

DESORPTION OF FREE RADICALS FROM POLYMER
PARTICLES IN EMULSION POLYMERIZATION

A THESIS

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GLOSSARY OF SYMBOLS

A_p :	Surface area of the swollen polymer particle ($\text{cm}^2/\text{particle}$)
A_s :	Area occupied by one emulsifier molecule ($\text{cm}^2/\text{molecule}$)
a :	Surface area through which the desorption takes place (cm^2)
C :	Mean free radical concentration in the middle of the monomer layer
C_a :	Concentration of free radicals at the inside surface of the swollen monomer layer
C'_a :	Concentration of free radicals at the outside surface of the swollen monomer layer
C_m :	Transfer constant for monomer (-)
C_s :	Transfer constant for chain transfer agents (-)
c :	Constant
c_d :	Distribution coefficient for monomer free radical between the polymer particles and the water phase (-)
D_p :	Diffusion coefficient for monomer free radical in the polymer particle (cm^2/sec)
D_w :	Diffusion coefficient for monomer free radical in the water phase (cm^2/sec)
d_0 :	Initial seed particle diameter (\AA) or (cm)
d_{an} :	Number average diameter of large polymer particles (\AA) or (cm)
d_{a0n} :	Number average diameter of large polymer particles at initial stage (\AA) or (cm)
d_{aw} :	Weight average diameter of large polymer particles (\AA) or (cm)

d_{bn} :	Number average diameter of small polymer particle (Å) or (cm)
d_{b0n} :	Number average diameter of small polymer particle (Å) or (cm)
d_{bw} :	Weight average diameter of small polymer particle (Å) or (cm)
d_p :	Diameter of polymer particle (Å) or (cm)
d_{ps} :	Diameter of swollen polymer particle (Å) or (cm)
d_m :	Diameter of micelle (cm/molecule)
f	Efficiency of initiator in initiating free radicals (-)
h :	Parameter in Eq. (14) and (16), defined $h = (8\alpha)^{1/2}$
$[I]$:	Concentration of initiator (molecule/cc-water)
k :	Constant
k_0 :	Specific rate constant for desorption process (cm/sec)
k_{0I} :	Rate constant of desorption process for initiator radical (l/sec)
k_1 :	Rate constant of free radical entry into micelles (cc-water/molecule · sec)
k_2 :	Rate constant of free radical entry into polymer particle (cc-water/molecule · sec)
k_a :	Rate constant for free radical absorption (l/sec)
k_d :	Desorption rate constant (l/sec)
k_{di} :	Decomposition rate constant (l/sec)
k_{mct} :	Chain transfer rate constant to the monomer (l/gmole · sec)
k_{mtp} :	Mutual termination rate constant in the polymer particle (l/gmole · sec)
k_{cct} :	Chain transfer rate constant to chain transfer agent (l/gmole · sec)

k_p :	Propagation rate constant in the polymer particle ($\ell/\text{gmole}\cdot\text{sec}$)
k_p' :	Propagation rate constant for monomer radicals ($\ell/\text{gmole}\cdot\text{sec}$)
k_{pw} :	Propagation rate constant in the water phase ($\ell/\text{gmole}\cdot\text{sec}$)
k_{tw} :	Termination rate constant in the water phase ($\ell/\text{gmole}\cdot\text{sec}$)
K_1 :	Constant dependent on the specific monomer involved and the polymerization conditions
$[M]_p$:	Monomer concentration in the polymer particle (gmole/ℓ)
M_s :	Micelle concentration in the water phase (molecule/ cc-water)
$[M]_w$:	Monomer concentration dissolved in the water phase (gmole/ℓ)
m :	Dimensionless parameter, defined by $m = \frac{k_d \cdot v}{k_{mtp}}$
N :	Number of polymer particles in the water phase (particle/cc-water)
N_A :	Avogadro's number (molecule/gmole)
N_n :	Number of polymer particles containing n free radicals (particle/cc-water)
N_T :	Total number of particles in the water phase (particle/cc-water)
n :	Number of free radicals
$[P]$:	Monomer amount converted to polymer (gmole/cc-water)
p :	Probability that the free radical does not escape from the polymer particles
q :	$1 - p$
$[R\cdot]$:	Free radical concentration in the polymer particles (molecule/cc-water)
$[R\cdot]_w$:	Free radical concentration in the water phase (molecule/cc-water)

- R_p : Polymerization rate (gmole/cc-water·sec)
 r : Radius of the polymer particle (cm)
 S : Concentration of emulsifier in the water phase (molecule/cc-water)
 U : Polydispersity of latex diameter (-)
 v : Volume of the polymer particle (ℓ)
 v_{ps} : Volume of swollen polymer particle (ℓ)
 x : Upper limit of chain length of the desorbed free radical (-)
 Y : Dimensionless parameter, defined by $Y = \frac{2 \cdot k_{tw} \cdot k_{mtp}}{k_a^2 \cdot N_T \cdot v}$
 α : Dimensionless parameter, defined by $\alpha = \frac{\rho_a \cdot v}{N_T \cdot k_{mtp}}$
 α' : Dimensionless parameter, defined by $\alpha' = \frac{\rho_i \cdot v}{N_T \cdot k_{mtp}}$
 γ : d_{bn}/d_{b0}
 δ : $= \left(1 + \frac{D_w}{D_p \cdot C_d}\right)^{-1}$
 ρ_a : Overall rate of entrance of radicals into all N polymer particles (molecule/cc-water·sec)
 ρ_i : Rate of generation of free radicals in the water phase (molecule/cc-water·sec)
 ϕ_I : Fraction for initiator radical to escape from a polymer particle
 ϕ_m : Fraction for a radical of monomer or transfer agent to escape from a polymer particle

SUMMARY

Competitive growth and polymerization rate experiments were carried out to study the free radical transport phenomena which influence the kinetics of emulsion polymerization. In the competitive growth experiments, the relative particle growths were measured under equilibrium monomer-swelling conditions. The growth rate was found to vary with square of the unswollen particle diameter at different temperatures. The same results were obtained when chain transfer agents were added. The results strongly support the theory that the polymerization locus in seeded emulsion polymerization is the surface of the polymer particle, and suggest that even with styrene emulsion polymerization the kinetics can follow Smith-Ewart Case I theory in which the desorption of free radicals occurs.

In the polymerization rate experiments, the factors which influence the size of the desorption rate constant, k_d , were examined. The value of k_d tended to decrease with increases in the polymerization temperature for styrene and MMA. The values of k_d were not zero even in the styrene system. The k_d values for styrene were higher than those of MMA. The addition of chain transfer agents

increased the values of k_d , and decreased the polymerization rate. k_d was shown to be a function of d_{ps}^2 (swollen polymer particle diameter) for the case where free radicals were assumed to be desorbed from the swollen monomer layer, not from the center of the polymer particle. k_d was also found experimentally to be proportional to d_{ps}^2 .

Values of k_d calculated by Ugelstad's model in the MMA system were higher than those calculated by the model used in this work. The deviation seems to be based on whether water-phase deactivation of free radicals due to the polymerization is considered or not.

CHAPTER I

INTRODUCTION

General

Emulsion polymerization is widely utilized to manufacture many products which are very important in our modern life, such as paints, adhesives, synthetic rubber, inks, etc. One of the principal advantages of the emulsion polymerization reaction is that it affords a means of increasing the polymer molecular weight without decreasing the polymerization rate. That is, emulsion polymerization has the advantage of being able to simultaneously attain both high molecular weights and high reaction rates.

The products of emulsion polymerization can, in some instances, be employed directly without further separations. Therefore, due to the importance of latex products, many researchers have worked to determine the complex chemical and physical mechanisms involved in the emulsion polymerization reaction. In 1929, information was disclosed in a patent which would now be regarded as true emulsion polymerization [1]. Since then, many efforts have been made to study emulsion polymerization, especially, during the decade 1940 ~ 1950. Since this period, our ideas concerning emulsion polymerization have evolved to a

reasonable understanding of the mechanisms and kinetics. Although much fundamental works remain to be done, commercial practice has been successfully established.

Some of the unresolved problems in emulsion polymerization are listed below [2]:

- (1) The development of a generalized mechanism which would apply to all emulsion polymerization systems.
- (2) The quantitative prediction of rates of particle nucleation.
- (3) The determination of the principal locus of the propagation reaction.
- (4) The understanding of the internal structure of the polymer particle.
- (5) The quantitative prediction of desorption of the free radicals from the polymer particles.

A more comprehensive understanding of these key aspects of emulsion polymerization is essential, not only to explain several physical phenomena encountered in this and related fields, but to provide more satisfactory engineering for reactor design.

Ugelstad [3] and other workers [4,5,6,7] have demonstrated that the kinetic behavior of emulsion polymerization can be strongly influenced by the desorption of free radicals from the polymer particles. This desorption phenomenon plays a dominant role in the deviation of the

kinetic behavior of vinyl chloride and vinyl acetate emulsion polymerization from the Smith-Ewart Case II theory [8]. The desorption of free radicals can be important even with styrene if the number of particles is large and the rate of free radical formation small [9]. Thus, the systematic study of desorption phenomenon in emulsion polymerization is required in order to explain clearly the phenomena observed in various emulsion polymerization systems.

Theory and Literature Review

A qualitative picture of the emulsion polymerization process was first developed by Harkins [10]. Harkins proposed that emulsifier micelles were the locus of the emulsion polymerization in the early part of the reaction, and that later the polymer particles became the locus. The free radicals formed in the water phase can diffuse into emulsifier micelles. When a free radical enters a micelle, polymerization is initiated and additional monomer is supplied to the reaction site by diffusion through the water phase from the large droplets of monomer. Emulsifier in the water phase is adsorbed on the surface of these growing polymer particles. After the surface of the polymer particles adsorbs all free emulsifier in the water phase, particle formation stops.

Harkins suggested that the polymerization rate was

closely related to the concentration of polymer particles. A schematic diagram of a conventional emulsion polymerization reaction during the particle formation period (Interval 1) is shown in Figure 1.

The first quantitative treatment of emulsion polymerization kinetics was presented by Smith and Ewart [8]. Their model was based on the Harkins theory of the emulsion polymerization. The Smith and Ewart theory assumed that the particle nucleation occurs in the monomer swollen emulsifier micelles. The particle nucleation stops when all free emulsifier in the water phase is adsorbed on the surface of the polymer particles, and thereafter new particles are not formed. The Smith-Ewart Case II expression for the number of particles formed is as follows:

$$N = k \left(\frac{\rho_i}{\mu} \right)^{0.4} \left(A_s \cdot [s] \right)^{0.6} \quad (1)$$

where N : the number of polymer particles in the water phase $\left(\frac{\text{particle}}{\text{cc-water}} \right)$

ρ_i : the rate of generation of free radicals $\left(\frac{\text{molecule}}{\text{cc-water} \cdot \text{sec}} \right)$

μ : the volumetric growth rate of a polymer particle $\left(\frac{\text{cm}^3}{\text{sec}} \right)$

A_s : the area occupied by one emulsifier molecule $\left(\frac{\text{cm}^2}{\text{molecule}} \right)$

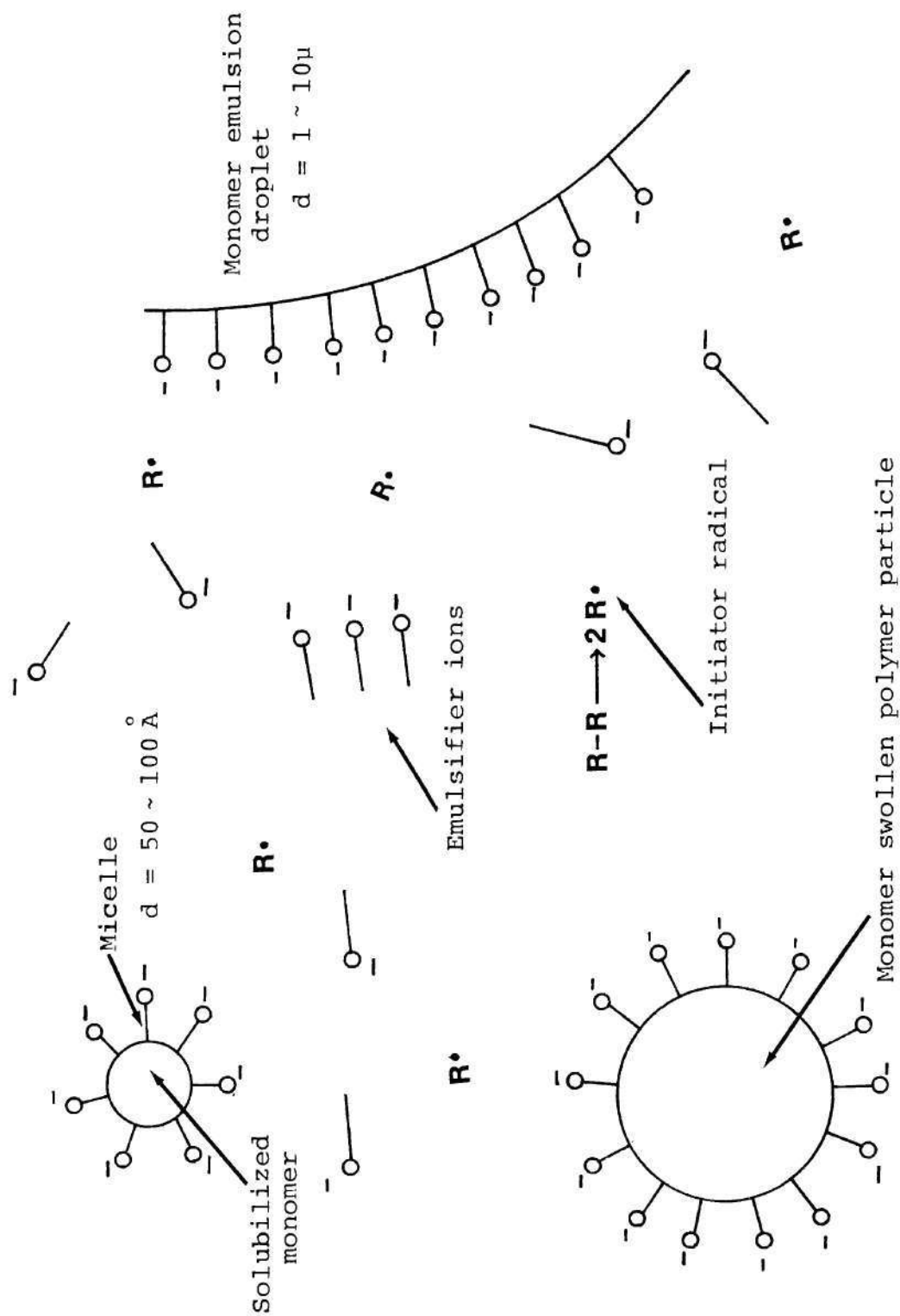


Figure 1. Schematic Diagram of a Conventional Emulsion Polymerization during Interval 1.

[s]: the concentration of emulsifier $\left(\frac{\text{molecule}}{\text{cc-water}}\right)$

k: a constant

The constant k lies between 0.37 and 0.53. The higher value is based on the assumption that only micelles capture radicals during Interval 1. The lower value is based on the assumption that both polymer particles and micelles capture radicals and that the number entering a particle or micelle per unit surface area per unit time is independent of the radius of the particle. The theoretical relationship given by Eq. (1) is in good agreement with data from the styrene system of the emulsion polymerization using persulfate ion initiator [8,12]. However, the theoretical relationship does not agree with experimental results for more water soluble monomers such as vinyl acetate [13,14, 15] and vinyl chloride [16,17].

In emulsion polymerization systems, the polymerization rate can be set equal to the rate of polymerization in the particle as follows:

$$R_p = \frac{d[P]}{dt} = k_p [M]_p \cdot [R\cdot] = k_p \cdot [M]_p \cdot \frac{\bar{n} \cdot N_T}{N_A} \quad (2)$$

where R_p : the polymerization rate $\left(\frac{\text{gmole}}{\text{sec} \cdot \text{cc-water}}\right)$

[P]: the amount of monomer converted to polymer
 $\left(\frac{\text{gmole}}{\text{cc-water}}\right)$

k_p : the propagation rate constant in the polymer

- particle $\left(\frac{\ell}{\text{gmole} \cdot \text{sec}}\right)$
- $[M]_p$: the monomer concentration in the polymer particle $\left(\frac{\text{gmole}}{\ell}\right)$
- $[R\cdot]$: the radical concentration in the polymer particles $\left(\frac{\text{gmole}}{\text{cc-water}}\right)$
- N_T : the total number of particles in the water phase $\left(\frac{\text{particle}}{\text{cc-water}}\right)$
- N_A : Avogadro's number $\left(\frac{\text{molecule}}{\text{gmole}}\right)$
- \bar{n} : average number of free radicals per polymer particle

The rate of particle growth can be obtained from Eq. (2) as:

$$\frac{dv}{dt} = 4\pi r^2 \cdot \frac{dr}{dt} = K_1 \cdot [M]_p \cdot \bar{n} \quad (3)$$

- where v : the volume of the polymer particle (ℓ)
- r : the radius of the polymer particle (cm)
- K_1 : a constant dependent on the specific monomer involved and the polymerization conditions.

According to the Smith-Ewart theory, the rate of entrance of free radicals into a single particle can be expressed as follows:

$$\left. \frac{dn}{dt} \right|_a = \frac{\rho_a}{N} \quad (4)$$

- where n : the number of free radicals
- ρ_a : the over-all rate of entrance into all N polymer

particles

N : the number of polymer particles

A free radical which enters a particle grows in the polymer particle until it is terminated or until desorption occurs. The rate of radical desorption from a polymer particle can be written as follows:

$$\left. \frac{dn}{dt} \right|_d = -k_0 \cdot a \cdot \left(\frac{n}{v} \right) \quad (5)$$

where k_0 : the specific rate constant for the this process

$\frac{n}{v}$: the concentration of free radicals in a polymer particle

a : the interfacial area through which the desorption takes place

If the termination of free radicals takes place only by the mutual termination, the rate of termination can be expressed as follows:

$$\left. \frac{dn}{dt} \right|_t = - 2k_{mtp} \cdot \left[n \cdot \frac{(n-1)}{v} \right] \quad (6)$$

where k_{mtp} : the mutual termination rate constant in the polymer particle

The factor 2 comes from the fact that two free radicals are destroyed in each termination. $\left(\frac{n-1}{v} \right)$ is the concentration of free radicals with which any one free

radical in the particle can react.

The change of the number of polymer particles containing n radicals can be expressed by considering the above three processes; free radical entry, desorption and termination, as follows:

$$\begin{aligned} \frac{dN_n}{dt} = & \left(\frac{\rho_a}{N_T} \right) N_{n-1} + k_0 \cdot \left(\frac{n+1}{v} \right) \cdot N_{n+1} + k_{mtp} \left[\frac{(n+2)(n+1)}{v} \right] N_{n+2} \\ & - \left(\frac{\rho_a}{N_T} \right) N_n - k_0 \cdot n \cdot N_n - k_{mtp} \left[\frac{n(n+1)}{v} \right] N_n \end{aligned} \quad (7)$$

where k_0 : is the desorption rate constant.

The desorption rate constant is defined as:

$$k_d = \frac{k_0 \cdot a}{v} \quad (8)$$

The above equation is valid for the non-steady state, however; Smith and Ewart did not obtain a general solution of Eq. (7). They set up the following recursion equation by assuming the steady-state condition; $\frac{dN_n}{dt} = 0$.

$$\begin{aligned} & \left(\frac{\rho_a}{N_T} \right) N_{n-1} + k_0 \left(\frac{n+1}{v} \right) \cdot N_{n+1} + k_{mtp} \left[\frac{(n+2)(n+1)}{v} \right] \cdot N_{n+2} \\ & = \left(\frac{\rho_a}{N_T} \right) \cdot N_n + k_0 \cdot n \cdot N_n + k_{mtp} \left[\frac{n(n+1)}{v} \right] \cdot N_n \end{aligned} \quad (9)$$

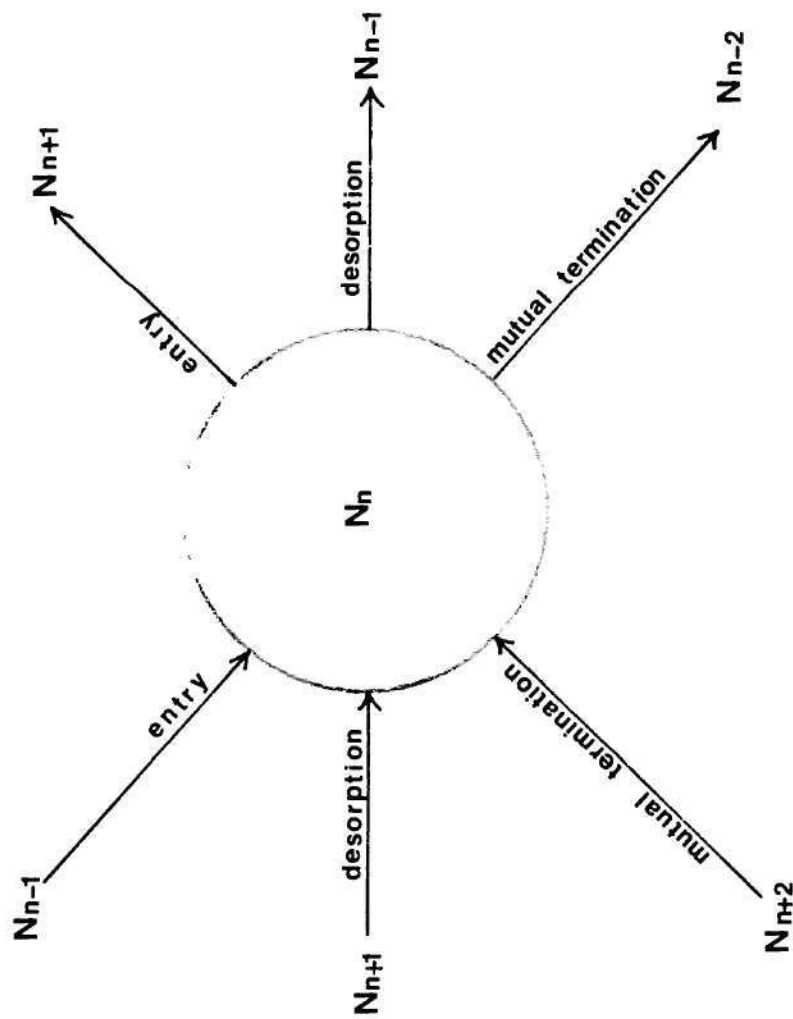
At steady state, the rate of entrance of free radicals into the polymer particles is equal to the rate at which free radicals are lost by desorption or termination. At any instant, all polymer particles in the system consist of particles which do not contain free radicals, N_0 , the particles which contain one free radical, N_1 , or, in general, the particles which contain n free radicals, N_n . When a free radical enters an N_{n-1} particle, it becomes a N_n particle. Desorption of a free radical from a polymer particle causes an N_{n+1} particle to become an N_n particle. When mutual termination occurs within a polymer particle, an N_{n+2} particle becomes an N_n particle. Since $\frac{dN_n}{dt}$ is zero at the steady state, the rate at which N_n particles are formed from N_{n-1} particles, N_{n+1} particles or N_{n+2} particles is equal to the rate at which they are lost. This is explained by the simple diagram in Figure 2.

Equation (9) was solved by Smith and Ewart for the following three limiting cases.

Case I. Average number of free radicals per polymer particle is small compared with 0.5. Under these conditions $N_0 \gg N_1 \gg N_n$, two different cases were considered.

1. Termination in the water phase dominating

$$\left(\frac{k_{mtp}}{v} \ll kd, \rho_i \approx 2 \cdot k_{tw} \cdot [R\cdot]_w^2 \right)$$



$$\left(\frac{\rho_a}{N_T}\right) N_{n-1} + k_d \left(\frac{n+1}{v}\right) N_{n+1} + k_{mtp} \left[\frac{(n+2)(n+1)}{v} \right] N_{n+2} \quad \left(\frac{\rho_a}{N_T}\right) N_n + k_d \cdot n \cdot N_n + k_{mtp} \left[\frac{n(n+1)}{v} \right] \cdot N_n$$

Figure 2. Formation and Loss of N_n Particles.

$$\bar{n} = \left(\frac{\rho_i}{2 \cdot k_{tw}} \right)^{1/2} \frac{a \cdot v}{N_T} \ll 0.5 \quad (10)$$

where ρ_i : the rate of radical production in
the water phase from the initiator
 $\left(\frac{\text{molecule}}{\text{cc-water} \cdot \text{sec}} \right)$
 k_{tw} : the termination rate constant in
the water phase $\left(\frac{l}{\text{gmole} \cdot \text{sec}} \right)$

2. Termination in the polymer particles dominating
 $\left(\frac{k_{mtp}}{v} \gg k_d \right)$

$$\bar{n} = \left(\frac{\rho_i}{2 \cdot N_T \cdot k_d} \right)^{1/2} \ll 0.5 \quad (11)$$

Case II. Average number of free radicals per polymer
particle is equal to 0.5. Under this condition
 $k_d \ll \frac{\rho_a}{N_T} \ll \frac{k_{mtp}}{v}$ and desorption is neglected,

$$\bar{n} = 0.5 \quad (12)$$

Case III. The number of free radicals per polymer particle
is large compared with 0.5. Under this condition
 $\frac{\rho_a}{N_T} \gg \frac{k_{mtp}}{v}$ and desorption is again neglected.

$$\bar{n} = \left(\frac{\rho_a \cdot v}{2 \cdot k_{mtp} \cdot N_T} \right)^{1/2} \gg 0.5 \quad (13)$$

Case II ($\bar{n} = 0.5$) gives the most satisfactory explanation for the emulsion polymerization of styrene. Case III ($\bar{n} > 0.5$) is closely related to the kinetics of bulk, solution and suspension polymerization. Case I agrees with the characteristics of the emulsion polymerization of monomers like vinyl chloride and vinyl acetate in which the desorption of free radicals from polymer particles is important. \bar{n} values considerably less than 0.5 have been found for these monomers [3,6,12,16].

A general solution of the Smith-Ewart equation (Eq. (9)) was first obtained by Stockmayer [18], applying a steady state assumption. If the desorption process of free radicals out of the polymer particle is not considered, the result for \bar{n} is,

$$\bar{n} = \frac{I_0(h)}{I_1(h)} \quad (14)$$

$$h = \sqrt{8\alpha}, \quad \alpha = \frac{\rho_a \cdot v}{N_T \cdot k_{mtp}} \quad (15)$$

where I_0 and I_1 : Bessel functions of the first kind.

O'Toole [19] extended the Stockmayer analysis and developed a physically more acceptable expression for \bar{n} as follows:

$$\bar{n} = \frac{h}{4} \cdot \frac{I_m(h)}{I_{m-1}(h)} \quad (16)$$

$$h^2 = 8\alpha, \quad \alpha = \frac{\rho_a \cdot v}{k_{mtp} \cdot N_T}, \quad m = \frac{k_d \cdot v}{k_{mtp}} \quad (17)$$

A number of workers have tried to obtain a general solution for Eq. (7). More complete and detailed reviews are given in several references [2,11,20,21].

In many models proposed, the importance of the desorption and the reabsorption of free radicals was not considered. Ugelstad and Nomura tackled the problem of desorption and reabsorption of free radicals, independently. They have derived theoretical expressions concerning the desorption rate of free radicals out of the polymer particles.

Ugelstad's Contribution

Ugelstad et al. [22] solved Eq. (7) with the following balance equation on the free radicals in the water phase.

$$\frac{d[R\cdot]_w}{dt} = \rho_i + \sum k_d \cdot n \cdot N_n - 2 \cdot k_{tw} [R\cdot]_w^2 - \rho_a \quad (18)$$

where ρ_a : is the rate of radical absorption

$[R\cdot]_w$: is the free radical concentration in the water phase.

At steady state, Eq. (18) becomes:

$$\rho_a = \rho_i + \sum k_d \cdot n \cdot N_n - 2 \cdot k_{tw} \cdot [R\cdot]_w^2 \quad (19)$$

$$\rho_a = k_a \cdot [R\cdot]_w \quad (20)$$

where k_a : the rate constant of free radical absorption.

By considering $[R\cdot]_w = \frac{\rho_a}{k_a}$ and $\sum n \cdot N_n = \bar{n} \cdot N_T$, from Eq. (19), one obtains the following dimensionless equation.

$$\alpha = \alpha' + m\bar{n} - Y \cdot \alpha^2 \quad (21)$$

where

$$\alpha = \frac{\rho_a \cdot v}{k_{mtp} \cdot N_T} \quad (22)$$

$$\alpha' = \frac{\rho_i \cdot v}{k_{mtp} \cdot N_T} \quad (23)$$

$$m = \frac{k_d \cdot v}{k_{mtp}} \quad (24)$$

$$Y = \frac{2 \cdot k_{tw} \cdot k_{mtp}}{k_a^2 \cdot N_T \cdot v} \quad (25)$$

\bar{n} has been evaluated as a function of α' , m and Y by means of Eq. (16) and Eq. (21). Typical results are shown in Figure 3, where $\log \bar{n}$ is given as a function of $\log \alpha'$ over a wide range of m values for the case of $Y=0$. Ugelstad suggested that termination in the water phase could be neglected under the normal conditions of emulsion

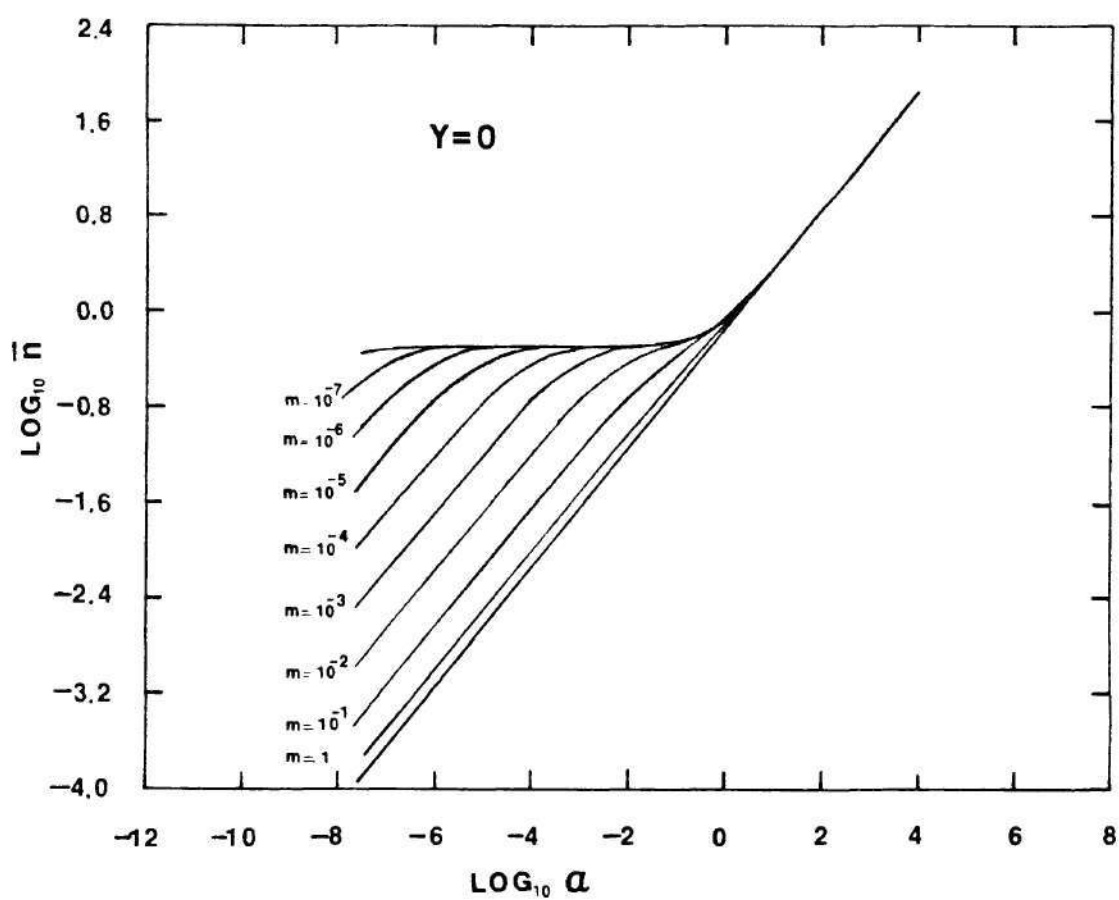


Figure 3. Average Number of Free Radicals per Polymer Particle \bar{n} as a Function of the Parameters α' and m for

$$Y = \frac{2 \cdot k_{mtp} \cdot k_{tw}}{k_a^2 \cdot N_T \cdot v} = 0.$$

polymerization [20].

