	number of radicals in a particle
N	number of particles per gram of latex
N_A	Avogadro's number, molecules/mole
r	radius of a latex particle, cm
r_c	rate of radical capture by a particle, events/sec
r_t	rate of termination inside a particle, events/sec
r_{ft}	rate of chain transfer inside a particle, events/sec
R	rate of radical generation, radicals/l-sec
$[R]$	free radical concentration, moles/l
S	total area of particles and micelles in the system, cm ² /l
$[S]$	surfactant concentration, moles/l
t	time, sec
V_p	volume of a particle, l
α	dimensional constant used to calculate the rate of radical capture
β	dimensional constant used to calculate the rate of termination
η	dimensional constant used to calculate the rate of chain transfer
$[\eta]$	intrinsic viscosity
ρ_o	density of monomer, gr/ml
ρ_p	density of a particle, gr/ml

τ mean residence time of the reactor, sec
 \emptyset volume fraction of monomer in a particle

INTRODUCTION

During World War II both the United States and Germany saw a need to develop a synthetic rubber in order to become self-sufficient in that commodity. Consequently, a massive research effort was directed at this end, and as a result, a process for producing a synthetic rubber was developed. This research program had a side effect of producing many engineers and scientists trained in the new field of polymerization. After the war these engineers and scientists directed their skills toward other areas of polymerization, resulting in a boom in the polymer industry. Today polymers and polymerization are a dominant sector of the chemical industry, employing over fifty percent of all chemists and chemical engineers (56).

In the government research program, one particular polymerization process was found to be best suited for producing an artificial rubber and was therefore studied extensively. This process was emulsion polymerization. In this process, water, monomer, a surfactant, and a water-soluble initiator are mixed together. The product of the resulting polymerization is a latex in which the polymer is present in tiny particles stabilized in the latex by the surfactant. Some of the advantages of such a process are apparent. Heat transfer from the site of polymerization by

the water phase is excellent, so that temperature control is not a problem. Since the product is a latex, it is directly usable in paints, coatings, and adhesives. Perhaps the most important advantage is that uniformly high molecular weight polymers are produced at high rates of reaction. This is a direct contrast with bulk, solution, and suspension polymerization processes in which high molecular weight polymers are produced only at very slow rates of reaction. There are also disadvantages with an emulsion polymerization process. For instance if the polymer itself is the desired product, the latex must be destroyed, and the polymer must be recovered and processed to remove the surfactant. In addition while most of the polymer is being produced in the latex particles, bulk polymerization may be occurring in the monomer droplets, and solution polymerization may be occurring in the monomer-water solution. The polymer produced in these last two locations has considerably different properties than that produced in the particles. Fortunately it forms a separate solid phase which can easily be removed from the latex. Perhaps the most troublesome problem of emulsion polymerization is that a product properties are often inconsistent from one run to another even though reaction conditions are not intentionally changed.

Despite its drawbacks emulsion polymerization is still

the basis for nearly all artificial rubber processes. Besides rubber, many paints, coatings, and adhesives are also produced by emulsion polymerization. Except in the rubber industry, most emulsion polymerization processes employ batch production rather than continuous production. The flexibility of a batch operation is certainly one reason for this. Another reason, and perhaps the most important, is the difficulty in operating and controlling a continuous emulsion polymerization system. Perhaps with additional research this can be overcome and continuous emulsion polymerization will see more commercial use.

Purpose and Goal of this Investigation

The advantages of being able to predict and control the properties of polymer produced under a given set of conditions are obvious. In emulsion polymerization, the size distribution of the latex particles and the molecular weight of the polymer are two key properties which would be desirable to predict and control. For this investigation molecular weight was the specific property of interest. The specific goal was to experimentally determine the relationship between molecular weight and particle size and to obtain a mathematical model which could be used to explain the experimental results. The purpose of the investigation was two-fold. One purpose of determining

relationship between molecular weight and particle size was to identify the sources of molecular weight poly-dispersity and thus to provide better predictions of the molecular weight distribution. The second purpose was to obtain additional insight into the mechanism of emulsion polymerization so that a more accurate model may be obtained.

THEORY AND LITERATURE REVIEW

Smith-Ewart Theory

A qualitative theory of emulsion polymerization was introduced by Harkins in 1947 (20). The following year Smith and Ewart's quantitative refinements to the theory were published. They retained the basics of Harkins' mechanism and included a mathematical analysis of the batch emulsion polymerization process (48). The work of these pioneers is still widely accepted as providing a reasonably satisfactory description of the batch process of emulsion polymerization. The basics of their theory will be given below.

The essential ingredients of an emulsion polymerization reaction are water, monomer, surfactant, and initiator. Initially the surfactant is present as clusters of 50-100 molecules which contain a small amount of monomer. The shape and size of these clusters, or micelles, is uncertain, but one may consider them to be spherical with a diameter of approximately 50 angstroms.

The monomer is present as droplets which are approximately 10 μ in diameter and are stabilized by surfactant molecules which cover the surface of the droplet.

The water soluble initiator decomposes slowly to provide a steady source of free radicals throughout the reaction. The free radicals are very reactive and will

combine chemically with monomer to initiate the growth of a polymer chain. The free radicals diffuse through the water until they come in contact with a micelle. Upon contact the free radical is absorbed into the micelle and reacts with the monomer initiating the polymerization reaction. The micelle with a polymer-monomer mixture in it is called a particle. As the particle grows, monomer diffuses from the monomer droplets to supply the reaction occurring in the particle.

The particles are stabilized in the latex by surfactant molecules which cover the surface of the particles. The source of the surfactant molecules is the micelles, which dissolve as needed to provide surfactant for stabilization. Eventually the total surface area of the particles becomes so large that all of the surfactant is required for stabilization of the latex particles. At this point micelles disappear, and nucleation of new particles ceases. The number of particles will remain constant for the remainder of the reaction, unless additional surfactant is introduced into the latex so that micelles again are formed.

Eventually a particle containing a growing polymer chain will capture a second free radical. The free radicals are extremely reactive, and a particle is very small so that the probability of having more than one growing

polymer chain in a particle is very small. As a result the time average number of free radicals in a particle is one-half.

Eventually the monomer droplets disappear. There is, however, a considerable amount of monomer still in the particles, and the reaction will continue until this monomer is polymerized. The final product is a latex containing tiny polymer spheres, ranging up to several thousand angstroms in diameter, stabilized in an aqueous base.

Remarks on Radical Capture and Termination

This description of the Smith-Ewart theory just presented is basic and very broad. Two points will be discussed in more detail, since they are of special interest in this investigation. Both have received considerable attention in the literature and are areas of uncertainty in the emulsion polymerization mechanism. These are radical capture by particles and micelles and termination inside the particles.

Smith and Ewart assumed that the process of radical capture was governed by the ordinary laws of diffusion (48). According to diffusion theory, particles would capture free radicals proportionally to the radius of the particle. Gardon has proposed that the capture of radicals is by a mechanism described by a collision theory (9). In this case

the surface area of a particle would determine the rate of radical capture. The models of Watterson et al. (54), Parts et al. (36), Harada et al. (19), and Sato and Taniyama (43, 44) all assume that radical capture is independent of particle size, although they have not emphasized this in their discussions. The simple model used by these investigators does not appear to have received much acceptance. It is difficult to differentiate between the radical capture models because they predict results which are not drastically different, so that experiments which would clearly differentiate are difficult to devise. Fitch and Shih attempted to determine which of the radical capture models is most nearly correct by studying the nucleation of particles (7). Their experimental results were closer to results predicted by the diffusion mechanism, but were nevertheless inconclusive. DeGraff and Poehlein attempted to distinguish between the collision model and the diffusion model by analysis of molecular weight data, but their results were also inconclusive (5).

The second process of special interest in this investigation is termination inside the particles. Smith and Ewart (48) realized that termination may not be instantaneous and that multiple radicals may exist simultaneously in a particle. Their mathematical description of a batch emulsion polymerization involved a quasi steady state

balance for the number of particles containing n free radicals. They were able to solve the numbers balance only for three limiting cases. The limiting case which best described their experimental data was based on the average number of free radicals in a latex particle being one-half. This corresponds to the assumption of instantaneous termination and the on-off growth mechanism of a latex particle. Stockmayer (49) and O'Toole (33) were later able to solve the quasi steady state numbers balance without the assumption of instantaneous termination, and they calculated the average number of free radicals in a particle as a function of particle size. Their calculations indicated that for very small particles the average number of free radicals is one-half, but as particle size increases the average number of radicals increases. The change with particle size is very gradual initially but as the particle size is further increased, the average number of free radicals in a particle becomes a very strong function of particle size. Gardon obtained nearly identical predictions of the average number of free radicals in a particle when he solved the time dependent numbers balance (11), verifying the validity of the steady state assumption of Stockmayer (49) and O'Toole (33).

Because of the difficulty, if not impossibility of determining the number of free radicals in a particle

directly, experimental verification of the presence of multiple radicals has necessarily dealt with observance of the rate of polymerization and molecular weight. Gardon (11) presents the most convincing analysis. He has applied his calculations of the average number of growing polymer chains in a particle to predictions of reaction rate and molecular weight in batch emulsion polymerization. By his analysis he was able to explain the details of the time dependent rate of polymerization and time dependent molecular weight behavior for several monomers.

Previous Investigations of Molecular Weight

Molecular weight in batch emulsion polymerization

Molecular weight is a key factor in determining the physical characteristics of a polymer. For this reason studies of molecular weight are frequently included in batch emulsion polymerization investigations. The primary emphasis has been the determination of the effects of initiator and surfactant concentrations on the molecular weight of the product and determination of the time dependent molecular weight behavior.

The first published study of the effect of initiator concentration, surfactant concentration, and temperature on molecular weight in a batch reactor was that by Smith

(47) who thoroughly examined the effects of these variables on molecular weight for batch polystyrene emulsion polymerization. Wiener (55) and Brodnyan et al. (3) performed similar, but less extensive studies, for vinylidene chloride and methyl methacrylate respectively. More recent investigators have begun to include theoretical calculations of molecular weight in their research. Watterson et al. (54) and Parts et al. (36) predicted molecular weights using a simple model which assumed that radical capture is independent of particle size. They predicted that molecular weight would rise to a maximum and then level off during the course of a batch reaction. Harada et al. (19) and Sato and Taniyama (44) used a model similar to Watterson's but much more detailed and complete. Harada, like Watterson et al., introduced an adjustable parameter and consequently were able to fit their calculated values to their experimental molecular weight-conversion data. Sato and Taniyama were also able to obtain agreement with their experimental and predicted molecular weight data, but it is not clear if their predictions were fitted to the data using their calculated parameters or if their predictions used values of parameters taken from the literature. Saidel and Katz (42) studied the affects of random radical arrival on molecular weight. They used a partially stochastic model to predict that molecular weight

as a function of conversion would rise to a maximum and then decrease. They did not collect experimental data but qualitatively compared their predicted values to values found in the literature and concluded that the trends were similar.

Gardon has performed the most extensive and impressive study of batch emulsion polymerization to date, both theoretically and experimentally (9, 10, 11, 12, 13, 14). His work is based primarily on the Smith-Ewart theory, but his comprehensive analysis also takes into account the effect of multiple radicals on polymer particles. His analysis of molecular weight in batch emulsion polymerization predicts that molecular weight is proportional to the surfactant-initiator ratio raised to the 0.6 power and that molecular weight increases to a maximum and then decreases during the course of the polymerization reaction. His laboratory data confirm the trends predicted by his calculations for several different monomers.

Several investigators have studied somewhat different aspects of molecular weight than those discussed above. Stryker et al. (50) investigated the emulsion polymerization of ethylene and determined that a chain transfer reaction between the growing polymer radicals and the emulsifier molecules was responsible for producing an unusually low molecular weight product and an inverse

dependence of molecular weight on emulsifier concentration. Morton et al. (31) fractionated a polystyrene latex according to particle size in order to determine the relationship between particle size and molecular weight in the same latex. They measured molecular weight for two latex fractions, having mean diameters of 800 Å and 400 Å and found molecular weights of 4.6×10^6 and 4.8×10^6 gr/mole respectively. They concluded that particle size had no effect on molecular weight.

Molecular weight in continuous emulsion polymerization

Studies of continuous emulsion polymerization systems have not been published as extensively as have studies of batch systems, although single continuous stirred tank reactors, multiple continuous stirred tank reactor systems, and tubular flow reactors are widely used industrially (6). Patents on continuous emulsion polymerization processes are copious and date back to 1937 when I. G. Farbenindustrie filed for a patent on a process for the manufacture of styrene-butadiene copolymer rubber (6). However in most commercial systems, reactor type and operating conditions are evidently determined by experience, since thorough kinetic studies of continuous emulsion polymerization have not been reported until recently (32).

The earliest published kinetic study of continuous

emulsion polymerization is that of Gershberg and Longfield (15). Experimentally they found that the rate of polymerization is independent of initiator concentration, while molecular weight is inversely proportional to initiator concentration. Consequently they concluded it is possible to increase the molecular weight without at the same time decreasing the rate of polymerization.

Several investigators have used models other than that of Smith and Ewart to predict the results of continuous emulsion polymerization. Sato and Taniyama (43) extended the model they had used to describe a batch reaction to a series of continuous stirred tank reactors. The model treated micelles and latex particles like molecules of a chemical species which reacted with free radicals in a manner independent of size. Both calculated and experimental results agreed with those of Gershberg and Longfield (15). Nomura et al. (32) used a model similar to that of Sato and Taniyama (43) to describe emulsion polymerization in a series of stirred tank reactors. Their experimental and predicted results were also similar to those of Gershberg and Longfield (15).

The most complete data for a continuous emulsion polymerization was obtained by DeGraff (4). He used an approach much like that of Gershberg and Longfield (15) for predicting the numbers of particles and reaction rates.

Molecular weights were predicted from the ratio of the calculated rate of reaction to the calculated rate of radical production. Although his individual predictions were in error by as much as a factor of two, his experimental and theoretical values both indicated that molecular weight increased with surfactant concentration to the first power and decreased with initiator concentration to the first power. His predictions of molecular weight as a function of residence time were quite different from his experimental data. His predictions indicated that molecular weight should vary approximately as residence time to the $-2/3$ power, while his experimental data showed that molecular weight was nearly independent of residence time.

Later DeGraff and Poehlein (5) used a different approach to calculate molecular weights for a continuous system. They used a molecular weight distribution derived by Katz et al. (22) together with a predicted particle size distribution to obtain an overall molecular weight distribution. This approach and the approach used by DeGraff (4) predicted nearly identical results.

THEORETICAL PREDICTIONS OF MOLECULAR WEIGHT

In the previous sections the concepts of emulsion polymerization have been described, and pertinent prior investigations have been reviewed. In this section these will be applied to predict the molecular weight of polymer produced in a continuous stirred tank reactor.

Our physical picture of emulsion polymerization is a series of randomly occurring events. It follows that the most direct model of emulsion polymerization would also be based on a series of randomly occurring events. Any continuous model for this type of process would necessarily require assumptions, the validity of which can be difficult to assess. In this work a Monte Carlo model has been developed which describes emulsion polymerization by a numerical simulation of the many randomly occurring events which determine the history of a latex particle. We have attempted in this model to include all physical factors felt to be important in particle and chain growth. For the limiting case of instantaneous termination a deterministic approach was used to develop an approximate analytic expression for molecular weight.

Monte Carlo Simulation

For the Monte Carlo simulation, the Smith-Ewart theory was used as the basic description of the mechanism of emulsion polymerization. The deviations from the Smith-Ewart theory and the assumptions used in the model are listed below:

1. The significant events in determining the history of a latex particle are radical capture, termination, and chain transfer to monomer.
2. For a given latex, the probability of any event occurring in a particle is dependent only on the state of the particle. The size of the particle and the number of free radicals in a particle determine its state.
3. Two events cannot take place simultaneously.
4. Free monomer is present in the latex at all times.
5. The total surface area of all particles and micelles in the latex is equal to the surface area associated with the total surfactant concentration in the latex.
6. The monomer concentration of the particles is constant at all times and is independent of particle size.
7. The volumetric rate of growth of a particle is dependent only on the number of free radicals in a particle for a given latex.

8. Free radicals are captured by particles at a rate proportional to the surface area of the particle.
9. When a particle leaves the reactor, it is instantly quenched by inhibitor killing all growing polymer chains.
10. In the reactor, termination of growing polymer chains in latex particles is by combination.
11. The exit age distribution of latex particles is that of an ideally mixed continuous stirred tank reactor.

The heart of this Monte Carlo simulation is a probability expression for the time at which the next event will occur in a latex particle. The probability expression depends on the rates of the events that can occur. Rate expressions for radical capture, termination and chain transfer are given below:

$$r_c = \left(\frac{4\pi r^2}{S}\right)R \quad (1)$$

$$r_t = k_t \left(\frac{n}{N_A V_p}\right) \left(\frac{n-1}{N_A V_p}\right) N_A V_p \quad (2)$$

$$r_{tf} = k_{tf} \left(\frac{n}{N_A V_p}\right) [M] V_p N_A \quad (3)$$

where

r_c = rate of radical capture by a particle, events/sec

- R = rate of production of free radical in the reactor, radicals/l sec
 S = total surface area, cm^2/l
 r = particle radius, cm
 r_{tf} = rate of chain transfer in a particle, events/sec
 k_{tf} = chain transfer rate constant, l/mole sec
 n = number of free radicals in the particle
 $[M]$ = monomer concentration in the particle, mole/l
 V_p = particle volume, l
 N_A = Avogadro's number, molecule/mole
 r_t = rate of termination in a particle, events/sec
 k_t = termination rate constant, l/mole sec.

In Equation 1 the assumption has been made that particles and micelles capture free radicals in proportion to their surface area and that the total surface area of the system is equivalent to S , the surface area of the surfactant molecules in the system.

To use these equations values for the constants must be available. The rate of radical production, R , can be determined by

$$R = 2k_d[I]N_A \quad (4)$$

where

k_d = initiator decomposition rate constant, sec^{-1}

$[I]$ = initiator concentration in the reactor mole/l.

The total surface area of the latex, S , can be calculated from

$$S = a_s [S] N_A \quad (5)$$

where

$[S]$ = the surfactant concentration in the reactor,
moles/l

a_s = the area covered by one molecule of surfactant,
 $\text{cm}^2/\text{molecule}$.

The monomer concentration in a particle can be expressed more conveniently in terms of ϕ , the volume fraction monomer in a particle.

$$[M] = 1000 \frac{\rho_o \phi}{M_o} \quad (6)$$

where

ρ_o = monomer density

M_o = molecular weight of monomer.