Ugelstad et al. [3] derived theoretically the expression of the desorption rate constant by considering a simplified model for evaluating \bar{n} at low values of $\bar{n} < 0.1$.

$$k_d = \frac{k_{mct}}{k_p'} \frac{3 \cdot D_w \cdot D_p}{[(c_d \cdot D_p + D_w)r^2]} \quad (26)$$

where k_{mct} : the chain transfer rate constant to the monomer

k_p' : the propagation rate constant for the monomer radical

D_p : the diffusion coefficient for monomer free radicals in the polymer particle

D_w : the diffusion coefficient for monomer free radicals in the water phase

c_d : the distribution coefficient for the monomer free radicals between the polymer particles and the water

r : the radius of the polymer particle.

Nomura's Contributions

Ugelstad did not consider the size effect of the oligomer free radical on its ability to desorb from the polymer particle. Nomura et al. [23,5] showed two different ways to derive the relationship by assuming that:

- 1) a free radical with no longer than x -monomer units can

desorb from and enter the particles with the same rate irrespective of its chain length, 2) a particle contains not more than one free radical, 3) instantaneous termination takes place when another radical enters the particle which already contains a free radical, 4) no distinction occurs between the free radicals with or without an initiator fragment, and 5) water phase reactions such as the propagation, termination and chain transfer can be neglected.

1. Material balance approach [23]

The following relationship was derived from a material balance on the polymer particles and the free radicals in the water phase, assuming steady state.

$$k_d = k_{0I} \left(\frac{N_I^*}{N_T} \right) + k_0 \left[\left(\frac{k_{mct}}{k_p} \right) + \left(\frac{k_{di}}{k_p} \right) \left(\frac{N_I^*}{N_T} \right) \right] \sum_{i=1}^x \left(\frac{k_p [M]_p}{k_p [M]_p + k_0 \bar{n}} \right)^i \quad (27)$$

where N_I^* : the number of polymer particles containing an initiator free radical I^*
 k_{di} : the initiator decomposition rate constant
 k_{0I} : the rate constant of initiator free radical desorption from the polymer particle
 k_0 : the rate constant of free radical desorption
 x : the upper limit of chain length of the desorbed free radical.

Nomura et al. assumed that the desorption of the free radicals was based on the molecular diffusion, and defined k_0 as follows:

$$k_0 = \frac{4\pi r^2 \left(\frac{r}{D_p} + \frac{c_d r}{D_w} \right)^{-1}}{\frac{4}{3} \pi r^3} = \frac{3 \cdot D_w \cdot \delta}{c_d \cdot r^2} \quad (28)$$

where

$$\delta = \left(1 + \frac{D_w}{D_p \cdot c_d} \right)^{-1} \quad (29)$$

Using the assumptions of Eq. (28), $k_0 \approx k_{0I}$ and $k_{di} \approx k_p$, Eq. (27) was simplified further as follows:

$$k_d = \frac{3D_w \cdot \delta}{c_d \cdot r^2} \left(\frac{k_{mct}}{k_p} \right) \quad (30)$$

2. Probability approach [5]

First, the following four processes were considered in the generation and disappearance of free radicals.

- 1) Initiation and propagation reactions.
- 2) Chain transfer reactions with the monomer, the polymer and chain transfer agents.
- 3) Termination reactions among free radicals within the polymer particles.
- 4) Radical desorption from the particle into the water phase.

In Nomura's approach, (2) and (3) above were neglected. The probability that the free radical escapes from a polymer particle within the time interval for the radical to add a monomer unit is designated as q . The probability, p , that the free radical will not escape within the same time interval is expressed as,

$$p = 1 - q \quad (31)$$

The probability that the radical will escape from a particle within the time interval for the radical to add to a monomer unit is defined as q . It was also assumed that the free radicals with a chain smaller than x units of the monomer could be desorbed and p and q were constant independent of x .

Considering the two processes; propagation and desorption, the probability, p was obtained as follows:

$$p = 1 - q = \frac{k_p [M]_p}{k_0 \cdot \bar{n} + k_p [M]_p} \quad (32)$$

If one assumes that oligomer units with lengths up to x can escape, the chance of escaping is

$$\Phi_m = q(1 + p + p^2 + \dots + p^{x-1}) = 1 - p^x \quad (33)$$

where ϕ_m : the probability that a radical of monomer or transfer agent will escape from a particle.

The value of ϕ_I for initiator radical is similarly given as follows:

$$\phi_I = \frac{k_{0I} \cdot \bar{n}}{k_{0I} \cdot \bar{n} + k_u \cdot [M]_p} \quad (34)$$

where k_u : the reaction rate constant of monomer initiation

The desorption rate constant, k_d , is given as follows:

$$\begin{aligned} k_d = & \left(\frac{\phi_m}{\bar{n}} \right) \left[k_{mct} [M]_p + k_{cct} [CT] \right] + \left(\frac{\phi_I}{\bar{n}} \right) \left(\frac{\rho_i}{N} \right) \frac{(1 - \bar{n})}{\bar{n}} \\ & + \left(\frac{\phi_m}{\bar{n}} \right) (1 - \phi_I) \left(\frac{\rho_i}{N} \right) \frac{(1 - \bar{n})}{\bar{n}} \end{aligned} \quad (35)$$

Furthermore, if x is equal to 1, Eq. (35) is simplified as:

$$\begin{aligned} k_d = & \left[\bar{n} + \frac{k_p [M]_p \cdot c_d \cdot r^2}{3 \cdot \delta \cdot D_w} \right]^{-1} \left[\frac{k_{mct}}{k_p} + \frac{k_{cct} [CT]}{k_p [M]_p} \right. \\ & \left. + \frac{\rho_i (1 - \bar{n})}{N \cdot k_p [M]_p \cdot \bar{n}} \right] \left(k_p [M]_p \right) \end{aligned} \quad (36)$$

Also, when the rate of free radical desorption from the polymer particle and the reactivity of monomer are very high, i.e., in the case of vinyl acetate or vinyl chloride,

it is assumed $k_p [M]_p \gg k_0 \bar{n}$. Equation (36) was simplified further to the following:

$$k_d = k_0 \left(\frac{k_{mct}}{k_p} \right) = \frac{12 \cdot D_w \cdot \delta}{c_d \cdot d_p^2} \left(\frac{k_{mct}}{k_p} \right) \quad (37)$$

Approach to the Problem in this Research

The purpose of this research was to obtain a better understanding of the free radical transport phenomena which influence the kinetics of the emulsion polymerization. More precisely we have attempted to identify and investigate the relationship among the different factors affecting the rate of desorption of the free radicals from the polymer particles. In this research, the following experiments were carried out with styrene and methylmethacrylate.

A. Competitive Growth Experiments for Emulsion Latexes

In these experiments, monodispersed latexes of different sizes were mixed and polymerized under equilibrium monomer-swelling conditions. The relative particle growths were measured. The transport of free radicals into and out of the polymer particles may be a function of the particle size. The competitive growth experiments help to determine this functionality. The effect of chain transfer agents were also investigated in these competitive particle growth experiments.

B. Polymerization Rate Experiments

In homogeneous bulk and solution free radical polymerization, when the chain transfer agents such as carbon tetrachloride, xylene, etc. are added, they reduce the molecular weight without significantly altering the rate of polymerization. The presence of a chain transfer agent in a polymer particle during emulsion polymerization will generate a small, mobile free radical which can move out of the polymer particle. The desorption of free radicals which are capable of initiation or propagation will effect the rate of polymerization. Thus, the effect of the chain transfer agent on the rate of polymerization was determined with several transfer agents with different sizes of monodispersed latexes. A kinetic model has been established and the desorption rate constant k_d was calculated quantitatively from the experimental data. The factors which influence the size of the desorption rate constant, k_d , were examined.

CHAPTER II

EXPERIMENT AND MATERIALS

Experiment Apparatus

All competitive growth experiments and polymerization rate experiments were carried out in a 250 ml pyrex, five-neck flask. The polymerization apparatus, shown in Figure 4, was used. The polymerization flask was fitted with an adapter in the central neck for a teflon-blade stirrer connected to an electrical stirring motor. One side neck was fitted with a cooling condenser. A second side neck was fitted with an adapter at the top to permit the prepurified grade nitrogen to enter through the glass tube that extends below the surface of the reaction fluid. The prepurified grade nitrogen was supplied by Union Carbide. The nitrogen was passed through a water solution of pyrogallol and sodium hydroxide (50 g pyrogallol and 250 g sodium hydroxide are dissolved into 1 liter water), concentrated sulfuric acid solution and silica gel.

Temperature control of the polymerization was carried out by a Therm-O-Watch controller (Instruments for Research and Industry, Cheltenham, PA) which was attached to the thermometer of the polymerization flask. When the sensing head is attached and adjusted, a slight change in

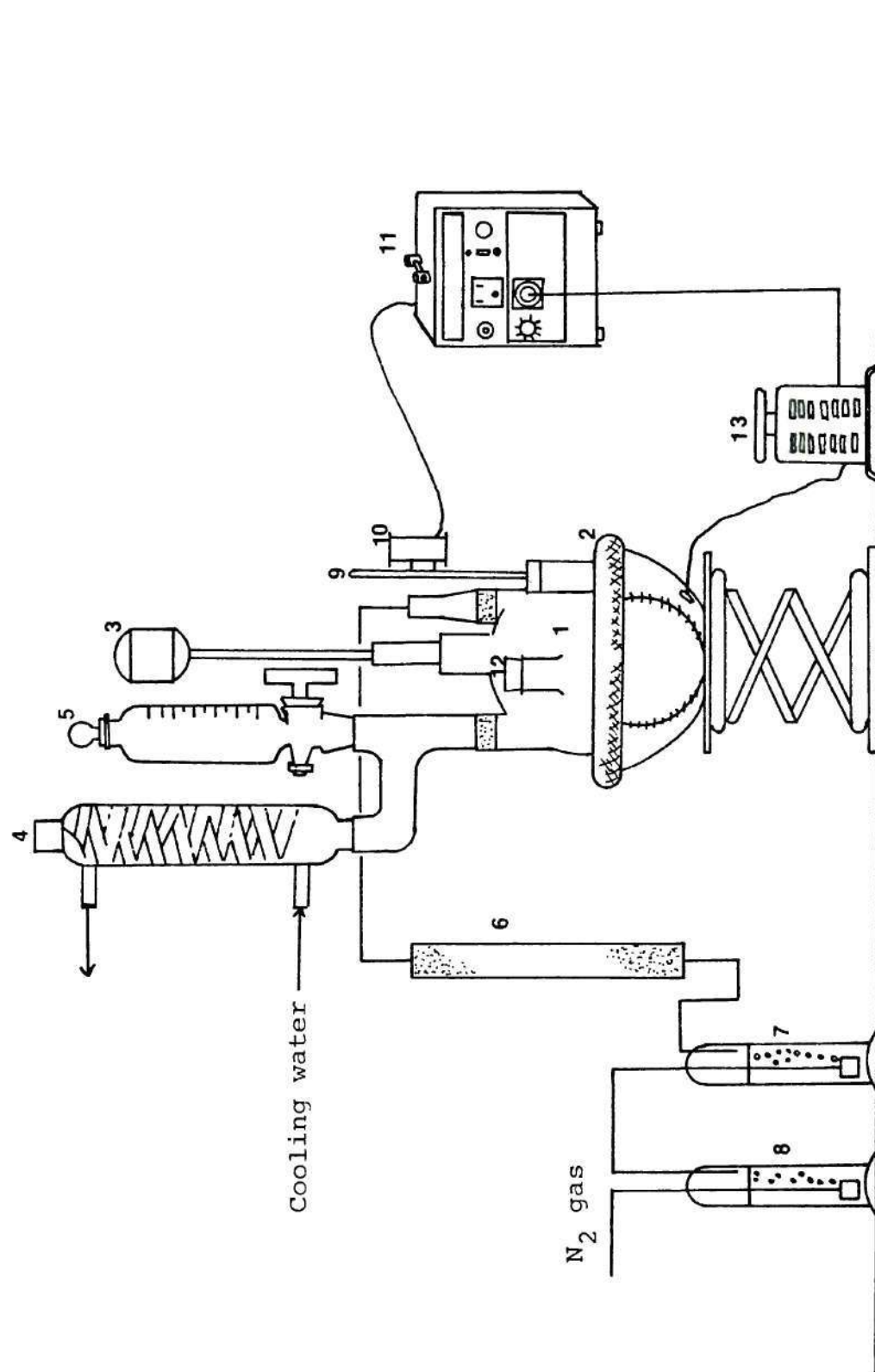


Figure 4. Emulsion Polymerization Apparatus.

Key to Figure 4

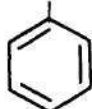
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1. Polymerization flask
 2. Mantle heater
 3. Stirring motor
 4. Condenser
 5. Funnel for monomer dropping
 6. Silica gel column
 7. N_2 gas washing by H_2SO_4
 8. N_2 gas washing by a water solution of pyrogallol and NaOH
 9. Thermometer
 10. Sensing head for Therm-O-Watch
 11. Amplifier for Therm-O-Watch
 12. Sampling Rubber Stopper
 13. Transformer
-

the position of mercury or other liquid alters the electrical capacitance and affects the electronic oscillator located in the sensing head. This in turn causes a relay in the amplifier to control the power supplied to the electric mantle heater under the polymerization flask.

Materials

All solvents used in this experiment were reagent grade and were not further purified. The deionized water was used as received from the deionization equipment without any further purification other than degassing by boiling and subsequent cooling while bubbling with the prepurified grade nitrogen. Styrene and methyl methacrylate were vacuum distilled to remove the stabilizer. The temperature of the distillation vapor never exceeded 40°C. Both monomers were stored in a refrigerator at 0°C to 5°C and were checked periodically for the presence of oligomers by the addition of approximately 5 ml of monomer to 100 ml of methanol.

Styrene: $\text{CH}=\text{CH}_2$



Stabilized laboratory grade styrene was supplied by Eastman Kodak Company.

Methyl methacrylate: $\text{CH}_2=\text{C}-\text{CH}_3$
|
 COOCH_3

Stabilized reagent grade methyl methacrylate was

by Fisher Scientific Company.

Potassium persulfate: $K_2S_2O_8$

Fisher certified grade potassium persulfate was used.

Sodium lauryl sulfate: $CH_3(CH_2)_{11}OSO_3Na$

Sodium lauryl sulfate from Aldrich Chemical Co. was used as an emulsifier.

Hydroquinone: $C_6H_4(OH)_2$

Purified hydroquinone from Fisher Scientific Company was used to quench the active radicals.

Pyrogallol: $C_6H_3-1,2,3-(OH)_3$

Certified A.C.S. grade pyrogallol was used.

Sodium hydroxide: $NaOH$

Laboratory grade sodium hydroxide was used.

CHAPTER III

EXPERIMENTAL PROCEDURE

Competitive Growth Experiments

1. Two monodisperse latexes are mixed to yield a latex with approximately equal numbers of each particle size in the 250 ml reaction flask shown in Figure 4 at the specified polymerization temperature.
2. Monomer, chain transfer agent (if it was a part of the recipe) is added to the reaction flask by using the funnel. The amount of the monomer charged was enough to satisfy the equilibrium monomer-swelling conditions during emulsion polymerization.
3. After all monomer has been added, the potassium persulfate (powder), weighed previously, is charged through the sample neck of the flask. The agitator and nitrogen purge are both functioning during this addition. The powder which sticks on the inside wall of the reaction flask is rinsed by the reaction mixture by using the sampling syringe. The temperature is kept at the constant polymerization temperature.
4. Samples are removed to determine particle sizes and the conversion at regular intervals during the polymerization. Conversion is determined by drying

the sample solution in the vacuum oven (max. 50°C). The drying is carried out overnight. A 0.1 wt% hydroquinone water solution is added to quench the living free radicals when the samples are removed. The amount of hydroquinone solution is 0.5 cc for 3.5 gram of the sample.

Polymerization Rate Experiments

1. Monodispersed latex is charged to the 250 ml reaction flask.
2. The procedures which follow are the same as those in competitive growth experiment.

Particle Size Measurements

Particle size was determined with a JEOL-100-C (JEOL Ltd.) transmission electron microscope. The sample from the reaction flask was diluted; 5~10 drops of the sample were dropped into 10 cc of deionized water. One drop of the highly diluted latex was placed on a stainless steel 200 mesh grid and dried at the room temperature under vacuum. The grid with the dried latex sample was Au-Pd shadowed by a Au-Pd Sputter Coater for MMA latexes, since polymethyl methacrylate particles of colloidal dimensions are rather unstable under an electron beam in high vacuum. The styrene latex was not shadowed. Particle size was measured directly from the electron micrograph negatives

using a ruler. Approximately 70~140 particles were counted for each latex.

Two types of the particle size averages were computed from the measurements. These included:

a) the number average diameter d_n

$$d_n = \frac{\sum n_i D_i}{\sum n_i} \quad (38)$$

where n_i is the number of particles whose diameter is D_i .

b) the weight average diameter d_w

$$d_w = \left(\frac{\sum n_i D_i^6}{\sum n_i D_i^3} \right)^{1/3} \quad (39)$$

The latex polydispersity is given by the uniformity ratio

$$U = \frac{d_w}{d_n}$$

If the uniformity ratio is less than 1.05, the latex is considered to be monodisperse.

CHAPTER IV

RESULTS AND DISCUSSION

Competitive Growth Experiments

All competitive growth experiments were carried out in a batch reactor in which the initial charge contained a mixture of two different size monodisperse latexes. Additional monomer and initiator were added to the mixture. Additional emulsifier was not used so that the new particles were not generated.

Reproducibility

Replica experiments (EX-13 and EX-17) were run to determine the reproducibility of the experimental data and to make sure that the experimental techniques were correct. Figure 5 (curves of the converted monomer amount and time) shows good reproducibility.

Experimental Results

Two monodisperse latexes, were mixed to give a seed latex with approximately equal numbers of each particle size. The number of particles and the average particle diameters were determined before mixing. These results are shown in Table 1. The transmission electron microscope (JEOL-100C) was used as outlined earlier.

Details concerning the preparation of these latexes

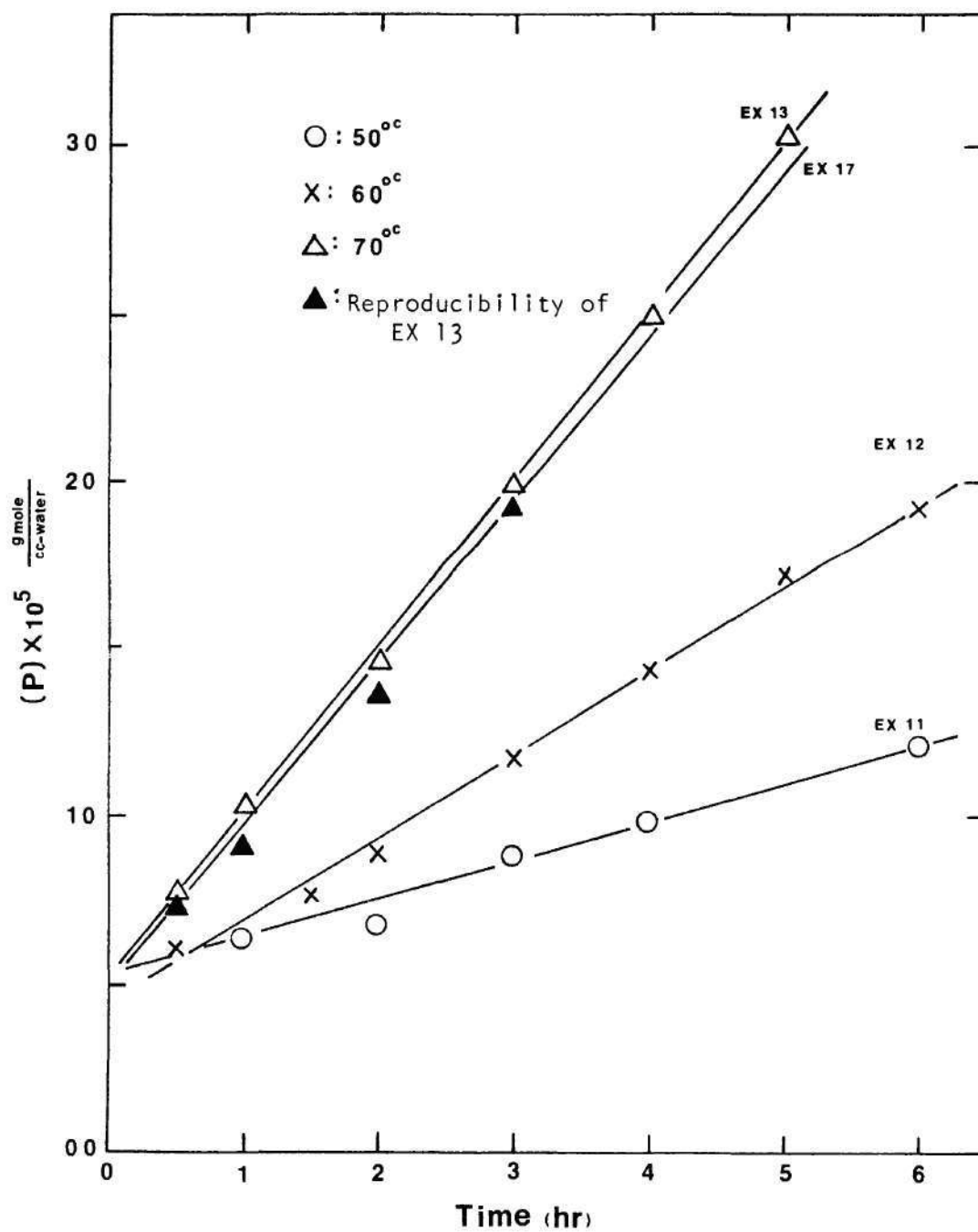


Figure 5. Relationship between Monomer Converted and Time in Competitive Growth Experiments for Styrene.

Table 1. Latex Particle Characterization

Latex	Styrene		Methylmethacrylate	
	Latex-8	Latex-9	Latex-47	Latex-53
Number Average Diameter d_n (Å)	800	1156	645	1153
Weight Average Diameter d_w (Å)	811	1161	659	1157
Number of Particles per cc-water	1.1945×10^{13}	9.677×10^{12}	6.5688×10^{13}	5.497×10^{12}
Polydispersity = U	1.013	1.005	1.022	1.003

is described in Appendix 2. These "seed" polymerizations were carried out at different temperatures (50°C, 60°C, 70°C for styrene and 55°C, 60°C, 70°C for methylmethacrylate). The effect of chain transfer agents on competitive particle growth was determined at 70°C for styrene and 60°C for methylmethacrylate. Carbon tetrachloride and xylene were used as the chain transfer agents. The recipe of seeded competitive growth is shown in Tables 2 and 3.

Figures 5 and 6 show the relationship between monomer converted and time for competitive growth experiments which do not contain chain transfer agents. The polymerization temperature influences the rate of polymerization for both monomers as would be expected. In the case of methylmethacrylate, an acceleration of polymerization rate was observed at 60°C and 70°C (see Figure 6). This could be a result of the well known gel effect. The gel effect causes a decrease in k_t (termination constant) which leads to an increase in the number of free radicals in the polymer particle. This will be discussed later in the section entitled "Polymerization Rate Experiment."

The effects of chain transfer agents are shown in Figures 7 and 8. Figure 7 indicates the effect of chain transfer agent on the rate of polymerization for styrene. Chain transfer agents such as carbon tetrachloride and xylene clearly cause a decrease in the rate of polymerization

Table 2. Recipe of "Seed" Competitive Polymerization for Styrene

	Without Chain Transfer Agent	With Chain Transfer Agent		
	EX-13 gram	EX-15 gram	EX-16 gram	EX-27 gram
Latex-8	50.000	50.000	50.000	50.000
Latex-9	61.404	61.404	61.404	61.404
Monomer	10.000	10.000	10.000	10.000
Initiator ($K_2S_2O_8$)	0.0068	0.0068	0.0068	0.0068
Carbon Tetrachloride	---	0.0425	0.2208	---
Xylene	---	---	---	0.6814
Total	121.4108	121.4533	121.6316	122.0922

Table 3. Recipe of "Seed" Competitive Polymerization for MMA

	Without Chain Transfer Agent	With Chain Transfer Agent	
	EX-58, EX-60 gram	EX-64, EX-65 gram	EX-66 gram
Latex-47	15.00	15.00	15.00
Latex-53	179.25	179.25	179.25
Monomer	20.00	20.00	20.00
Initiator ($K_2S_2O_8$)	0.01	0.01	0.01
Carbon Tetrachloride	---	1.60	---
Xylene	---	---	1.60
Total	214.260	215.860	215.860

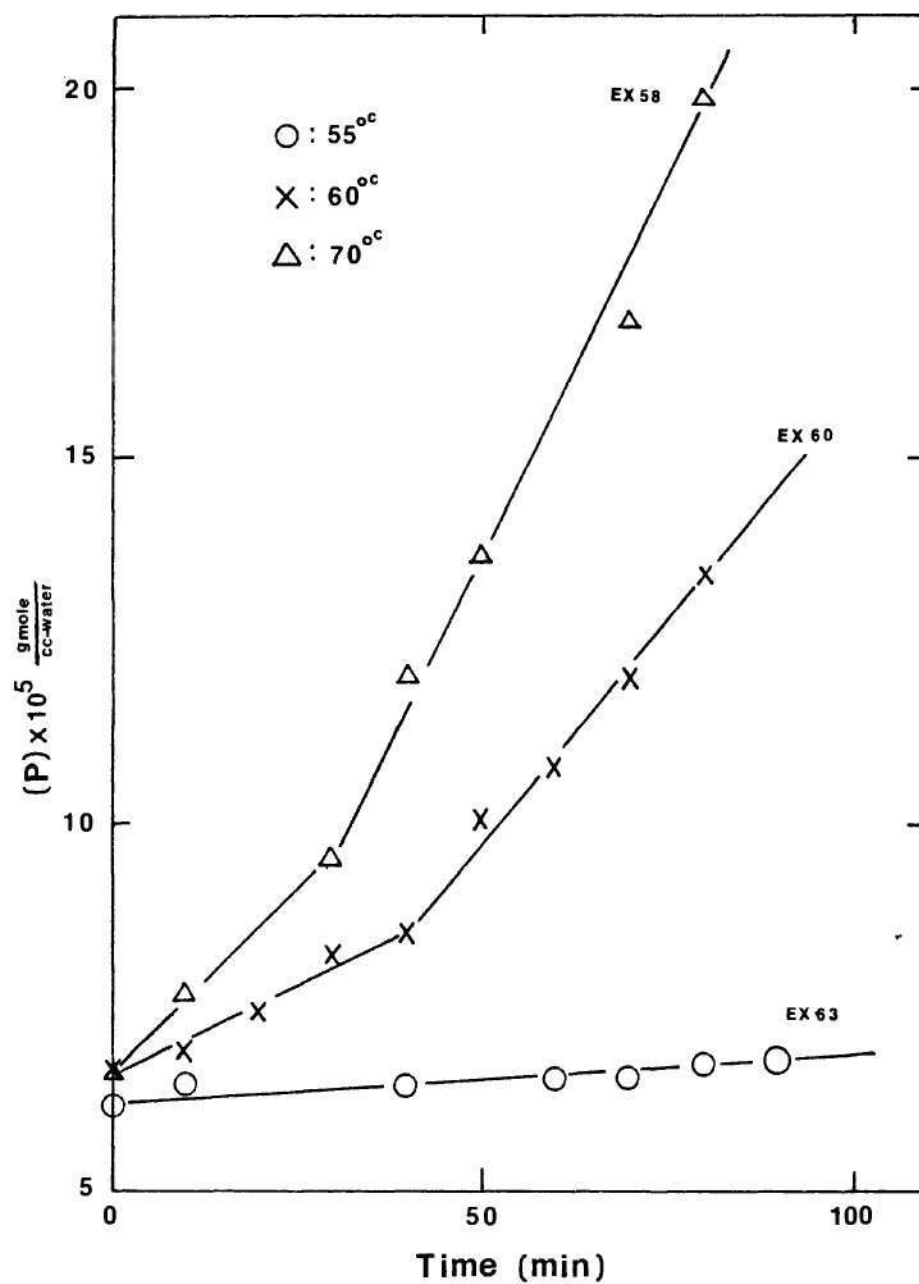


Figure 6. Relationship between Monomer Converted and Time in Competitive Growth Experiments for MMA.

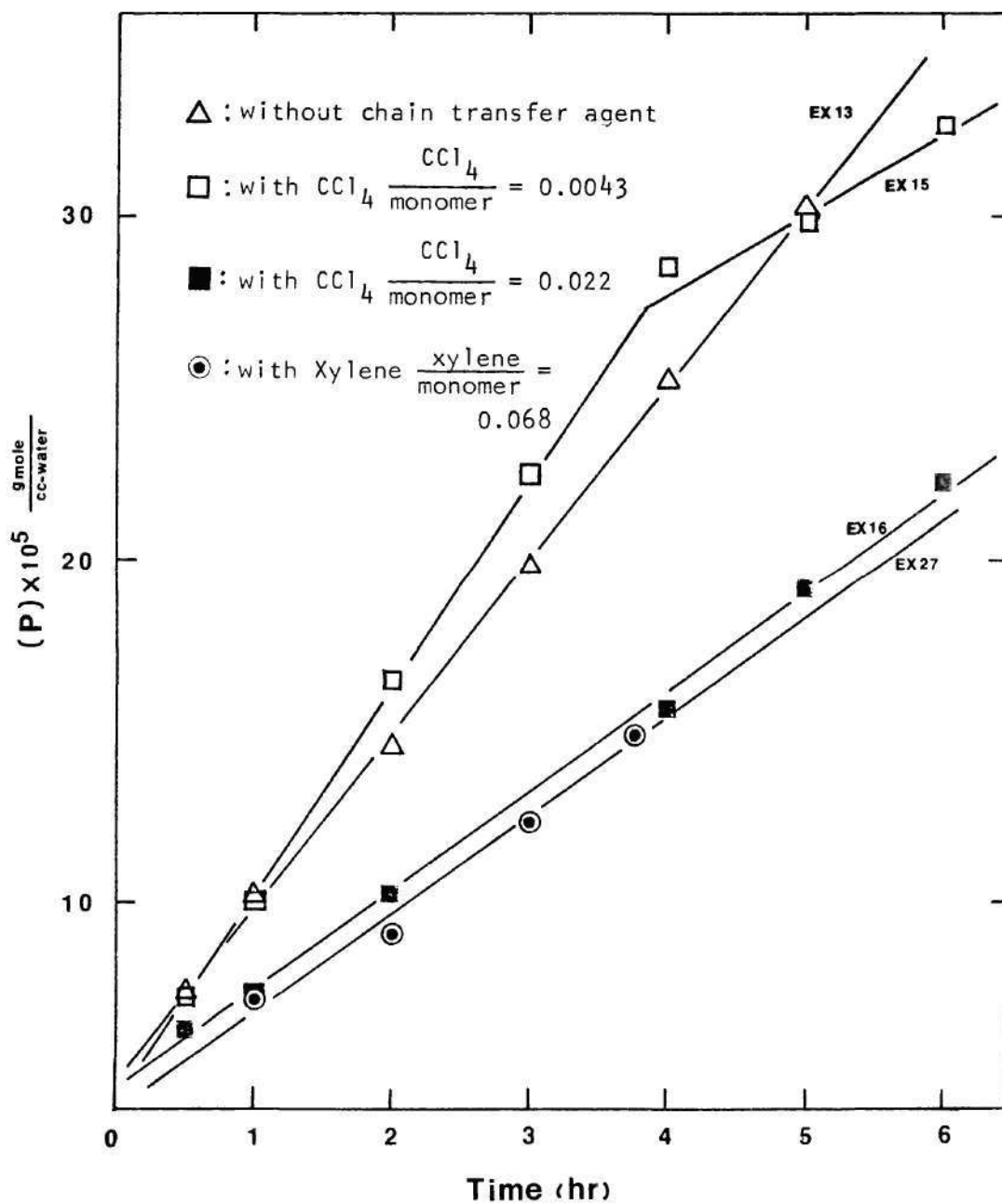


Figure 7. Effect of Chain Transfer Agent on Competitive Growth of Styrene Particles at 70°C.

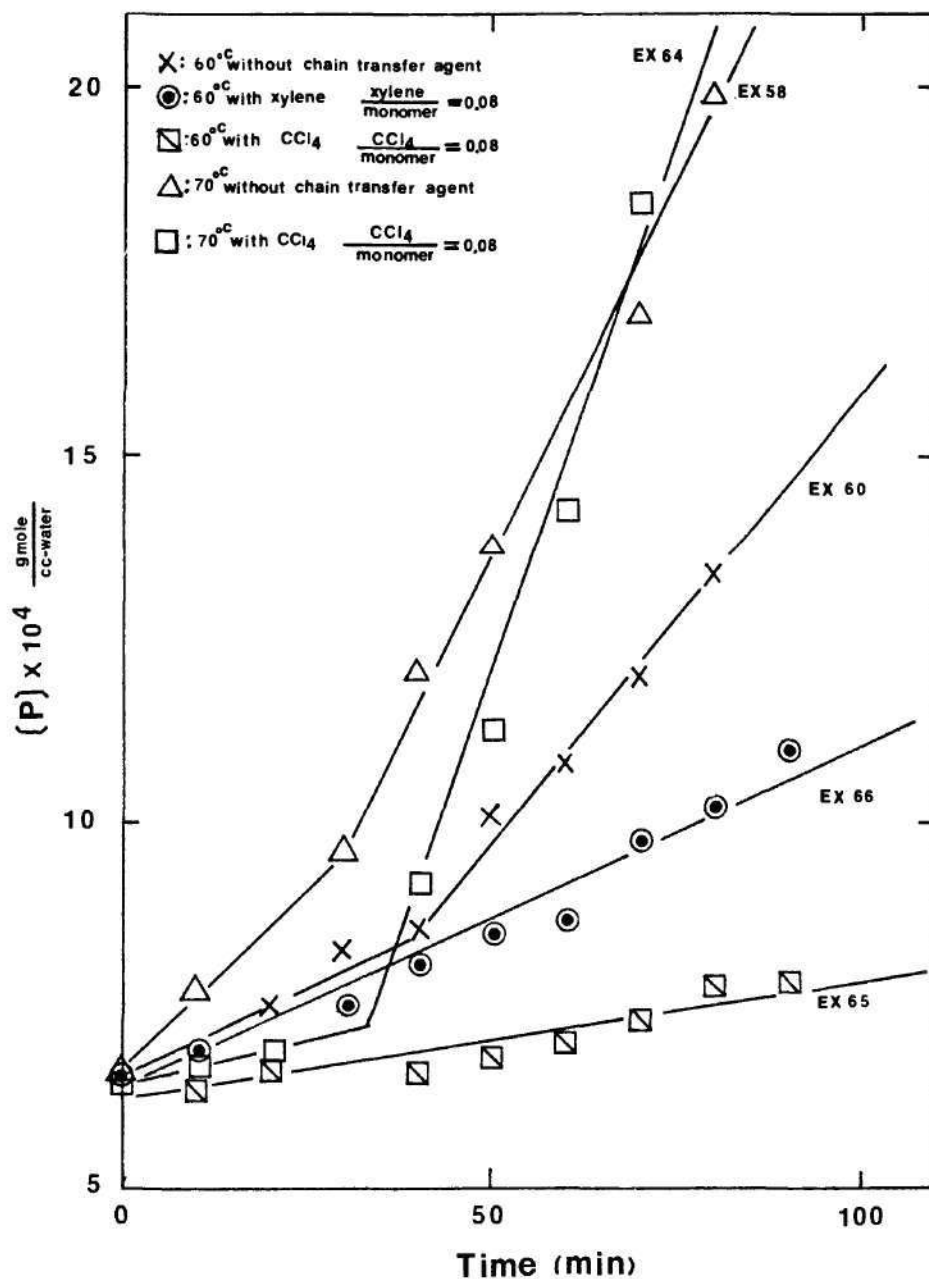


Figure 8. Effect of Chain Transfer Agent on Competitive Growth of MMA Particles.

when a reasonable amount of chain transfer agent is added. As indicated by EX-15, when a small amount of carbon tetrachloride was added, the rate of polymerization increased slightly compared with that in EX-13 (without chain transfer agent). After 4 hours, the rate of polymerization decreased. No explanation is offered for this observation. The average particle diameter and polydispersity during polymerization were determined by using the transmission electron microscopy. The electron micrographs of "seed" competitive polymerization products are shown in Figure 9.

Vanderhoff and co-workers [24,25,26] fitted the competitive growth data to an equation of the following form:

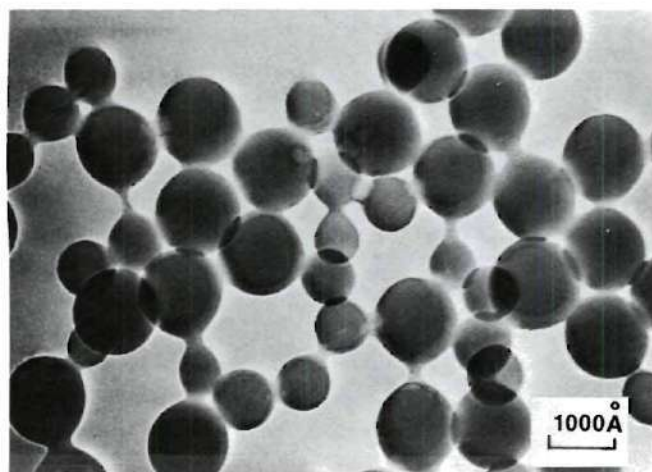
$$\frac{dv}{dt} = k \cdot d_p^c \quad (40)$$

where v is the particle volume, d_p is the diameter and k and c are constant. Vanderhoff et al. determined that $c = 0.0$ for small particles below 1500\AA and $c = 2.5$ for particle sizes significantly larger than 1500\AA . c was 3.0 when an oil soluble initiator (benzoyl peroxide) was used. The water soluble initiator (potassium persulfate) was used in the former experiments.

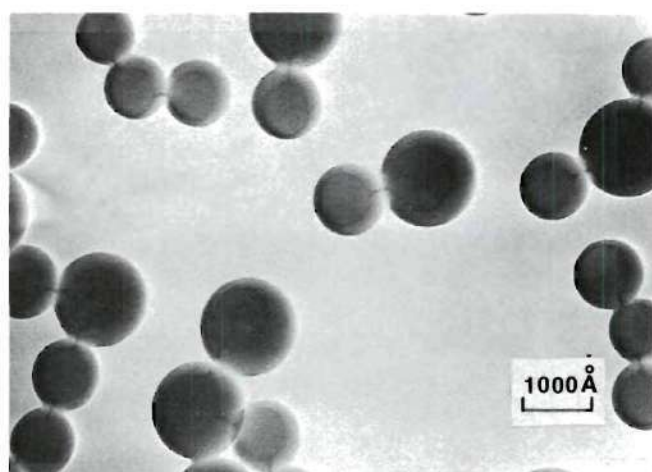
Our data were analyzed by first determining c with Vanderhoff's calculation method. The calculation is shown in Appendix 2. Diameter ratios are shown in

Figure- 9 Electron Micrograph from which Competitive Growth
Measurement were made . (Mag. 100,000 X)

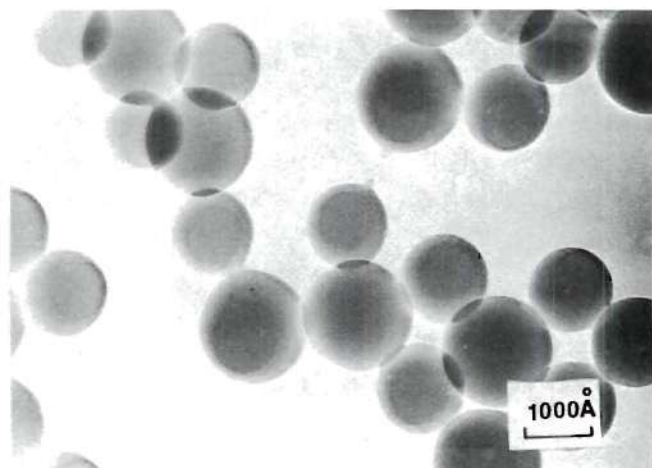
Styrene



0.5 hrs



2.0 hrs



5.0 hrs

Tables 4, 5, 6 and 7. The index c is very useful for studying the phenomenon of radical absorption and desorption. The following relation is widely accepted [27]:

$$\frac{dv}{dt} \approx K[M]_p \bar{n} = R_p \quad (41)$$

where \bar{n} is the average number of free radicals per polymer particle, $[M]_p$ the monomer concentration in the polymer particle, K a constant dependent on the monomer propagation rate and monomer swelling of the latex particles. Equation (41) shows that the volumetric growth rate of a particle is directly proportional to the average number of free radicals \bar{n} . If the kinetics of emulsion polymerization obeys Smith-Ewart theory Case II kinetics, the value of c will be 0.0 because \bar{n} is a constant, 0.5. In this case, the volumetric growth rate can be expressed as:

$$\frac{dv}{dt} = k_1 \cdot d^{0.0} = k_2 \cdot v^{0.0} \quad (42)$$

Experimentally, Smith [28] found that the rate was independent of the polymer particle size in the small particle system. However, as we know, the volumetric growth rate of the polymer particle is affected by the number of free radicals in the polymer particle. The quantity is based on the balance of absorption and desorption of free radicals.

Table 4. Competitive Growth Data from Experiments Without Chain Transfer Agent in Styrene Seed Polymerization.

Time (hour)	50°C				60°C				70°C			
	Large Particle (a)		Small Particle (b)		Large Particle (a)		Small Particle (b)		Large Particle (a)		Small Particle (b)	
	$\frac{d_{an}}{d_{a0n}}$ (Å)	$\frac{d_{aw}}{d_{a0w}}$ (Å)	$\frac{d_{bn}}{d_{b0n}}$ (Å)	$\frac{d_{bw}}{d_{b0w}}$ (Å)	$\frac{d_{an}}{d_{a0n}}$ (Å)	$\frac{d_{aw}}{d_{a0w}}$ (Å)	$\frac{d_{bn}}{d_{b0n}}$ (Å)	$\frac{d_{bw}}{d_{b0w}}$ (Å)	$\frac{d_{an}}{d_{a0n}}$ (Å)	$\frac{d_{aw}}{d_{a0w}}$ (Å)	$\frac{d_{bn}}{d_{b0n}}$ (Å)	$\frac{d_{bw}}{d_{b0w}}$ (Å)
0.0	1156	1161	1.005	800	811	1.013	1.445		+	+	+	+
0.5									1211	1215	1.003	849
1.0	1222	1228	1.005	835	846	1.013	1.464	773	1376	1330	1.003	983
1.5												
2.0	1221	1225	1.003	843	861	1.021	1.448	853	1442	1446	1.003	1120
3.0	1301	1305	1.003	911	924	1.016	1.428	934	1575	1582	1.004	1271
4.0	1339	1343	1.003	936	948	1.013	1.431	1125	1830	1838	1.004	1510
5.0								1217	1938	1946	1.004	1612
6.0	1451	1458	1.005	1078	1090	1.011	1.366	1299	1987	2001	1.007	1712
$\frac{d_{an}}{d_{a0n}}$	1.255								1.719			
$\frac{d_{bn}}{d_{b0n}}$				1.348				1.624				2.140

Table 5. Competitive Growth Data from Experiments with Chain Transfer Agent in Styrene Seed Polymerizations at 70°C.

		Carbontetrachloride (EX-16)				Xylene (EX-27)				
		Large Particle (a)		Small Particle (b)		Large Particle (a)		Small Particle (b)		
Time (hour)	d_{an} (Å)	d_{aw} (Å)	U	d_{bn} (Å)	d_{bw} (Å)	U	d_{bn} (Å)	d_{bw} (Å)	U	
0.0	1156	1161	1.005	800	811	1.013	+	+	+	
0.5	1215	1220	1.004	801	818	1.021	1159	1166	1.006	
1.0	1292	1299	1.005	890	911	1.024	1174	1188	1.012	
2.0	1359	1366	1.005	994	1008	1.014	1351	1357	1.004	
3.0	1497	1513	1.011	1171	1184	1.011	1453	1463	1.007	
3.75	--	--	--	--	--	--	1576	1582	1.004	
4.0	1554	1558	1.003	1208	1219	1.009	--	--	--	
5.0	1682	1687	1.003	1361	1373	1.009	--	--	--	
6.0	1796	1810	1.008	1491	1502	1.007	--	--	--	
6.5	--	--	--	--	--	--	2010	2022	1.006	
$\frac{d_{an}}{d_{a0n}}$	1.554		--		--		1.739		--	
$\frac{d_{bn}}{d_{b0n}}$	--		1.864		--		--		2.126	

Table 6. Relationship between $\frac{d_{an}}{d_{a0n}}$ versus $\gamma = \frac{d_{bn}}{d_{b0n}}$ in the Polymerization without Chain Transfer Agent.

$\frac{d_{an}}{d_{a0n}}$	γ^*	$\frac{d_{an}}{d_{a0n}}$	γ	$\frac{d_{an}}{d_{a0n}}$	γ
1.445	1.000	+	+	+	+
1.464	1.044	1.477	0.966	1.426	1.061
1.448	1.054	1.451	1.066	1.349	1.229
1.428	1.139	1.392	1.168	1.288	1.400
1.431	1.170	1.317	1.406	1.239	1.589
1.346	1.348	1.268	1.521	1.212	1.888
		1.253	1.624	1.202	2.015
				1.161	2.140

*: $\gamma = \frac{d_{bn}}{d_{b0n}}$

Table 7. Relationship between $\frac{d_{an}}{d_{a0n}}$ versus $\gamma = \frac{d_{bn}}{d_{b0}}$ in the Polymerization with Chain Transfer Agents.

Carbon tetrachloride		Xylene	
$\frac{d_{an}}{d_{bn}}$	γ	$\frac{d_{an}}{d_{bn}}$	γ
1.445	1.000	←	←
1.517	1.001	1.519	0.954
1.452	1.113	1.486	0.988
1.367	1.243	1.347	1.254
1.278	1.464	1.304	1.393
1.286	1.510	1.273	1.548
1.236	1.701	1.182	2.126
1.205	1.864		

Gardon [29] suggested that free radicals enter the polymer particles in direct proportion to the particle surface area. The free radicals which enter into the swollen polymer particles may not diffuse easily into the center of the polymer particle because of the high viscosity. Vanderhoff [30] has shown that in the emulsion polymerization of styrene, more than 50% of all the polymer chain ends are located at the surface of the particle. Medvedev [31] also suggested that the radicals cannot penetrate the interior of the particles due to the high viscosity and thus that polymerization occurred at the particle surface. Brodnyan [32] demonstrated that the polymerization rate was shown to be linearly related to the total surface area of all the particles.

Therefore, it is assumed that the surface area of the polymer particle affects the volumetric growth rate. That is

$$\frac{dv}{dt} = k_3 \cdot d^{2.0} \quad (43)$$

In Figures 10 and 11, the theoretical variation of d_{an}/d_{bn} with $\gamma = d_{bn}/d_{b0}$ for various values of c are shown when $\alpha = 1.445$. The experimental results are also shown. According to the experimental data, c is approximately equal to 2.0 even if the polymerization temperature is changed (50°C,

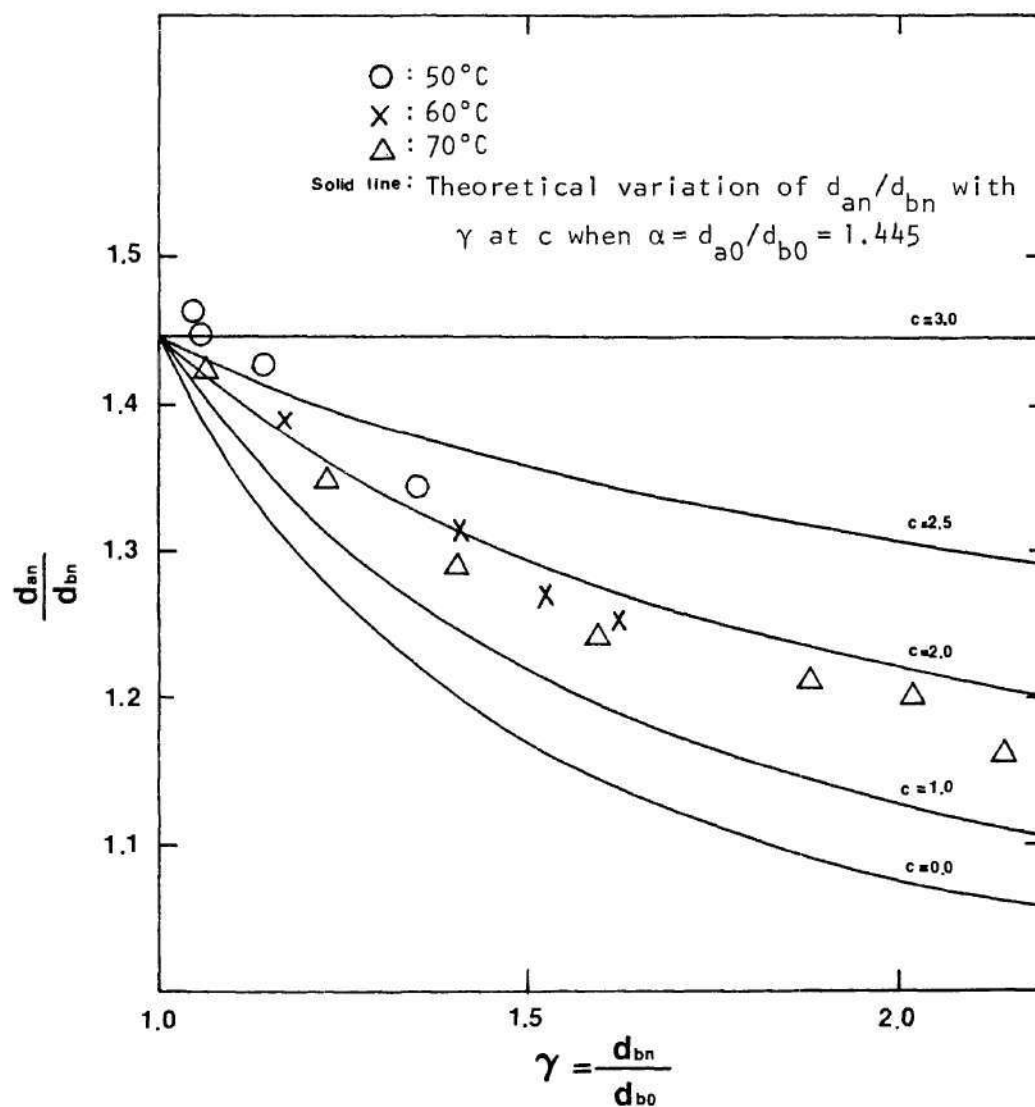


Figure 10. Competitive Growth without Chain Transfer Agent for Styrene Seed Polymerizations.

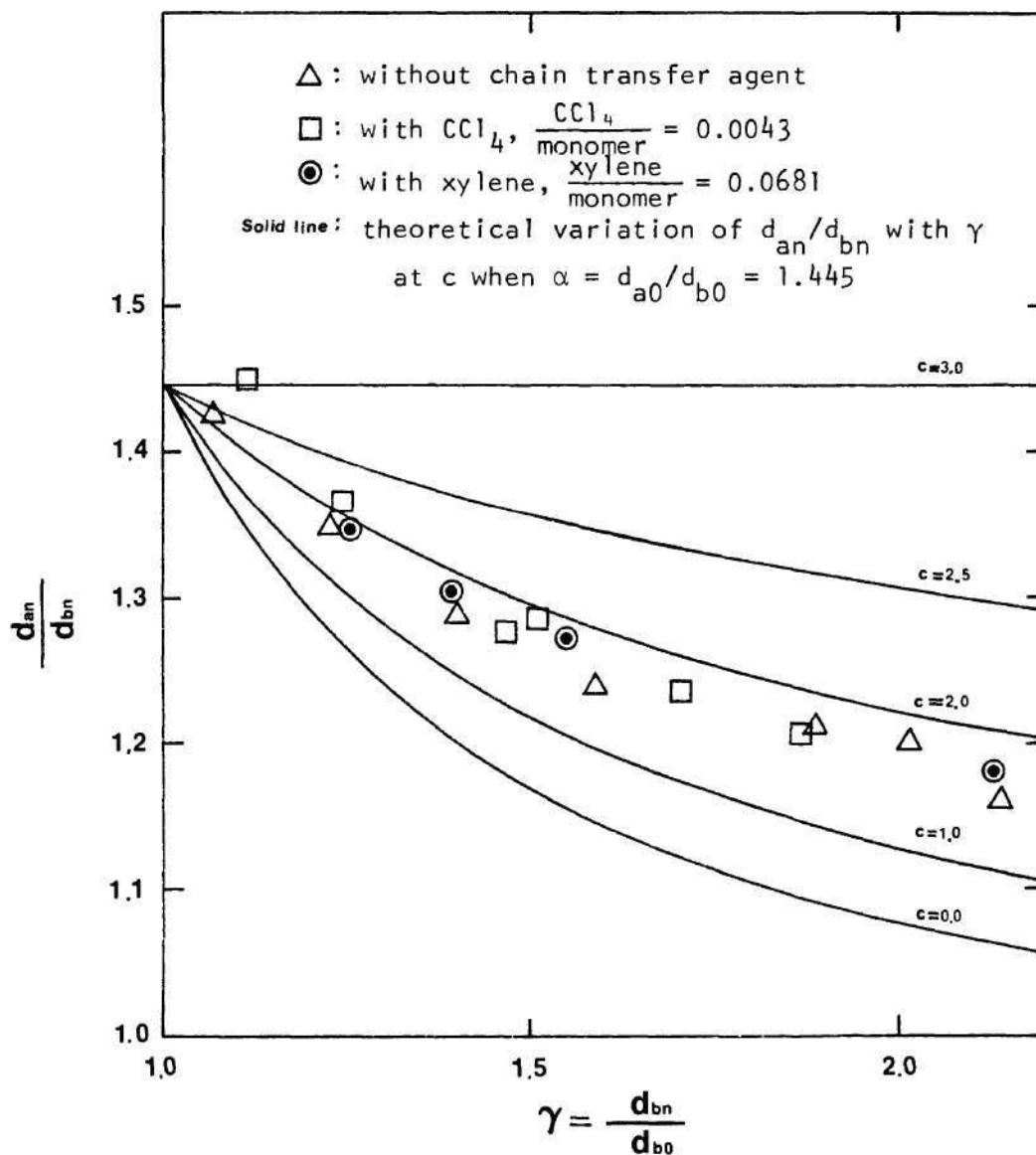


Figure 11. Competitive Growth with Chain Transfer Agents for Styrene Seed Polymerizations at 70°C.

60°C and 70°C) and the chain transfer agent (carbon tetrachloride, xylene) is added. This means that the volumetric growth rate of the polymer particle is proportional to the surface area of the polymer particle. This agrees with the assumption mentioned before. Also, this means that \bar{n} is not constant (0.5), which means that desorption and accumulation of free radicals may occur, even in styrene polymerization. The result ($c = 2.0$) does not agree with Vanderhoff's result. Poehlein and Vanderhoff [27] showed theoretically that the factor of c was 2.5 when \bar{n} was significantly larger than 0.5 (Smith-Ewart Case III where the desorption of free radicals is not significant). Recently, Gilbert and Napper [33] showed that \bar{n} could be less than 0.5 for styrene emulsion polymerization under suitable conditions (e.g., low initiator concentrations and/or small particle sizes). Therefore, the discrepancy may suggest that our styrene polymerization kinetics obeys Smith-Ewart theory Case I in which the desorption of free radicals occurs.

In Figures 12 and 13, the comparisons of particle growth rate (particle diameter vs. time) without and with chain transfer agents are shown. The chain transfer agents clearly decrease the particle growth rate. The desorption of free radicals from polymer particles is quite likely proceeded by the chain transfer reaction with small

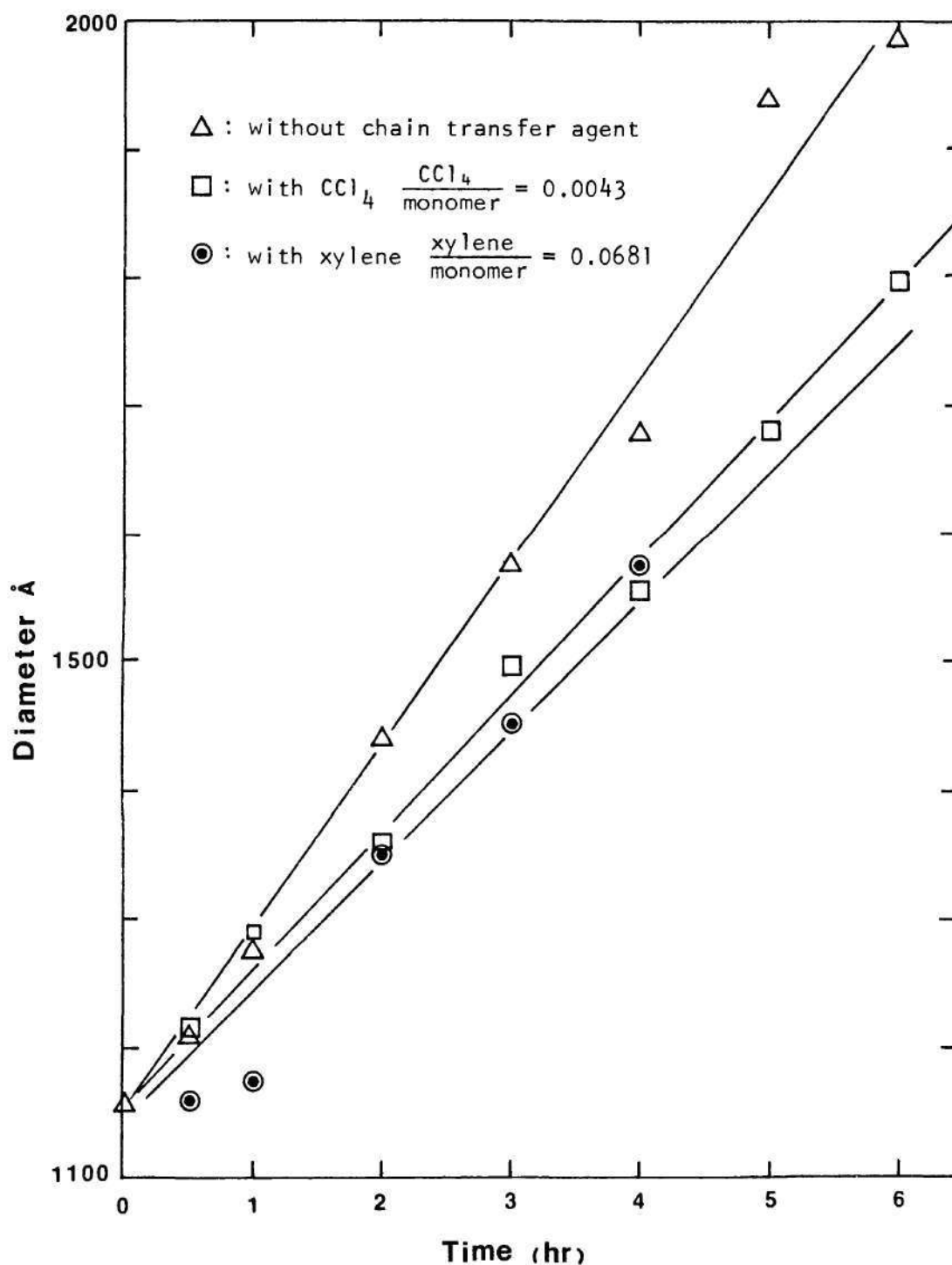


Figure 12. Comparison of Growth Rates (Diameter vs. Time) without and with Chain Transfer Agents for Large Particles (Initial Diameter $d_0 = 1156\text{\AA}$) at 70°C (Styrene).