Our rate expressions can be more simply expressed as

$$r_c = \left(\frac{4\pi r^2}{S} \right) R = \alpha r^2 \quad (7)$$

$$r_t = \frac{k_t n(n-1)}{N_A V p} = \frac{\beta n(n-1)}{r^3} \quad (8)$$

$$r_{tf} = 1000 n \rho_o k_{tf} \theta / M_o = \eta n \quad (9)$$

where

$$\alpha = \frac{4\pi R}{S} \quad (10)$$

$$\beta = \frac{3000 k_t}{4\pi N_A} \quad (11)$$

$$\eta = \frac{1000 k_{tf} \rho_o \theta}{M_o} \quad (12)$$

Since the probability of any event occurring in a small time increment δt is $r_i \delta t$, the probability of that event not occurring in the time increment δt is $(1 - r_i \delta t)$ where r_i represents the rate at which any single event occurs. The probability that no event occurs in the time increment δt is

$$P(\text{no event occurs in } \delta t) = 1 - (r_c + r_t + r_{tf}) \delta t \quad (13)$$

The probability that no event occurs in a finite time $t_2 - t_1 = \sum \delta t_i$ is the product of the individual terms.

$$P(\text{no event occurs in time } \Delta t) = P = \prod_{\text{all } i} [1 - (r_c + r_r + r_{tf}) \delta t_i] \quad (14)$$

In the limit for very small values of δt , this becomes

$$P = \exp\left(- \int_{t_1}^{t_2} (r_c + r_t + r_{tf}) dt\right) \quad (15)$$

Because the rates of capture and termination are functions of particle size, the time integral in Equation 17 will be transformed to an integral over particle radius through use of the particle growth equation. The growth equation for a single polymer particle may be taken to be

$$\frac{d\left(\frac{4}{3} \pi r^3 (1-\emptyset) \rho_p\right)}{dt} = \frac{k_p n \emptyset \rho_o}{1000 N_A} \quad (16a)$$

or

$$\frac{dr^3}{dt} = Kn \quad (16b)$$

where k_p is the polymerization rate constant in l/mole sec and

$$K = \frac{3k_p \rho_o \emptyset}{4000 \pi N_A \rho_p (1-\emptyset)} \quad .$$

Using Equations 7, 8, 9 and 16, Equation 15 can be evaluated.

$$P = \exp\left[- \frac{3\alpha}{5Kn} (r_2^5 - r_1^5) - \frac{3\beta(n-1)}{K} \ln \frac{r_2}{r_1} - \frac{\eta}{K} (r_2^3 - r_1^3)\right] \quad (17)$$

When the particle contains no free radicals, the rates of chain transfer and termination are zero, and the particle size does not change. Therefore the following expression is obtained.

$$P = \exp\left[-\frac{\alpha}{r^2}(t_2 - t_1)\right] \quad n=0 \quad (18)$$

If the rates of capture, termination, and chain transfer change negligibly between events, the following approximation can be used.

$$P = \exp\left[\left(-\frac{\alpha}{r^2} - \frac{3\beta(n-1)}{r^3} - n\eta\right)(t_2 - t_1)\right] \quad (r > 750 \text{ \AA}) \quad (19)$$

For calculational purposes this equation was used for particles with radius greater than 750 Å with negligible error.

Equations 17, 18, and 19 can be arranged in terms of the radius at the time an event will occur in a particle or the time at which the event will occur.

$$\begin{aligned} -\ln P + \frac{3\alpha}{5Kn} r_1^5 + \frac{3\beta(n-1)}{K} \ln r_1 + \frac{\eta}{K} r_1^3 \\ = \frac{3\alpha}{5Kn} r_2^5 + \frac{3\beta(n-1)}{K} \ln r_2 + \frac{\eta}{K} r_2^3 \quad n \neq 0 \end{aligned} \quad (20)$$

$$-\frac{r_1^2 \ln P}{\alpha} = t_2 - t_1 \quad n = 0 \quad (21)$$

$$\frac{-\ln P}{\left[\frac{\alpha}{r^2} + \frac{\beta n(n-1)}{r^3} + n\eta\right]} = t_2 - t_1 \quad \begin{array}{l} r > 750 \text{ \AA} \\ n \neq 0 \end{array} \quad (22)$$

Time and particle size are related through the integrated particle growth equation

$$r_2^3 - r_1^3 = K(t_2 - t_1)n \quad . \quad (23)$$

For use with Equation 22, an approximate expression for the integrated particle growth equation was used.

$$r_2 - r_1 = \frac{K}{3r_1^2} (t_2 - t_1)n \quad (24)$$

This was necessary because of the round off error obtained when Equation 23 was used to calculate the radius of large particles.

Equations 20, 21, 22, 23, and 24 are the basic equations used in the Monte Carlo simulation. For the simulation a random number was generated for use as the probability P , and the appropriate equations were solved to obtain the size and age of the particle when the next event occurred. Use of all equations, except Equation 20, is straight forward. Solving Equation 20 for the radius of the particle at the next transition is an iterative process. Since the function

$$F(r) = \frac{3\alpha r^5}{5Kn} + \frac{3\beta(n-1)}{K} \ln r + \frac{\eta}{K} r^3 \quad (25)$$

is monotonically increasing with r and a lower bound for r is known, r_2 can be determined as accurately as desired by trial and error. Numerically this is a simple and rapid procedure.

Once it has been determined when the event will occur, it must be determined which event will occur. This must be a random determination and can be based on the conditional probabilities of radical capture, termination, or chain transfer, which are given below.

$$P_c = \frac{r_c}{(r_c + r_t + r_{tf})} \quad (26)$$

$$P_t = \frac{r_t}{(r_c + r_t + r_{tf})} \quad (27)$$

$$P_{tf} = \frac{r_{tf}}{(r_c + r_t + r_{tf})} \quad (28)$$

The occurrence of an event causes a change in the size and/or number of growing chains in a polymer particle. When a capture event occurs, a new chain of length zero is created. When a termination event occurs, two of the growing polymer chains are chosen at random for termination and the number of growing chains is reduced by two. The length of

the dead polymer chain is the sum of the lengths of the two terminating chains. When chain transfer occurs, the number of growing chains remains unchanged. One of the growing chains is selected at random. Its size is set to zero and a dead polymer chain is created with the size of the transferring chain.

The initial state is chosen to be a particle 50 Å in diameter with one growing polymer chain of size zero in it. The complete history of a particle was constructed by repeatedly determining when the next event would occur and the size of the particle at that time. The number and size of the growing polymer chains were also calculated.

Simply determining the history of the particle, however, is only part of the problem. To extract useful information from the simulation of the growth of a single particle, an elaborate bookkeeping procedure is necessary. The number and length of all growing chains must be known. The number of dead polymer chains and the sum of the weights of the dead polymer chains must also be known if number average molecular weights are to be calculated. If weight and viscosity average molecular weights are of interest, the sum of the squares of the weights and the sum of the weights to the $(1+a)$ power are also needed. Here a is the power parameter in the Mark-Houwink equation, which is given below.

$$[\eta] = KM_v^a \quad (29)$$

This equation is commonly used to obtain the viscosity average molecular weight from the intrinsic viscosity of a dilute polymer solution.

In order to determine properties of the entire latex, the properties of the particle as a function of size must be weighted according to the numbers of particles of that size in the product and summed over all particle sizes. Numerically this procedure was carried out by utilizing diameter intervals. As a particle "grew" through a diameter interval, the following sums were recorded for that interval:

1. $n \sum x_i$
2. $\sum x_i \sum M_j$
3. $\sum x_i \sum M_j^{1+a}$
4. $\sum x_i \sum M_j^2$
5. $\sum \sum x_i$.

Here

$$x = (e^{-t_1/\tau} - e^{-t_2/\tau}) = \text{the fraction of particles leaving the reactor between times } t_1 \text{ and } t_2$$

n = the number of living and dead polymer chains in a particle and

M_j = the molecular weight of the j^{th} polymer chain.

The inner summation is over all live and dead polymer chains in the particle. The outer summation is over the events which occurred while the particle was in that interval. When a particle passed from one interval to the next, the growth of live chains in the particle for one interval was based on the time spent in that interval. Inclusion of live chains in these summations was based on the assumption that when a particle left the reaction vessel, it would be quickly quenched by inhibitor which would instantly terminate the growing chains.

The history of a latex particle was followed for five residence times of the reactor. Over 99 percent of the particles would have been discharged from an ideally stirred vessel in this time.

The data accumulated for the history of one or more particles allows calculation of the following:

1. Number, weight and viscosity average molecular weights as function of particle diameter.
2. Number, weight, and viscosity average molecular weights of the latex.
3. Particle size distribution of the latex.

4. Viscosity average molecular weight of all particles above a given diameter as a function of weight fraction of total latex polymer represented by those particles.

Item 4 is of less general interest, but is of specific interest to this investigation since experimental data was obtained in this form.

A flow diagram for the numerical computation is given in Figure 1. A listing of the computer program is given in the Appendix.

Before the Monte Carlo simulation can be confidently used, an estimate is needed of the reliability of the predictions. To obtain an estimate of the standard deviation of the particle diameters and the molecular weights of the latex, Monte Carlo simulations were obtained for ten particles. The results were analyzed to obtain the mean and standard deviation of each predicted quantity. The results are summarized in Table 1.

One way to increase the reliability of the results would be to run the Monte Carlo simulation for more than one particle and to estimate the product properties from the combined data. This would decrease the standard deviation of the predicted quantities by approximately \sqrt{n} where n is the number of replications. Since a large portion of the standard deviation is due to events which take

Figure 1. Flow diagram for Monte Carlo simulation of growth of a latex particle

DIA = diameter of a particle
DNEW = diameter of a particle when next event occurs
n = number of growing polymer chains in a particle
M(i) = molecular weight of a dead polymer chain
c(j) = molecular weight of a live polymer chain
NCHAIN = number of terminated chains

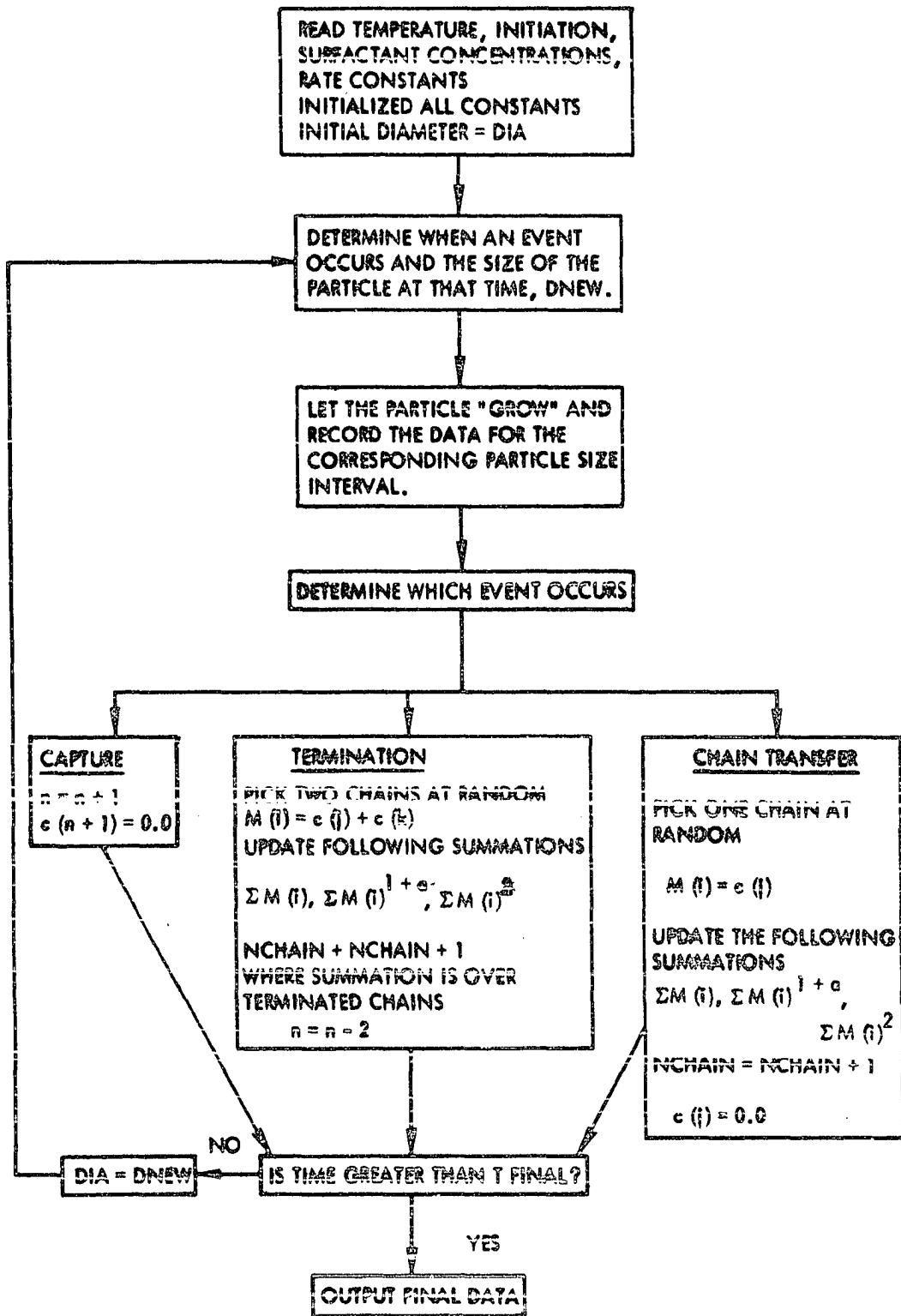


Table 1. Mean and standard deviation for Monte Carlo data
 $k_p = 756$ l/mole sec
 $k_t = 4.92 \times 10^8$ l/mole sec
 $k_{tf} = 0.0454$ l/mole sec
 $\tau = 32.9$ min

Variable	For a single particle (based on 10 runs)		For multiple particles (based on 2 runs)	
	Mean	Standard Deviation (9df)	Mean	Standard Deviation (1df)
D_n^a	1344 Å	60	1358	1.5
D_a^b	1524	36	1527	2.0
D_v^c	1665	26	1665	1.6
M_n	0.905×10^6	0.026×10^6	0.921×10^6	0.037×10^6
M_v	1.739	0.103	1.799	0.073
M_w	1.930	0.139	1.998	0.076

$$D_n^a = \frac{\sum n_i D_i}{\sum n_i} .$$

$$D_a^b = \frac{\sum n_i D_i^2}{\sum n_i D_i} .$$

$$D_v^c = \frac{\sum n_i D_i^3}{\sum n_i D_i^2} .$$

place early in the history of the particle, an alternative method of decreasing the variances would be to replicate only this portion of the particle history. For the implementation of this technique the data was replicated 27 times for diameters 50 Å to 1000 Å, five times for diameters 1000 Å to 1600 Å, and two times for diameters above 1600 Å. The means and standard deviations for these calculations based on two replications are shown in Table 1 and compared to the means and standard deviations of data calculated when one particle was observed, the standard deviation of the various mean diameters has decreased from 26-60 Å when the history of individual particles were used to several angstroms when multiple particles are used. The standard deviations of the molecular weights are less affected. The improvement using the multiple particle technique was made with only a small increase in computer cost over that for an individual particle.

Approximate Analytic Expressions

The Monte Carlo simulation just presented can be used to predict the behavior of a continuous emulsion polymerization reactor. However it is a numerical technique and is less convenient to use than an analytic expression. In this section analytic expressions will be derived for the number and weight average molecular weights of polymer in

a particle and polymer in the latex with the assumption that chain termination in the latex particles is instantaneous.

If the rates of radical capture and chain transfer do not change significantly during the lifetime of a growing polymer chain, the probability that no event occurs in a particle from time zero to time t is

$$P(\text{no event occurs from } t=0 \text{ to } t=t) = e^{-(r_c + r_{tf})t} \quad (30)$$

If this period of time is followed by the occurrence of an event in the next time increment δt , the probability is

$$P(\text{next event occurs between time } t \text{ and } t+\delta t) = (r_c + r_{tf}) e^{-(r_c + r_{tf})t} \delta t \quad (31)$$

The molecular weight of a growing polymer chain is given as

$$M = k_p \bar{\rho}_0 t \quad (32)$$

where t is the time of growth of the polymer chain. In a particle of radius r , the time of growth is not single valued, but has a statistical distribution given by Equation 31. If the mean of this distribution is used in Equation 32, the number average molecular weight of polymer produced under stationary conditions is obtained.

$$\bar{M}_{ns} = k_p \phi \rho_o \int_0^{\infty} t (r_c + r_{tf}) e^{-(r_c + r_{tf})t} dt \quad (33)$$

If the rates of radical capture and chain transfer do not change significantly during the lifetime of a growing chain, we can obtain

$$\bar{M}_{ns} = \frac{k_p \phi \rho_o}{(r_c + r_{tf})} \quad (34)$$

The weight average molecular weight of polymer produced under stationary conditions, \bar{M}_{ws} , can be derived similarly

$$\bar{M}_{ws} = \frac{\int_0^{\infty} (k_p \phi \rho_o t)^2 (r_c + r_{tf}) e^{-(r_c + r_{tf})t} dt}{\int_0^{\infty} (k_p \phi \rho_o t) (r_c + r_{tf}) e^{-(r_c + r_{tf})t} dt} \quad (35)$$

$$= \frac{2k_p \phi \rho_o}{(r_c + r_{tf})} \quad (36)$$

$$= 2 \bar{M}_{ns} \quad .$$

For a polymer particle the number and weight average molecular weights can be determined by an appropriate summation over all chains in the particle, as given in the following equations.

$$\bar{M}_{np} = \frac{\sum_i n_i M_i}{\sum_i n_i} \quad (37)$$

$$\bar{M}_{wp} = \frac{\sum_i w_i M_i}{\sum_i w_i} \quad (38)$$

Here n_i and w_i are the number and weight of chains with molecular weight M_i in a particle. The number of chains, n_i , is $(r_c + r_{tf})/2$. The weight of chains, w_i , is

$$\left(\frac{r_c + r_{tf}}{2}\right) M_n \quad .$$

Combining these expressions for n_i and w_i and Equations 34, 36, 37, and 38 and changing the summations in Equations 37 and 38 to integrations yields the following expressions.

$$\bar{M}_{np} = \frac{\frac{1}{2} \int_0^t (r_c + r_{tf}) \frac{k_p \phi \rho_0}{(r_c + r_{tf})} dt}{\frac{1}{2} \int_0^t (r_c + r_{tf}) dt} \quad (39)$$

$$\bar{M}_{wp} = \frac{\frac{1}{2} \int_0^t 2(r_c + r_{tf}) \frac{(k_p \phi \rho_0)^2}{(r_c + r_{tf})^2} dt}{\frac{1}{2} \int_0^t (r_c + r_{tf}) \frac{k_p \phi \rho_0}{(r_c + r_{tf})} dt} \quad (40)$$

Over the life of a particle, the rate of radical capture changes according to Equation 1.

$$r_c = \frac{4\pi R}{S} r^2 \quad (1)$$

By the use of Equations 1, 39, 40 and the Smith-Ewart particle growth equation

$$\frac{dr^3}{dt} = \frac{K}{2} \quad , \quad (41)$$

to change from integration over time to integration over particle size, we can obtain the number and weight average molecular weight of a particle of size r .

$$\bar{M}_{np} = \frac{k_p \phi \rho_o}{\left(\frac{12\pi R}{5S} r^2 + r_{tf}\right)} \quad (42)$$

$$\bar{M}_{wp} = \frac{6Sk_p \phi \rho_o}{4\pi R r^3} \left[r - \left(\frac{r_{tf} S}{4\pi R}\right)^{1/2} \tan^{-1} \left(\frac{4\pi R r^2}{r_{tf} S}\right)^{1/2} \right] \quad (43)$$

The number and weight average molecular weight can be calculated from Equations 37 and 38 if the summations are taken over all chains in the latex. An equivalent method would be to weight the contribution of a particle by the number of particles of that size (or, equivalently, of age) in the latex. By expressing the fraction of particles with age t using the exit age distribution, the number and

weight average molecular weights of the latex can be written as

$$\bar{M}_n = \frac{\frac{1}{2} \int_0^{\infty} (r_c + r_{tf}) \frac{k_p \phi \rho_o}{(r_c + r_{tf})} \frac{e^{-t/\tau}}{\tau} dt}{\frac{1}{2} \int_0^{\infty} (r_c + r_{tf}) \frac{e^{-t/\tau}}{\tau} dt} \quad (44)$$

$$\bar{M}_w = \frac{\frac{1}{2} \int_0^{\infty} 2(r_t + r_{tf}) \frac{(k_p \phi \rho_o)^2}{(r_c + r_{tf})^2} \frac{e^{-t/\tau}}{\tau} dt}{\frac{1}{2} \int_0^{\infty} (r_t + r_{tf}) \frac{k_p \phi \rho_o}{(r_c + r_{tf})} \frac{e^{-t/\tau}}{\tau} dt} \quad (45)$$

These equations reduce to

$$\bar{M}_n = \frac{k_p \phi \rho_o}{\frac{2^{4/3} \pi R (K\tau)^{2/3}}{S} \Gamma(1.666) + r_{tf}} \quad (46)$$

$$\bar{M}_w = \frac{k_p \phi \rho_o S}{\pi R (K\tau)^{2/3}} \int_0^{\infty} \frac{e^{-2z} dz}{\left[z^{2/3} + \frac{r_{tf} S}{4\pi R (K\tau)^{2/3}} \right]} \quad (47)$$

When the rate of chain termination is zero, both the number and weight average molecular weights vary as S/R and $\tau^{-2/3}$. As expected this dependence decreases as chain transfer becomes more important, until at the limit both number and weight average molecular weights are independent of S/R and τ .