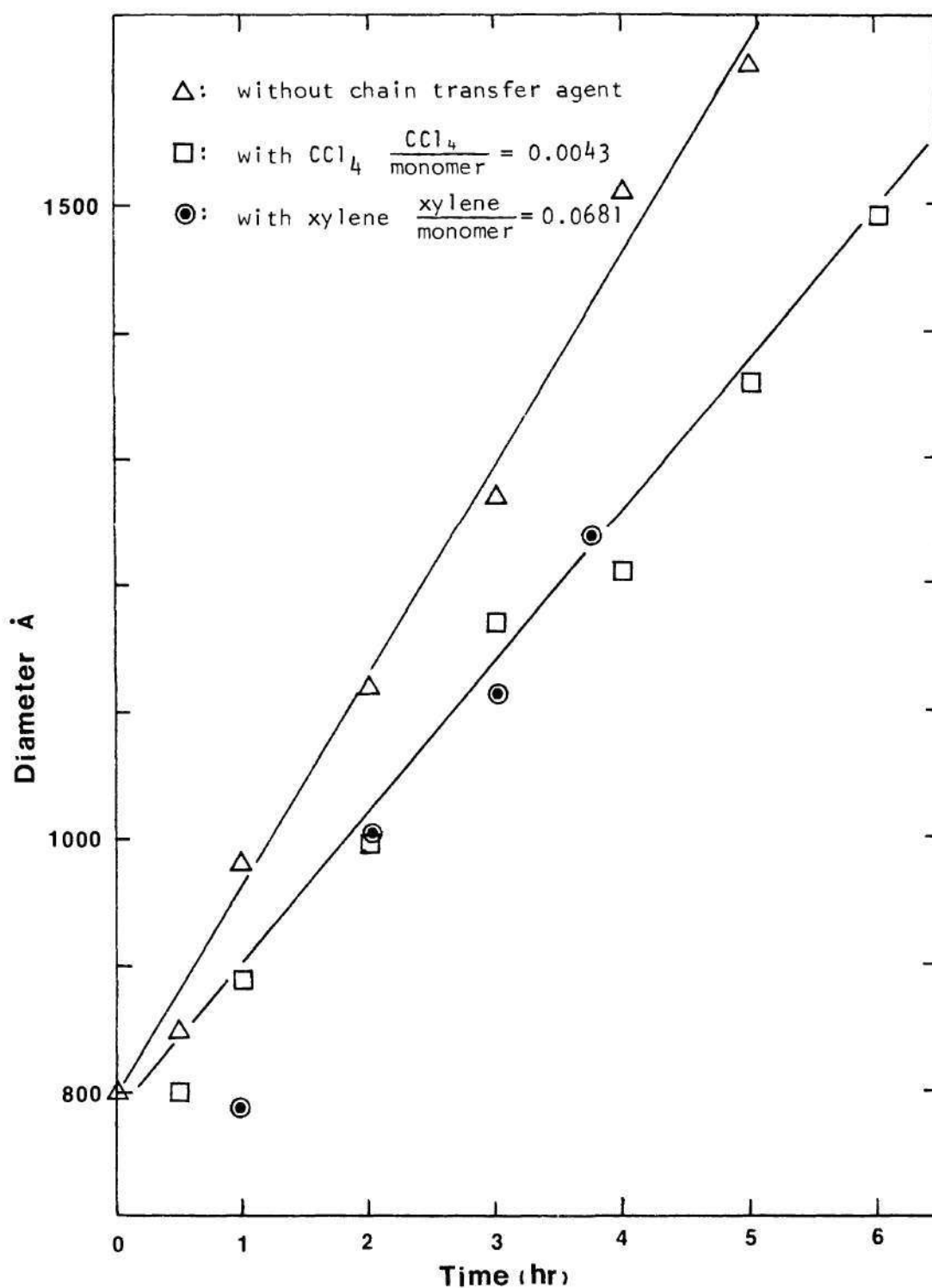


Figure 13. Comparison of Growth Rates (Diameter vs. Time) without and with Chain Transfer Agents for Small Particles (Initial Diameter $\bar{d}_0 = 800\text{\AA}$) at 70°C (Styrene)

molecules. As shown in Figures 14, 15, 16 and 17, $\frac{dv}{dt}$ changes for large and small particles, even when the polymerization temperature is altered and chain transfer agents are added. This means that \bar{n} changes during polymerization in the styrene system although the overall polymerization rate $R_p = \frac{d[P]}{dt}$ is fairly linear as shown in Figure 5. This result agrees with Sundberg's [34] and Gerrens' [35] results for styrene which showed that \bar{n} changes during polymerization.

The monomer concentration in the polymer particle $[M]_p$ is assumed to be constant although it is well known that polystyrene latex particles are swelled to equilibrium with styrene monomer and that the equilibrium swelling rate generally increases with increasing polymer particle diameter [36].

Both styrene and MMA were studied in the competitive growth experiment. The styrene system was analyzed. However, the MMA system could not be analyzed due to trouble with the transmission electron microscope. The analysis of MMA will be continued in the next project.

Polymerization Rate Experiments

The purpose of this work was to determine quantitatively the desorption behavior of free radicals from polymer particles. First, the average number of free

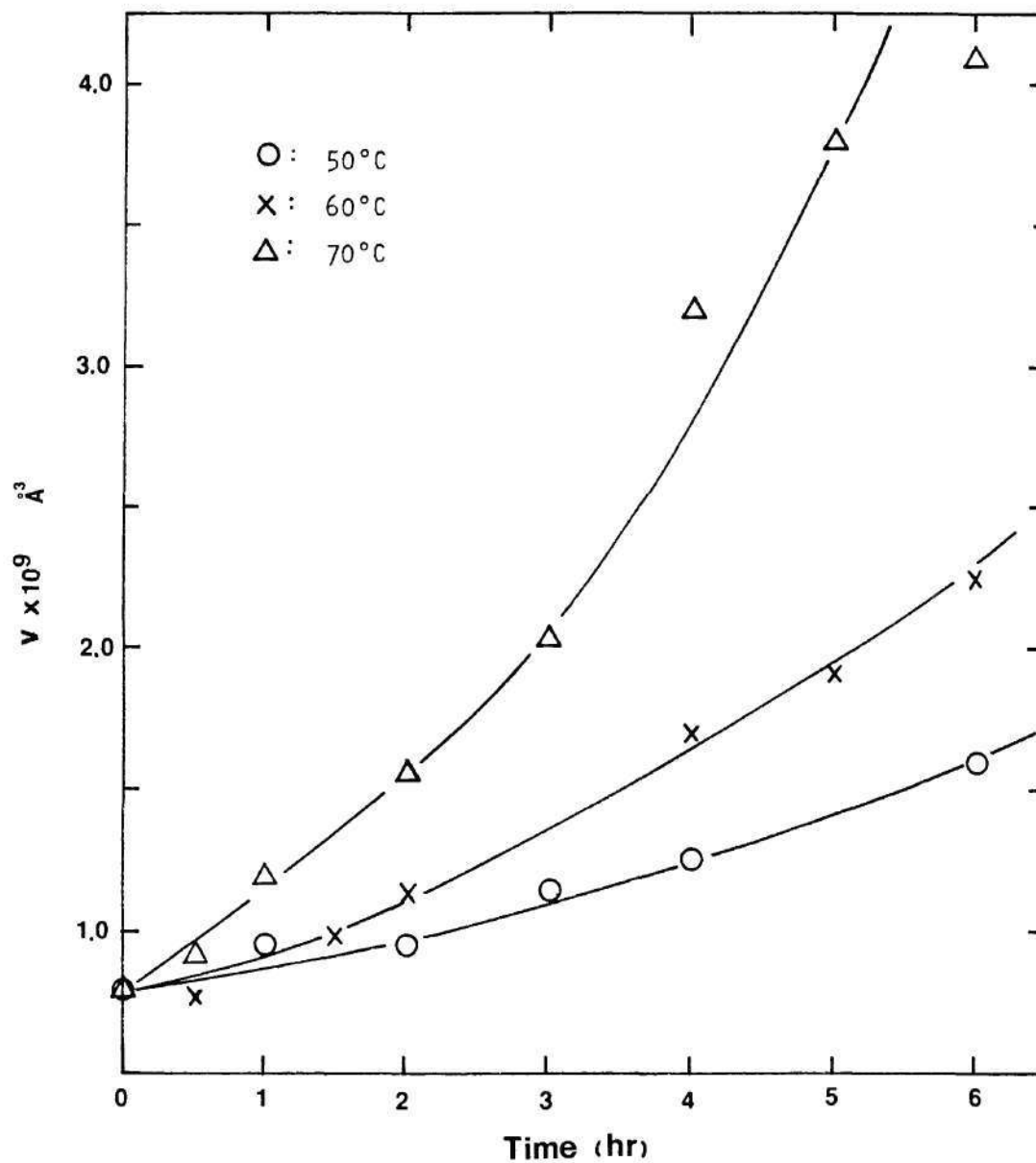


Figure 14. Competitive Growth Rates (Volume vs. Time) for Large Particles (Initial Diameter $d_0 = 1156\text{\AA}$) (Styrene).

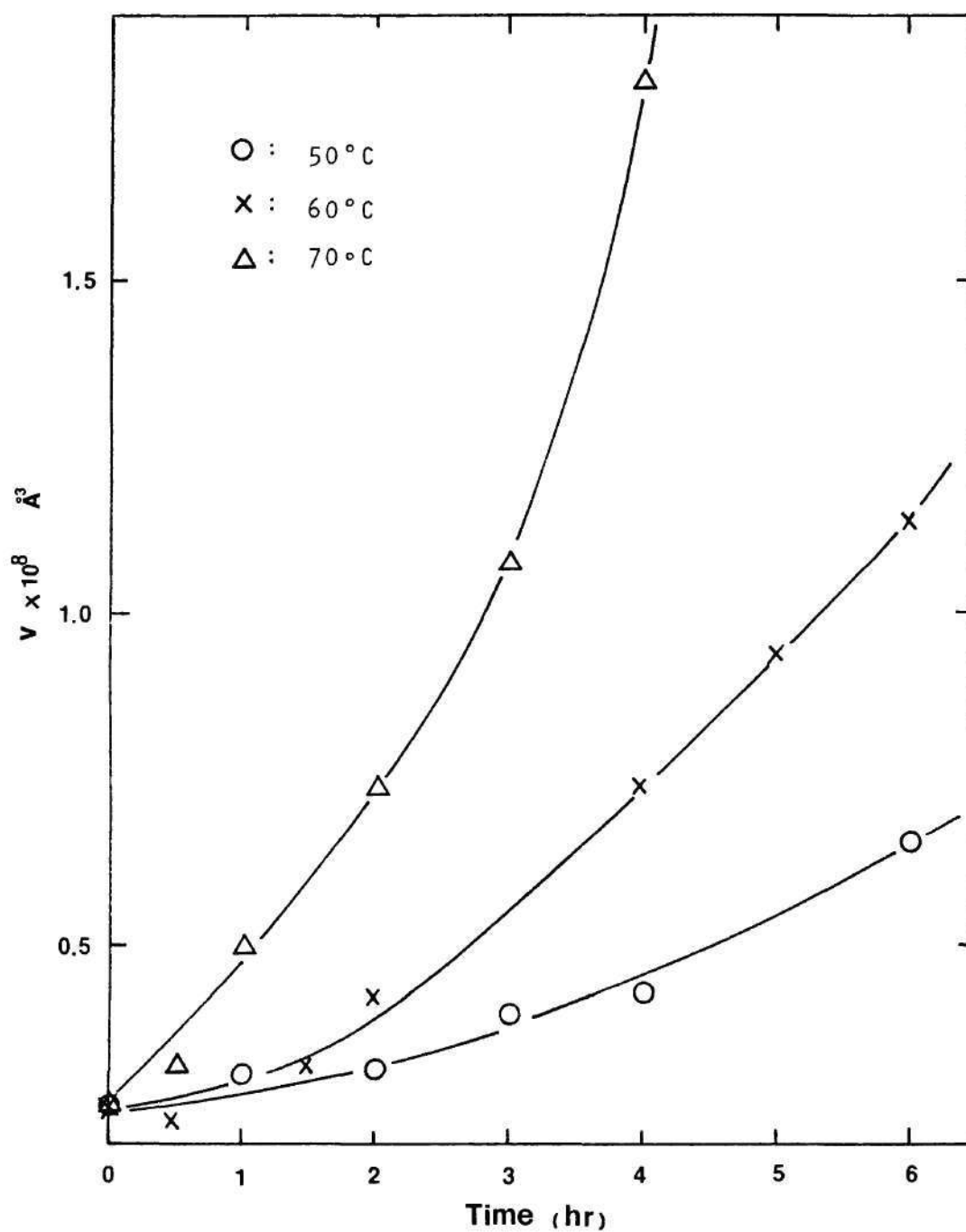


Figure 15. Competitive Growth Rates (Volume vs. Time) for Small Particles (Initial Diameter $d_0 = 800\text{\AA}$) (Styrene).

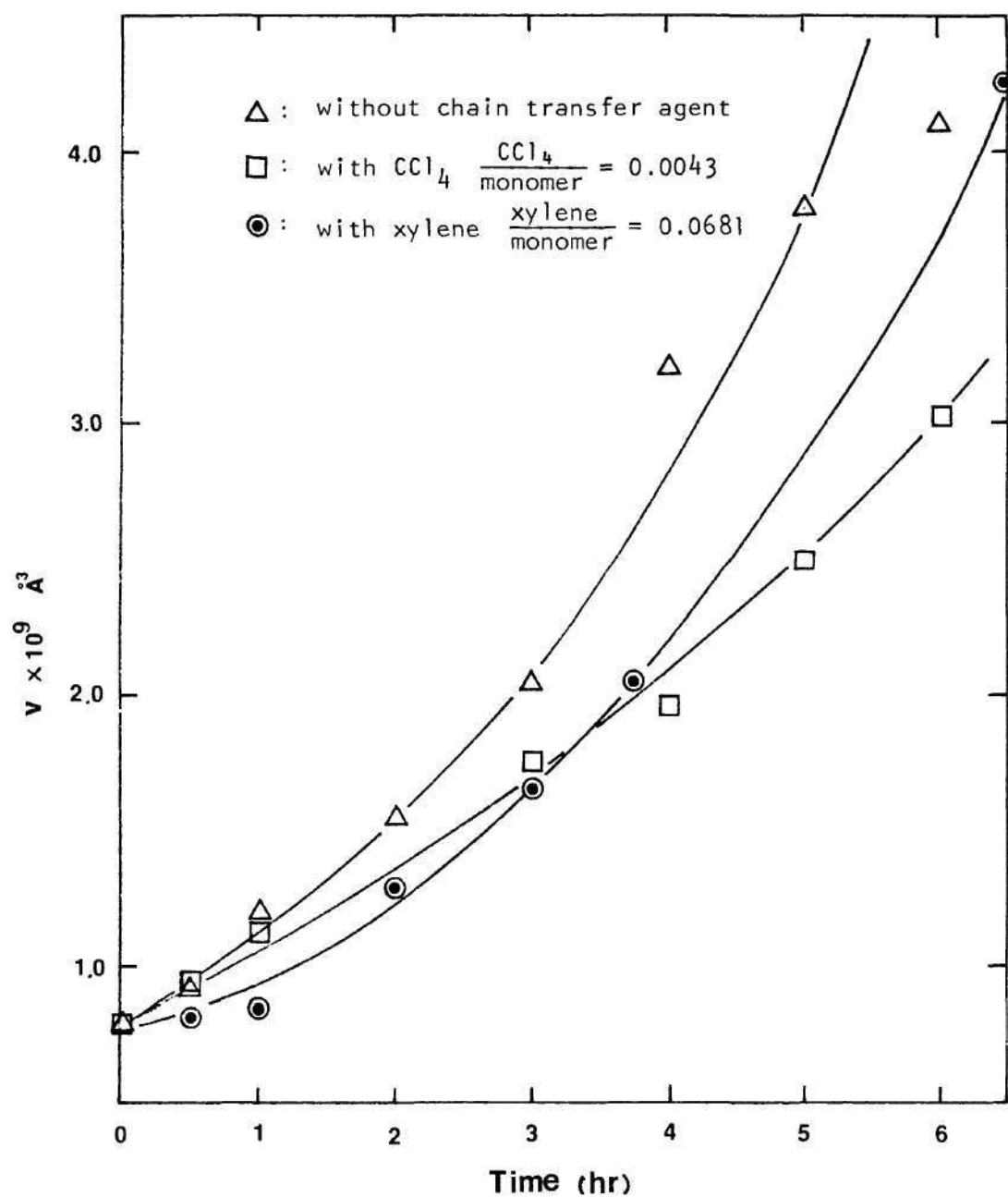


Figure 16. Competitive Growth Rates (Volume vs. Time) without and with Chain Transfer Agents for Large Particles (Initial Diameter $d_0 = 1156 \text{ Å}$) at 70°C (Styrene).

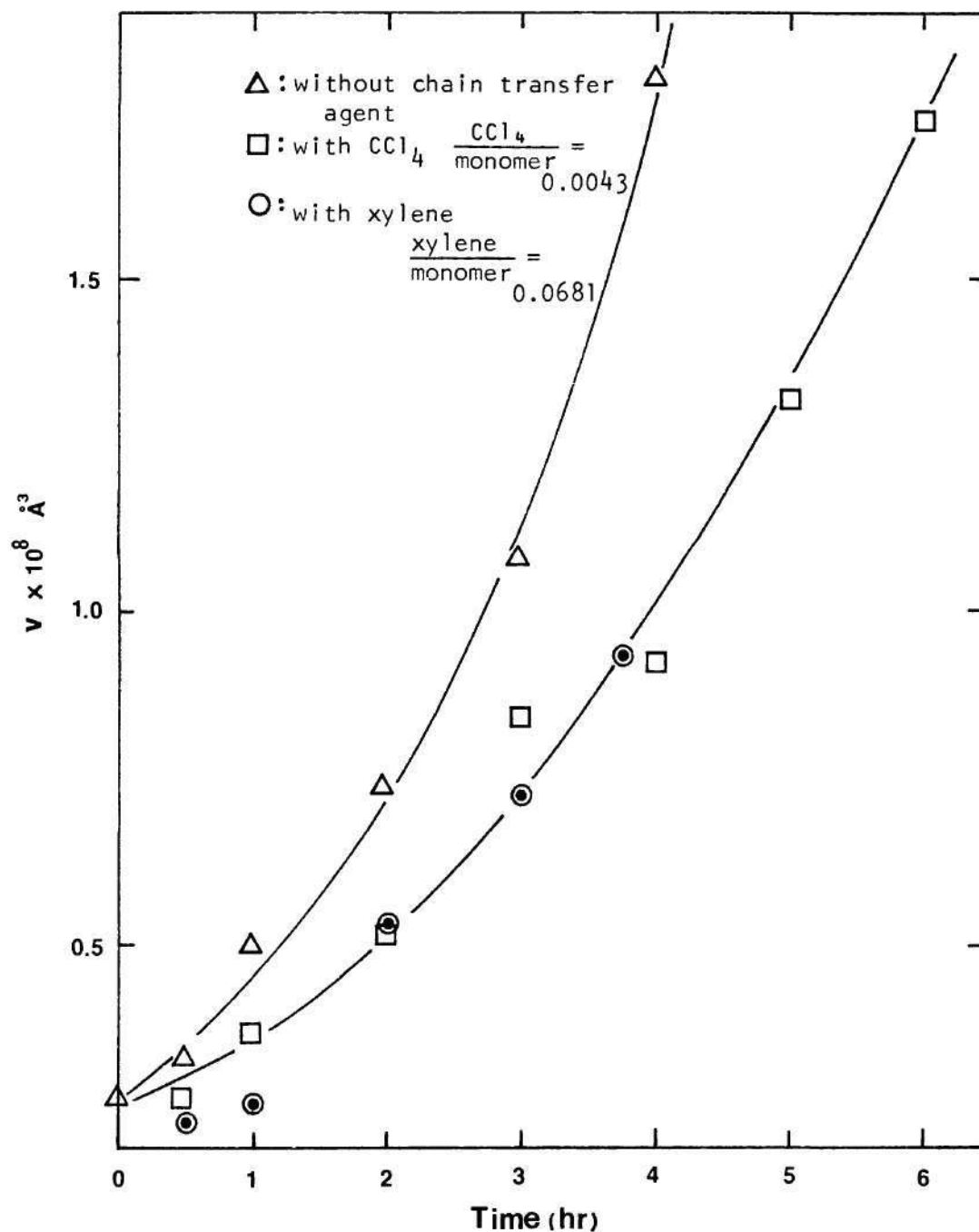


Figure 17. Competitive Growth Rates (Volume vs. Time) without and with Chain Transfer Agents for Small Particles (Initial Diameter $d_0 = 800\text{\AA}$) at 70°C (Styrene).

radicals in the polymer particles was calculated from the value of the polymerization rate obtained experimentally. The experimental values, \bar{n} , were used to determine the desorption rate constant, k_d , from the \bar{n} vs. k_d relationship which was derived from kinetic models.

Calculation of \bar{n}

In an emulsion polymerization, the polymerization rate, R_p , can be expressed by:

$$R_p = \frac{d[P]}{dt} = k_p \cdot [M]_p \cdot [R\cdot] = k_p \cdot [M]_p \cdot \left(\frac{\bar{n} \cdot N_T}{N_A} \right) \quad (44)$$

where $[P]$ is the amount of monomer converted to polymer, k_p is the propagation rate constant, $[M]_p$ is the monomer concentration in the polymer particles, $[R\cdot]$ is the number of active free radicals in the polymer particles, N_T is the total number of polymer particles per cc-water, and N_A is Avogadro's number. If the number of particles is held constant, the rate of polymerization, R_p , is proportional to \bar{n} , which is controlled by free radical absorption, desorption, and termination mechanisms.

Equation (44) can be modified as follows:

$$\bar{n} = \frac{R_p \cdot N_A}{k_p \cdot [M]_p \cdot N_T} = \frac{\left(\frac{d[P]}{dt} \right) N_A}{k_p \cdot [M]_p \cdot N_T} \quad (45)$$

Thus, the slope of $[P]$ versus time must be determined to

evaluate \bar{n} . Figures 18 through 36 show the relationships of $[P]$ versus time which have been obtained in the polymerization rate experiments. The rate of polymerization, $R_p = \frac{d[P]}{dt}$, is relatively constant in the styrene system, but at least two different polymerization rate ranges were obtained in the MMA (methylmethacrylate) experiments. A possible reason for these two rates will be discussed later. The slope, $\frac{d[P]}{dt}$, was calculated by using a linear regression analysis. The calculation is shown in Appendix 5. The values of k_p used in the calculation of \bar{n} were:

$$k_p = 2.16 \times 10^7 \times \exp \left(- \frac{7760}{RT} \right) \text{ for styrene [Ref. 37]}$$

$$k_p = 1.9 \times 10^7 \times \exp \left(- \frac{6840}{RT} \right) \text{ for MMA [Ref. 38]}$$

The values of $[M]_p$ were [39]:

$$[M]_p = 5.4 \text{ gmole/l-particle for styrene}$$

$$[M]_p = 7.0 \text{ gmole/l-particle for MMA}$$

Morton et al. [36] demonstrated that the volume fraction of the monomer in the swollen particle was effected by the temperature. However, since the change of $[M]_p$ due to temperature is small, $[M]_p$ was assumed to be a constant. This assumption is widely accepted.

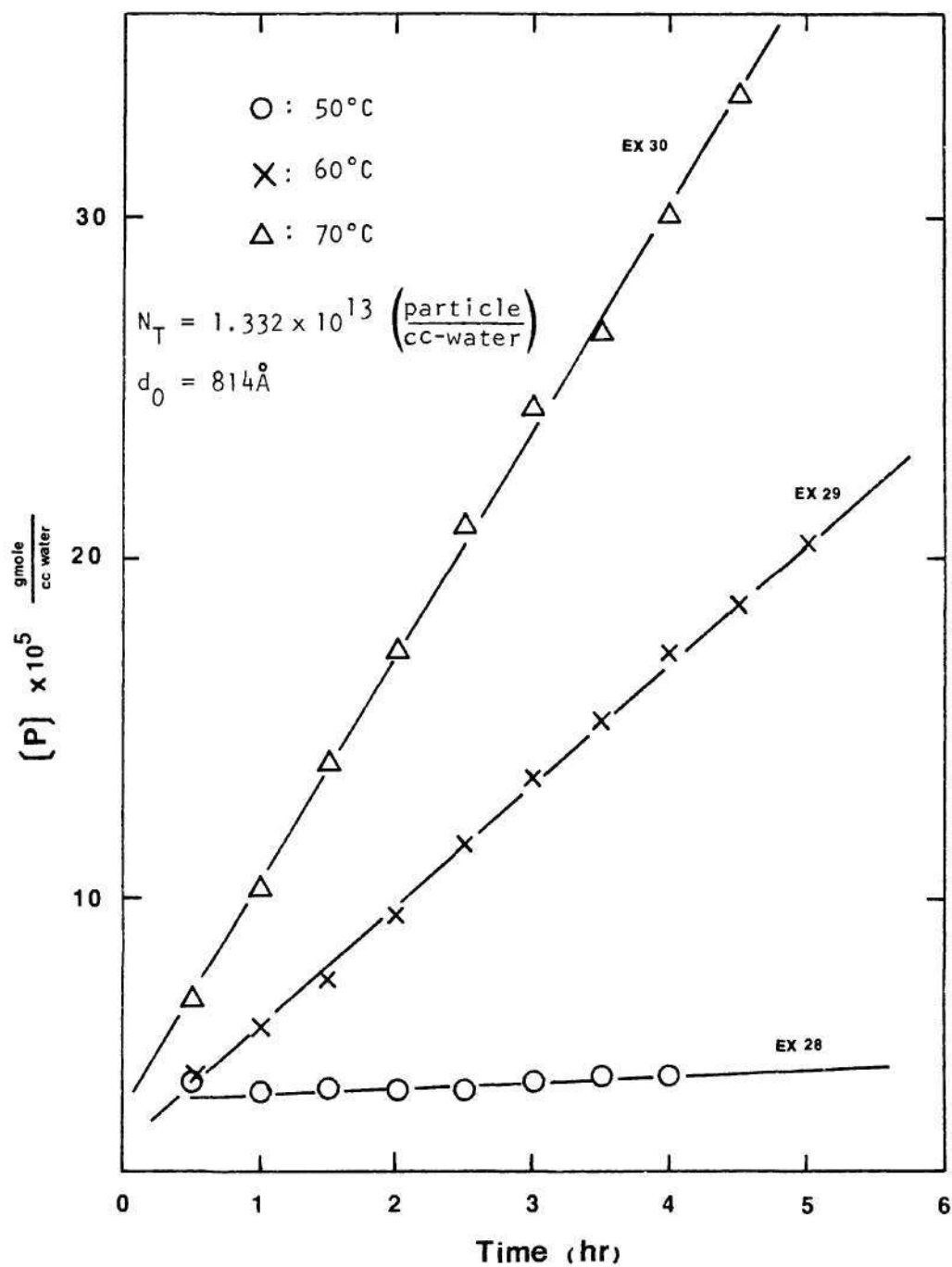


Figure 18. Effect of Temperature on the Relationship of $[P]$ vs. Time for Styrene.

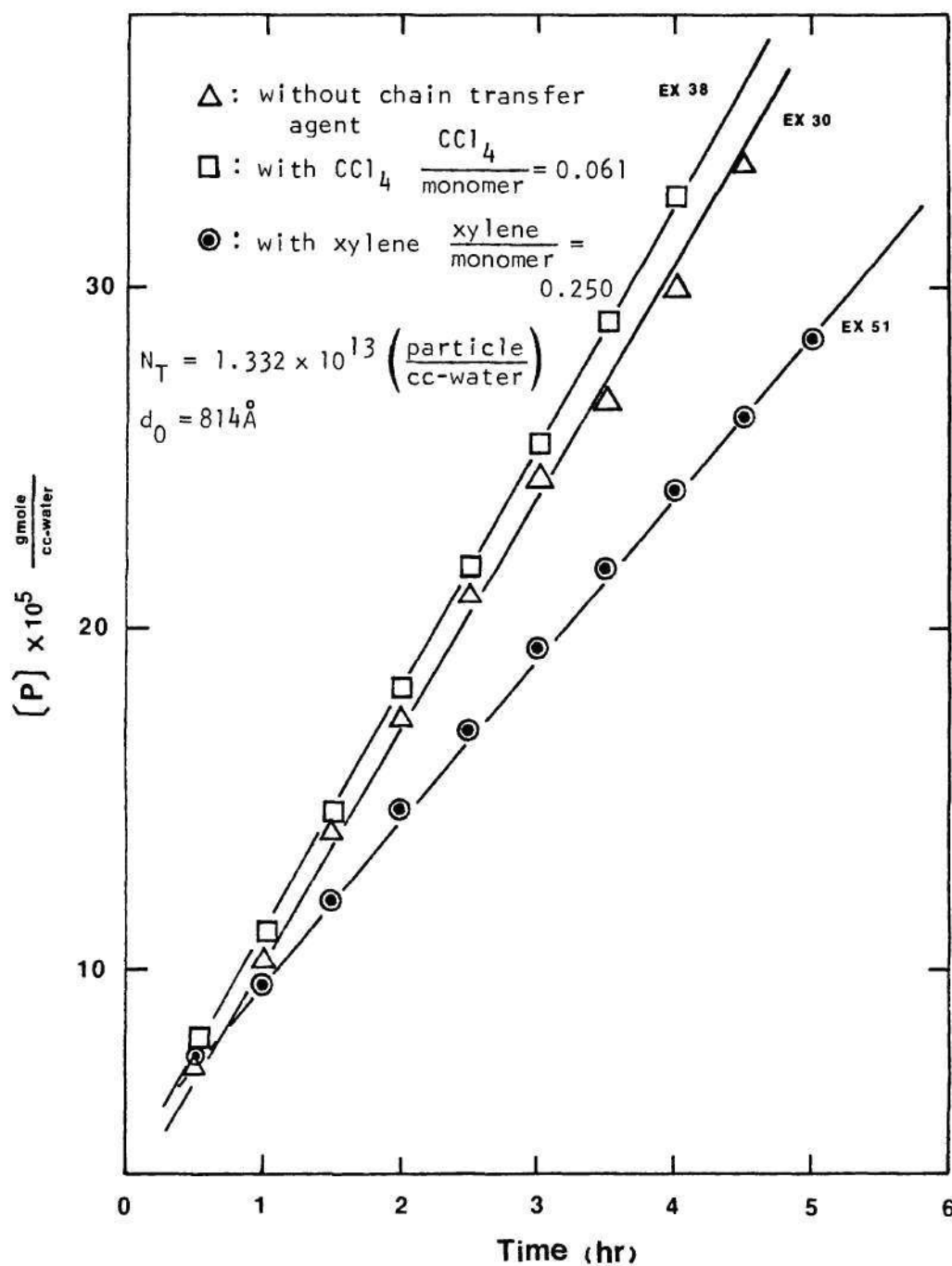


Figure 19. Effect of Chain Transfer Agents on the Relationship of $[P]$ vs. Time for Styrene at 70°C .

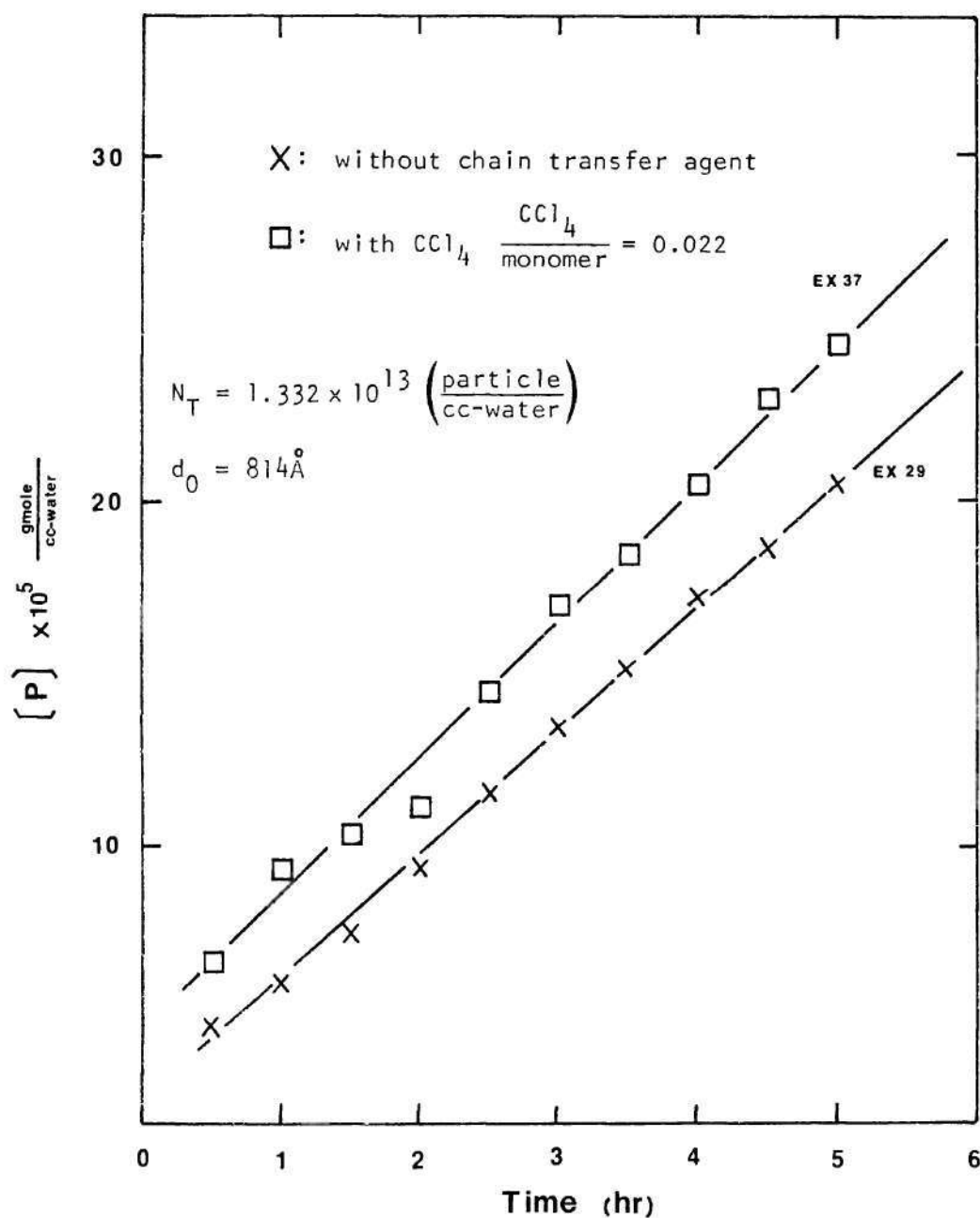


Figure 20. Effect of Chain Transfer Agent on the Relationship of $[P]$ vs. Time for Styrene at 60°C .