EXPERIMENTAL INVESTIGATION

Apparatus, Materials, and Techniques

Batch latexes were prepared in a one quart, wide mouth bottle with a screw top. In the top were cut openings for a three blade stainless steel stirrer, a thermometer, a single stainless steel baffle, a nitrogen purge line, and a sampling port. The reactor was placed in a constant temperature bath so that the contents of the reactor were maintained at 60 ± 2 °C. Prior to reaction the water and the monomer were purged by bubbling prepurified nitrogen through them for approximately 30 minutes. The reactor was blanketed by nitrogen at a pressure of about 20 cm of water throughout the reaction to minimize the chance of oxygen entering the system. The reaction was stopped by removing the reactor from the temperature bath and adding an amount of tertiary butyl catechol to the reaction vessel moderately in excess of that necessary to counteract the initiator.

Continuously prepared latexes were produced in a 290 ml cylindrical glass vessel with a round bottom. The top of the vessel was a Teflon plate with openings for a glass stirring rod with a Teflon paddle, a thermometer, feed lines for water solution and monomer, a thermoregulator, and a nitrogen purge line. The reaction vessel was heated by a Glas-Col electrical heater which was controlled

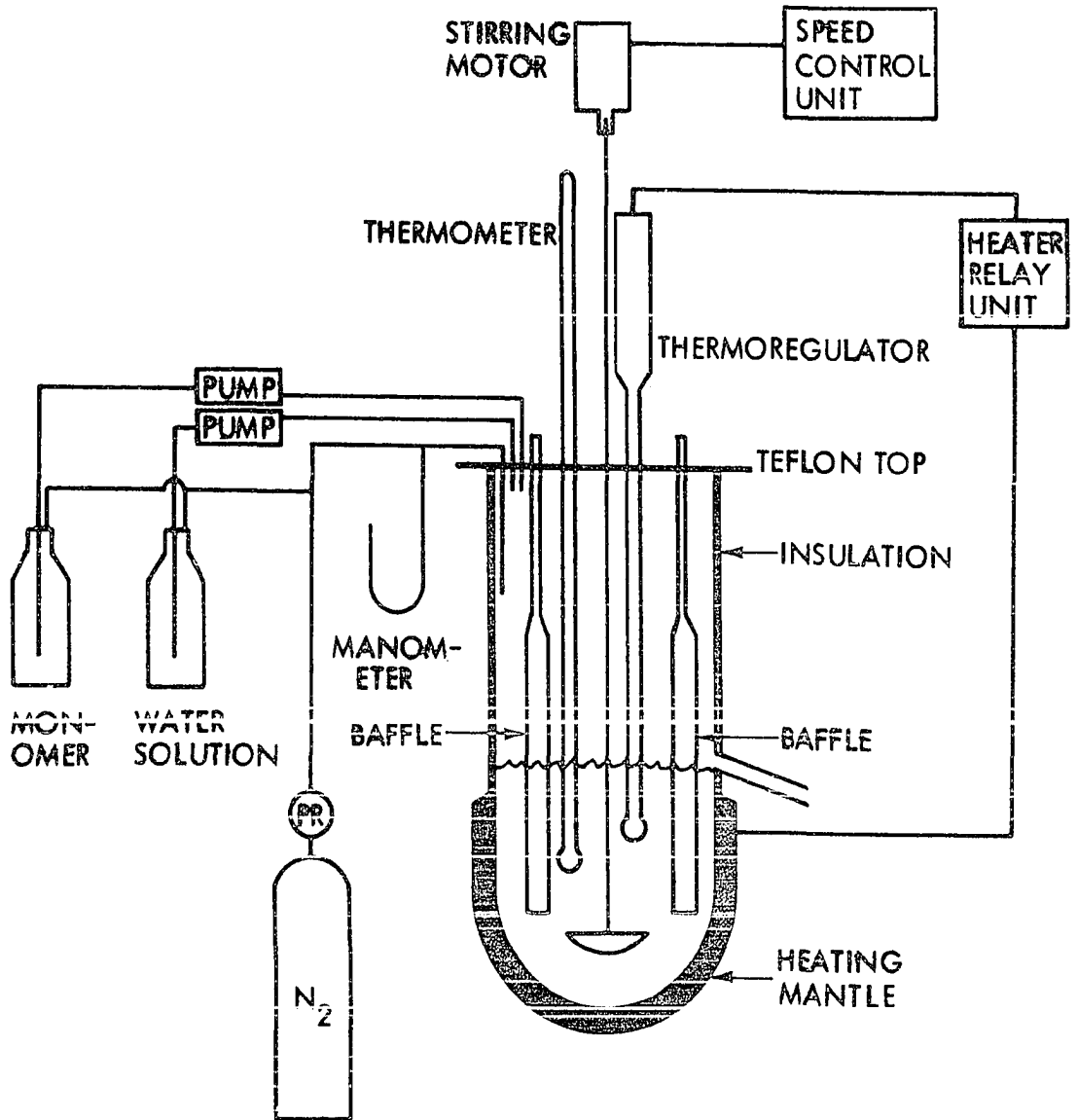
via a relay by the thermoregulator. A variac was used to adjust the output of the heater. Reaction vessel temperatures were maintained at 60 ± 0.5 °C. Feed solutions were pumped by two Milton-Roy positive displacement mini-pumps. The stirring rate was maintained at 200 RPM by a Cole-Parmer constant speed stirring unit. Throughout the run prepurified nitrogen blanketed the reactor at a pressure of about 5 cm of water. A schematic of the continuous apparatus is shown in Figure 2.

Batch particle size distributions were obtained by ultracentrifuge analysis using a technique similar to that developed by Peppard (39). A Beckman Model E analytical ultracentrifuge was used with schlieren optics. Particle densities were obtained by centrifuging the latex in two media having different densities. Water and 10 percent sucrose solution were used for the two media. Some of the particle size distributions were verified from electron microscope photographs of the latex.

The particle size distribution for the continuously produced latexes could not be obtained by ultracentrifuge analysis, since these latexes were too turbid. Electron microscope photographs were used to determine these particle size distributions.

Polymer molecular weights were obtained by dilute solution viscometry. For preliminary batch experiments

Figure 2. Schematic of reactor used for preparation of continuous latexes



the one point method of Maron was used to determine intrinsic viscosities (26), but for continuous experiments intrinsic viscosities were obtained by extrapolation of viscosity-concentration curves to zero concentration. Viscosities of the solution were measured according to ASTM recommended procedures (1). Molecular weights were calculated using Equation 29

$$[\eta] = KM_v^a \quad . \quad (29)$$

Here $[\eta]$ is intrinsic viscosity and M_v is viscosity average molecular weight. The values of the constants K and a are those of Goldberg et al. (16). Toluene was used as the solvent at 30°C.

Latex fractionation according to particle size was achieved using the technique of fractional creaming with sodium alginate. This technique will be described in detail in a later section.

The polymer in the batch latexes was recovered by diluting the latex with water and adding sodium chloride until the solids coagulated. The mixture was then filtered, and the residue was washed alternately with hot deionized water and methanol until the effluent did not taste of salt. While this method for determining the presence of sodium chloride is rather crude, it is very quick and has a lower detection limit of several hundred

parts per million. The residue was washed several additional times with hot deionized water before it was dried. While this procedure removed the sodium chloride, it did not remove all of the sodium alginate. Consequently it was necessary for the polymer residue to be dissolved in toluene and filtered to remove any traces of sodium alginate. The polymer in continuously produced latexes was recovered by coagulation of the latex with sodium chloride. To remove the impurities with reasonable time expended it was necessary to wash the residue with acetone until a pure product was recovered. This step is certainly undesirable since the lower molecular weight fractions of polymer would also be removed. One sample was purified with methanol in order to determine if error introduced by washing with toluene could be tolerated. The methanol purification required many washings of the polymer and lasted 5-6 hours. Comparison of the results from the methanol purification and the acetone purification showed that the effect of acetone washing of polymer had negligible effect on the viscosity average molecular weight.

Prior to polymerization, the styrene was distilled by vacuum distillation at approximately 75 °C and 690 mm Hg vacuum with a reflux ratio estimated to be about 2/1. It was stored in a refrigerator until it was used or for 60 days at which time it was redistilled.

The water used was deionized tap water which was passed through a Barnstead water purification cartridge to remove organic impurities.

Table 2 shows the source and purity of the chemicals used in the experimental investigation.

Table 2. Source and purity of reagents used in the experimental investigation

Chemical	Source	Grade
Potassium Persulfate	Matheson, Coleman, and Bell	Reagent
Tertiary Butyl Catechol	Eastman Kodak	Practical
Sodium Pentachlorophenate (Santobrite)	Monsanto	Technical
Sucrose	Baker	Reagent
Sodium Lauryl Sulfate	Sargeant	Technical
Nitrogen	Cook Welding Supplies	Prepurified
Toluene	Baker	Reagent
Styrene	Cope Plastics	Ungraded
Sodium Alginate (Kelcosol)	Kelco	Ungraded

Latex Fractionation

Two potential methods of latex fractionation were tested before the fractional creaming technique was developed. The first technique involved the use of a column packed with porous glass beads. The beads were 120/200 mesh and had a mean interval pore diameter of 1000 \AA . The supplier was Electro-Nucleonics, Inc. A column packed with these porous glass beads should have been able to fractionate a latex according to particle size, since the larger particles would go around the beads while small particles would enter the pores in the beads. Consequently larger particles should have a residence time in the column less than that of smaller latex particles. To test the column two monodispersed latexes having mean diameters of approximately 1200 \AA and 500 \AA were produced using the procedure of Williams and Grancio (57). A mixture of the two was passed through the column. Design calculations for the column showed that a wide separation should occur, and two well separated latex fractions should emerge from the column. When the experiment was performed, only one latex band flowed out of the column. After this experiment was performed several times with the same results, an India ink tracer was passed through the column. The particles of carbon black in the ink were small enough to pass through the pores in the glass beads, so that the retention

volume for very small particles could be determined experimentally. However, the retention volume of the ink was the same as that for the latex and also very close to a calculated retention volume for large particles. This suggested that the latex particles had plugged the pores in the glass beads.

The second attempted method of fractionation was by a centrifugation technique widely used in biochemical research to separate very similar macromolecules. It was suggested by Dr. Malcolm Rougvie of the Department of Biochemistry at Iowa State University. The technique involved centrifuging a mixture of two monodisperse latexes in a cell with an imposed density gradient. The function of the density gradient was to provide stability under centrifugation and to minimize convection in the centrifuging medium. The density gradient was produced by placing in the cell a sucrose solution whose concentration decreased linearly from the top to the bottom of the cell. After a density gradient was placed in the centrifuging cell, a layer of a latex mixture, similar to that used in the experiments with the packed column, was gently placed on top of it, and the cell was centrifuged at 15,000 RPM. After the centrifuging was completed, the cell was removed and examined. Samples were taken from several different positions in the cell and analyzed using the analytical

ultracentrifuge. This procedure was performed for a series of experiments in which sample sizes, density gradients, and centrifuging times were varied, but no separation was achieved.

The third method investigated for fractionation of a latex according to particle size is called fractional creaming. The technique used in this investigation was similar to that used by Schmidt and Biddison for determining particle size distributions of latexes (45). The procedure itself is quite simple. It consists of merely adding a measured amount of sodium alginate to a latex sample. Upon setting, the mixture will separate into two phases. One phase will contain the larger particles, and the other phase will contain the smaller particles. When a batch-produced latex was fractionated, the layer containing the large particles was found at the bottom of the separating vessel. When a continuously-produced latex was fractionated, the layer containing the large particles was the top layer. The relative amounts of polymer in each phase is a function of the amount of a sodium alginate added. Therefore a series of samples can be prepared in which the amount of alginate is successively increased. The mean diameter of the particles in each phase will shift with each additional increment of alginate added. In this way a series of samples can be obtained in which the weight

fraction of polymer increases and the mean particle diameter decreases throughout the series.

While the basic idea is very simple, the actual procedure used in the experiments is a bit more complicated. Therefore a detailed description is given below.

1. To 300-400 gr of latex were added 4.0 gr of sodium lauryl sulfate. The mixture was diluted with water to a volume of 1 liter.
2. To 50 ml of the diluted latex mixture a weighed sample of sodium alginate solution was added. The entire mixture was diluted to a total weight of 200 gr. The sodium alginate solution was approximately 1.0 percent sodium alginate by weight. It also contained 0.1 percent sodium pentachlorophenate, the purpose of which was to prevent bacterial growth. The amount of sodium alginate added to the sample ranged from 30 to 60 grams of 1.0 percent solution. The exact amount was determined by trial and error. When a series of fractionations was desired, the minimum level of sodium alginate was established for the first sample and was increased by 3 or 4 grams for each successive sample.
3. These solutions were put into separatory vessels and allowed to set for one to two days to allow

separation of the phases to take place. The best separatory vessels were found to be glass tubes approximately 120 cm in length and with an inside diameter of 1.5 cm. These worked well for measuring the volumes of the phases and for allowing for separation of the two phases.

4. The height of each phase was measured, and the volume of each was calculated.
5. The two phases were separated by removing the top phase by suction.
6. Samples of both phases were dried to determine the solids concentration of each.
7. A mass balance was used to determine the total solids content of both phases and the fraction of the total solids in each phase. For the purposes of these calculations, the sodium lauryl sulfate and the sodium alginate were assumed to be present in each layer at the same concentration.

After the technique was developed, an experiment was performed, the purpose of which was to determine the effectiveness of the fractionation and to compare the weight fractions of polymer calculated from a mass balance with that obtained by analysis of electron microscope photographs. A batch latex was fractionated using the procedure outlined above, and electron microscope photographs were

taken of the latex in the top and bottom phases. From these photographs the weight average diameters of the top and bottom phases were determined to be 750 Å and 920 Å respectively. The difference between these values indicates that fractionation did indeed occur. However, the separation was not perfect. When the particle size distributions for the two phases were compared, a cut off diameter of approximately 800 Å was obtained. This value represents an overlap of the two distributions of 20-25 percent. That is 20-25 percent of the material in the top phase that would be in the bottom phase in an ideal separation and vice versa. This was also found to be typical of the quality of separation of a continuously-produced latex.

A mass balance was applied to the experimental data for the batch separation and the weight fraction of polymer in the bottom phase was calculated to be 20.1 percent. The weight fraction of polymer in the bottom phase was calculated by analysis of the electron microscope photographs to be 26 percent.

Description of an Experiment

The idea behind the experiments is very simple--to fractionate a latex according to particle size and measure the molecular weight of each fraction so that molecular

weight could be determined as a function of particle size. However the experimental procedure involved a number of operations and was somewhat more complex than a brief description of the experiment would indicate. Therefore a detailed description of an experiment will be given below.

1. A latex was produced by either a batch or a continuous process.
2. The particle size distribution of this latex was obtained by use of an analytical ultracentrifuge or an electron microscope for batch-produced and continuously-produced latexes respectively.
3. The technique of fractional creaming was used to fractionate 5 to 10 samples of the latex. Each sample contained a larger amount of sodium alginate than the previous, so that a series of fractionated latexes was obtained, each containing successively more polymer and having a smaller mean particle diameter.
4. For each sample the two phases were separated, and the polymer was recovered from the phase containing the largest particles.
5. The viscosity average molecular weight of each of these samples and of the entire latex was determined.

RESULTS

Batch Emulsion Polymerization

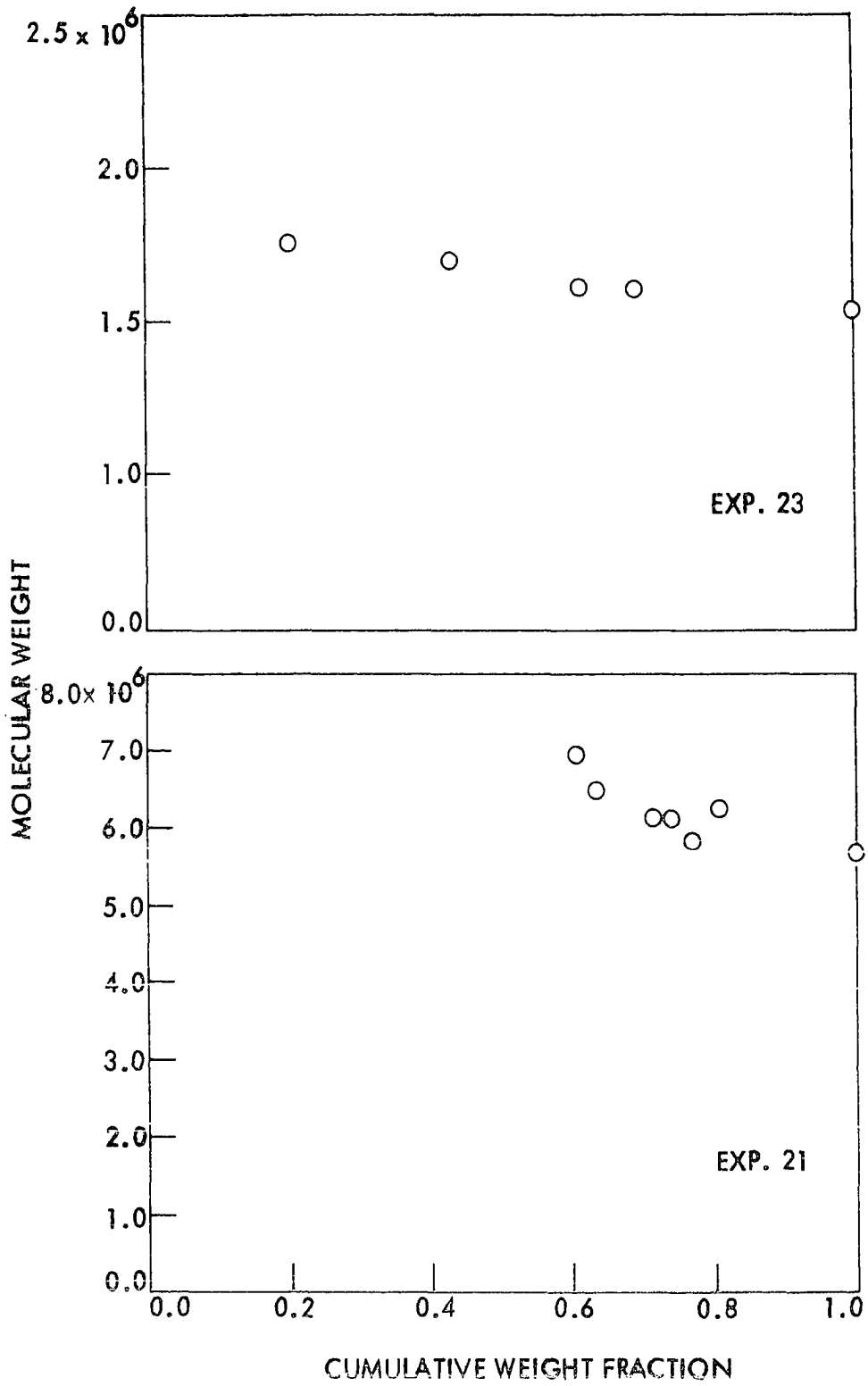
Two batch experiments were performed as described in the previous section. The recipes for the polymerizations are given below for the two experiments.