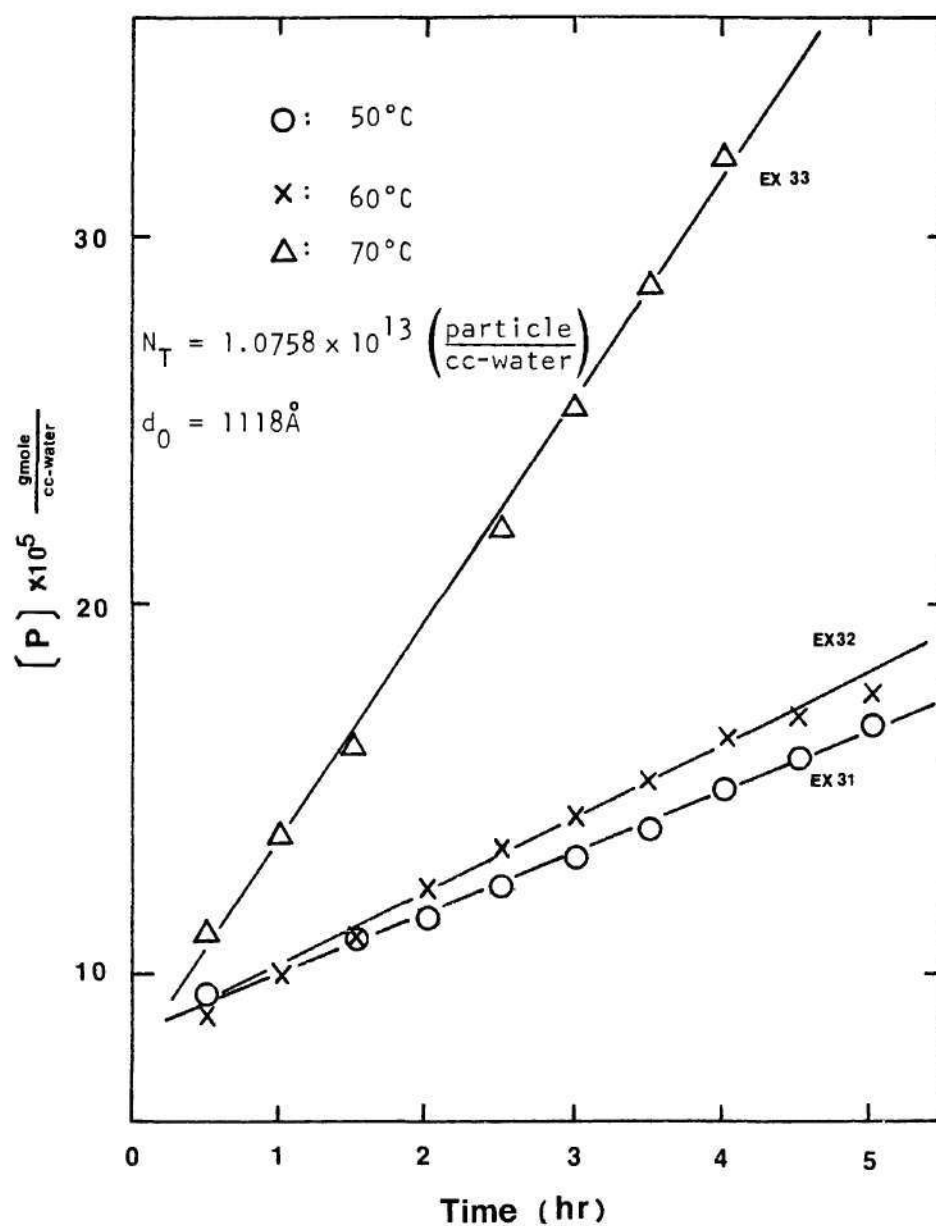


Figure 21. Effect of Temperature on the Relationship of $[P]$ vs. Time for Styrene.

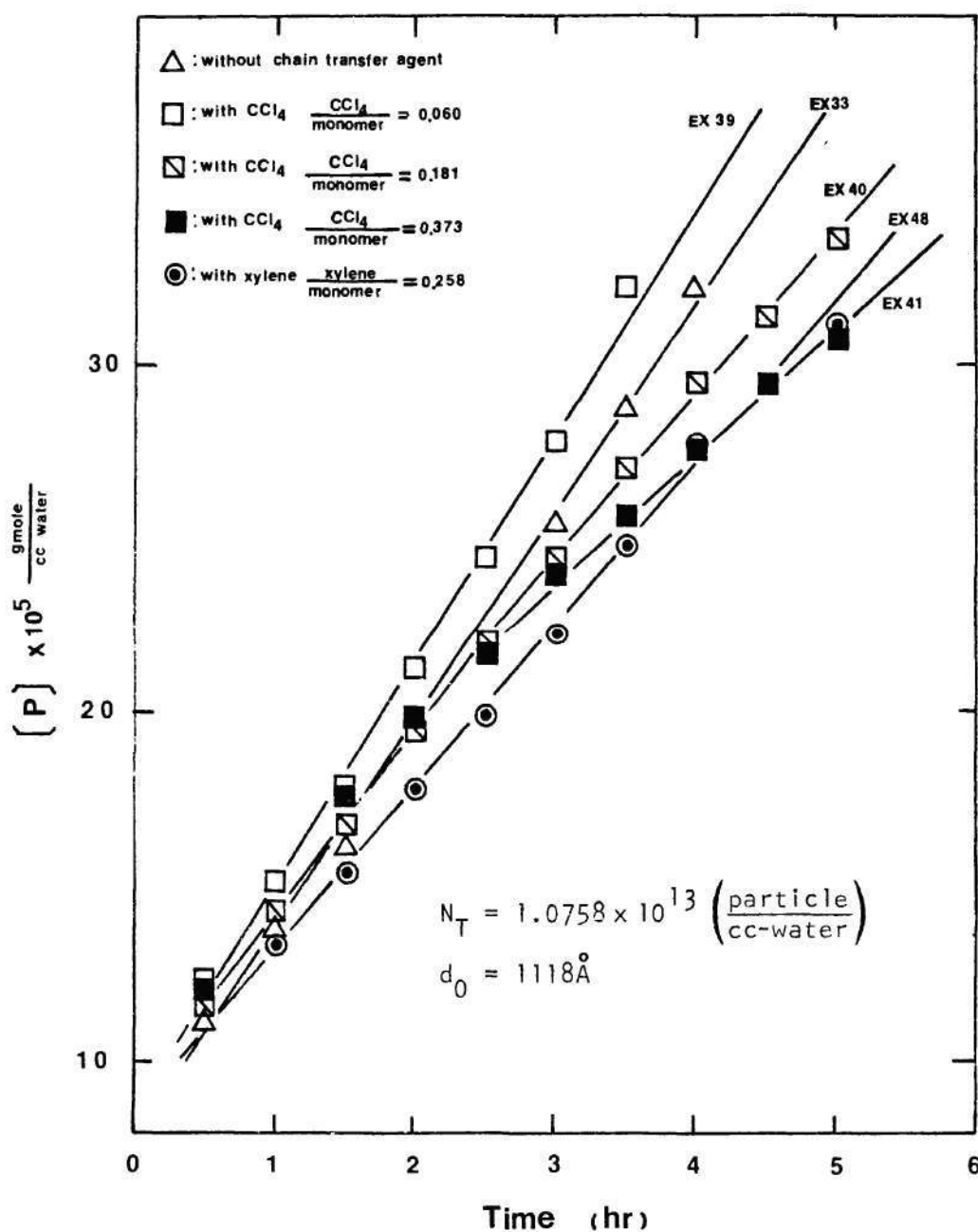


Figure 22. Effect of Chain Transfer Agents on the Relationship of $[P]$ vs. Time for Styrene at 70°C .

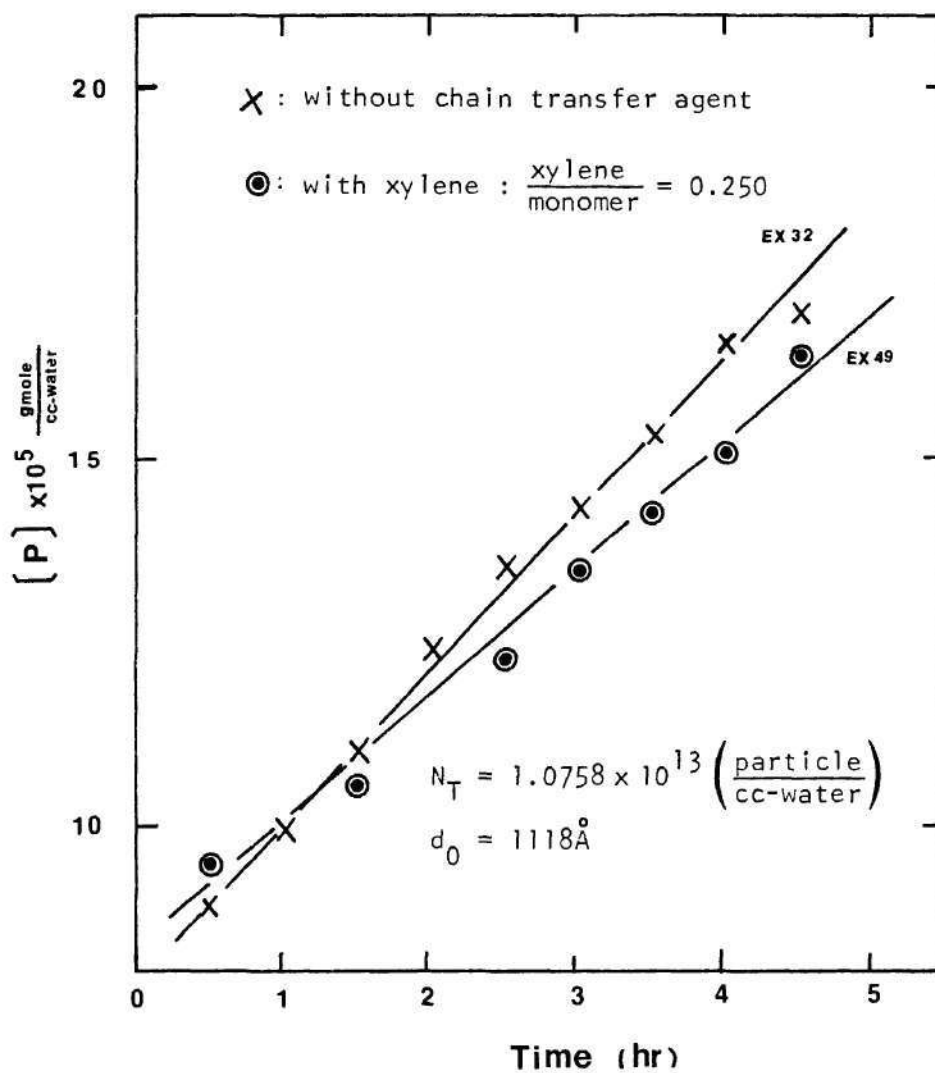


Figure 23. Effect of Chain Transfer Agent on the Relationship of $[P]$ vs. Time for Styrene at 60°C .

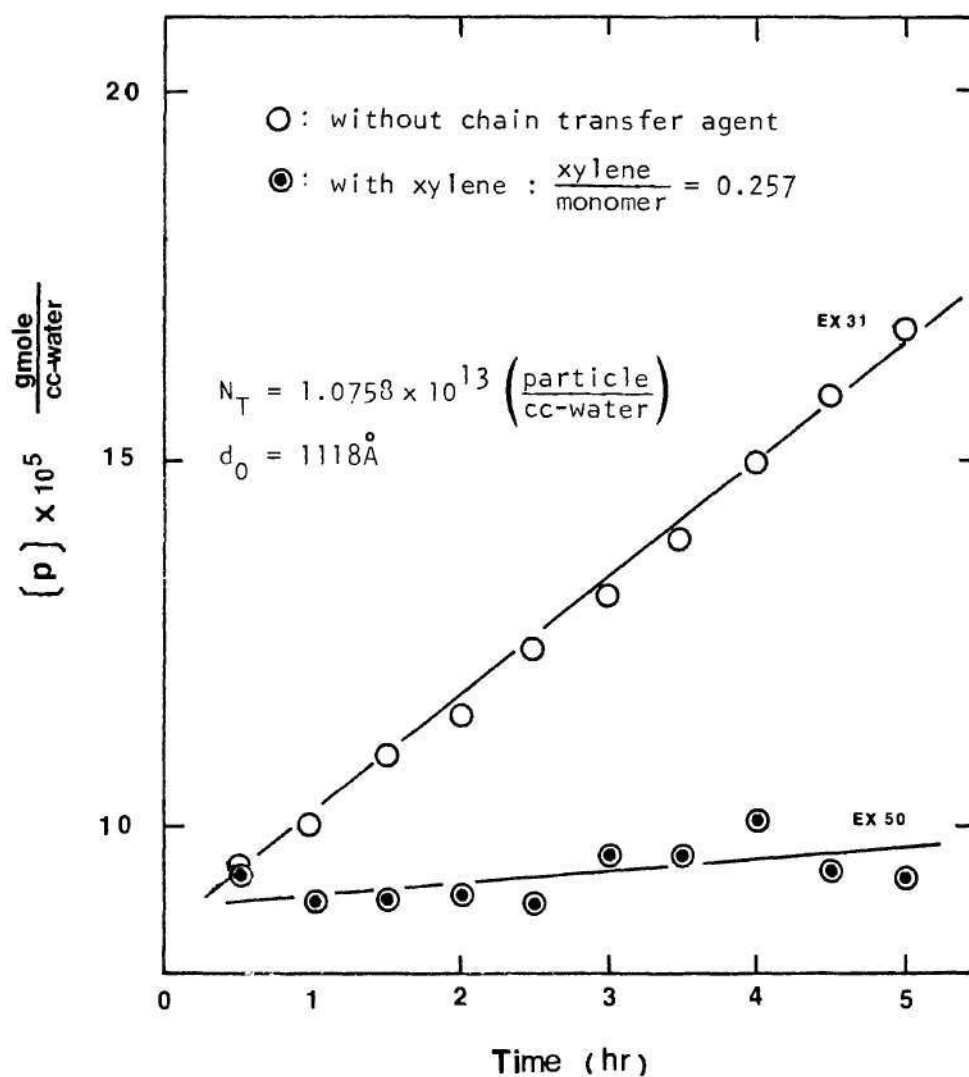


Figure 24. Effect of Chain Transfer Agents on the Relationship of $[P]$ vs. Time for Styrene at 50°C .

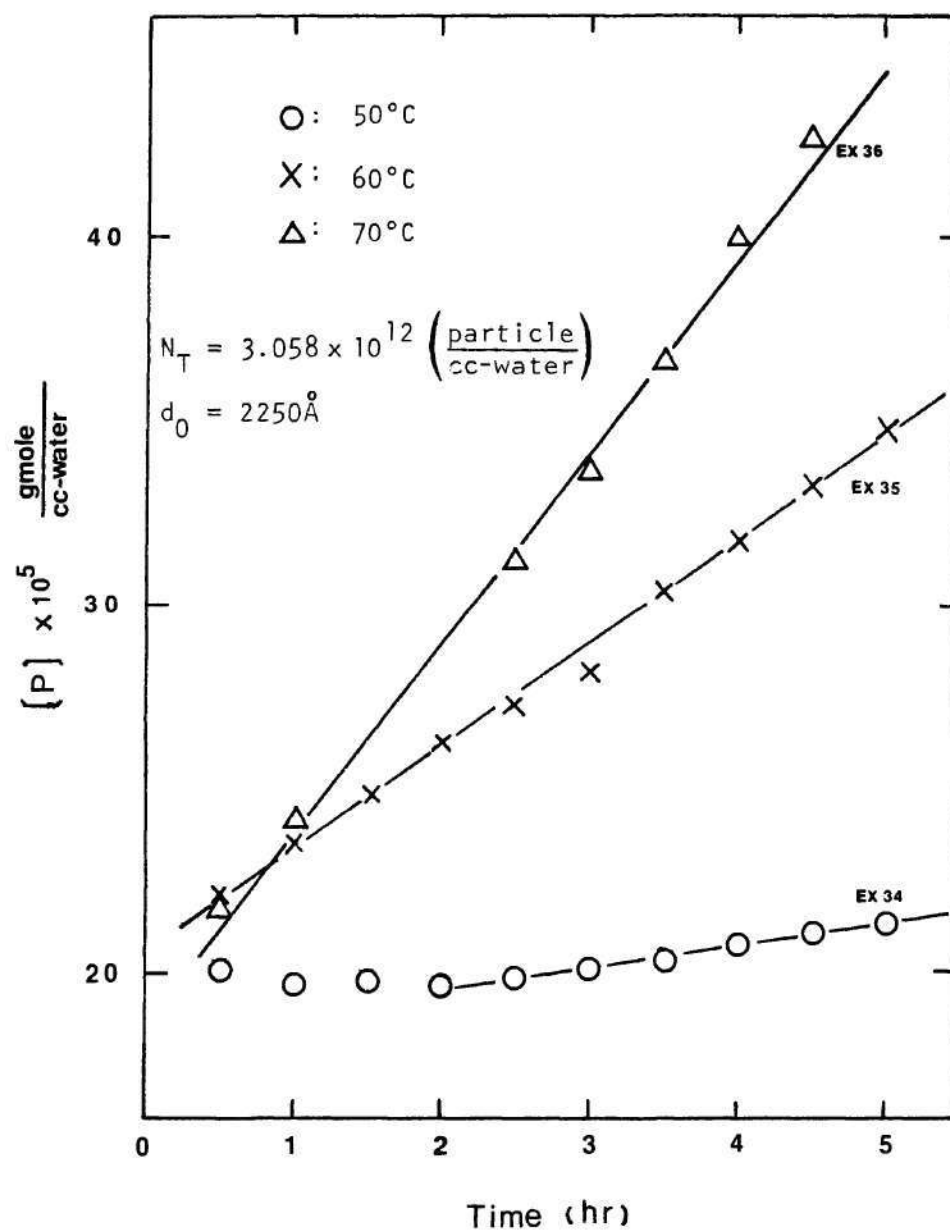


Figure 25. Effect of Temperature on the Relationship of $[P]$ vs. Time for Styrene.

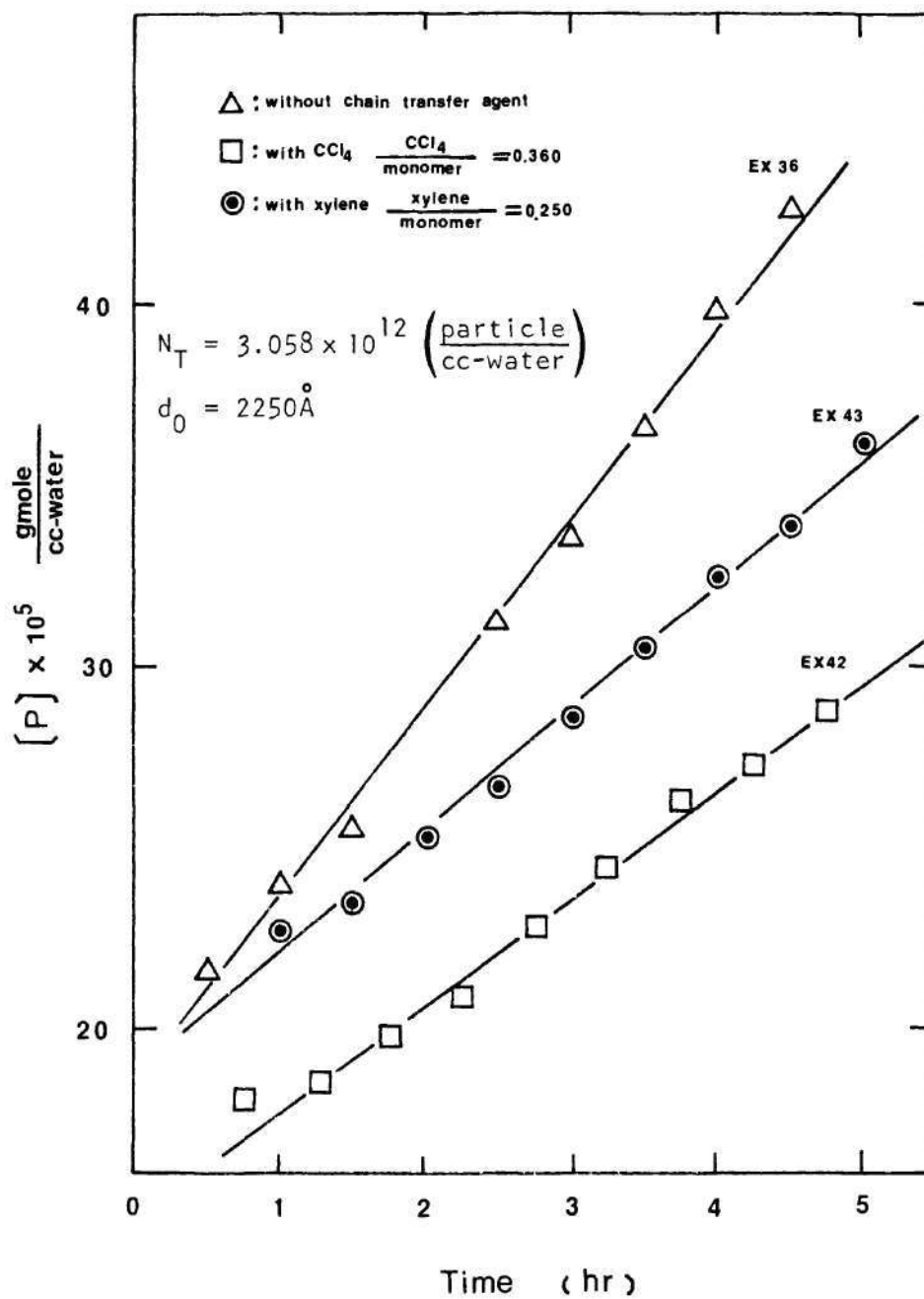


Figure 26. Effect of Chain Transfer Agents on the Relationship of $[P]$ vs. Time for Styrene at 70°C .

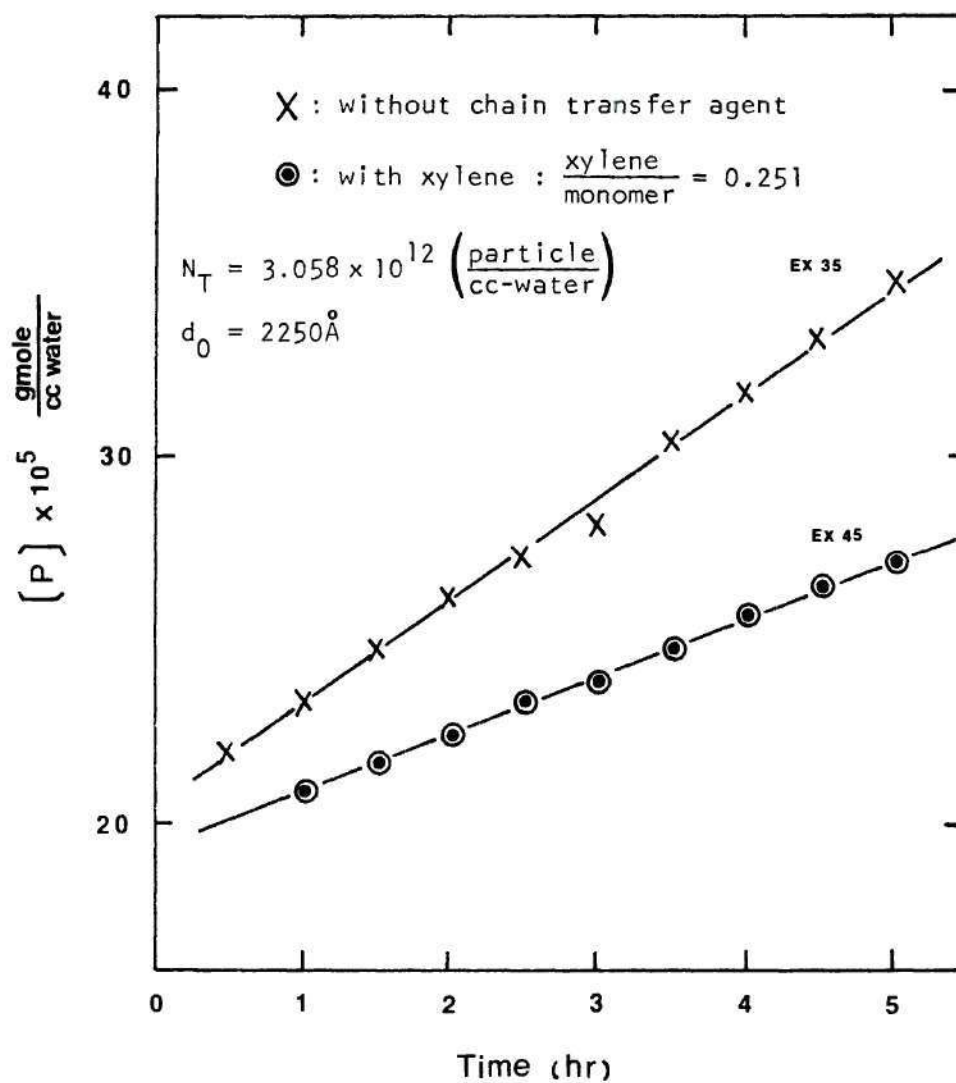


Figure 27. Effect of Chain Transfer Agents on the Relationship of $[P]$ vs. Time for Styrene at 60°C .

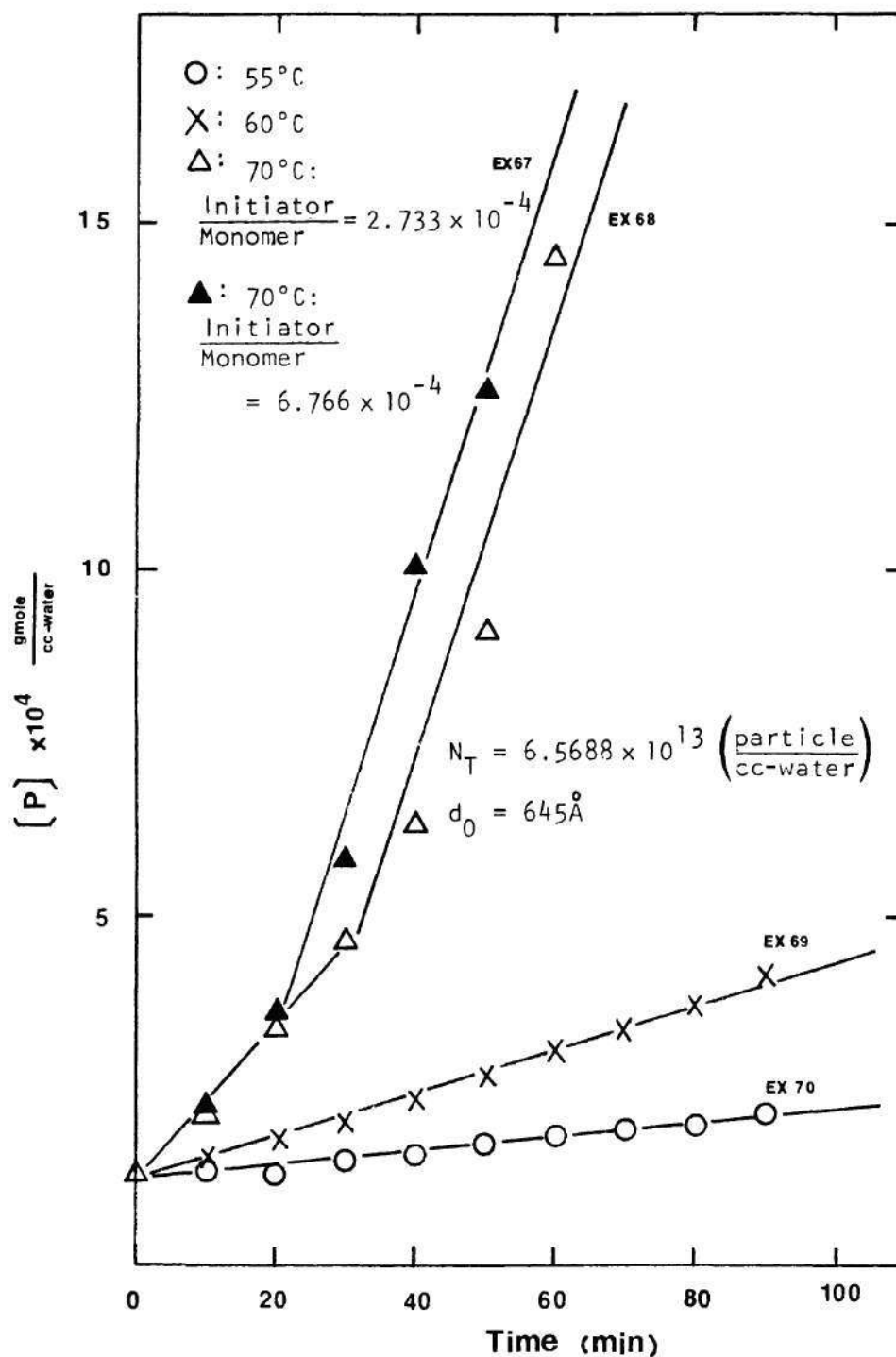


Figure 28. Effect of Temperature on the Relationship of $[P]$ vs. Time for MMA.