	<u>Exp 21</u>	<u>Exp 23</u>
Water	180	180
Styrene	100	100
Potassium persulfate	0.15	1.0
Sodium lauryl sulfate	5.0	5.0

Both polymerizations were allowed to react to completion. Viscosity average molecular weights of the polymer produced in experiments 21 and 23 are 5.70×10^6 and 1.54×10^6 respectively. The initiator level was increased in experiment 23 to reduce the molecular weight of the polymer, because it was anticipated that at high molecular weights chain transfer would be a dominant factor and would result in molecular weight being insensitive to particle size.

Figure 3 shows the molecular weight plotted versus cumulative weight fraction for experiments 21 and 23. Unfortunately the data for experiment 21 is incomplete, but nevertheless these data for the two experiments appear to show the same trend. The highest molecular weight is found at the lowest cumulative weight fractions indicating that

Figure 3. Viscosity average molecular weight as a function of cumulative weight fraction of polymer for batch emulsion polymerization



the highest molecular weight polymer is in the largest particles. A detailed analysis of this data was performed to infer the molecular weight as a function of particle size, but it was found that the results were extremely dependent on the shape of the curve drawn through the molecular-weight fraction data. Consequently this type of analysis is not reliable. However it can be concluded from the data that molecular weight is not a strong function of particle size and that the highest molecular weight is found in the largest particles.

Based on considerations of the process of radical capture alone, one would expect molecular weight to be a decreasing function of particle size for both the diffusion and the collision mechanisms of radical capture. The fact that such a direct contrast exists between experimental data and theoretical expectations implies that some other phenomenon is responsible. Perhaps the explanation lies partially with the cause of particle size polydispersity in a batch reactor. Particles are larger than average because they have either grown for a longer time or because they contained multiple free radicals causing them to grow faster. Either of these situations would cause a higher than average molecular weight polymer to be associated with particles that are larger than average. It would be surprising however, if this alone could explain the trend

of the data in these experiments.

Even if this data could be analyzed with more certainty, the meaning would probably be clouded since 30-50 percent of the polymerization occurs after the free monomer in the latex disappears. Polymerization is not well understood under these conditions, but it is thought to be substantially different than in monomer-rich particles.

Continuous Emulsion Polymerization

Four experiments were conducted using the continuous stirred tank reactor and associated apparatus described previously. The recipe used in these runs is given below.

water	180 parts by weight
styrene	100
potassium persulfate	1.0
sodium lauryl sulfate	5.0

The four runs were at 60°C and with residence times as shown.

<u>Experiment</u>	<u>Residence Time (min)</u>
24	32.9
25	63.4
26	47.2
27	47.2

After the latexes were produced, they were fractionated using the process of fractional creaming; the polymer was recovered from the latex fractions; and the viscosity average molecular weights were measured. In all experiments the reaction was carried out for at least nine residence times before a sample was taken for analysis. Electron microscope photographs were taken of the latex samples, and particle size distributions were obtained.

A tabular summary of particle size data, overall molecular weights, conversions and numbers of particles is given in Table 3 for the four continuous experiments. The number, area and volume average diameters were calculated from the following equations.

$$\bar{D}_n = \frac{\sum n_i D_i}{\sum n_i} \quad (48)$$

$$\bar{D}_a = \frac{\sum n_i D_i^2}{\sum n_i D_i} \quad (49)$$

$$\bar{D}_v = \frac{\sum n_i D_i^3}{\sum n_i D_i^2} \quad (50)$$

The values shown in Table 3 have been corrected to reflect the fact that latex samples are dried before they can be viewed with an electron microscope, and, as a result,

Table 3. Summary of experimental data for continuous emulsion polymerization

Experiment	Residence time (min)	$\bar{D}_n(\text{\AA})$	$\bar{D}_a(\text{\AA})$	$\bar{D}_v(\text{\AA})$	$\bar{M}_v(\frac{\text{gr}}{\text{mole}})$	Conversion	Number of particles per ml of latex
24	32.9	1410	1550	1680	1.17×10^6	16.5%	8.56×10^{13}
25	63.4	1950	2150	2310	1.01×10^6	40.2%	7.92×10^{13}
26	47.2	1710	1860	2050	0.92×10^6	25.0%	7.44×10^{13}
27	47.2	1650	1800	1920	1.12×10^6	28.4%	9.52×10^{13}

particles that are observed do not contain any monomer.

In making these corrections a value of the volume fraction monomer, $\phi = 0.65$, was used, and monomer and polymer volumes were considered additive.

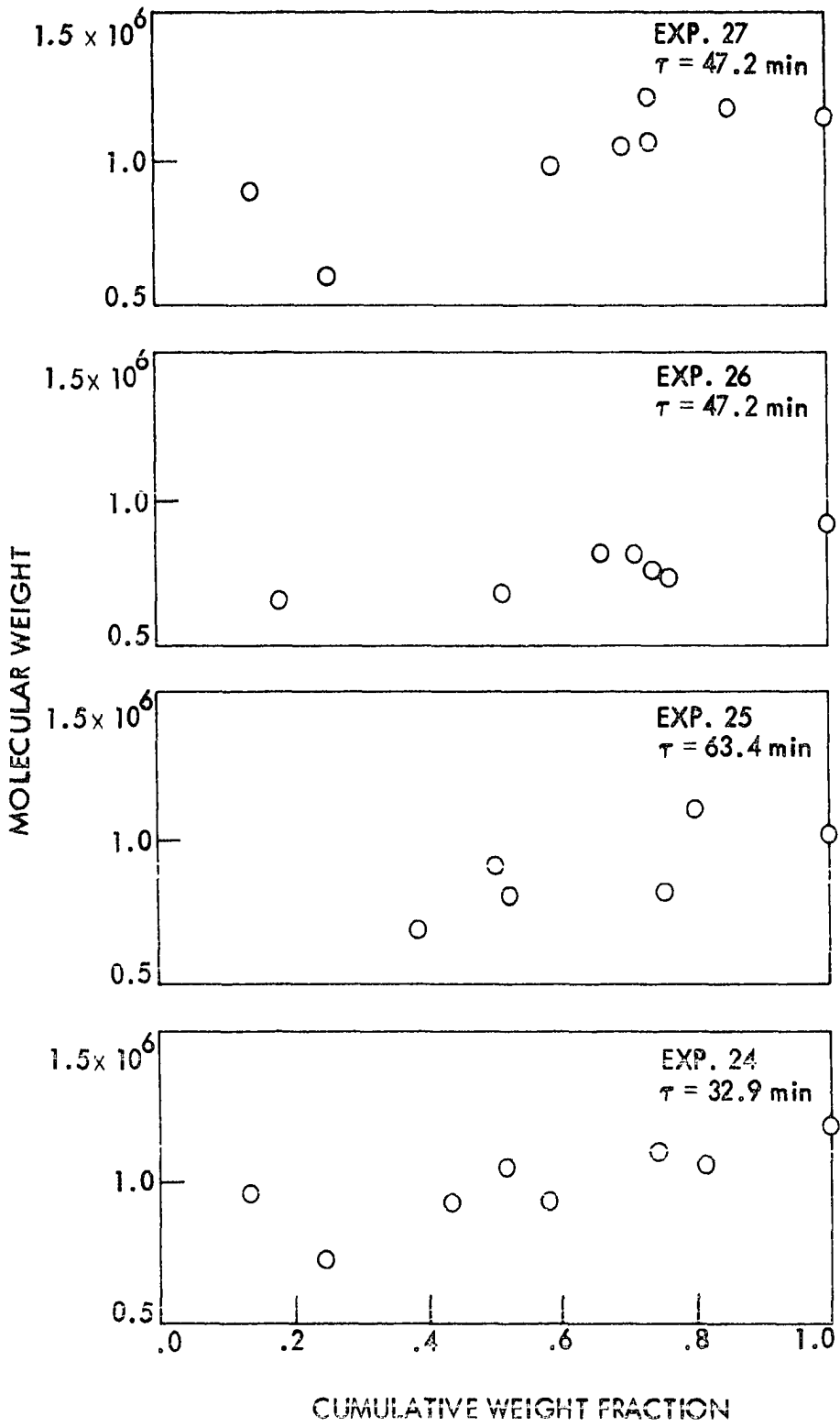
Figure 4 shows the molecular weight of the fractionated latex samples plotted versus the weight fraction of total polymer. The detailed shape of the curve drawn through the data points is uncertain due to the scatter, but the increasing trend is evident. The trend indicates that the lowest molecular weight is found in the largest particles, and as the mean particle size in the sample decreases, the molecular weight increases. Looking at Equations 42 and 43, the approximate analytic expressions for molecular weight as a function of particle size, we see that a decreasing trend is predicted.

Before the Monte Carlo simulation could be used, estimates of the following parameters were required.

1. Volume fraction of monomer in a particle, ϕ .
2. Surface area per soap molecule, a_s .
3. Decomposition rate constant for initiator, k_d .
4. Polymerization rate constant, k_p .
5. Termination rate constant, k_t .
6. Chain transfer rate constant, k_{tf} .

Of these parameters, a_s , k_d , and k_{tf} have been reported by

Figure 4. Experimental viscosity average molecular weights as a function of cumulative weight fraction for continuous emulsion polymerization



numerous investigators whose results are in general, if not excellent, agreement. The other parameters have also been widely investigated, but published results have been very divergent. As a consequence it became necessary in this investigation to determine which of the literature values could best be used to describe the experimental data. In some cases it was necessary to adjust the literature values slightly to obtain a good fit with experimental results. These adjustments were of the order of 10 percent or less. Table 4 summarizes the values of the parameters used in this investigation.

Early in this investigation, the volume fraction of monomer was considered to be a function of particle size, as calculated by Morton et al. (31). Their theoretical predications for a latex particle are based on an equilibrium balance between the interfacial surface tension and the swelling force. Their equation contains two parameters, the interfacial surface tension and a polymer-solvent interaction parameter, both of which are difficult to estimate accurately. The surface tension is particularly difficult, since it can be a function of not only surfactant concentration, but also the temperature, the concentration of salts in the latex, and even the conditions of synthesis (14). Using the values for the two parameters given by Gardon (14), the equation of Morton et al. (31) predicts ϕ

Table 4. Summary of the parameters used in this investigation
T = 60 °C

Parameter	Values	Source
a_s	61 Å ² /molecule	Brodnyan and Brown (2)
k_d	4.99 x 10 ⁻⁶ sec ^{-1a}	Kolthoff and Miller (25)
k_p	756 ^b	Smith (47)
k_t	$k_t/k_p^2 = 861$	Tobolsky and Offenbach (51)
k_{tf}	6.0 x 10 ⁻⁵ k_p	Johnson and Tobolsky (21) Mayo et al. (28) Saha et al. (41) Tobolsky and Offenbach (51)
\emptyset	0.65 ^b	Gardon (10)
ρ_p	1.056	Matheson et al. (27)
ρ_o	0.869	Patnode and Scheiber (37)

^aObtained by interpolation of author's data.

^bAdjusted slightly to provide a better fit to our experimental data.

to be a monotonically increasing function of particle size with a value greater than 0.8 for particles with diameter of 2000 Å. If this is taken to be the mean value for all particles in the reactor, it is evident that a maximum conversion of approximately 20 percent can be reached before free monomer disappears. Experimentally, however, conversions of approximately 40 percent were obtained in this

investigation before the free monomer vanished. This corresponds to an approximate value of $\emptyset = 0.60$. The discrepancy may be explained by use of incorrect values for the parameters used in the theoretical equation or by the monomer content of particles being rate controlled rather than equilibrium controlled. Because of these uncertainties, a constant value of $\emptyset = 0.65$ was used for all calculations in this investigation.

The value of the polymerization rate constant, k_p , given in the literature is strongly dependent on the type of polymerization used in obtaining the data. Typical of most solution and bulk polymerization investigations, Matheson et al. calculated $k_p = 176$ l/mole sec at 60°C (27). The value of the polymerization rate constant calculated from emulsion polymerization data is usually higher than that calculated from bulk or solution polymerization. For instance extrapolation of the values of k_p given by Smith (47) to 60°C yield $k_p = 737$ l/mole sec; the value obtained by Paoletti and Billmeyer is $k_p = 300$ l/mole sec at 60°C (35). With such widely differing values of k_p published in the literature, it was decided that initial Monte Carlo runs should be made for the two extreme values.

Termination rate constants for polystyrene emulsion polymerization have not been the subject of much study, since termination has often been considered to be

instantaneous. This is equivalent mathematically to assuming that k_t is infinite. Gardon was the only investigator found to report k_t for emulsion polymerization (12). He determined the ratio $k_t/k_p = 141$. Comparable values of this ratio determined from bulk polymerization experimentation of Tobolsky and Offenbach are 3-4 orders of magnitude larger (51). The values determined from bulk and solution polymerization are so large that the Monte Carlo simulation results were the same as obtained using an infinite value of k_t . Therefore, for initial computer runs values of k_t based on Gardon's (12) value of k_t/k_p and on Tobolsky and Offenbach's (51) value of k_t/k_p^2 were used.

The following table summarizes the rate constants used in the initial Monte Carlo simulations (Table 5).

Initial Monte Carlo runs made with a simplified model which did not include chain transfer yielded average molecular weights of 4-6 million, with individual chains having molecular weights as high as 40 million. Since no evidence of this extreme behavior was found in the literature or obtained experimentally in this investigation, we were alerted to the possibility of an omission in our model. When chain transfer was added, more reasonable molecular weight behavior was predicted.

The computer runs based on Gardon's (12) value of k_t/k_p showed strong disagreement with experimental data

Table 5. Summary of rate constants used for initial Monte Carlo simulations
 $k_{tf} = 6.0 \times 10^{-5} k_p$

k_p (1/mole sec)	k_t (1/mole sec)
176 ^a	2.67×10^7 ^b
176 ^a	2.48×10^4 ^c
737 ^d	4.67×10^8 ^b
737 ^d	1.04×10^5 ^c

^aMatheson et al. (27).

^bBased on $k_t/k_p^2 = 861$, given by Tobolsky and Offenbach (51).

^cBased on $k_t/k_p = 141$, given by Gardon (12).

^dSmith (47).

for both molecular weight and particle size. For the run using $k_p = 756$ l/mole sec, computer output indicated that a particle 2000 Å in diameter would contain 15-20 free radicals. The multiple free radicals were the cause of the disagreement with the experimental data. Figure 5 shows the viscosity average molecular weight plotted versus cumulative weight fraction. The strong disagreement with the experimental data shown in Figure 4 is obvious, both in the magnitudes of predicted molecular weights and in the shape of the curve. The predicted and experimental particle size

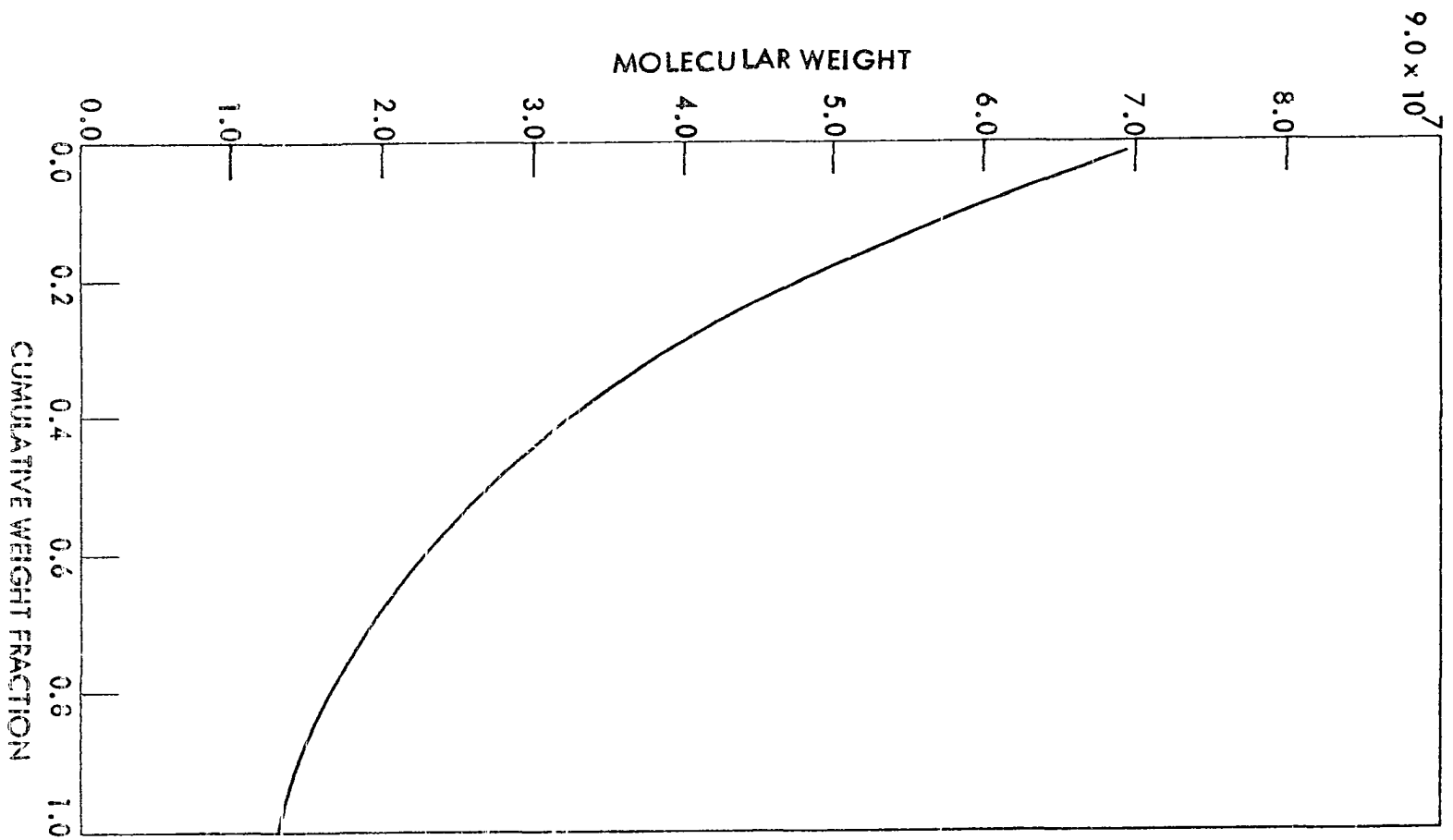
Figure 5. Predicted molecular weight as a function of weight fraction based on Gardon's (12) value of k_t/k_p

$$k_p = 176 \text{ l/mole sec}$$

$$k_t = 2.48 \times 10^4 \text{ l/mole sec}$$

$$k_{tf} = 0.01056 \text{ l/mole sec}$$

$$\tau = 32.9 \text{ min}$$



data are shown below for comparison.