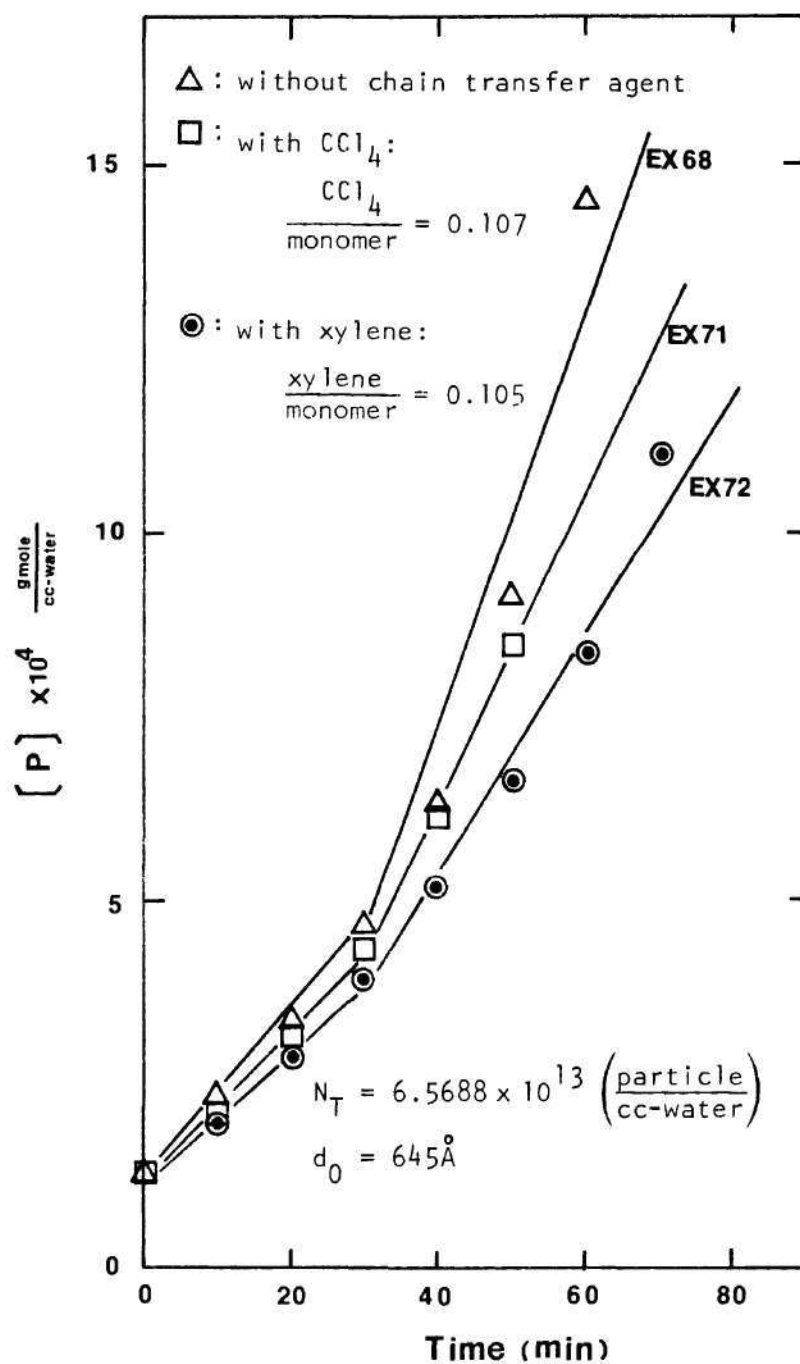


Figure 29. Effect of Chain Transfer Agents on the Relationship of $[P]$ vs. Time for MMA at 70°C .

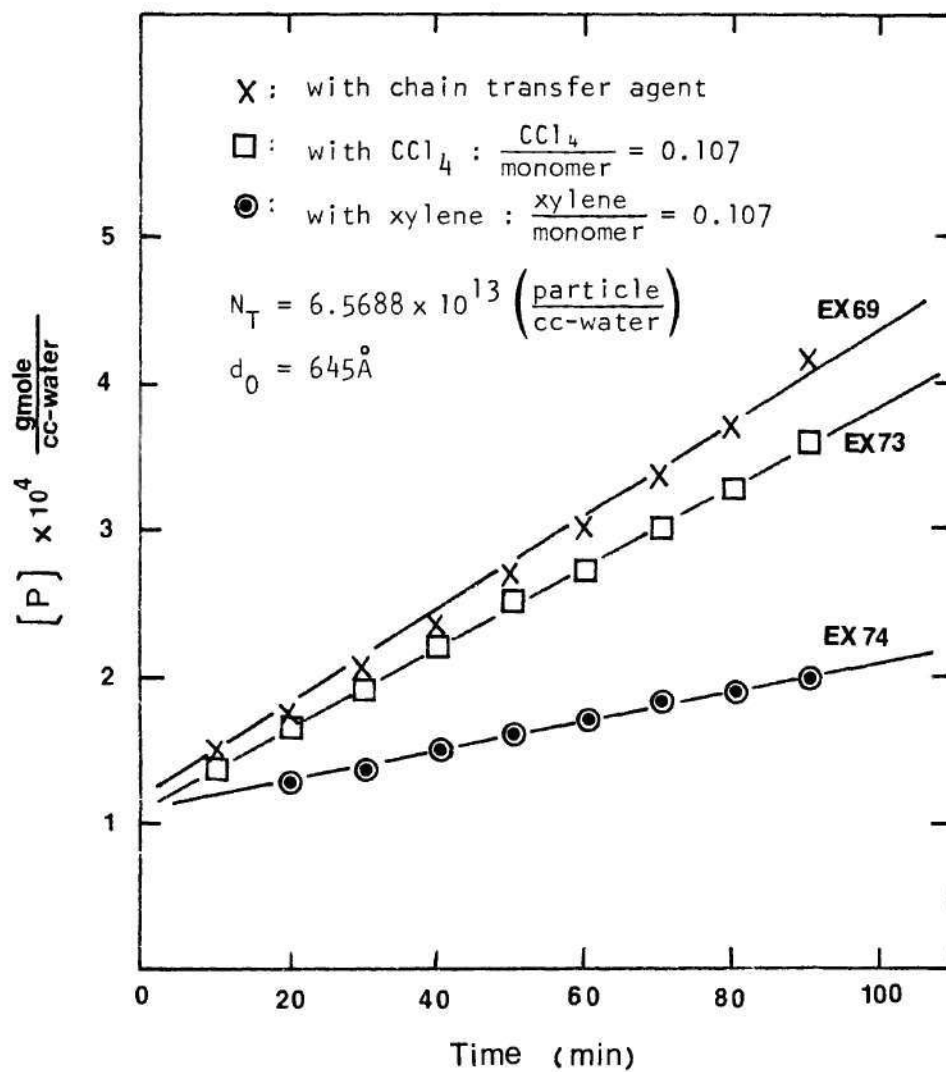


Figure 30. Effect of Chain Transfer Agents on the Relationship of $[P]$ vs. Time for MMA at 60°C .

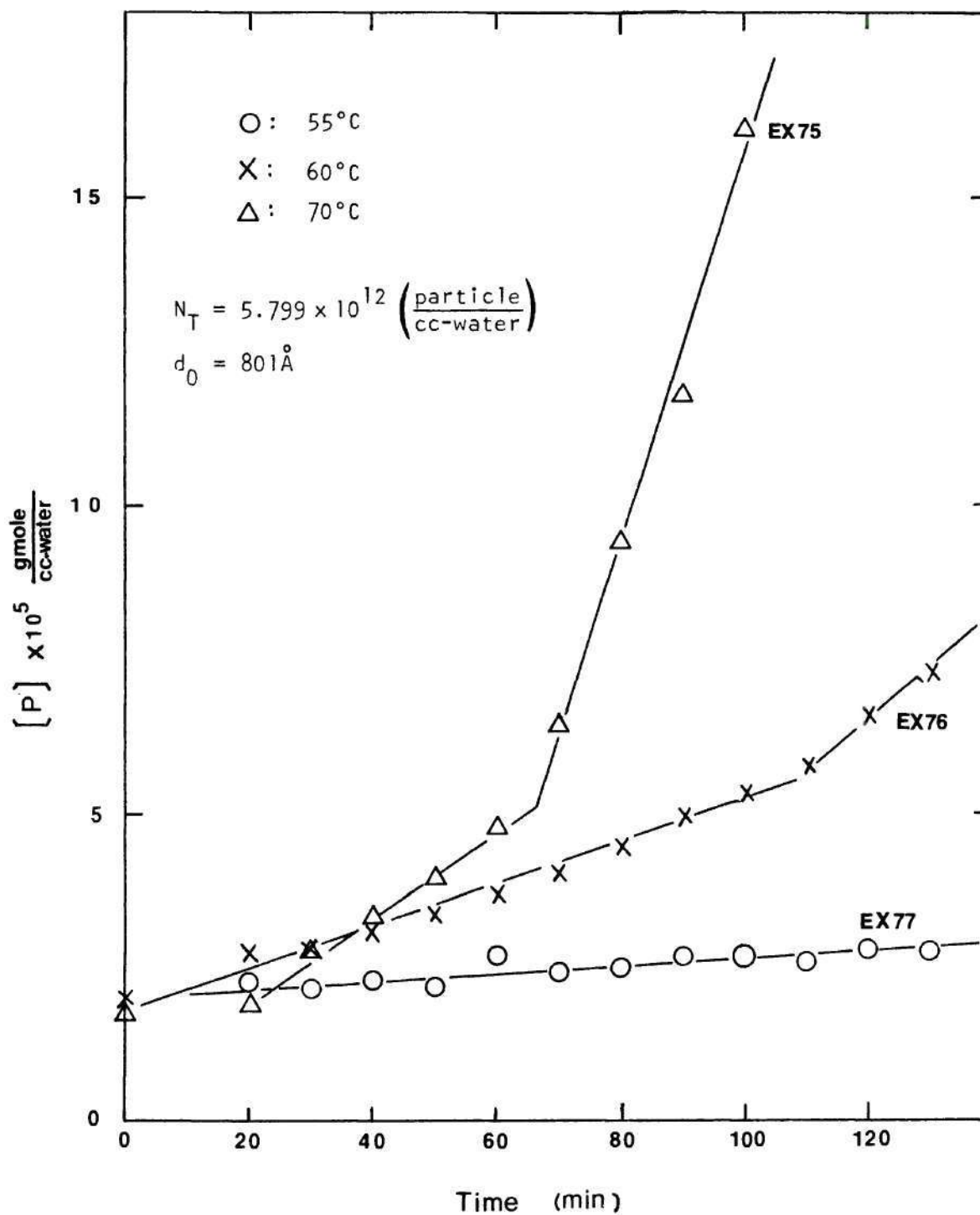


Figure 31. Effect of Temperature on the Relationship of $[P]$ vs. Time for MMA.

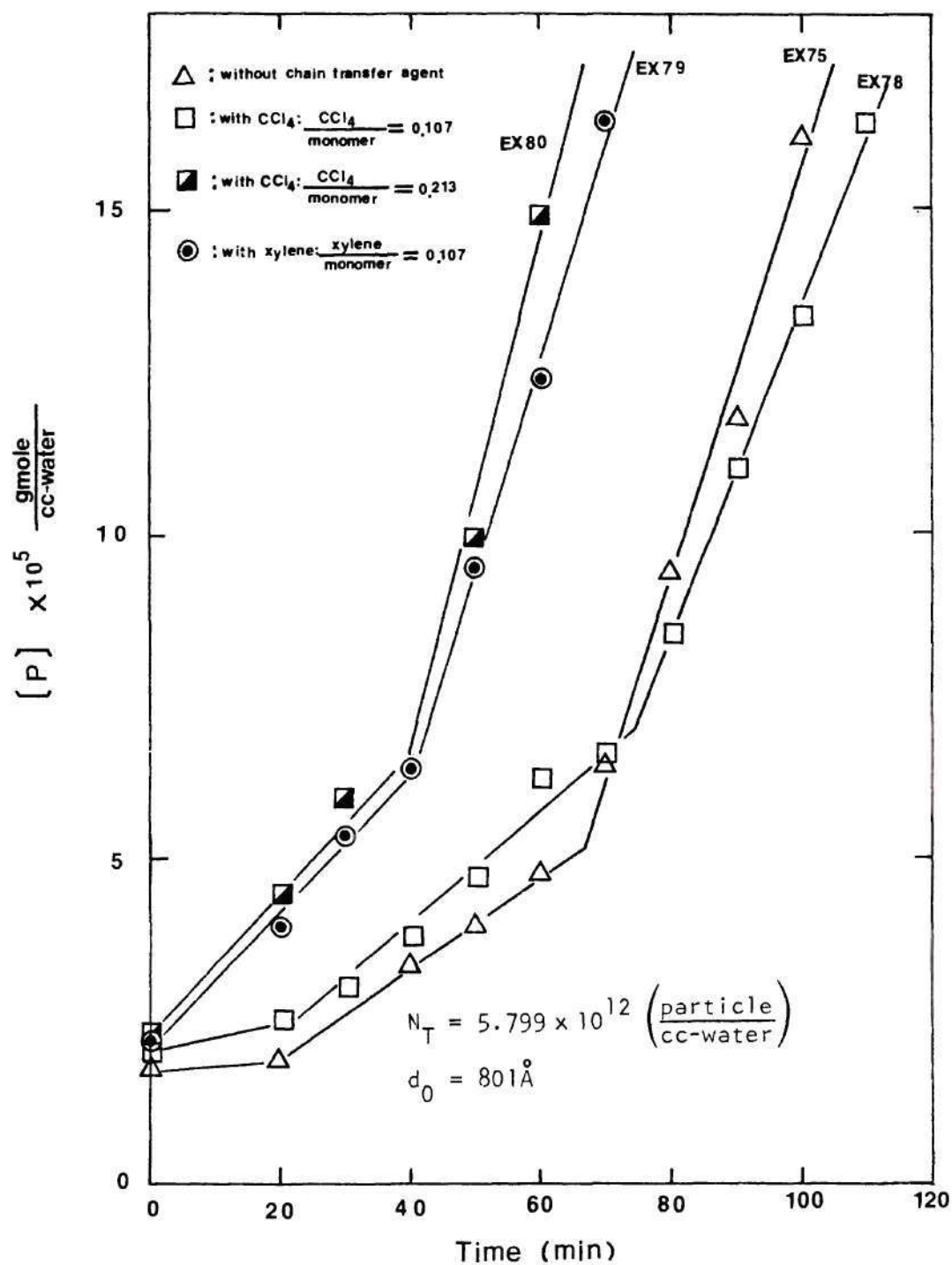


Figure 32. Effect of Chain Transfer Agents on the Relationship of $[P]$ vs. Time for MMA at 70°C .

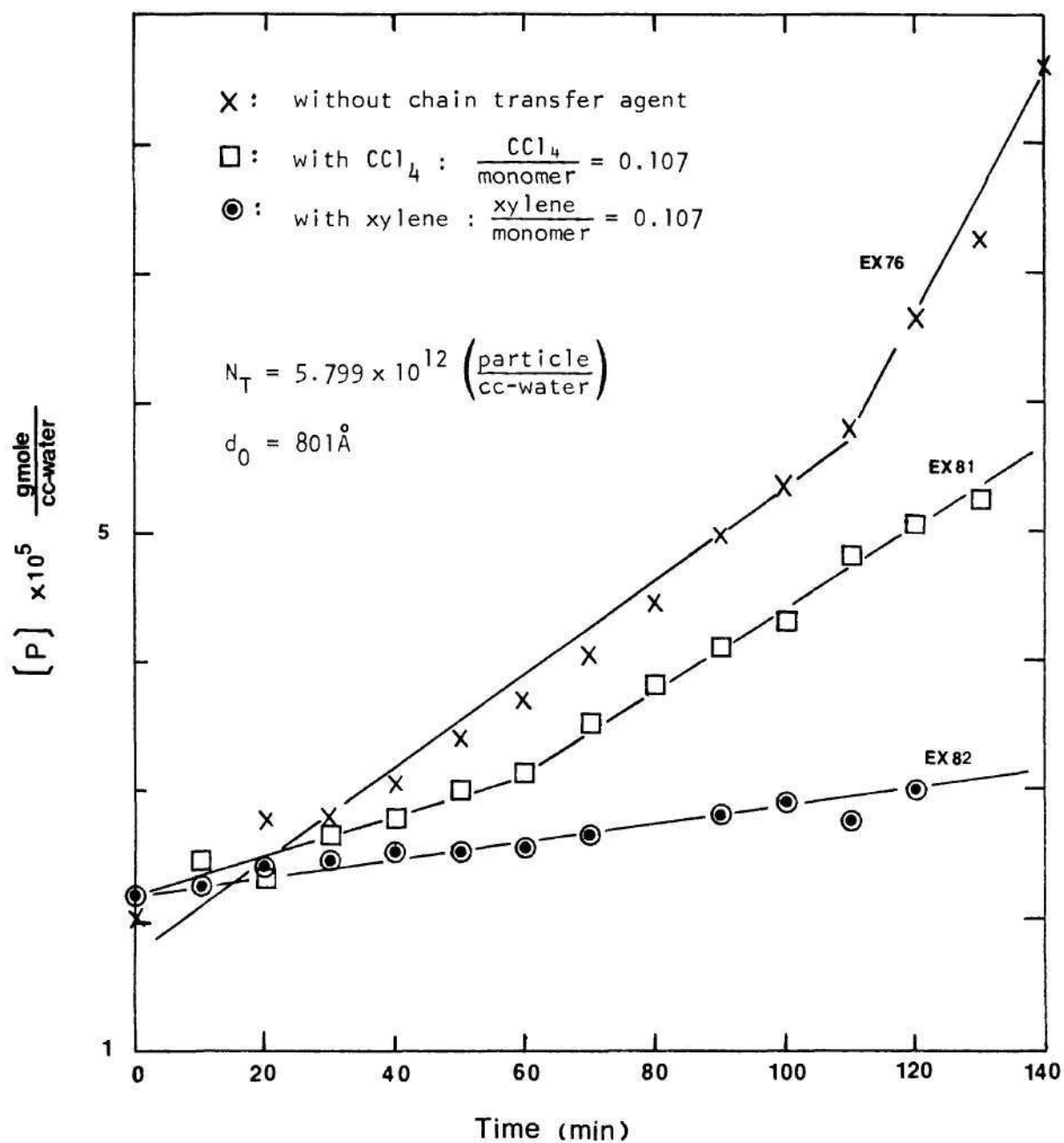


Figure 33. Effect of Chain Transfer Agents on the Relationship of $[P]$ vs. Time for MMA at 60°C .

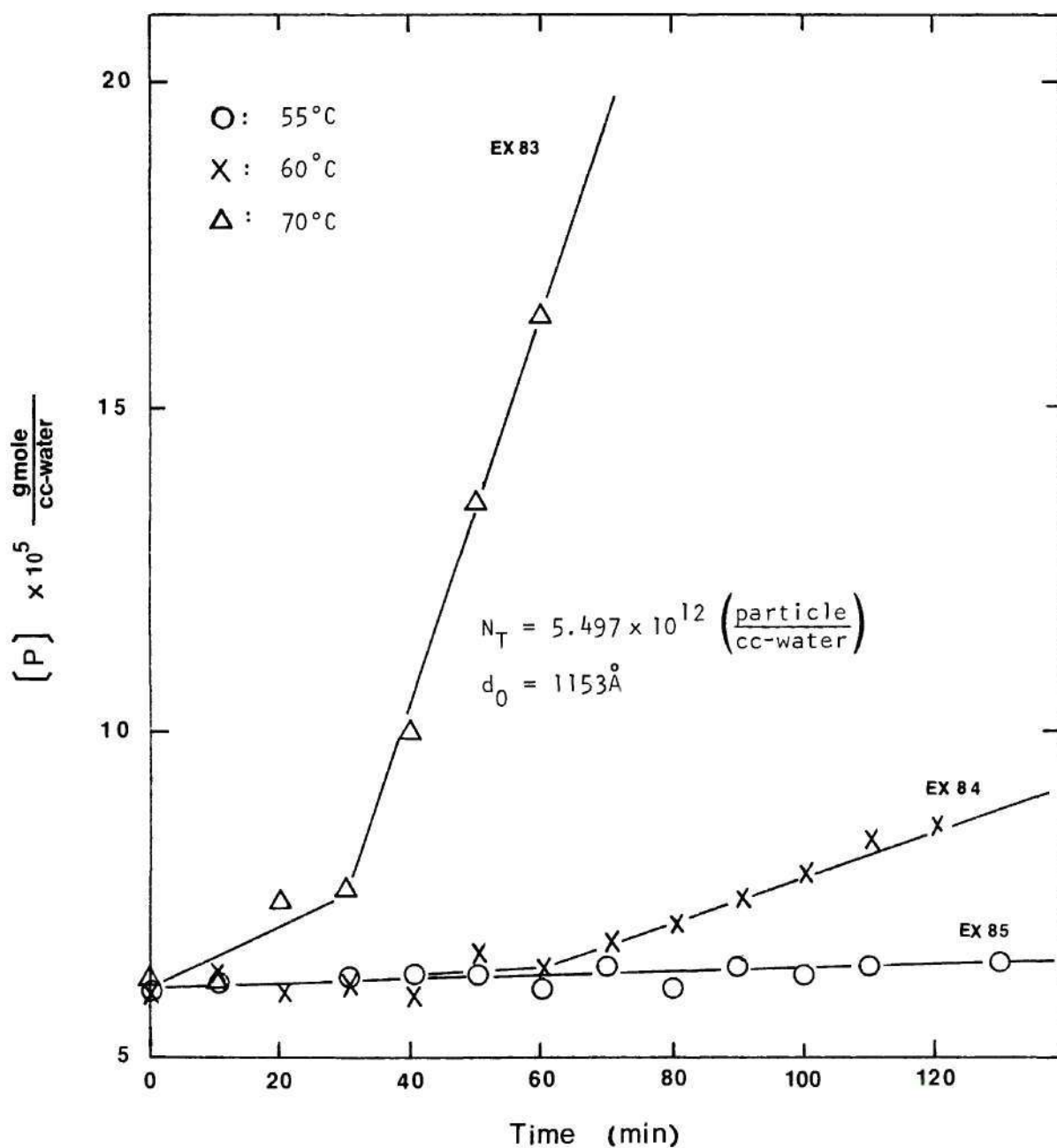


Figure 34. Effect of Temperature on the Relationship of $[P]$ vs. Time for MMA.

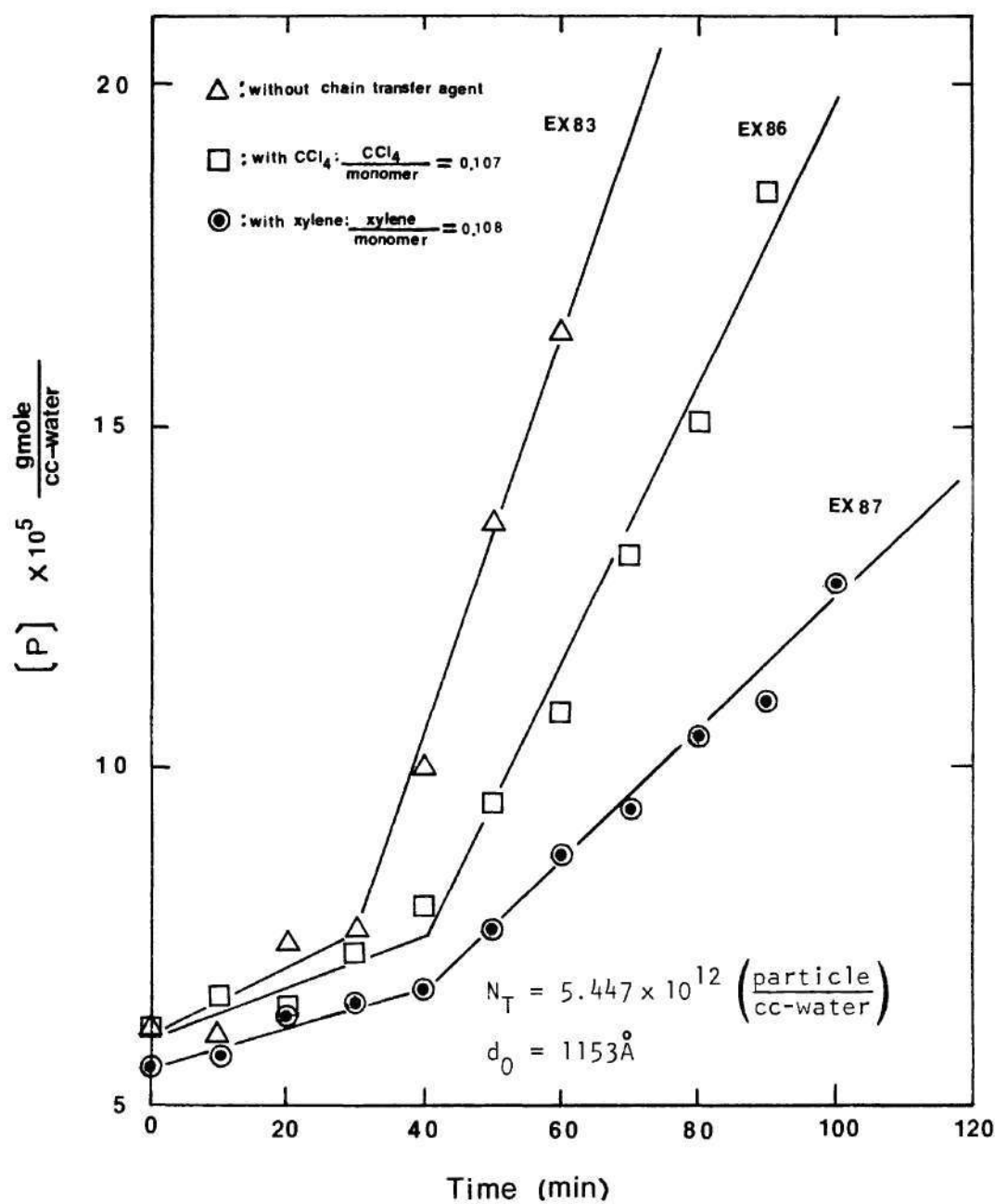


Figure 35. Effect of Chain Transfer Agents on the Relationship of $[P]$ vs. Time for MMA at 70°C .

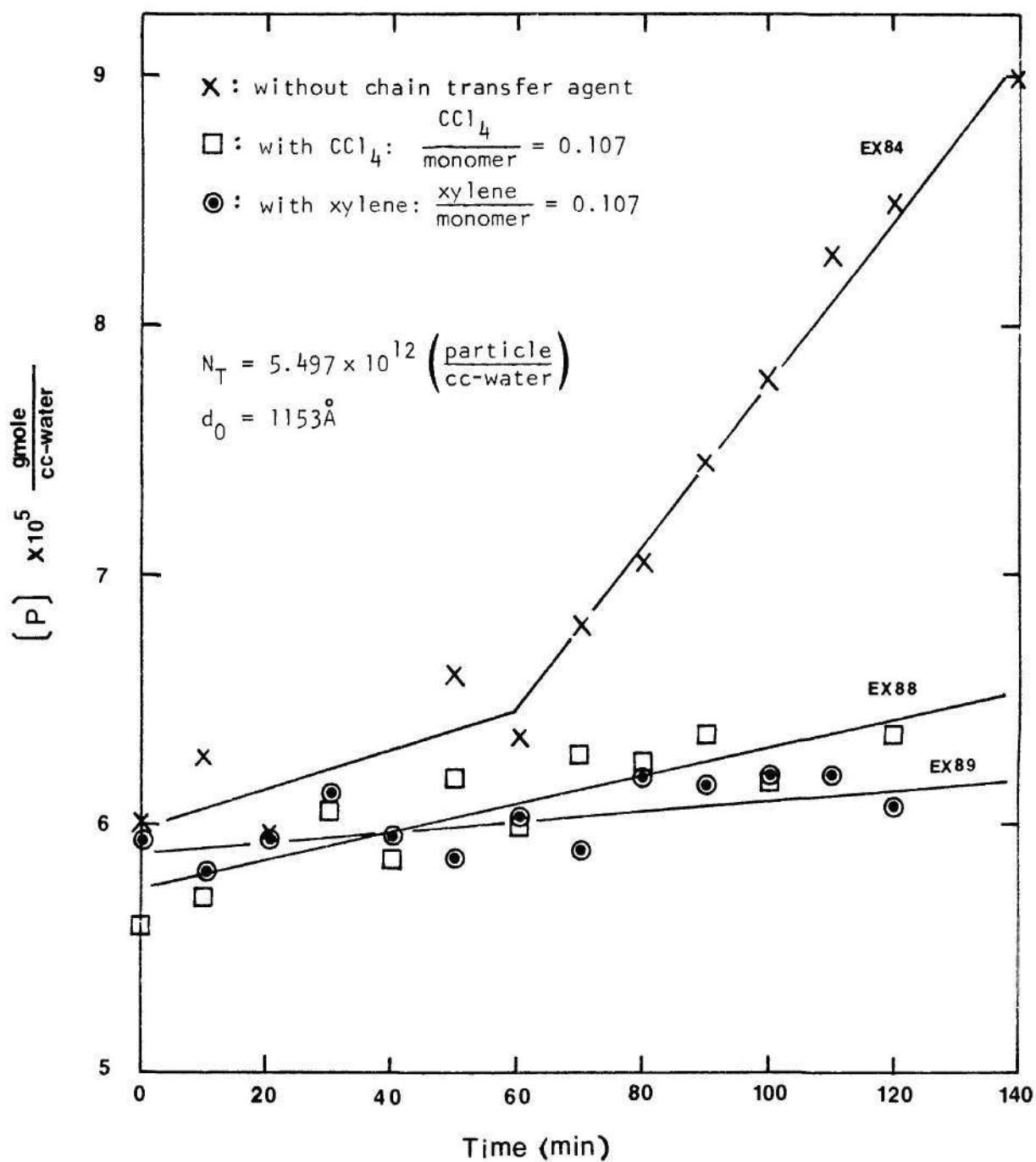


Figure 36. Effect of Chain Transfer Agents on the Relationship of $[P]$ vs. Time for MMA at 60°C .

The calculated values of \bar{n} are shown in Tables 8 and 9. The relationships of \bar{n} vs. d_0 (unswollen initial seed particle diameter) and \bar{n} vs. temperature are plotted in Figures 37 through 41. In the styrene system, \bar{n} increases as the initial seed particle diameter (d_0) increases at 50°C, 60°C and 70°C. On the other hand, in the MMA system, \bar{n} decreases as the initial seed particle diameter (d_0) increases at 55°C, 60°C and 70°C. The temperature effect for MMA is the same as for styrene. Sunberg [34], in his studies of seeded emulsion polymerization of styrene, reported trends which are quite similar to our results for styrene.

In our experiments, the seed polymerizations were carried out under the equilibrium swelling condition by the monomer except near the end of the polymerization. The limiting condition of the equilibrium swelling for MMA is that the $\frac{\text{monomer}}{\text{polymer}}$ wt. ratio must be over 0.59. As shown in the MMA polymerization experiments (Figures 28 through 36), an acceleration of the polymerization rate was observed. Since the polymerization of MMA is subject to a strong gel effect in bulk [40], it is not surprising that the same behavior is observed in emulsion polymerization. However, according to our results, the acceleration of the polymerization rate appeared under conditions of full equilibrium swelling. Zimmt [41] showed the same behavior occurred at less than 10% conversion; especially with large particles.

Table 8. Calculated Values of \bar{n} for Styrene.

	With/Without Chain Transfer Agent	\bar{n}		
		50°C	60°C	70°C
$D_0 = 814\text{\AA}$	Without Chain Transfer Agent	0.0556 (EX-28)	0.479 (EX-29)	0.634 (EX-30)
$N_T = 1.332 \times 10^{13}$	With Carbon Tetrachloride		0.540 (EX-37)	0.678 (EX-38)
$\left(\frac{\text{particle}}{\text{cc-water}}\right)$	With Xylene			0.448 (EX-51)
$D_0 = 1118\text{\AA}$	Without Chain Transfer Agent	0.390 (EX-31)	0.331 (EX-32)	0.732 (EX-33)
$N_T = 1.0758 \times 10^{13}$	With Carbon Tetrachloride			0.06* (EX-39) 0.732 0.181* First slope 0.605 (EX-40) Second slope 0.545 0.373* First slope 0.567 (EX-41) Second slope 0.454
$\left(\frac{\text{particle}}{\text{cc-water}}\right)$				
	With Xylene	0.0275 (EX-50)	0.307 (EX-44)	0.538 (EX-48)
$D_0 = 2250\text{\AA}$	Without Chain Transfer Agent	0.461 (EX-34)	1.628 (EX-35)	2.231 (EX-36)
$N_T = 3.058 \times 10^{12}$	With Carbon Tetrachloride			1.178 (EX-42)
$\left(\frac{\text{particle}}{\text{cc-water}}\right)$	With Xylene		0.851 (EX-45)	1.353 (EX-43)

*: $\frac{\text{CCl}_4}{\text{monomer}}$ weight ratio in the recipe

Table 9. Calculated Values of \bar{n} for MMA.