	D_n	D_a	D_v	D_v/D_n
experimental	1410 Å	1550	1680	1.192
predicted	1078 Å	1434	1847	1.715

Again the strong disagreement is obvious.

The numerical data obtained using very large values of k_t showed much better agreement with the trend of the experimental molecular weight data for both $k_p = 176$ and $k_p = 737$ l/mole sec. Of the two values of k_p , predicted particle size data using Smith's (47) value showed the best agreement with experimental particle size data, but mild disagreement did exist. By using $k_p = 756$ l/mole sec the predicted mean particle sizes showed good agreement with the experimental data with a residence time of 32.4 minutes, but at larger residence times predicted mean particle sizes were smaller than the experimental values. Since multiple radicals in particles would be more likely for small values of k_t , this discrepancy could be caused by use of a value of k_t which was too large. It was anticipated that multiple radicals would have the most significant effect in the experimental data at the largest residence time. Therefore a reasonable approach for deciding on a value of k_t would be to use $k_p = 756$ l/mole sec and adjust k_t so that the experimental and predicted particle

size data agreed for residence times of 47.2 and 63.4 min. More emphasis would be placed on the data for the largest residence time, since in this experiment multiple radical effects would be most pronounced.

Computer runs were made for $k_t = 7.5 \times 10^6$, 5.0×10^6 , and 2.5×10^6 in addition to the run at $k_t = 4.92 \times 10^8$ for the residence time of 63.4 min. For residence times of 32.4 and 47.2 minutes, computer runs were made with $k_t = 5.0 \times 10^6$ and 4.92×10^8 . The effects of k_t on the molecular weight as a function of particle size and on the particle size distribution can be seen in Figures 6 and 7. In Figure 6 the results of the analytic expression based on the assumption of instantaneous termination is also shown. Looking at the general shape of the curves, molecular weight is an increasing function of particle size for small particles, but a maximum is reached followed by a decrease in molecular weight as particle size increases further.

The Monte Carlo model shows that very small latex particles contain polymer of low molecular weight. These particles are so small that even if there is only one polymer chain in the particle, the molecular weight of that chain is relatively low. The shape of the curve is very similar for small particles for all values of k_t used in these calculations. However, for large particles the shapes of the curves are very noticeably different due to the

Figure 6. Monte Carlo simulation predictions of molecular weight as a function of particle size

$$\tau = 63.4 \text{ min}$$

$$k_p = 756 \text{ l/mole sec}$$

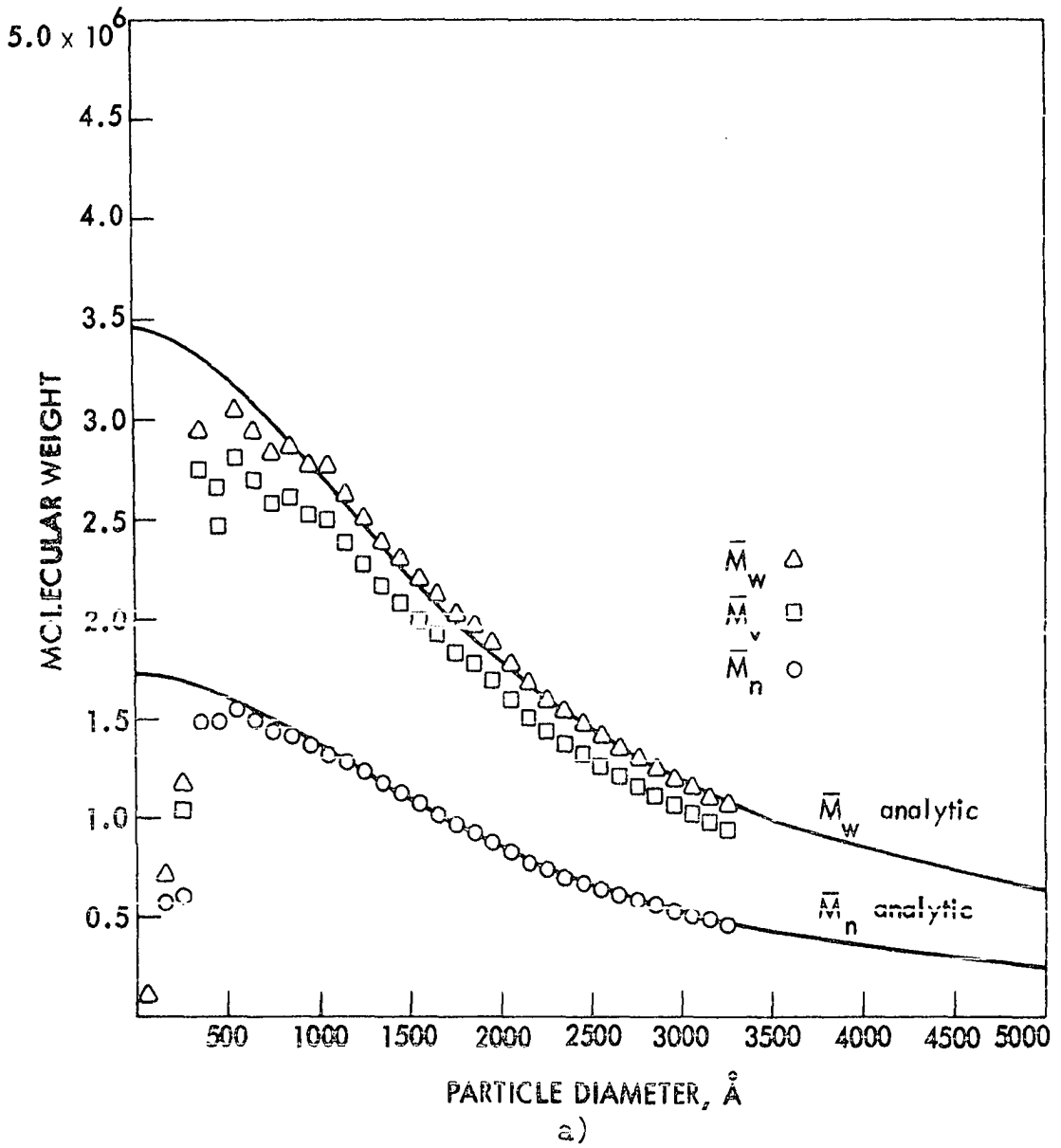
$$k_{tf} = 0.0454 \text{ l/mole sec}$$

a) $k_t = 4.92 \times 10^8 \text{ l/mole sec}$

b) $k_t = 7.5 \times 10^6 \text{ l/mole sec}$

c) $k_t = 5.0 \times 10^6 \text{ l/mole sec}$

d) $k_t = 2.5 \times 10^6 \text{ l/mole sec}$



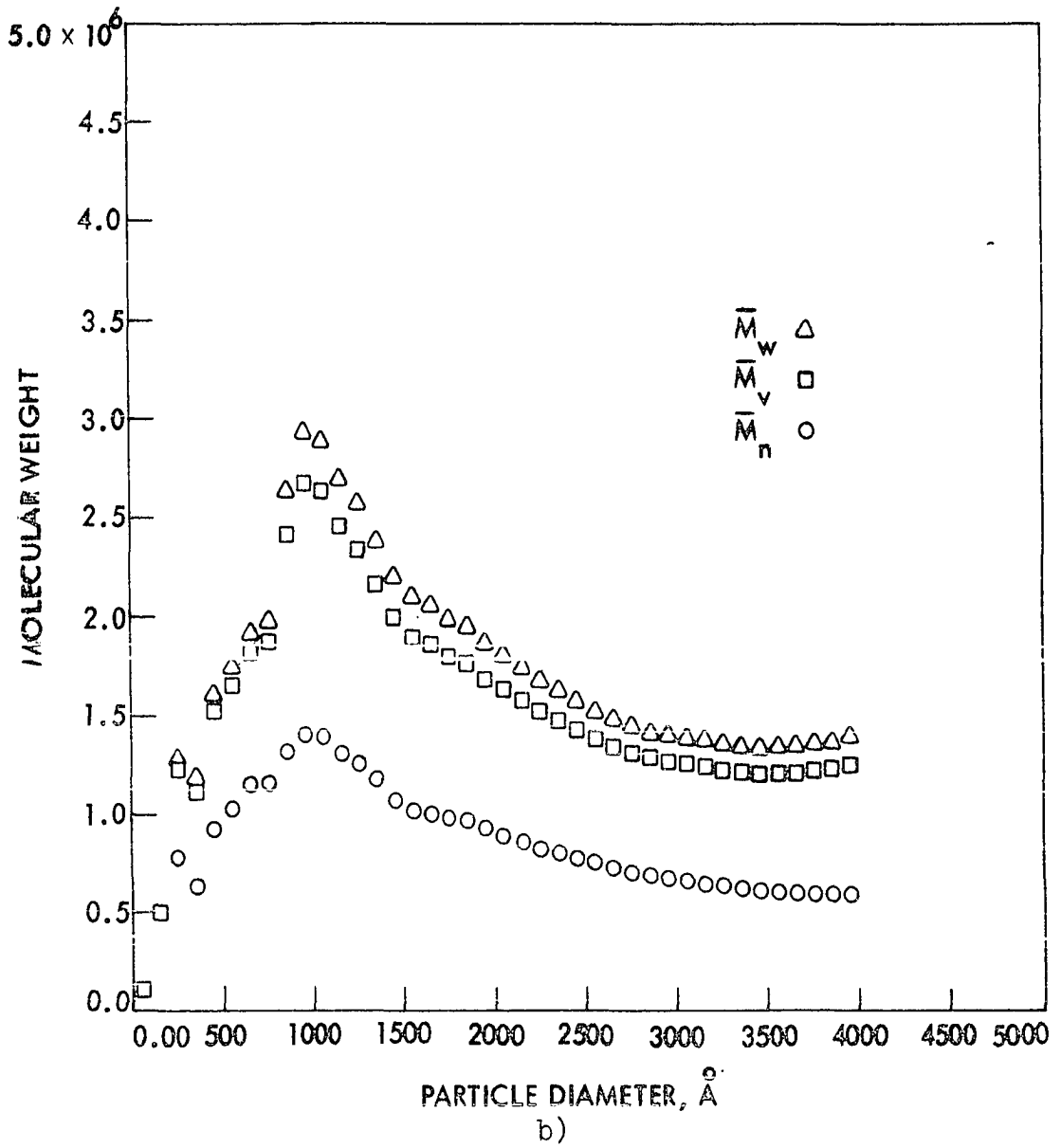


Figure 6 (Continued)

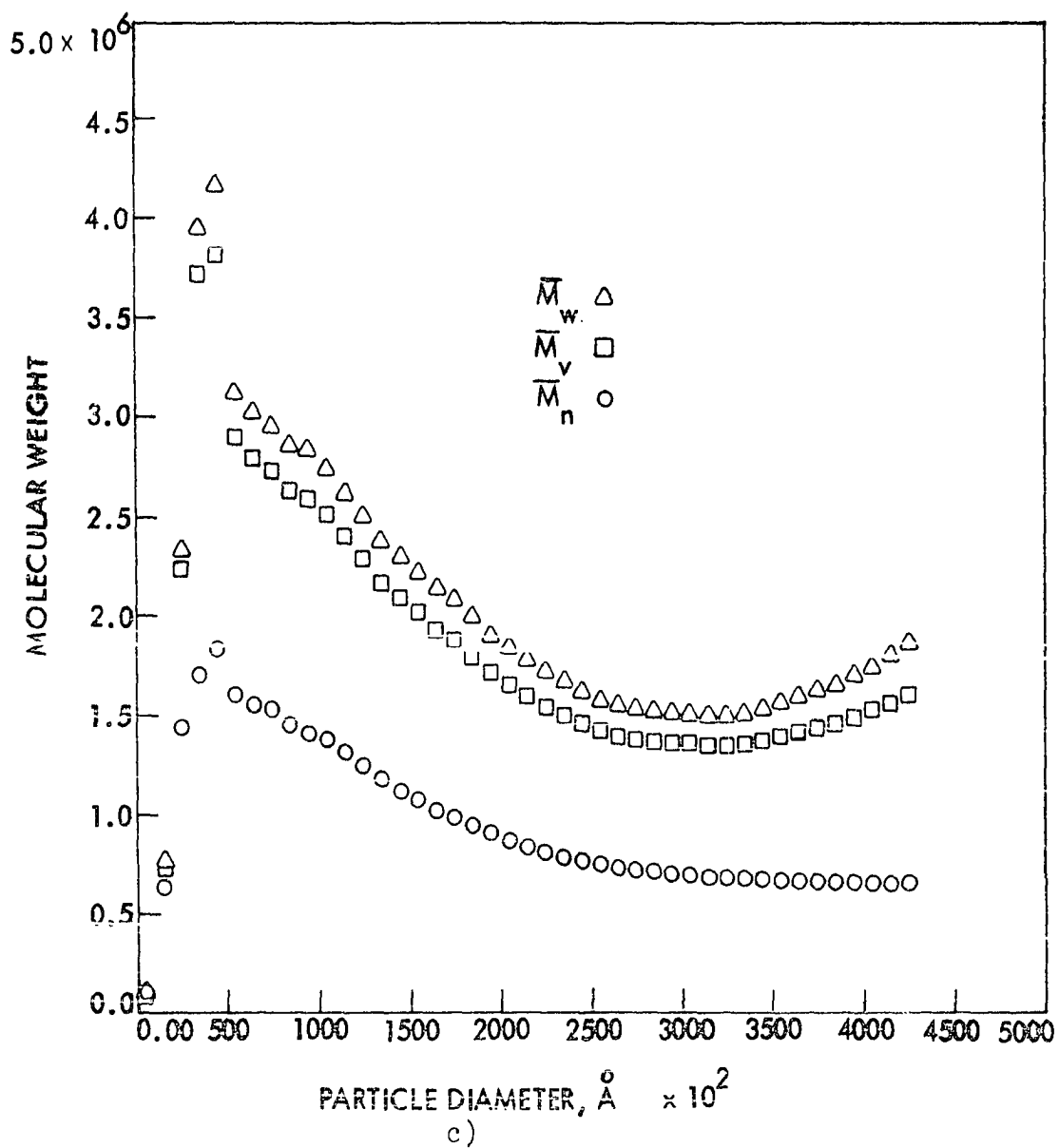


Figure 6 (Continued)

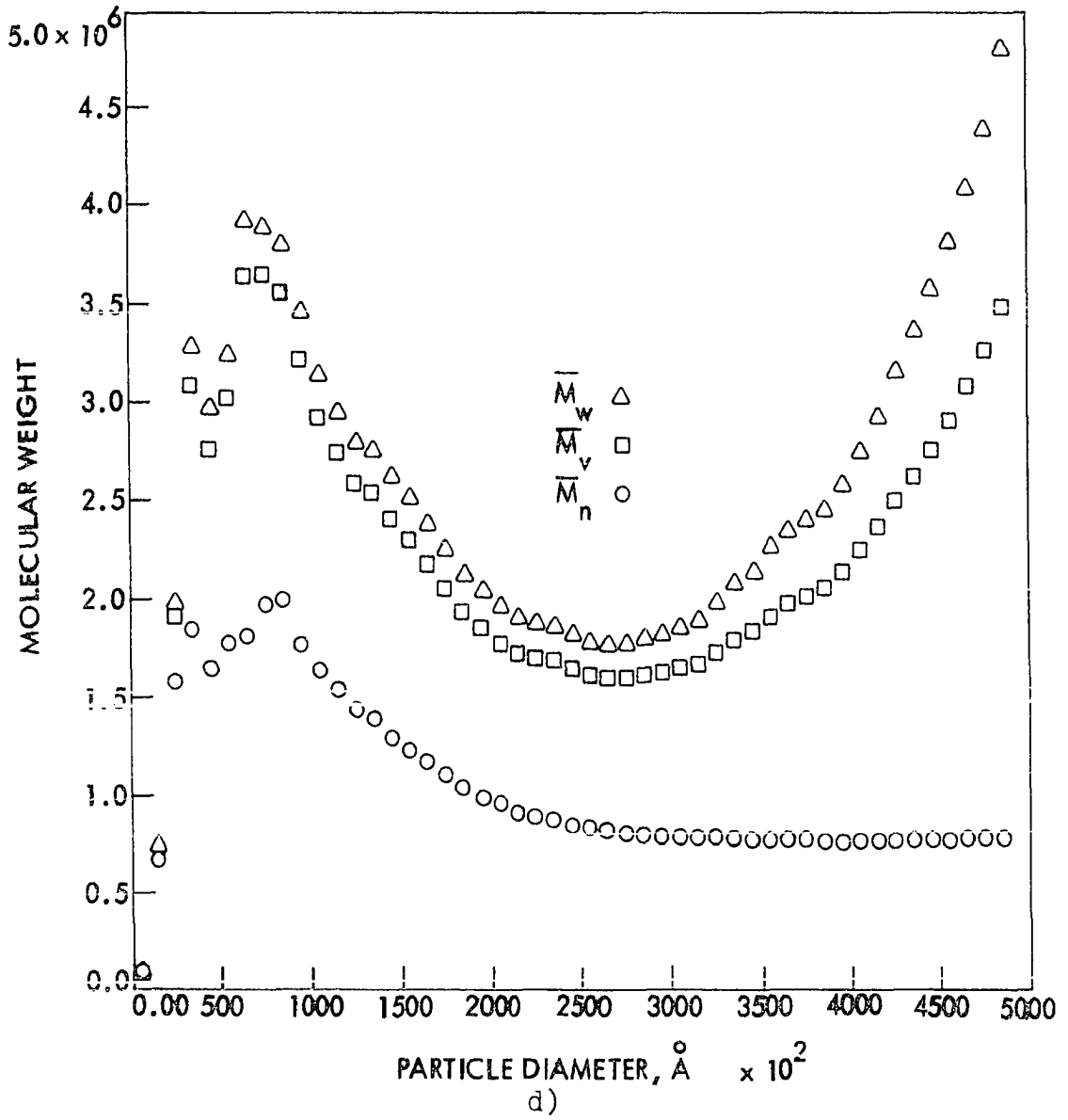


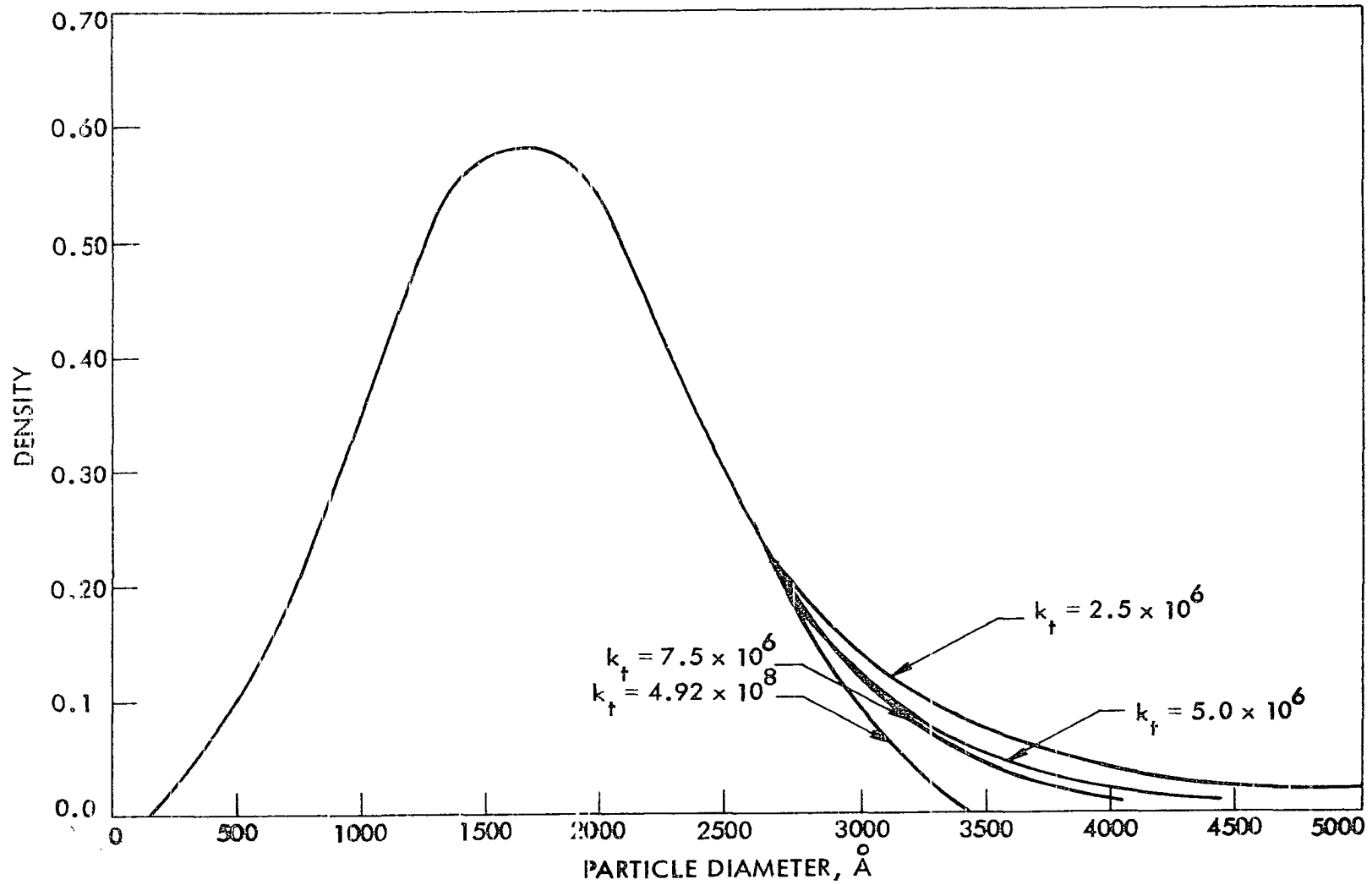
Figure 6 (Continued)