	\bar{n}					
	55°C	60°C	70°C			
With/Without Chain Transfer Agent	First Slope	First Slope	Second Slope	First Slope	Second Slope	
$D_0 = 645\text{\AA}$						
Without Chain Transfer Agent	0.0466 (EX-70)	0.114 (EX-69)		2.733×10^{-4} *	0.306×10^{-4} * (EX-68) 2.733×10^{-4} *	1.017 (EX-68) 0.850×10^{-4} * (EX-67)
$N_T = 6.5688 \times 10^{13}$						
(particle/cc-water)						
With Carbon Tetrachloride		0.0936 (EX-73)			0.277 (EX-71)	0.528 (EX-71)
With Xylene		0.0318 (EX-74)			0.237 (EX-72)	0.452 (EX-72)
$D_0 = 801\text{\AA}$						
Without Chain Transfer Agent	0.0295 (EX-77)	0.136 (EX-76)	0.290 (EX-76)		0.206 (EX-75)	0.931 (EX-75)
$N_T = 5.799 \times 10^{12}$						
(particle/cc-water)						
With Carbon Tetrachloride		0.0598 (EX-81)	0.123 (EX-81)	0.107**	0.212 (EX-78)	0.743 (EX-78)
With Xylene		0.0239 (EX-82)		0.213**	0.321 (EX-80)	1.265 (EX-80)
$D_0 = 1153\text{\AA}$						
Without Chain Transfer Agent	0.0112 (EX-85)	0.0246 (EX-84)	0.143 (EX-84)		0.172 (EX-83)	1.401 (EX-83)
$N_T = 5.497 \times 10^{12}$						
(particle/cc-water)						
With Carbon Tetrachloride		0.0213 (EX-88)			0.127 (EX-86)	0.610 (EX-86)
With Xylene		0.0090 (EX-89)			0.095 (EX-87)	0.294 (EX-87)
*: Initiator Monomer	weight ratio in the recipe.			CCl ₄ Monomer	**:	weight ratio in the recipe.

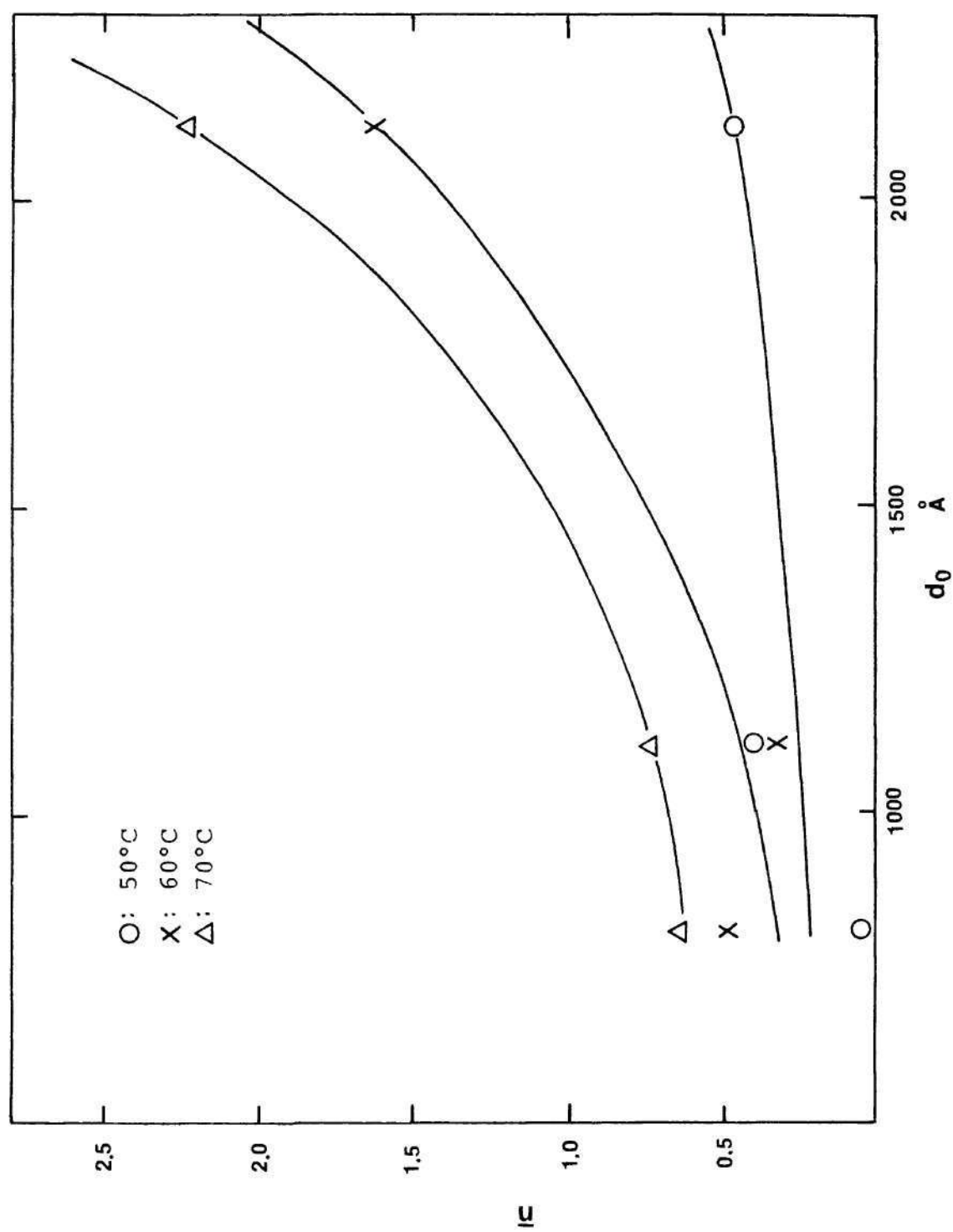


Figure 37. Relationship of \bar{n} vs. d_0 for Styrene.

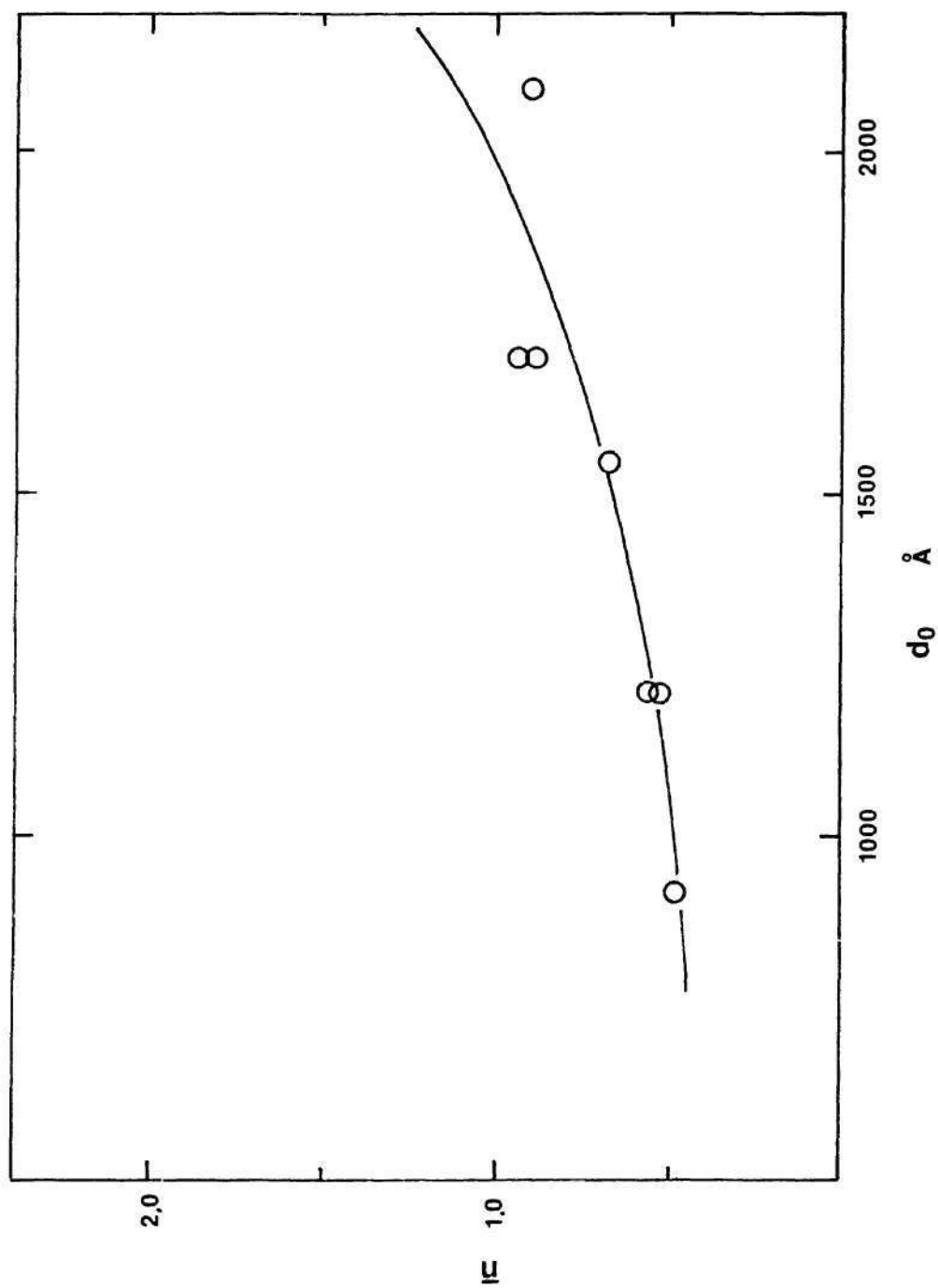


Figure 38. Relationship of \bar{n} vs. d_0 for Styrene from Sundberg's Experiments at 50°C.

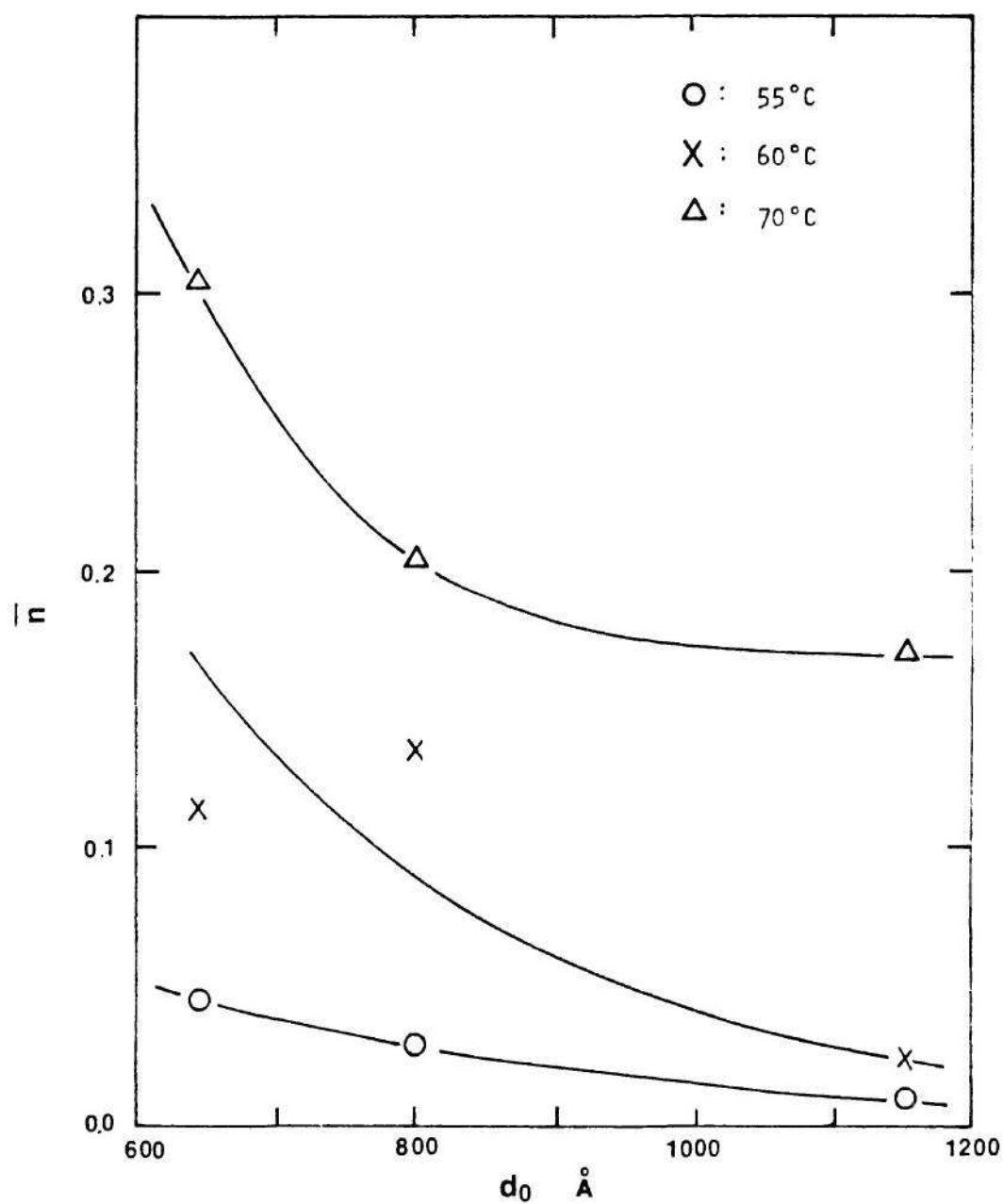


Figure 39. Relationship of \bar{n} vs. d_0 for MMA by Plotting Values of First Slope.

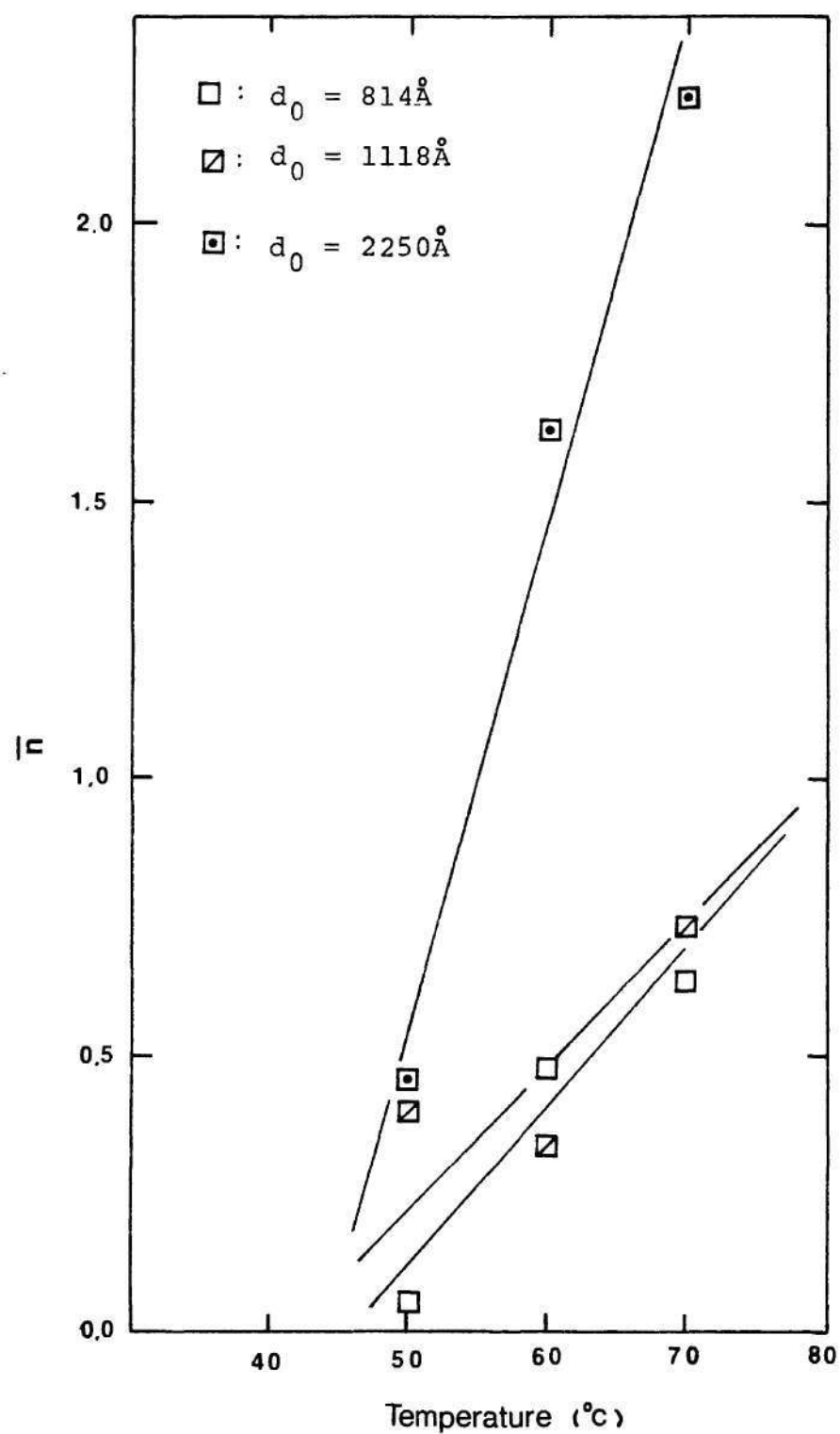


Figure 40. Relationship of \bar{n} vs. Temperature for Styrene.

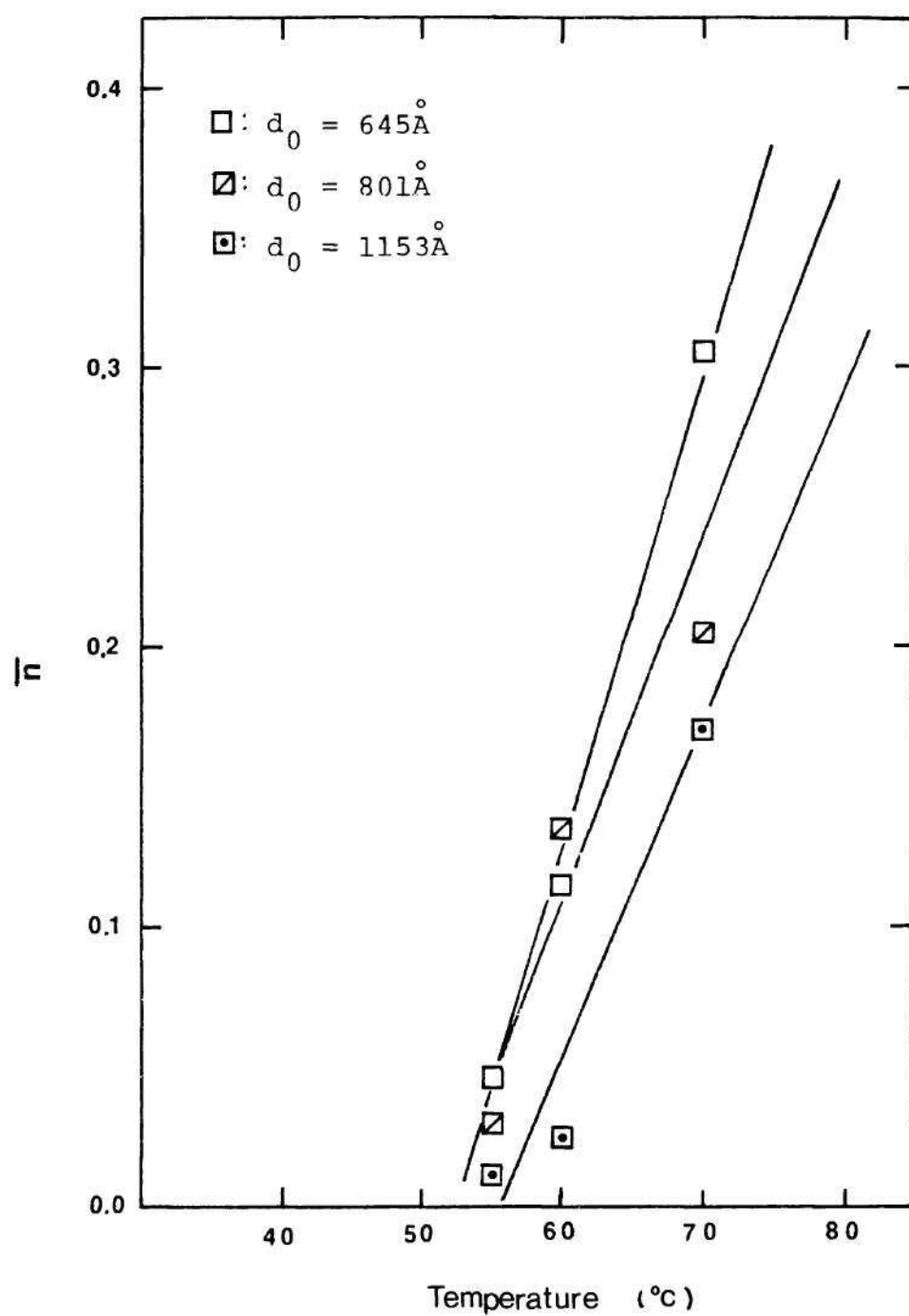


Figure 41. Relationship of \bar{n} vs. Temperature for MMA.

The causes of the above behavior in MMA emulsion polymerization are not clearly explained. However, generally the following reasons are considered:

- 1) Slow mutual termination rate of free radicals in the polymer particle: If the monomer concentration in the polymer particle $[M]_p$ is assumed as a constant, the viscosity of the monomer layer on the core polymer particle doesn't change. Therefore, the mutual termination rate of free radicals is decreased for reasons other than high viscosity. If the swollen polymer particle has a layer of the oligomers on the core, the free radicals may be trapped in that layer and the movement of these free radicals would be restricted. This restriction causes a decrease in the mutual termination rate. A layer of MMA oligomers would be more easily formed than a similar styrene layer because the propagation rate constant of MMA ($616.16 \frac{l}{gmole \cdot sec}$ at $60^\circ C$) is much higher than that ($174.43 \frac{l}{gmole \cdot sec}$ at $60^\circ C$) of styrene. Melville and Horie [42,43] reported that trapped free radicals initiated block copolymerization when another monomer was added without any additional initiator. If $[M]_p$ is increased as the polymer particle diameter increases, the volume in which the free radicals can move is increased. This could also cause a decrease in the mutual termination

rate of free radicals.

- 2) MMA monomer is dissolved into the water phase much more than styrene monomer as follows:

Styrene 0.0271 wt% (25°C) [44] or $0.005 \frac{\text{gmole}}{\ell}$ [39]

MMA 1.59 wt% (20°C) [45] or $0.15 \frac{\text{gmole}}{\ell}$ [39]

If the polymerization of the monomer dissolved in the water phase is retarded by oxygen or other retarders, the rate of polymerization will be simply accelerated when retarders are depleted. Schulz [46] demonstrated that methacrylate free radicals react rapidly with oxygen in the water phase.

Theoretical Kinetic Model

The elemental chemical/physical processes which effect the polymerization have been studied by a number of workers [47,48,49] and are defined as follows:

- (1) Decomposition of initiator in the water phase

$$r_i = 2 \cdot k_{di} \cdot f \cdot [I] \quad (46)$$

where r_i : generation rate of radicals in the water phase $\left(\frac{\text{molecule}}{\text{cc-water} \cdot \text{sec}} \right)$

k_{di} : decomposition rate constant of
initiator $\left(\frac{1}{\text{sec}}\right)$

f : efficiency of initiator in
initiating polymerization

$[I]$: concentration of initiator
 $\left(\frac{\text{molecule}}{\text{cc-water}}\right)$

- (2) Bimolecular termination of free radicals in the water phase

$$r_{tw} = 2 \cdot k_{tw} \cdot [R\cdot]_w^2 \quad (47)$$

where r_{tw} : termination rate of free radicals
in the water phase $\left(\frac{\text{molecule}}{\text{cc-water} \cdot \text{sec}}\right)$

$[R\cdot]_w$: free radical concentration in the
water phase $\left(\frac{\text{molecule}}{\text{cc-water}}\right)$

k_{tw} : termination rate constant in the
water phase $\left(\frac{l}{\text{molecule} \cdot \text{sec}}\right)$

- (3) Free radicals in the water phase enter into a micelle which contains monomer and initiates the polymerization. The micelle is converted to a polymer particle.

$$r_{\text{poly} \cdot \text{particle}} = k_l \cdot M_s \cdot [R\cdot]_w \quad (48)$$

where $r_{\text{poly} \cdot \text{particle}}$: generation rate of

$$\begin{aligned}
 & \text{polymer particles } \left(\frac{\text{number}}{\text{cc-water} \cdot \text{sec}} \right) \\
 k_1: & \text{ rate constant for free radical} \\
 & \text{entry into micelles } \left(\frac{\text{cc-water}}{\text{number} \cdot \text{sec}} \right) \\
 M_s: & \text{ micelle concentration in the water} \\
 & \text{phase } \left(\frac{\text{number}}{\text{cc-water}} \right)
 \end{aligned}$$

k_1 can be calculated as follows, if it is assumed that the boundary layer thickness of a micelle is equal to the radius of micelle.

$$k_1 = 2\pi \cdot D_w \cdot d_m \quad (49)$$

where d_m : diameter of micelle (cm)

D_w : free radical diffusion coefficient
in the water phase $\left(\frac{\text{cm}^2}{\text{sec}} \right)$

- (4) Polymer particles which contain n free radicals are converted into polymer particles which contain $(n+1)$ free radicals. The rate r_{n+1} is:

$$r_{n+1} = k_2 \cdot N_n \cdot [R\cdot]_w \quad (50)$$

where r_{n+1} : $\left(\frac{\text{number}}{\text{cc-water} \cdot \text{sec}} \right)$

k_2 : rate constant of free radicals
entry into polymer particle
 $\left(\frac{\text{cc-water}}{\text{molecule} \cdot \text{sec}} \right)$

k_2 can be obtained the same as k_1 ,

$$k_2 = 2\pi \cdot D_w \cdot d_{ps} \quad (51)$$

where d_{ps} : diameter of swollen polymer particle
 $\left(\frac{\text{cm}}{\text{particle}}\right)$

- (5) In a polymer particle, the radicals react with monomer via the propagation reaction. The monomer reaction rate r_{mp} is:

$$r_{mp} = k_p \cdot [M]_p \cdot \bar{n} \cdot N_T = k_p \cdot [M]_p \sum_{n=0}^{\infty} n N_n \quad (52)$$

where k_p : propagation rate constant in the
 polymer particle $\left(\frac{\ell}{\text{gmole} \cdot \text{sec}}\right)$

$[M]_p$: monomer concentration in the $\left(\frac{\text{gmole}}{\ell}\right)$
 polymer particle

- (6) The radicals which exist in the water phase react with the monomer which is dissolved in the water phase.

$$r_{wp} = k_{pw} \cdot [M]_w \cdot [R\cdot]_w \quad (53)$$

where r_{wp} : monomer reaction rate in the water
 phase $\left(\frac{\text{molecule}}{\text{cc-water} \cdot \text{sec}}\right)$

k_{pw} : propagation rate constant in the
 water phase $\left(\frac{\ell}{\text{gmole} \cdot \text{sec}}\right)$

$[M]_w$: monomer concentration in the water

$$\text{phase} \left(\frac{\text{gmole}}{\ell} \right)$$

- (7) Two free radicals can be extinguished by mutual termination in a polymer particle which contains n free radicals. A polymer particle which contains $(n - 2)$ free radicals is produced by this process.

$$r_{\text{mtp}} = k_{\text{mtp}} \cdot \frac{n(n-1) \cdot N_n}{v_{\text{ps}} \cdot N_A} \quad n \geq 2 \quad (54)$$

where k_{mtp} : mutual termination reaction rate constant $\left(\frac{\ell}{\text{molecule} \cdot \text{sec}} \right)$

v_{ps} : volume of swollen polymer particle $\left(\frac{\ell}{\text{particle}} \right)$

$\frac{(n-1)}{v_{\text{ps}}}$: concentration of free radicals with which any of n free radicals in a locus can react.

- (8) Chain transfer reactions between free radicals and monomer or chain transfer agents can also occur in a polymer particle. Monomer free radicals or chain transfer agent radicals are generated.

$$r_{\text{ct}} = \left\{ k_{\text{mct}} \cdot [M]_p + k_{\text{c.ct}} [CT]_p \right\} \cdot \sum_{n=0}^{\infty} n \cdot N_n \quad (55)$$

where r_{ct} : chain transfer reaction rate
 $\left(\frac{\text{molecule}}{\text{cc-water} \cdot \text{sec}} \right)$
 k_{mct} : chain transfer reaction rate constant to monomer $\left(\frac{l}{\text{gmole} \cdot \text{sec}} \right)$
 $k_{c \cdot ct}$: chain transfer reaction rate constant to chain transfer agent
 $\left(\frac{l}{\text{gmole} \cdot \text{sec}} \right)$
 $[CT]_p$: concentration of chain transfer agent $\left(\frac{\text{gmole}}{l} \right)$

- (9) Polymer particles which contain n free radicals are converted to polymer particles which contain $(n-1)$ free radicals by the desorption of a free radical from the polymer particle,

$$r_d = k_0 \cdot A_p \cdot \left(\frac{n}{v_{ps}} \right) \cdot N_n \equiv k_d \cdot n \cdot N_n \quad (56)$$

where r_d : desorption rate of free radicals
 $\left(\frac{\text{molecule}}{\text{cc-water} \cdot \text{sec}} \right)$
 A_p : surface area of the swollen polymer particle $\left(\frac{\text{cm}^2}{\text{particle}} \right)$
 v_{ps} : volume of the swollen polymer particle
 $\frac{n}{v_{ps}}$: concentration of free radicals
 k_0 : specific rate constant in the

desorption process $\left(\frac{\text{cm}}{\text{sec}}\right)$
 k_d : desorption rate constant $\left(\frac{1}{\text{sec}}\right)$

The following material balances, based on the above nine polymerization processes, are set up for seeded emulsion polymerization.

- (1) Material balance of free radicals in the water phase. The change of free radicals in the water phase is expressed by using Eqs. (46,47, 50,53,56) as follows:

$$\frac{d[R\cdot]_w}{dt} = r_i - r_{tw} + r_d - r_{n+1} - r_{wp} \quad (57)$$

Eq. (57) is rearranged to be

$$\begin{aligned} \frac{d[R\cdot]_w}{dt} = & 2 \cdot k_{di} \cdot f \cdot [I] \cdot N_A - 2 \cdot k_{tw} \cdot [R\cdot]_w^2 \\ & + k_d (N_1 + 2N_2) - k_2 \cdot N_T \cdot [R\cdot]_w \cdot \frac{1}{N_A} \\ & - k_{pw} \cdot [M]_w \cdot [R\cdot]_w \end{aligned} \quad (58)$$

- (2) Material balance of polymer particles, N_1 , which contain one free radical:

$$\frac{dN_1}{dt} = \frac{k_2 \cdot N_0 \cdot [R\cdot]_w}{N_A} + 2 \cdot k_d \cdot N_2$$

$$- \frac{k_2 \cdot N_1 \cdot [R\cdot]_w}{N_A} - k_d \cdot N_1 \quad (59)$$

- (3) Material balance of polymer particles, N_2 , which contain two free radicals:

$$\frac{dN_2}{dt} = \frac{k_2 \cdot N_1 \cdot [R\cdot]_w}{N_A} - 2 \cdot \frac{k_{mtp}}{v_{ps} \cdot N_A} \cdot N_2 - 2 \cdot k_d \cdot N_2 \quad (60)$$

The values of N_1 and N_2 can be calculated with Eq. (58), Eq. (59), and Eq. (60) at steady state since the derivatives are zero. The average number of free radicals, \bar{n} , can be calculated from the value of N_1 and N_2 at the specified value of k_d as follows:

$$\bar{n} = \frac{\sum_{n=1}^{\infty} n \cdot N_n}{N_T} \approx \frac{N_1 + 2 \cdot N_2}{N_T} \quad (61)$$

Several assumptions were utilized in the above treatment.