Figure 7. Monte Carlo predictions of particle size distribution

$$k_p = 756$$

$$k_{tf} = 0.0454$$

$$\tau = 63.4$$



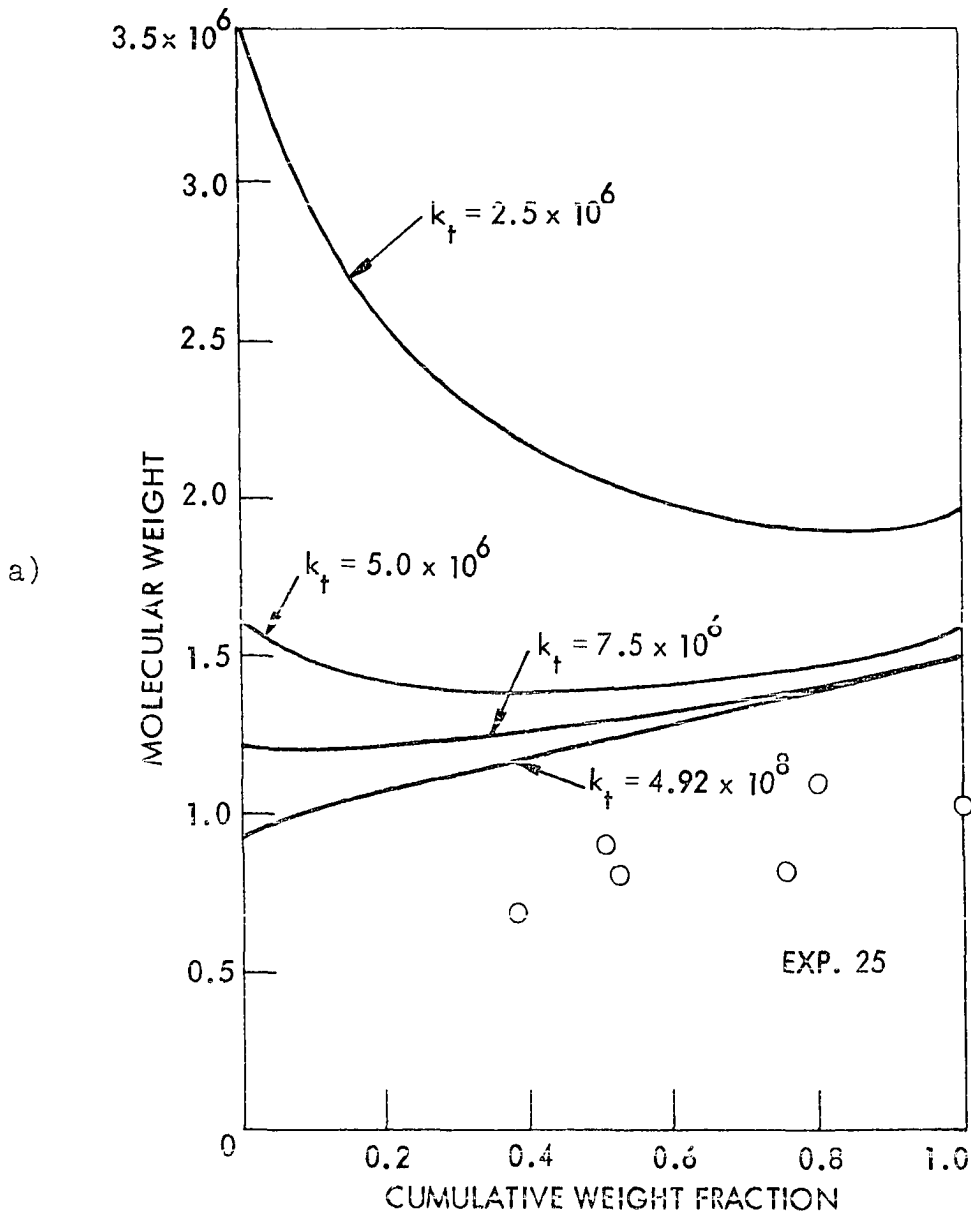
presence of multiple radicals in large particles. Multiple radicals cause the molecular weight of the polymer to increase very rapidly with particle size. This is in line with the predictions of Stockmayer (49), O'Toole (34), and Gardon (11) who showed that in the particle size range in which the average number of free radicals is significantly greater than one-half, the multiple radical effect is a very strong function of particle size.

The effect of multiple radicals on the particle size distribution is much less noticeable than on molecular weight. Figure 7 shows the predicted particle size distributions for the various values of k_t . Experimentally the curves would probably not be distinguishable, since the differences among them are small and are only observed in the tails of the distributions.

The most dramatic effect of the value of k_t is seen in the predicted relationship between molecular weight and cumulative weight fraction as shown in Figure 8 along with the corresponding experimental data. Our Monte Carlo simulation shows that the shape of the predicted curve is very sensitive to values of k_t . Consequently it is expected that the shape of the experimental curve would be very sensitive to the presence of multiple free radicals in the latex particles. Clearly the experimental data more nearly matches the predicted data for large values of k_t , but it is

Figure 8. Experimental and predicted values of viscosity
average molecular weight versus weight frac-
tion of polymer
 $k_p = 756 \text{ l/mole sec}$
 $k_{tf} = 0.0454 \text{ l/mole sec}$

- a) $\tau = 63.4$
- b) $\tau = 47.2$
- c) $\tau = 32.9$



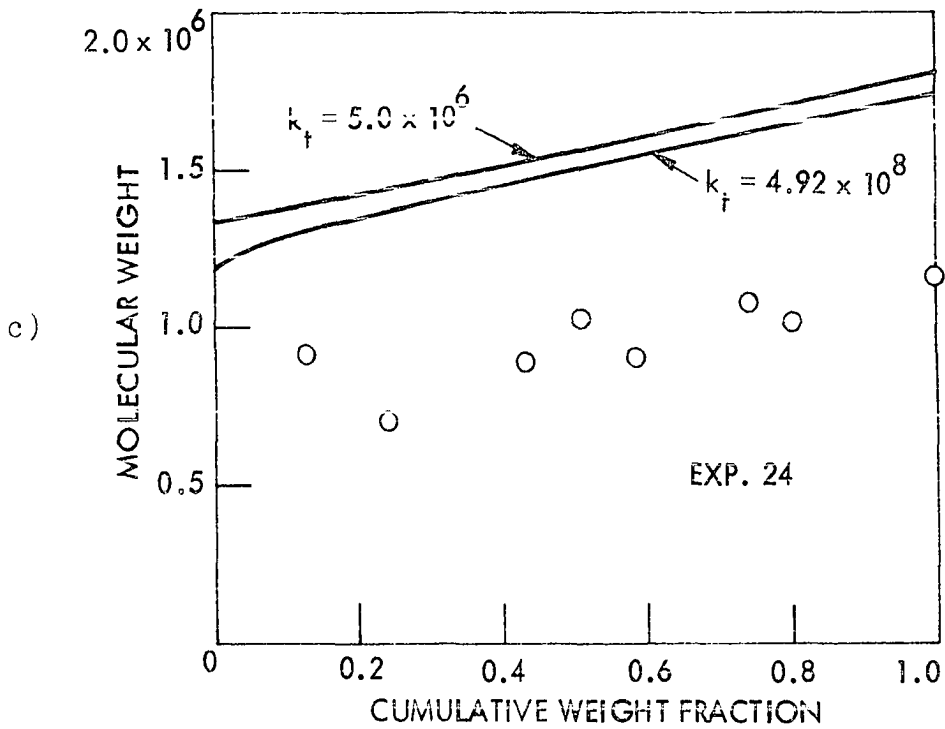
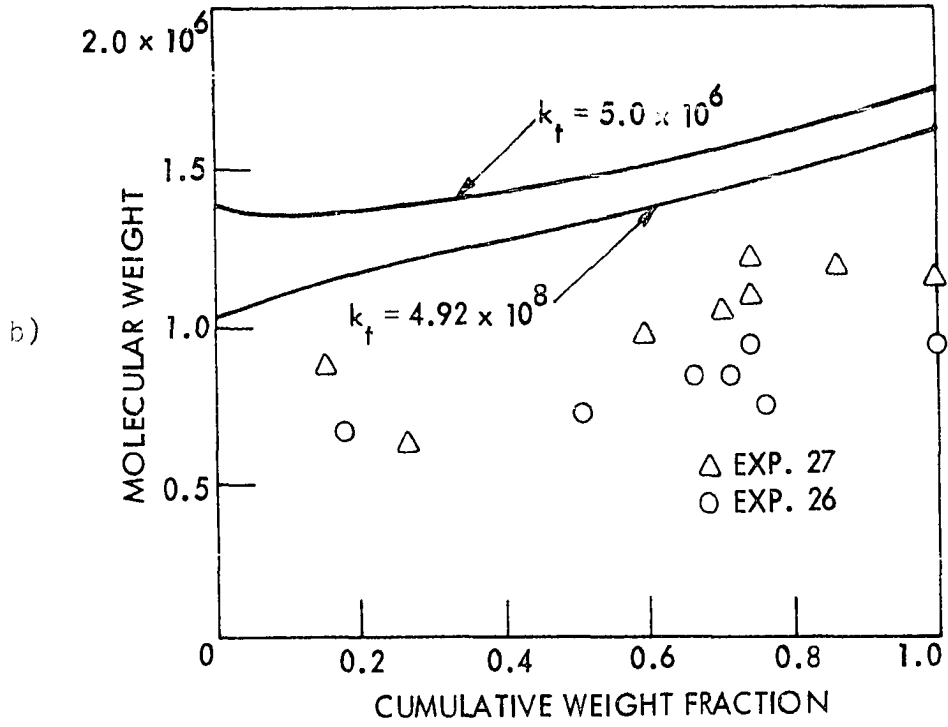


Figure 8 (Continued)

not obvious which of the predicted curves is most similar to the experimental data. In all cases the predicted values of molecular weight are higher than the experimental values. Such disagreement between experimental and calculated values of molecular weight is common for a priori predictions. Therefore in trying to match the experimental curves and predicted data, more emphasis was placed on matching the shape of the predicted curve to the form of the experimental data rather than in minimizing the absolute differences between the predicted and observed values.

The method used to compare the trends of the experimental and predicted data was based on an analysis of the differences between the experimental and predicted molecular weights. Let d_i represent the difference between the i^{th} experimental molecular weight and the corresponding predicted molecular weight. If the experimental data showed no scatter, a computer predicted curve would exist for which all d_i would be equal assuming the model was correct. If the predicted curve did not fit the data, the values of d_i 's would not be the same. This suggests that the variance or standard deviation of the d_i 's would be useful for determining which value of k_t will produce a curve most similar in shape to a curve drawn through the experimental data. The variance of d is

$$s_d^2 = \frac{\sum (d_i - \bar{d}_i)^2}{n - 1} \quad (51)$$

where n is the number of experimental data points. The standard deviation, s_d , is the square root of the variance. The computer curve for which the standard deviation of d is minimum should be the best fit to the experimental data. Table 6 gives a summary of these calculations. Looking first at the calculations for the residence time of 63.4 min, we can see that the standard deviation of d_i decreases as k_t increases with the minimum corresponding to $k_t = 4.92 \times 10^8$ l/mole sec. This suggests that the data for this experiment is best described when termination is

Table 6. Standard deviation of d
 $k_p = 756$ l/mole sec

exp	τ	k_t			
		4.92×10^8	7.5×10^6	5.0×10^6	2.5×10^6
24	32.9	0.0899		0.0899	
25	63.4	0.1034	0.1084	0.1189	0.2462
26	47.2	0.0678		0.0509	
27	47.2	0.1032		0.1299	

taken to be instantaneous. Similar analysis of the data of the other experiments is less conclusive, but in none of the experiments is there an indication of strong deviations from results predicted under conditions of instantaneous termination.

Table 7 shows the predicted and experimental number, area and volume average particle diameters. The ratio of volume to number average diameters is also given. This ratio may be the most important indication of nonideal behavior. For the largest value of k_t this ratio is constant, independent of residence time. For $k_t = 5.0 \times 10^6$ the ratio shows a steady increase as residence time is increased indicating the presence of proportionally more large particles. The experimental data for the four experiments show a constant value for the volume average to number average diameters. It is also interesting to note that the experimental ratios of volume to number average diameters are less than those obtained from the computer simulation, indicating that a narrower size distribution is obtained experimentally than is predicted. The experimental values are closest to agreement for theoretical predicts where $k_t = 4.92 \times 10^8$ is used. These observations suggest that termination in the particles is instantaneous.

Table 7. Monte Carlo particle size data

$$k_p = 756$$

$$k_{tf} = 0.0454$$

k_t	$\tau = 32.9$	$\tau = 47.2$	$\tau = 63.4$
4.92×10^8	$D_n^a = 1357$	1539	1702
	$D_a^b = 1525$ $R^c = 1.225$	1733 $R = 1.228$	1915 $R = 1.226$
	$D_v^d = 1663$	1889	2085
7.5×10^6			1756
			2011 $R = 1.273$
			2238
5.0×10^6	1368	1560	1774
	1556 $R = 1.253$	1795 $R = 1.282$	2062 $R = 1.311$
	1715	2001	2324
2.5×10^6			1871
			2207 $R = 1.361$
			2544
exp'l data	1410	1710	1950
	1550 $R = 1.192$	1860 $R = 1.199$	2140 $R = 1.184$
	1680	2050	
		1650	
		1800 $R = 1.163$	
		1920	

$$a \quad D_n = \frac{\sum n_i D_i}{\sum n_i} \quad .$$

$$b \quad D_a = \frac{\sum n_i D_i^2}{\sum n_i D_i} \quad .$$

$$c \quad R = \frac{D_v}{D_a} \quad .$$

$$d \quad D_v = \frac{\sum n_i D_i^3}{\sum n_i D_i^2} \quad .$$

Molecular Weight Predictions

Of general interest is the success of a model in the prediction of latex molecular weight as a function of the reaction variables. Figure 9 shows the number and weight average molecular weights of the latex as a function of residence time, as obtained by use of the Monte Carlo simulation. These curves were obtained using $k_t = 4.92 \times 10^8$ l/mole sec and correspond to conditions of instantaneous termination. The analytic expressions for molecular weight give nearly identical results. For comparison the corresponding experimental data are also shown. For very small residence times chain transfer is controlling, and the curves are nearly horizontal, but as the residence time gets large, chain transfer decreases in importance and the slope of the molecular weight curve approaches $-2/3$ as predicted by Equation 46. The experimental data of this investigation is also shown on the graph and does not appear to be inconsistent with the trends of the predicted curves. However predicted values of molecular weight are somewhat higher than the experimental values. This discrepancy is typical of molecular weight calculations in emulsion polymerization. It is commonly attributed to decreased free radical efficiency.

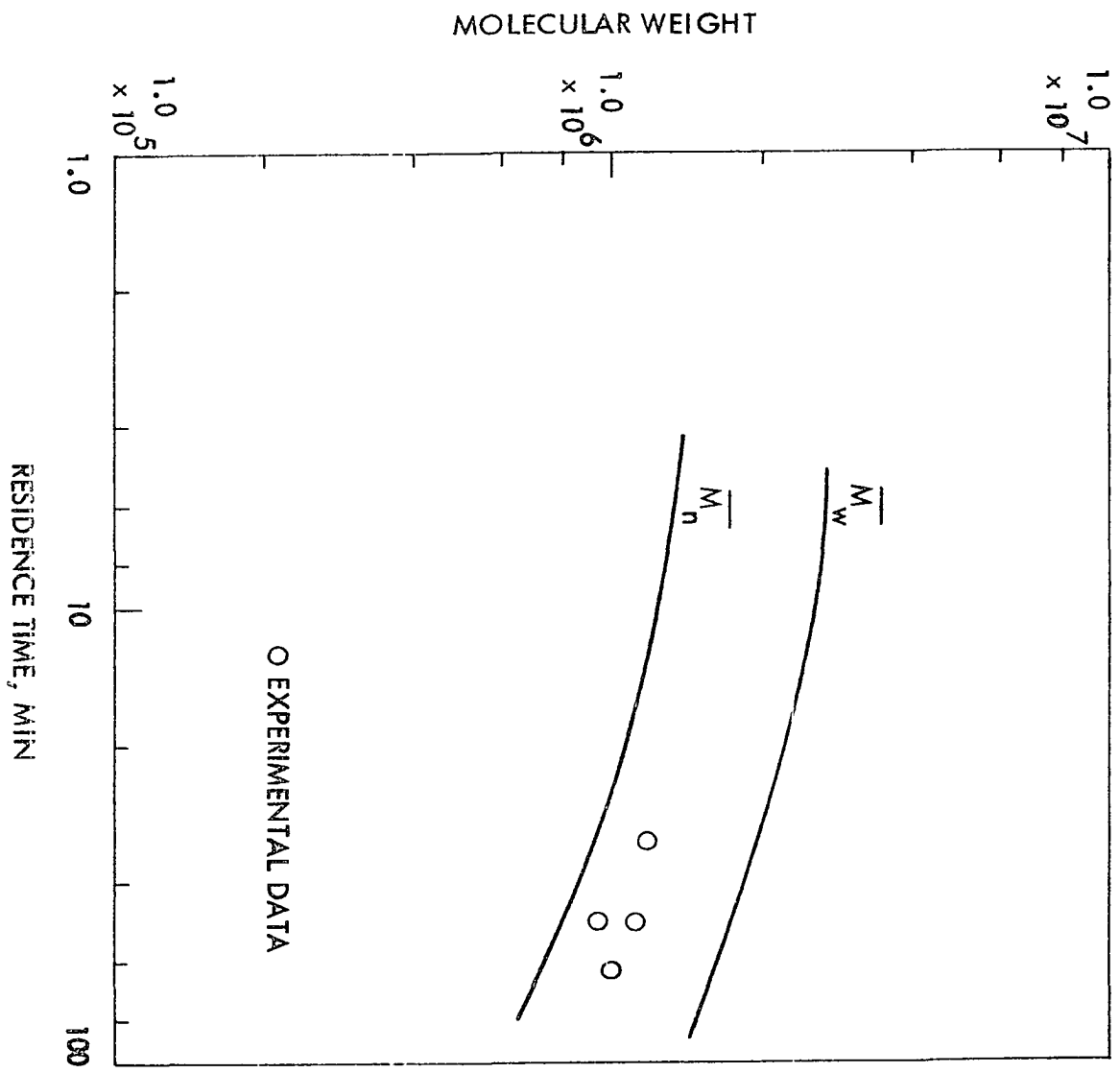
The experimental data of DeGraff (4) can be qualitatively compared with the results calculated by our model,

Figure 9. Molecular weight as a function of residence time as predicted by the Monte Carlo simulation under conditions of instantaneous termination

$$k_p = 756 \text{ l/mole sec}$$

$$k_t = 4.92 \times 10^8 \text{ l/mole sec}$$

$$k_{tf} = 0.0454$$



but DeGraff's data was collected under different experimental conditions and cannot be compared quantitatively. DeGraff concluded from his experimental data that molecular weight of the latex is independent of particle size. However his data show considerable scatter and are not inconsistent with our predictions.

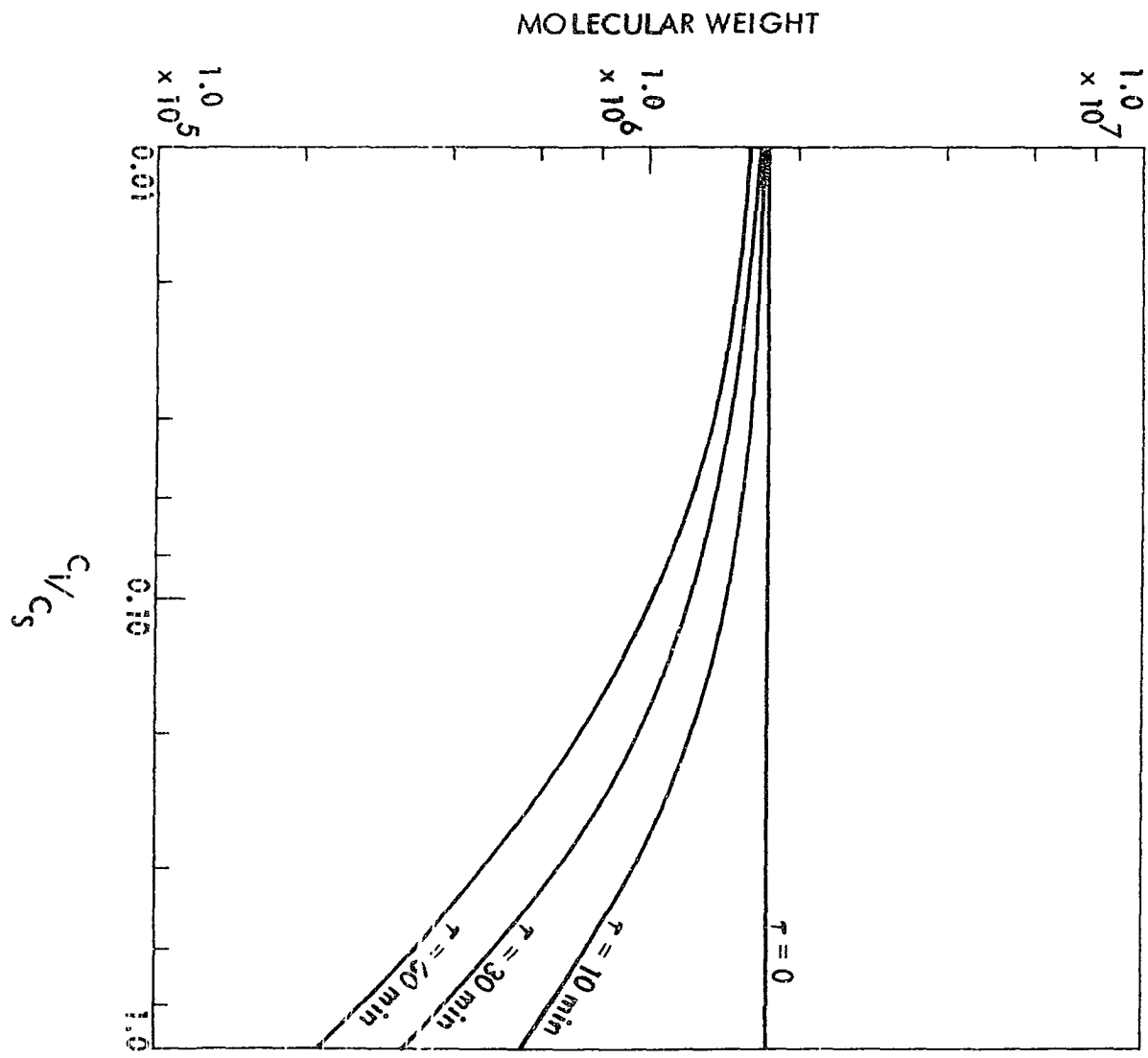
The relationship between number average molecular weight and the initiator to surfactant ratio is shown in Figure 10 for several residence times. These curves were generated using the analytic expression for number average molecular weight given in Equation 46. For very small initiator concentrations, chain transfer is the dominant factor in determining molecular weight, but as the initiator level is increased, the process of radical capture becomes more important and is the controlling factor for large initiator concentrations. As before the data of DeGraff (4) can be qualitatively compared to our predicted results. DeGraff found that molecular weight varies linearly with both surfactant concentration and initiator concentration when plotted on logarithmic coordinates. However, when his molecular weight data is expressed in terms of the initiator to surfactant ratio, the trend of his data is consistent with our predictions.

Figure 10. Number average molecular weight as a function of the initiator-surfactant ratio as predicted by the analytic molecular weight model

$$k_p = 756 \text{ l/mole sec}$$

$$k_t = 4.92 \times 10^8 \text{ l/mole sec}$$

$$k_{tf} = 0.0454 \text{ l/mole sec}$$



DISCUSSION

Consideration of all the data presented in the previous section leads on to the conclusion that noninstantaneous termination has had minimal, if any, effect on the product produced in this investigation. Experimental molecular weight data from this investigation is not inconsistent with predictions based on instantaneous termination. Analysis of the particle size data provides additional evidence that termination is instantaneous. If all experimental evidence is considered, it can be concluded that termination in the particles is extremely rapid under conditions of this investigation and that for calculational purposes termination can be considered to be instantaneous without introduction of noticeable error.

A comparison of the batch and continuous experimental results shows that the molecular weight-particle size relationship is different for the two cases. In the batch experiments large particles were found to have the highest molecular weight while in the continuous experiments large particles had the lowest molecular weight. A reason hypothesized for partial explanation of the batch results was that the stochastic variation responsible for producing larger than average particles also is responsible for producing larger than average molecular weights. In a

continuous system, however, dependency of the rates of radical capture and chain termination on particle size is the cause of molecular weight being a function of particle size.

Use of the Monte Carlo simulation has shown that the assumption that a particle grows one-half of the time cannot be validly used for very small particles. With our model the average particle was observed to grow from 50 Å to approximately 500 Å before the second free radical was captured. Obviously the free radical population of particles in this range is much closer to one than to one-half.

Despite the apparent success of the Monte Carlo simulation for describing the growth of an individual polymer particle, predictions of conversion are grossly in error. Two possible sources of the error are use of an incorrect value of ϕ and use of S to represent the total surface area of the latex. Table 8 summarizes the experimentally calculated values for ϕ and the total surface area of the particles. Both appear to vary with residence time. The volume fraction of monomer is largest for small residence times, a result contrary to the predictions of Morton et al. (31). For all experiments the total surface area of the particles is lower than the surface area based on surfactant concentration, S , but the experimentally determined value of particle surface increased with residence time. The observed changes of experimental particle surface area

Table 8. Experimentally determined values of volume fraction of monomer and particle surface area

exp	24	25	26	27
τ	32.9	63.4	47.2	47.2
conv	16.5%	40.2%	25.0%	28.4%
\emptyset	0.79	0.60	0.73	0.72
Total surface area of particles	0.59×10^5	1.03×10^5	0.74×10^5	0.89×10^5

$$S = a_s N_A [S] = 2.27 \times 10^5 \text{ cm}^2/\text{ml latex}$$

may explain the change of \emptyset with residence time. The increased particle areas at larger residence times should result in lower interfacial surfactant concentration. This lower surfactant concentration, according to Morton's (30) theory, will in turn establish a lower equilibrium volume fraction of monomer in a latex particle. This is consistent with the observed experimental change of \emptyset with residence time. It should be noted at this time that S is also used in the calculation of molecular weight the results of which have been found in this investigation and in the literature consistently larger than those observed experimentally.

CONCLUSIONS

1. Experimental data from this investigation indicate that molecular weight is a modest function of particle size in a polystyrene latex produced in a continuous stirred tank reactor. The experimental data indicate that the smallest molecular weight is found in the largest particles.
2. Limited experimental data obtained for batch emulsion polymerization of polystyrene suggest that molecular weight is a modest function of particle size for a completely reacted latex. One of two experiments indicates that higher molecular weights are found in the largest particles, while a second experiment is inconclusive.
3. The Monte Carlo simulation of emulsion polymerization in a continuous stirred tank reactor is useful for prediction of the molecular weight and particle size characteristics of the latex.
4. Comparison of the experimental data and predictions of the Monte Carlo simulation show no evidence of the presence of multiple free radicals in latex particles.
5. Approximate analytic expressions for number average and weight average molecular weights were derived based on the assumption of instantaneous termination. Calculations based on these expressions are nearly

identical to predictions of the Monte Carlo simulation.

6. Chain transfer was a significant factor in accurate predictions of the molecular weight of polystyrene produced by emulsion polymerization.
7. The assumption that the total surface area of particles in a latex as determined by the surfactant concentration in a latex was found to be in error in this investigation.

RECOMMENDATIONS

1. A latex fractionation technique should be developed which would fractionate a latex according to particle size in such a way that a series of latex samples nearly homogeneous in particle diameter is obtained.
2. The relationship between molecular weight and particle size should be studied for a monomer other than styrene, in which the effects of multiple radicals in particles would be more likely to be found. Methyl methacrylate and vinyl acetate are possibilities.
3. The monomer content of particles should be investigated to determine if
 - a) monomer content is affected by the amount of surfactant present
 - b) monomer content is a function of particle size
 - c) monomer content of particles is an equilibrium or rate controlled quantity.
4. The commonly made assumption that the total surface area of the latex is limited by surfactant concentration should be examined. This may be combined with a study of nucleation phenomenon in a continuous stirred tank reactor operating under transient conditions.
5. Additional kinetic studies are needed to determine why the polymerization rate constant determined by emulsion

polymerization differs so greatly from values of the same constant determined for bulk or solution polymerization. Kinetic studies of particle growth in batch monodisperse latexes may be useful.

6. A batch latex produced with excess of free monomer should be separated into fractions according to particle size. Comparison of the results of such an experiment with the batch results obtained in this investigation may yield information about polymerization in monomer starved particles.

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APPENDIX

Computer program for Monte Carlo simulation of
emulsion polymerization of styrene in
a continuous stirred tank reactor

```

C
C
C
C MCNTE CARLO SIMULATION OF EMULSION POLYMERIZATION IN A
C CONTINUOUS STIRRED TANK REACTOR
C
C
C
C DEFINITION OF TERMS
C
C AS = AREA ASSOCIATED WITH ONE MOLECULE OF SURFACTANT, CM**2 PER MOLECULE
C AVGN = AVOGADRO'S NUMBER
C C(J) = MOLECULAR WEIGHT OF THE J TH GROWING POLYMER CHAIN
C CHAING = GROWTH OF A POLYMER CHAIN, GRAMS PER MOLE
C CI = CONCENTRATION OF INITIATOR, GRAMS PER 100 GRAMS OF WATER
C CIM = CONCENTRATION OF INITIATOR, MOLES PER LITER
C CONV = PERCENT CONVERSION
C CS = CONCENTRATION OF SURFACTANT, GRAMS PER 100 GRAMS OF WATER
C CSM = CONCENTRATION OF SURFACTANT, MOLES PER LITER
C CT1 = MOLECULAR WEIGHT OF THE FIRST CHAIN SELECTED FOR TERMINATION
C CT2 = MOLECULAR WEIGHT OF THE SECOND CHAIN SELECTED FOR TERMINATION
C CUMWT = CUMULATIVE WEIGHT FRACTION
C D(INT) = MEAN DIAMETER FOR A DIAMETER INTERVAL
C DAVG = AVERAGE DIAMETER, ANGSTROMS
C DBAR = NUMBER AVERAGE PARTICLE DIAMETER
C D2BAR = AVERAGE PARTICLE DIAMETER SQUARED
C D3BAR = AVERAGE PARTICLE DIAMETER CUBED
C DEL = DIAMETER INCREMENT IN A SEARCH ROUTINE
C DENM = DENSITY OF MONOMER, GRAMS PER ML
C DENP = DENSITY OF POLYMER, GRAMS PER ML
C DIA = PARTICLE DIAMETER, ANGSTROMS
C DLIMIT = DIAMETER AT WHICH THE GROWTH OF A PARTICLE IS NO LONGER FOLLOWED
C DNEW = PARTICLE DIAMETER WHEN THE NEXT EVENT OCCURS, ANGSTROMS
C DTIME = AMOUNT OF TIME UNTIL NEXT EVENT, SEC
C DTIMEI = TIME A PARTICLE 'SPENDS' IN A DIAMETER INTERVAL
C I = NUMBER OF EVENTS

```

```

C   INT = INTERVAL NUMBER
C   IEND = DIAMETER INTERVAL WHICH A PARTICLE WILL BE IN AT THE END OF THE NEXT
C         EVENT
C   IX = STARTING NUMBER FOR GENERATING A RANDOM NUMBER
C   KKK = PARTICLE COUNT INDEX
C   MN = NUMBER AVERAGE MW OF THE LATEX
C   MV = VISCOSITY AVERAGE MW OF THE LATEX
C   MW = WEIGHT AVERAGE MW OF THE LATEX
C   MNINT(INT) = NUMBER AVERAGE MW FOR A DIAMETER INTERVAL
C   MVINT(INT) = VISCOSITY AVERAGE MW FOR A DIAMETER INTERVAL
C   MNINT(INT) = WEIGHT AVERAGE MW FOR A DIAMETER INTERVAL
C   N = NUMBER OF GROWING POLYMER CHAINS IN THE PARTICLE
C   NCHAIN = NUMBER OF TERMINATED POLYMER CHAINS
C   PARTN = NUMBER OF PARTICLES PER GRAM OF LATEX
C   PH = -ALOG(HYDROGEN ION CONCENTRATION)
C   PHI = VOLUME FRACTION OF MONOMER IN A PARTICLE
C   PLVINT = FRACTION OF PARTICLES LEAVING THE VESSEL BETWEEN TIMEI AND
C           (TIMEI + DTIMEI)
C   POLY = RATE OF POLYMERIZATION IN THE REACTOR, GRAMS PER MIN
C   RATEC = RATE OF RADICAL CAPTURE, EVENTS PER SEC
C   RATEI = RATE OF TERMINATION, EVENTS PER SEC
C   RATEI = RATE OF CHAIN TRANSFER, EVENTS PER SEC
C   RKP = RATE CONSTANT FOR POLYMERIZATION, LITERS PER MOLE PER SEC
C   RKT = RATE CONSTANT FOR TERMINATION, LITERS PER MOLE PER SEC
C   RKT = RATE CONSTANT FOR CHAIN TRANSFER TO MONOMER, LITERS PER MOLE PER SEC
C   TIMEI = AGE OF A PARTICLE WHEN IT IS IN A DIAMETER INTERVAL
C   TEMP = TEMPERATURE, DEG CENTIGRADE
C   RN = RANDOM NUMBER
C   RR = RATE OF RADICAL GENERATION, RADICALS PER SEC PER LITER OF WATER
C   SUMM1(INT) = SUM OF MW FOR A DIAMETER INTERVAL
C   SUMM2(INT) = SUM OF MW**2 FOR A DIAMETER INTERVAL
C   SUMMV(INT) = SUM OF MW**1.62 FOR A DIAMETER INTERVAL
C   SUMPB(INT) = SUM OF THE PROBABILITIES ASSOCIATED WITH AN INTERVAL
C   SUMCHN(INT) = NUMBER OF CHAINS RECORDED IN AN INTERVAL
C   SUMD = SUMMATION OVER ALL INTERVALS OF D(INT)*SUMPB(INT)
C   SUMD2 = SUMMATION OVER ALL INTERVALS OF SUMPB(INT)*D(INT)**2

```

```

C      SUMD3 = SUMMATION OVER ALL INTERVALS OF SUMPRB(INT)*D(INT)**3
C      SUM1 = SUM OF SUMM1(INT) OVER ALL INTERVALS
C      SUM2 = SUM OF SUMM2(INT) OVER ALL INTERVALS
C      SUMV = SUM OF SUMMV(INT) OVER ALL INTERVALS
C      SUMC = SUM OF SUMCHN(INT) OVER ALL INTERVALS
C      TAU = RESIDENCE TIME, MIN
C      TFINAL = FINAL AGE OF THE PARTICLE
C      TWT = SUM OF THE MW OF ALL TERMINATED CHAINS
C      TWTV = SUM OF MW*1.62 FOR ALL TERMINATED POLYMER CHAINS
C      TWT2 = SUM OF MW**2 FOR ALL TERMINATED POLYMER CHAINS
C      V = REACTOR VOLUME, ML
C      WTC = MOLECULAR WEIGHT OF THE TERMINATED CHAIN
C
C
C      THE FOLLOWING STATEMENTS GENERATE A RANDOM NUMBER:
C      IX=IX*65539
C      IF(IX.LT.0)IX=IX+2147483647+1
C      RN=IX*0.4656613E-9
C
C
C      THIS PROGRAM REQUIRES THE FOLLOWING DATA INPUT:
C
C      CARD 1
C          IX, I10 FORMAT
C      CARD 2
C          1. TAU, E15.6 FORMAT
C          2. CS, E15.6 FORMAT
C          3. CI, E15.6 FORMAT
C      CARD 3
C          1. RKP, E15.6 FORMAT
C          2. RKT, E15.6 FORMAT
C          3. RKTf, E15.6 FORMAT
C
C      IX MAY BE ANY ODD INTERGER FROM 1 TO 10 DIGITS IN LENGTH. IT IS RECOMMENDED
C      THAT THE LAST VALUE OF IX GENERATED BY THIS PROGRAM BE USED FOR THE
C      INITIAL VALUE IN THE NEXT RUN OF THIS PROGRAM.

```

C
C

```
DIMENSION SUMM1(50),SUMM2(50),SUMMV(50),SUMPRB(50)
DIMENSION SUMCHN(50),CUMVT(50),D(50),C(40)
REAL MNINT(50),MVINT(50),MWINT(50)
REAL MN,MV,MW
PH=3.5
AVGN=6.023E23
DENP=1.0563
DENM=0.869
PHI=0.65
AS=61.0E-16
V=290.0
KKK=0
READ(5,170)IX
READ(5,1) RKP,RKT,RKTF
2 READ(5,1,END=105)TAU,CS,CI,TEMP
1 FORMAT(4E15.6)
170 FORMAT(I10)
192 FCRMAT(I1)
WRITE(6,23)TAU,CS,CI,TEMP
WRITE(6,24) RKP,RKT,RKTF
WRITE(6,26)IX
23 FORMAT('1',4E15.6)
24 FORMAT(' ',4E14.6)
26 FORMAT(' ',I13)
DO 100 II=1,50
SUMPRB(II)=0.0
SUMM1(II)=0.0
SUMM2(II)=0.0
SUMMV(II)=0.0
SUMCHN(II)=0.0
100 CONTINUE
193 TEMP=TEMP+273.3
CSM=CS/28.838
CIM=CI/27.033
```



```

RKD=4.636E16*EXP(-33500.0/1.986/TEMP)+2.281E13*EXP(-26000.0/1.986
1/TEMP)/10.0**PH
RR=2.0*RKD*CIM*AVGN
S=AVGN*CSM*AS
RK=3.0*RKP*DENM/4.0/3.1416/AVGN/DENP*PHI/(1.0-PHI)*1000.0
ALPHA=RR*4.0*3.1416/S/4.0E16
BETA=RKT*3.0/AVGN/4.0/3.1416*8.0E24*1000.0
ETA=RKTF*DENM*1000./104.14*PHI
C1=3.0*ALPHA/5.0/RK/8.0E24
C2=3.0*BETA/RK/8.0E24
C3=ETA/RK/8.0E24
C4=RKF*DENM*PHI*1000.0
C5=4.0*3.1416*DENP*AVGN/3.0/8.0E24*(1.0-PHI)
C6=RK*8.0E24
WRITE(6,103)C1,C2,C3,C4,C5,C6
WRITE(6,103)ALPHA,BETA,ETA
103  FORMAT(5E14.6)
WRITE(6,106)RR,S,RKD,RK,RKP,RKT,RKTF,CS,CI,TAU
106  FORMAT(//'RR=' ,E14.6/'S=' ,E14.6//'RKD=' ,E14.6/'RK=' ,
1E14.6/'RKP=' ,E14.6/'RKT=' ,E14.6/'RKTF=' ,E14.6//
2'CS=' ,E14.6/'CI=' ,E14.6/'TAU=' ,E14.6//)
TAU=TAU*60.0
TFINAL=TAU*5.0
C THE FOLLOWING TWO STATEMENTS ARE OPTIONAL
WRITE(6,102)
102  FORMAT(//T4,'EVENT',T17,'D TIME',T32,'TIME',T42,'DIAMETER',T52,
1'RADICALS',T72,'MW')
DLIMIT=5000.0
201  IF(KKK.GE.27)GO TO 500
IF(KKK.EQ.2) I LAST=INT
TIME=0.0
TWT=0.0
TWT2=0.0
TWTV=0.0
NCHAIN=0
N=1

```

```

DNEW=50.0
I=1
INT=1
C(1)=0.0
E2=1.0
IF(KKK.GE.2) DLIMIT=1600.0
IF(KKK.GE.7) DLIMIT=1000.0
KKK=KKK+1
C
C DETERMINE WHEN THE EVENT WILL OCCUR
C
16 DIA=DNEW
IF(DIA.GT.DLIMIT) GO TO 201
IX=IX*65535
IF(IX.LT.0) IX=IX+2147483647+1
RN=IX*0.4656613E-9
IF(RN.EQ.0) GO TO 110
IF(DIA.LT.1500.0) GO TO 167
160 RATEC=ALPHA*DIA*DIA
RATET=BETA*N*(N-1)/(DIA**3)
RATETF=ETA*N
DTIME=-ALOG(RN)/(RATEC+RATET+RATETF)
DNEW=DIA+RK*N*DTIME/3.0/DIA/DIA*8.0E24
TIME=TIME+DTIME
I=I+1
GO TO 162
167 TERM1=C1*(DIA**5)/N+C2*(N-1)*ALOG(DIA)+C3*(DIA**3)
CONST=-ALOG(RN)+TERM1
DEL=1.0
DNEW=DIA
161 DNEW=DNEW+DEL
TERM2=C1*(DNEW**5)/N+C2*(N-1)*ALOG(DNEW)+C3*(DNEW**3)
IF(TERM2.LT.CONST) GO TO 161
DNEW=DNEW-DEL
DEL=DEL/10.0
IF(DEL.GT.0.002) GO TO 161

```

```

IF(DNEW.LT.(DIA+0.05)) GO TO 160
DTIME=((DNEW**3)-(DIA**3))/N/C6
TIME=TIME+DTIME
I=I+1
GO TO 11
110 RATEC=ALPHA*DIA**2
DTIME=-ALOG(RN)/RATEC
TIME=TIME+DTIME
DNEW=DIA
I=I+1
GO TO 168
C
C CALCULATE THE CONTRIBUTION THIS PARTICLE MAKES TO THE PRODUCT LATEX
C
162 IEND=DNEW/100.C+1
IF(IEND.LT.INT) IEND=INT
IF(IEND.GE.50) GO TO 201
IF(IEND.GT.(INT+1)) GO TO 11
IF(IEND.GT.INT) GO TO 164
DAVG=(DNEW+DIA)/2.0
TIMEI=TIME
CHAING=C4*DTIME
GO TO 166
164 DINT=INT*100.0
DTIMEI=DTIME*(DINT-DIA)/(DNEW-DIA)
TIMEI=TIME-DTIME+DTIMEI
DAVG=(DINT+DIA)/2.0
CHAING=C4*DTIMEI
GO TO 166
168 DTIMEI=DTIME
IEND=INT
TIMEI=TIME
CAVG=DNEW
166 E1=E2
E2=EXP(-TIMEI/TAU)
PLVINT=E1-E2

```

```

SUMM1 ( INT ) =SUMM1 ( INT ) +TWT *PLV INT
SUMM2 ( INT ) =SUMM2 ( INT ) +TWT2 *PLV INT
SUMMV ( INT ) =SUMMV ( INT ) +PLV INT *TWT V
SUMPRB ( INT ) =SUMPRB ( INT ) + PLV INT
SUMCHN ( INT ) =SUMCHN ( INT ) + PLV INT * ( NCHAIN +N )
IF ( N . EG . C ) GO TO 4
DO 151 J =1 ,N
C ( J ) =C ( J ) +CHAING
SUMM1 ( INT ) =SUMM1 ( INT ) +C ( J ) *PLV INT
SUMM2 ( INT ) =SUMM2 ( INT ) +C ( J ) **2 *PLV INT
SUMMV ( INT ) =SUMMV ( INT ) +PLV INT * ( C ( J ) **1 .62 )
151 CONTINUE
152 IF ( INT . GE . IEND ) GO TO 31
DTIMEI =DTIME * ( DNEW -D INT ) / ( DNEW -D IA )
TIMEI =TIME
DAVG = ( DNEW +D INT ) /2 .0
CHAING =C4 *DTIMEI
INT =INT +1
DINT =INT *100 .0
GO TO 166
11 IEND =DNEW /100 .0 +1
IF ( INT . EQ . IEND ) GO TO 157
DINT =INT *100 .0
DELD3 = ( DINT **3 -D IA **3 )
DTIMEI =DELD3 /C6 /N
CHAING =C5 /N *DELD3
TIMEI =TIME +DTIMEI -DTIME
DAVG = ( DINT +D IA ) /2 .0
GO TO 142
157 TIMEI =TIME
DAVG = ( DNEW +D IA ) /2 .0
CHAING =C5 /N * ( DNEW **3 -D IA **3 )
142 E1 =E2
E2 =EXP ( -TIMEI /TAU )
PLVINT =E1 -E2
SUMM1 ( INT ) =SUMM1 ( INT ) +TWT *PLV INT

```

```

SUMM2 (INT) =SUMM2 (INT) +TWT 2 *PLV INT
SUMMV (INT) =SUMMV (INT) + FLV INT *TWTV
SUMPRE (INT) =SUMPRE (INT) +FLV INT
SUMCHN (INT) =SUMCHN (INT) +PLV INT * (NCHAIN +N)
IF (N .EQ. 0) GO TO 31
DO 140 J =1 ,N
C ( J) =C ( J) +CHAIN G
SUMM1 (INT) =SUMM1 (INT) +C ( J) *PLV INT
SUMM2 (INT) =SUMM2 (INT) +C ( J) **2 *PLV INT
SUMMV (INT) =SUMMV (INT) + FLV INT * (C ( J) **1.62)
140 CONTINUE
149 IF (INT .EQ. IEND) GO TO 31
INT =INT +1
IF (INT .EQ. IEND) GO TO 141
DLAST =DINT
DINT = INT *1.00 .C
DAVG =DINT -.50 .C
DELD3 = (DINT **3 -DLAST **3)
DTIMEI =DELD3 /C6 /N
TIMEI =TIME I +DTIMEI
CHAIN G =C5 /N *DELD3
GO TO 142
141 DELD3 = (DNEW **3 -DINT **3)
DTIMEI =DELD3 /C6 /N
TIMEI =TIME I +DTIMEI
CHAIN G =C5 /N *DELD3
DAVG = (DNEW +DINT) /2 .0
GO TO 142
C
C DETERMINE WHICH EVENT OCCURS
C
31 RATEC =ALPHA *DNEW **2
RATE T =BETA *N *( N -1) /DNEW **3
RATE F =ETA *N
PCAP =RATE C / (RATE C +RATE T +RATE F)
PTERM =RATE T / (RATE C +RATE T +RATE F)

```

```

        IX=IX*65539
        IF (IX.LT.0) IX=IX+2147483647+1
        RN=IX*0.4656613E-9
        IF (RN-PCAP)4,4,112
112   IF (RN-PCAP-P TERM)40,40,155
C
C   RADICAL CAPTURE CALCULATIONS
C
4     N=N+1
        C(N)=0.0
C   THE FOLLOWING TWO STATEMENTS ARE OPTIONAL
        WRITE(6,3) I,DTIME,TIME,DNEW,N
3     FORMAT(' ',I6,3F14.2,I8,2IX,'   CAPTURE')
        IF (TIME.LT.TFINAL) GO TO 16
        GO TO 201
C
C   TERMINATION CALCULATIONS
C
40    IF (N.EQ.2) GO TO 5
        IX=IX*65539
        IF (IX.LT.0) IX=IX+2147483647+1
        RN=IX*0.4656613E-9
        DO 6 J=1,N
            IF (J/N.GT.RN) GO TO 7
6     CONTINUE
7     CT1=C(J)
        C(J)=C(N)
        N=N-1
        IX=IX*65539
        IF (IX.LT.0) IX=IX+2147483647+1
        RN=IX*0.4656613E-9
        DO 8 J=1,N
            IF (J/N.GT.RN) GO TO 9
8     CONTINUE
9     CT2=C(J)
        C(J)=C(N)

```

```

        N=N-1
        WTC=CT1+CT2
        GO TO 22
5       WTC=C(1)+C(2)
        N=0
22      NCHAIN=NCHAIN+1
        TWT=TWT+WTC
        TWT2=TWT2+WTC**2
        TWTV=TWTV+WTC**1.62
C      THE FOLLOWING TWO STATEMENTS ARE OPTIONAL
        WRITE(6,10)I,DTIME,TIME,DNEW,N,WTC
10      FORMAT(' ',I6,3F14.2,I8,E21.4,' TERMINATION')
        IF(TIME.LT.TFINAL) GO TO 16
        GO TO 201

C
C      CHAIN TRANSFER CALCULATIONS
C
153     IX=IX*65539
        IF(IX.LT.0)IX=IX+2147483547+1
        RN=IX*0.4656613E-9
        DO 154 J=1,N
        IF(J/N.GT.RN) GO TO 155
154     CONTINUE
155     TWT=TWT+C(J)
        TWT2=TWT2+C(J)**2
        TWTV=TWTV+C(J)**1.62
        NCHAIN=NCHAIN+1
C      THE FOLLOWING TWO STATEMENTS ARE OPTIONAL
        WRITE(6,156)I,DTIME,TIME,DNEW,N,C(J)
156     FORMAT(' ',I6,3F14.2,I8,E21.4,' CHAIN TRANSFER')
        C(J)=0.0
        IF(TIME.LT.TFINAL) GO TO 16
        GO TO 201

C
C      OUTPUT ACCUMULATED DATA
C

```

```

500 DO 501 INT=17, ILAST
    SUMM1(INT)=SUMM1(INT)*13.5
    SUMM2(INT)=SUMM2(INT)*13.5
    SUMMV(INT)=SUMMV(INT)*13.5
    SUMCHN(INT)=SUMCHN(INT)*13.5
    SUMPRES(INT)=SUMPRES(INT)*13.5
501 CONTINUE
    DO 502 INT=11, 16
    SUMM1(INT)=SUMM1(INT)*3.85714
    SUMM2(INT)=SUMM2(INT)*3.85714
    SUMMV(INT)=SUMMV(INT)*3.85714
    SUMCHN(INT)=SUMCHN(INT)*3.85714
    SUMPRES(INT)=SUMPRES(INT)*3.85714
502 CONTINUE
    WRITE(6,101)
101  FORMAT(/T4,'INT',T13,' DIAMETER',T27,'MN',T42
1     'MV',T56,'MW')
    WRITE(7,170) ILAST
    SUM1=0.0
    SUM2=0.0
    SUMV=0.0
    SUMC=0.0
    SUMD=0.0
    SUMD2=0.0
    SUMD3=0.0
    SUMPLV=0.0
    DO 54 INT=1, ILAST
    WRITE(7,171) SUMM1(INT), SUMM2(INT), SUMMV(INT), SUMPRES(INT),
1 SUMCHN(INT)
171  FORMAT(5E14.6)
    D(INT)=INT*100.0-50.0
    MNINT(INT)=SUMM1(INT)/SUMCHN(INT)
    MWINT(INT)=SUMM2(INT)/SUMM1(INT)
    MVINT(INT)=(SUMMV(INT)/SUMM1(INT))*1.6129
134  WRITE(6,53) INT, D(INT), MNINT(INT), MVINT(INT), MWINT(INT)
53   FORMAT(' ',I5,F15.2,3E14.6)

```



```

SUM1=SUM1+SUMM1(INT)
SUM2=SUM2+SUMM2(INT)
SUMV=SUMV+SUMMV(INT)
SUMC=SUMC+SUMCHN(INT)
SUMD=SUMD+D(INT)*SUMPRB(INT)
SUMD2=SUMD2+D(INT)*D(INT)*SUMPRB(INT)
SUMD3=SUMD3+(D(INT)**3)*SUMPRB(INT)
SUMPLV=SUMPLV+SUMPRB(INT)
54  CONTINUE
MN=SUM1/SUMC
MV=(SUMV/SUM1)**1.6129
MW=SUM2/SUM1
DBAR=SUMD/SUMPLV
D2BAR=SUMD2/SUMD
D3BAR=SUMD3/SUMD2
WRITE(6,107) DBAR,D2BAR,D3BAR,MN,MV,MW,SUMPLV
107  FORMAT(//' NUMBER AVERAGE DIAMETER = ',F20.2/
1' AREA AVERAGE DIAMETER =',F20.2/
2' VOLUME AVERAGE DIAMETER =',F20.2//
3' NUMBER AVERAGE MOLECULAR WEIGHT =',E14.6/
4' VISCOSITY AVERAGE MOLECULAR WEIGHT =',E14.6/
5' WEIGHT AVERAGE MOLECULAR WEIGHT =',E14.6//
6' SUMPLV =',F14.6)
PARTN=S/(S/RR/TAU+4.0*3.1416*SUMD2/SUMPLV/4.0E16)*180.0/286.0/
11.0E3
POLY=SUM1/SUMPLV/AVGN
CONV=POLY*PARTN*286.0
POLY=PCLY*PARTN*60.0*V/TAU
WRITE(6,109) PARTN,POLY,CONV
109  FORMAT(' NUMBER OF PARTICLES = ',E14.6,' PEP ML OF LATEX'/
1' GRAMS OF POLYMER PRODUCED PER MINUTE = ',E14.6/
2' PERCENT CONVERSION =',E14.6)
WRITE(6,108) IX
108  FORMAT(/' IX =',I20)
CALL GRAPH(ILAST,D,MNINT,3,107,7.0,5.0,0.0,0.0,0.0,0.0,0.0,0.0,0.0,0.0)
1'PARTICLE DIAMETER, A', 'MOLECULAR WEIGHT:', ' '; ' ', 'NUMBER AVERAGE; ')

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```

CALL GRAPH(ILAST,D,MVINT,12,107.000,0.000,0.000,0.000,0.000,
1';',',',',',',',', 'WEIGHT AVERAGE;')
CALL GRAPH(ILAST,D,MVINT,10,107.000,0.000,0.000,0.000,0.000,
1';',',',',',',',', 'VISCOSITY AVERAGE;')
CALL GRAPH(ILAST,D,SUMPRB,3,7,700,500,0.000,0.000,0.000,
1'PARTICLE DIAMETER, A', 'DENSITY;', 'PARTICLE SIZE;', 'DISTRIBUTION;')
2)
SMV=SUMMV(ILAST)
SM1=SUMM1(ILAST)
CUMWT(ILAST)=SUMM1(ILAST)/SUM1
MVINT(ILAST)=(SUMMV(ILAST)/SUMM1(ILAST))*1.6129
WRITE(6,30)
30 FORMAT(/'      INT',T11,'SUMM1',T25,'SUMM2',T39,'SUMMV',T53,
1'SUMPRB',T67,'SUMCHN')
INT=1
WRITE(6,32)INT,SUMM1(INT),SUMM2(INT),SUMMV(INT),SUMPRB(INT),
1SUMCHN(INT)
32 FORMAT(' ',I4,5E14.6)
DO 200 INT=2,ILAST
L=ILAST-INT+1
WRITE(6,32)INT,SUMM1(INT),SUMM2(INT),SUMMV(INT),SUMPRB(INT),
1SUMCHN(INT)
CUMWT(L)=CUMWT(L+1)+SUMM1(L)/SUM1
SM1=SM1+SUMM1(L)
SMV=SMV+SUMMV(L)
MVINT(L)=(SMV/SM1)*1.6129
200 CONTINUE
CALL GRAPH(ILAST,CUMWT,MVINT,3,7,700,500,0.000,0.000,0.000,
1'WEIGHT FRACTION;', 'MOLECULAR WEIGHT;',',',',',',')
GO TO 2
105 STOP
END

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