Assumption 1: The number of free radicals in the polymer particles is a maximum of two. The particle population consists of particles which do not contain free radicals (N_0), particles which contain one free radical (N_1) and particles which contain two free radicals (N_2).

Assumption 2: The bimolecular termination of free radicals in the water phase can be neglected. This assumption is made even though Napper and Gilbert [33] point out that the

mutual termination of oligomeric free radicals in the water phase is increased significantly as the initiator concentration increases. As pointed out by Flory [50], the average lifetime of a radical from generation to capture by a polymer particle or micelle must be of the order of 10^{-5} sec. On the other hand, taking a typical value for the mutual termination rate constant of free radicals, $k_t = 5 \times 10^{-14} \left(\frac{\text{cm}^3}{\text{molecule} \cdot \text{sec}} \right)$, and assuming a stationary concentration of 10^8 radicals per cc-water, the rate loss of free radicals of termination appears to be many orders of magnitude less than the rate of generation of free radicals, $r_i = 6.0 \times 10^{11} \left(\frac{\text{molecule}}{\text{cc-water} \cdot \text{sec}} \right)$.

$$r_{tw} = 2 \cdot k_t \cdot [R\cdot]_w^2 = 2 \times 5 \times 10^{-14} \times [10^8]^2 = 10^3 \left(\frac{\text{molecule}}{\text{cc-water} \cdot \text{sec}} \right)$$

Thus, r_i is much larger than r_{tw} and mutual termination in the water phase can be ignored.

There is a second reason for neglecting water-phase termination of free radicals. When the decomposition rate constant of an initiator, k_{di} , is determined [51], the mutual termination of initiator free radicals occurs, at least to some extent, in the water phase. Thus, the value of k_{di} obtained experimentally already includes the effect of the mutual termination of initiator free radicals. If the experimental value of k_{di} is used in our kinetic treatment, the mutual termination rate of free radicals in

the water phase is neglected as shown below.

$$r_{i_ACTUAL} - r_{tw} \approx r_{i_EXPERIMENTAL} = 2fk_{di}[I]$$

Assumption 3: Unimolecular termination between free radicals and emulsifier or other ingredients is neglected.

If mutual termination of free radicals in the water phase is neglected, Eq. (58), at steady state, can be written as:

$$\begin{aligned} \frac{d[R\cdot]_w}{dt} = & - \left\{ \frac{k_2 \cdot N_T}{N_A} + k_{pw} \cdot [M]_w \right\} [R\cdot]_w + k_d \cdot (N_1 + 2N_2) \\ & + 2 \cdot k_{di} \cdot f \cdot [I] \cdot N_A = 0 \end{aligned} \quad (62)$$

$[R\cdot]_w$ is obtained from Eq. (62) to be:

$$[R\cdot]_w = \frac{k_d \cdot (N_1 + 2N_2) + 2 \cdot k_{di} \cdot f \cdot [I] \cdot N_A}{\frac{k_2 \cdot N_T}{N_A} + k_{pw} \cdot [M]_w} \quad (63)$$

Substituting $N_0 \approx N_T - N_1 - N_2$ and $[R\cdot]_w$ from Eq. (63) into Eq. (59) at steady state yields the following relationship.

$$\begin{aligned} \frac{dN_1}{dt} = & \frac{k_d(N_1 + 2N_2) + 2 \cdot k_{di} \cdot f \cdot [I] \cdot N_A}{k_2 \cdot N_T + k_{pw} \cdot [M]_w \cdot N_A} (k_2 \cdot N_T - 2 \cdot k_2 \cdot N_1 \\ & - k_2 \cdot N_2) + k_d(N_1 + 2N_2) = 0 \end{aligned} \quad (64)$$

Also, at steady state, Eq. (60) can be rewritten by substituting for $[R\cdot]_w$ as follows:

$$\frac{dN_2}{dt} = \frac{k_2 \cdot N_1 (k_d \cdot N_1 + 2 \cdot k_d \cdot N_2 + 2 \cdot k_{di} \cdot f \cdot [I] \cdot N_A)}{k_2 \cdot N_T + k_{pw} \cdot [M]_w \cdot N_A} - \left(2 \cdot \frac{k_{mtp}}{v_{ps} \cdot N_A} + 2 \cdot k_d \right) N_2 = 0 \quad (65)$$

Thus, \bar{n} can be calculated for a fixed value of k_d by solving nonlinear algebraic equations like Eq. (64) and Eq. (65). The calculation method, which utilizes a computer, is shown in Appendix 6. The results are shown in Figures 42 through 47. Thus, values of k_d can be obtained from the experimental value of \bar{n} . The results of these calculations are shown in Table 10 and Table 11.

Temperature Effect on k_d

The value of k_d tends to decrease with increases in the polymerization temperature for styrene and MMA. When chain transfer agents are added, k_d increases. In the case of bulk polymerization, like the polymerization locus in emulsion polymerization, the viscosity of the system becomes high as the polymerization conversion increases. The high viscosity causes low mobility of the free radicals in the polymer particles. Therefore, the desorption of the free radical is eventually retarded by the higher

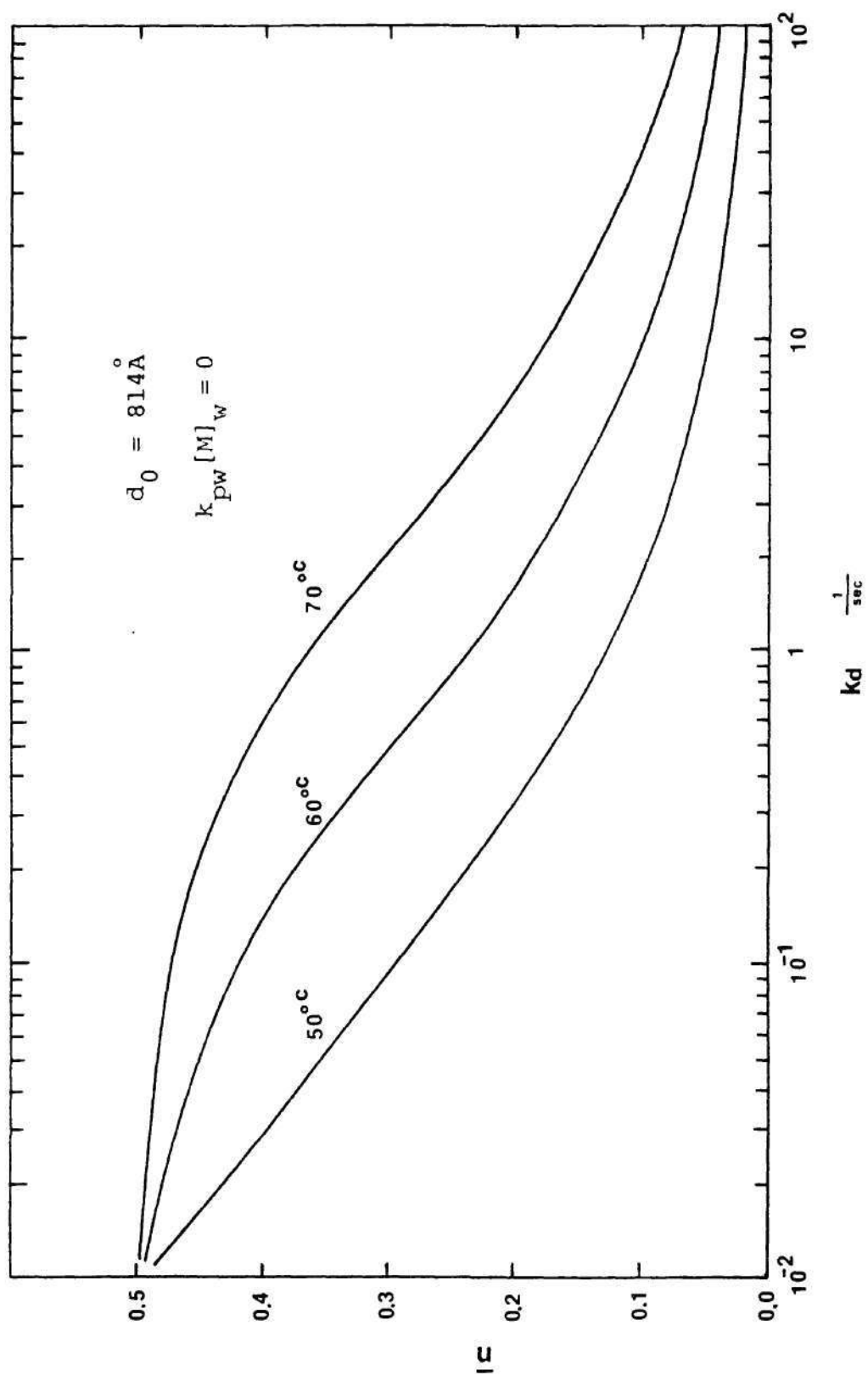


Figure 42. Relationship Between \bar{n} vs. k_d (Styrene) at 50°C, 60°C and 70°C.

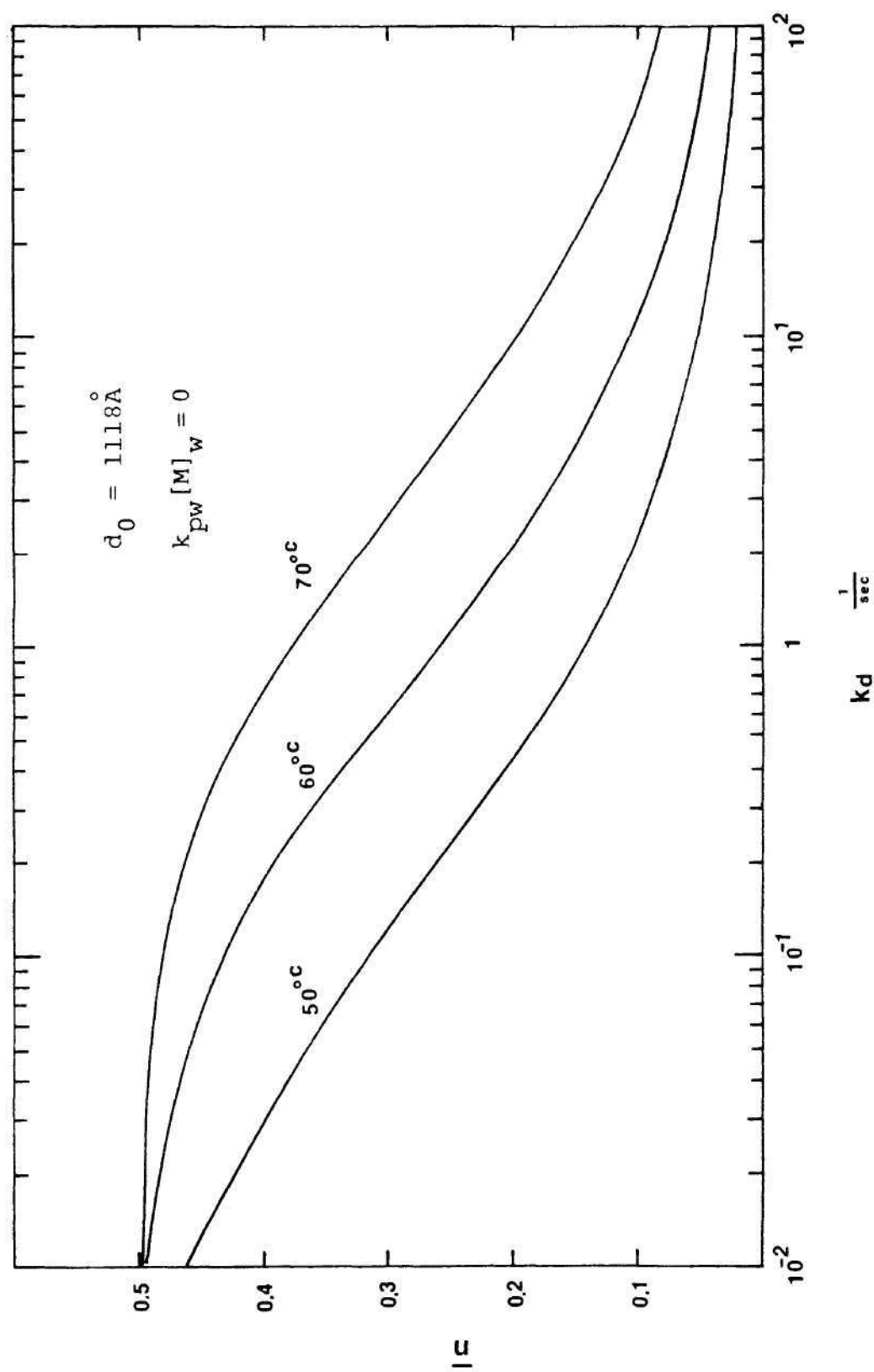


Figure 43. Relationship Between \bar{n} vs. k_d (Styrene) at 50°C , 60°C and 70°C .

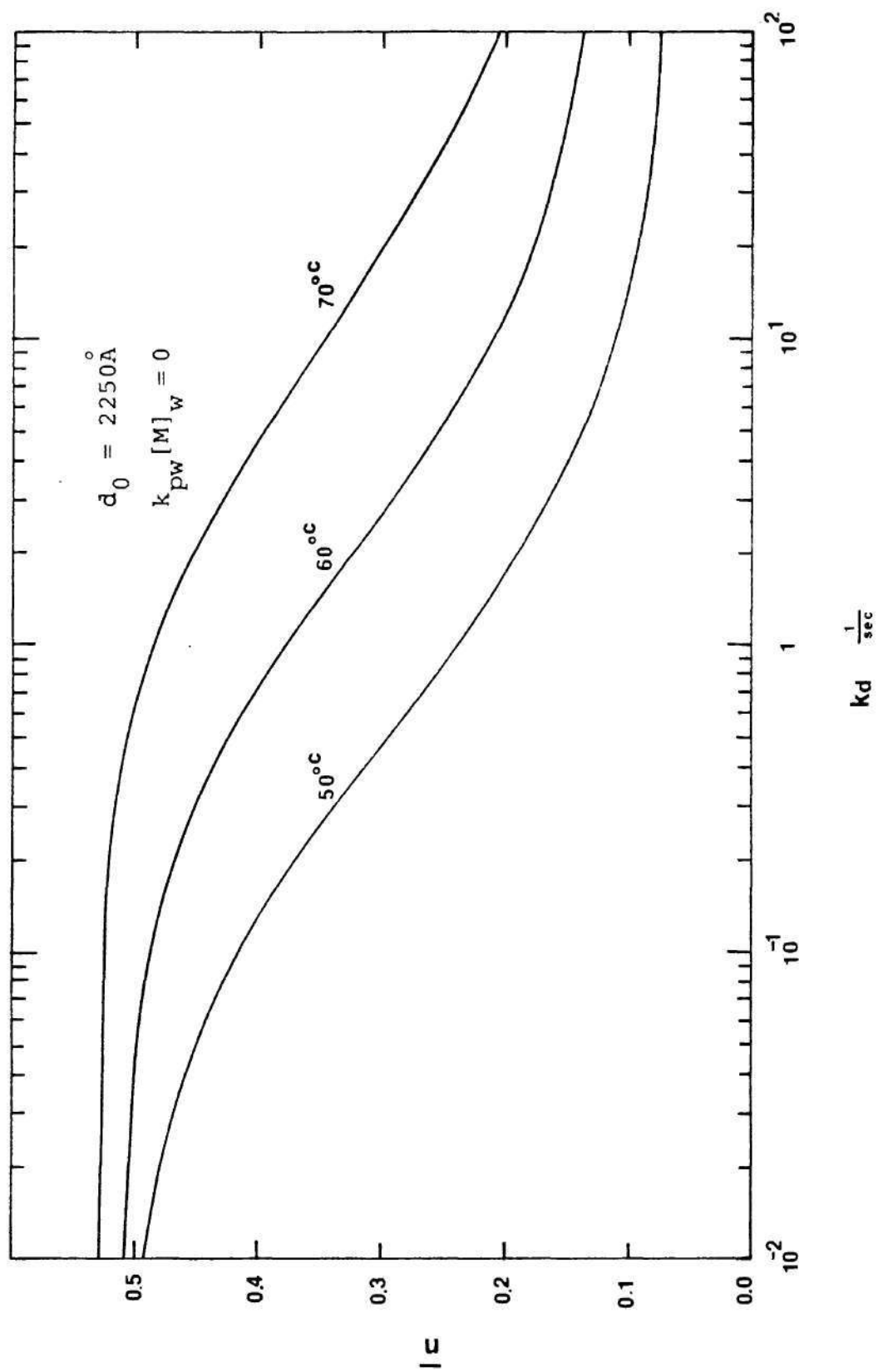


Figure 44. Relationship Between $\bar{\eta}$ vs. k_d (Styrene) at 50°C, 60°C and 70°C.

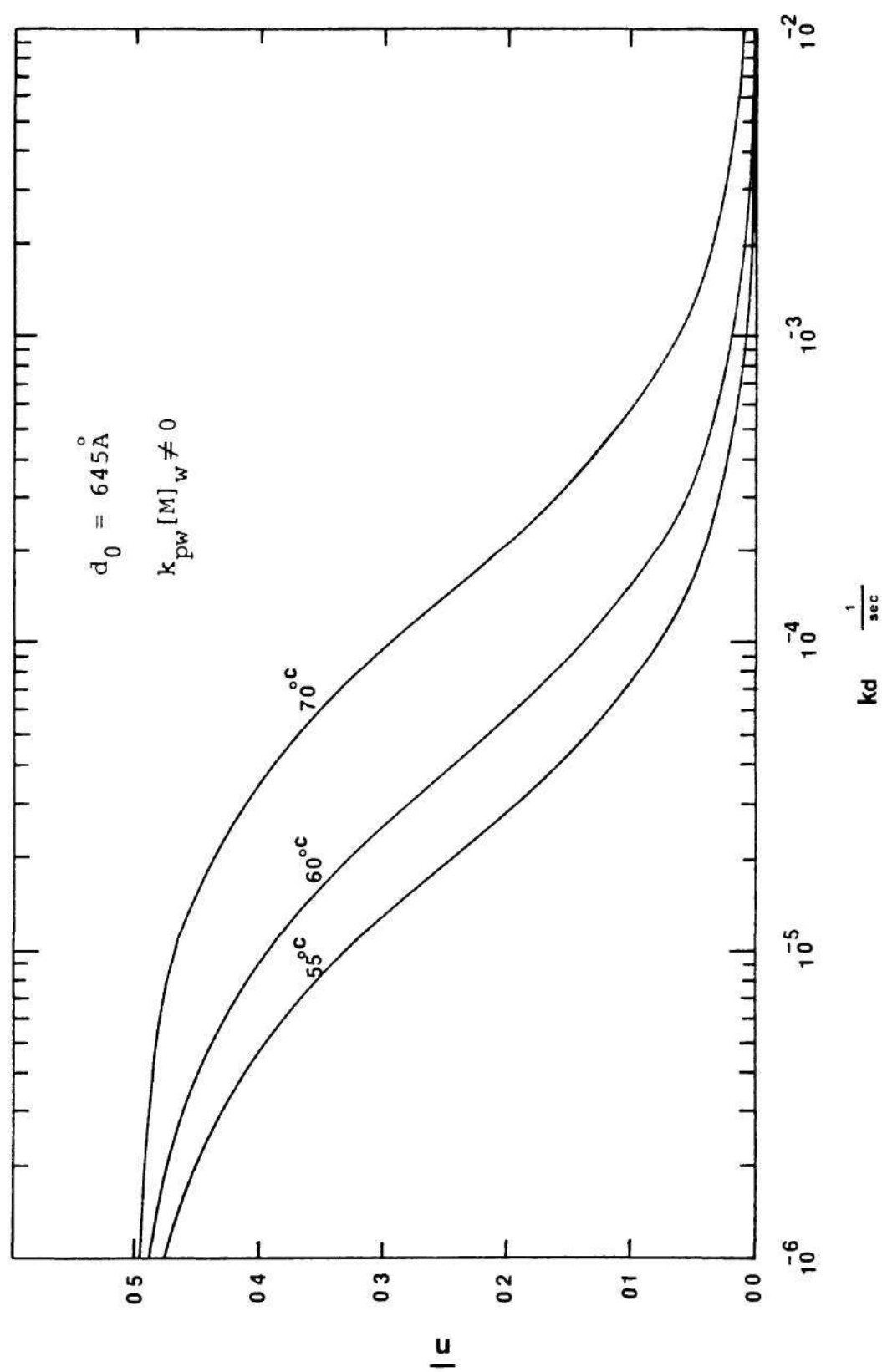


Figure 45. Relationship Between \bar{n} vs. k_d (MMA) at 55°C, 60°C and 70°C.

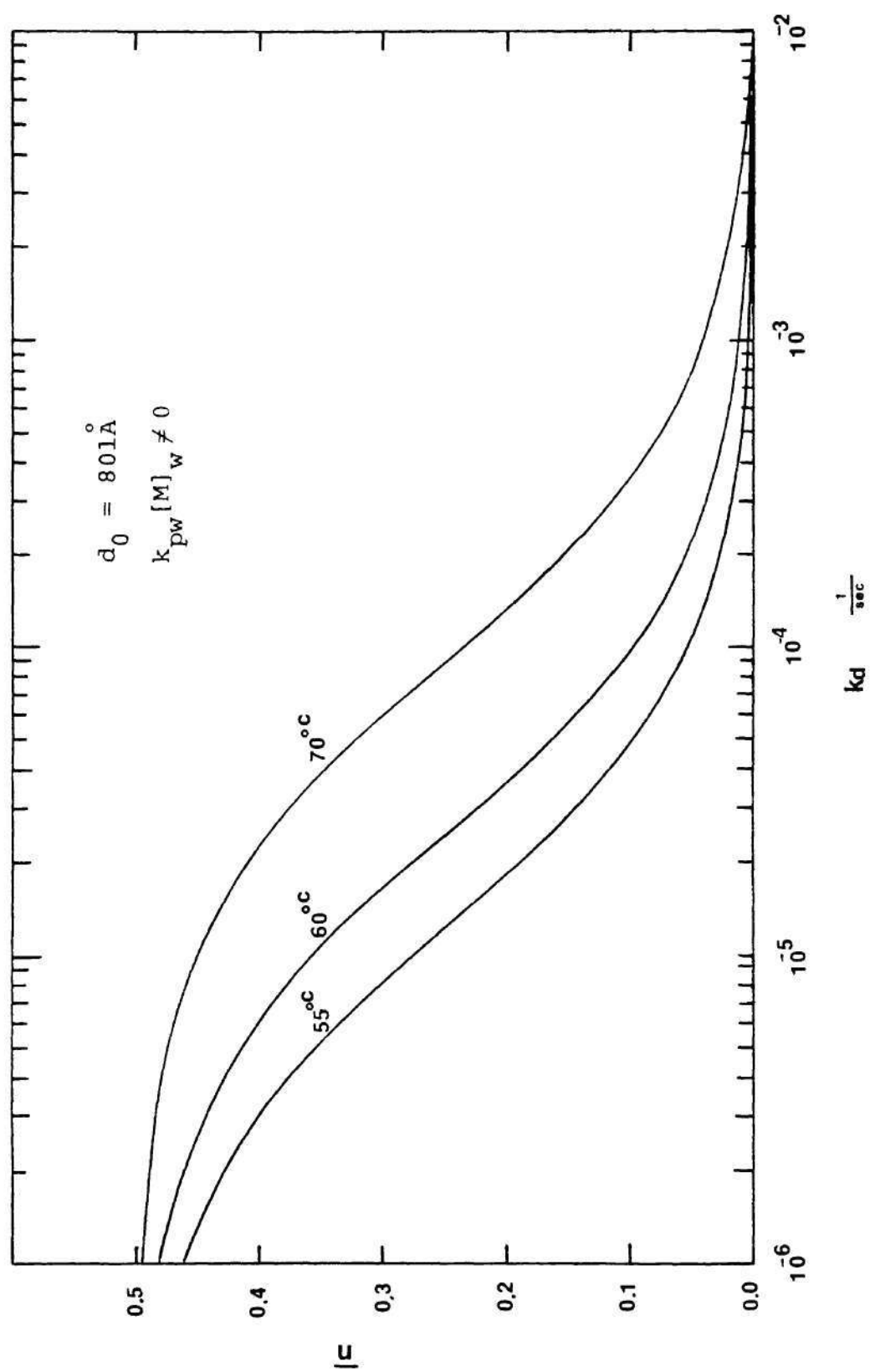


Figure 46. Relationship Between \bar{n} vs. k_d (MMA) at 55°C, 60°C and 70°C.

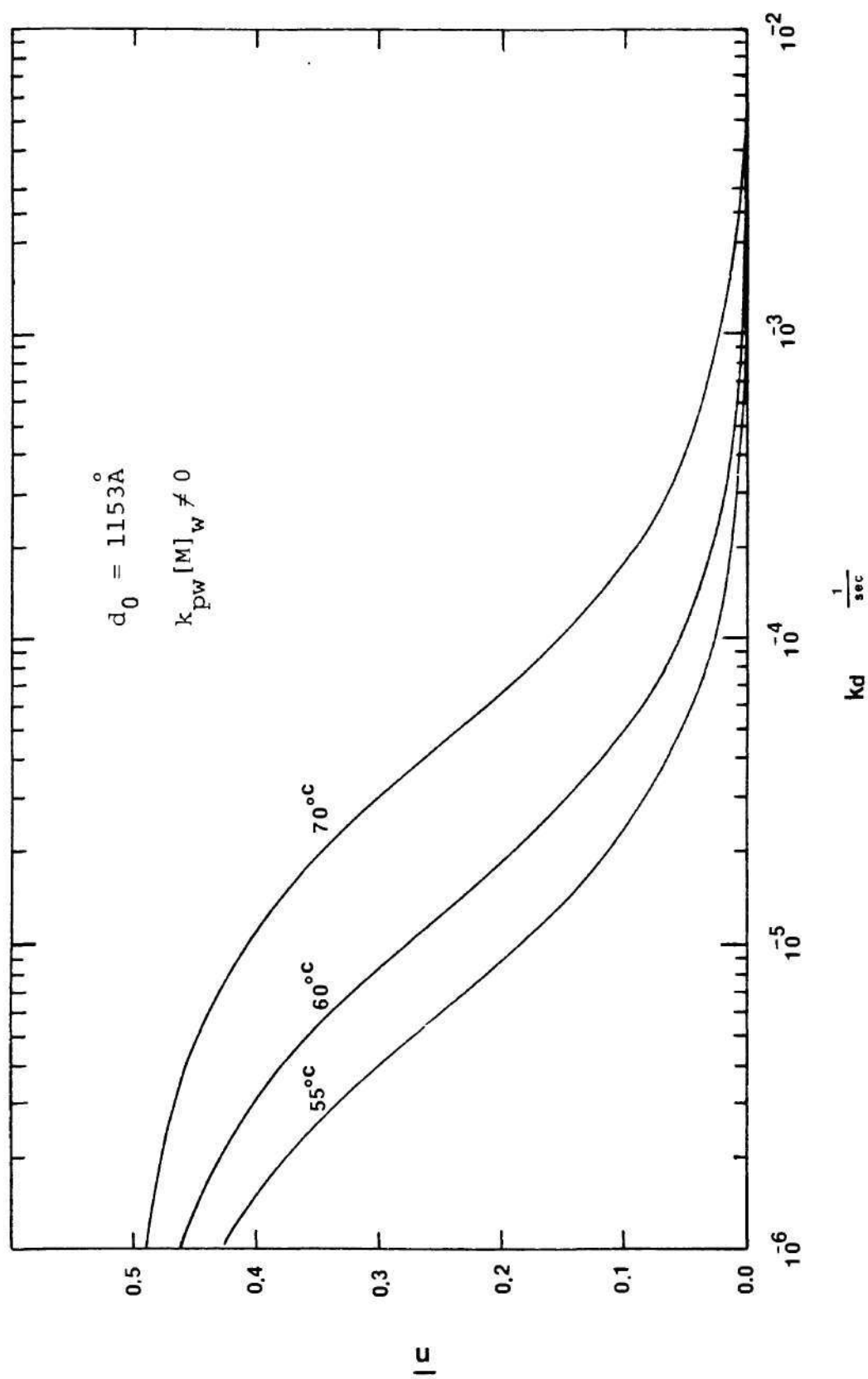


Figure 47. Relationship Between \bar{n} vs. k_d (MMA) at 55°C, 60°C and 70°C.

Table 10. k_d Values Obtained from Experimental \bar{n} Values (Styrene).

	With/Without Chain Transfer Agent	k_d (l/sec)		
		50°C	60°C	70°C
$d_0 = 814^{\circ}$	Without Chain Transfer Agent	6.5 (EX-28)	2.0×10^{-2} (EX-29)	0 (EX-30)
$N_T = 1.332 \times 10^{13}$	With Carbon Tetrachloride		0 (EX-37)	0 (EX-38)
$\left(\frac{l}{cc\text{-}water}\right)$	With Xylene			2.4×10^{-1} (EX-51)
$d_0 = 1118^{\circ}$	Without Chain Transfer Agent	3.5×10^{-2} (EX-31)	4.4×10^{-1} (EX-32)	0 (EX-33)
$N_T = 1.0758 \times 10^{13}$	With Carbon Tetrachloride			0.06* (EX-39)
$\left(\frac{l}{cc\text{-}water}\right)$				0.181* (EX-40)
				First Slope 0
				Second Slope 0
				0.373* (EX-41)
				First Slope 0
				Second Slope 2.6×10^{-1}
	With Xylene	45.0 (EX-50)	5.7×10^{-1} (EX-49)	0 (EX-48)
$d_0 = 2250^{\circ}$	Without Chain Transfer Agent	4.0×10^{-2} (EX-34)	0 (EX-35)	0 (EX-48)
$N_T = 3.058 \times 10^{12}$	With Carbon Tetrachloride			0 (EX-42)
$\left(\frac{l}{cc\text{-}water}\right)$	With Xylene		0 (EX-45)	0 (EX-43)

*: $\frac{CCl_4}{monomer}$ weight ratio in the recipe

Table 11. k_d Values Obtained from Experimental \bar{n} Values (MMA)

	With/Without Chain Transfer Agent	k_d (1/sec)			
		55°C	60°C	70°C	
		First Slope	First Slope	First Slope	Second Slope
$d_0 = 645^\circ$	Without Chain Transfer Agent	1.9×10^{-4} (EX-70)	1.3×10^{-4} (EX-69)	$2.733 \times 10^{-4*}$ 9.0×10^{-5} (EX-68)	$2.733 \times 10^{-4*}$ 0 (EX-68)
				$6.766 \times 10^{-4*}$ 1.0×10^{-4} (EX-67)	$6.766 \times 10^{-4*}$ 0 (EX-67)
$N_T = 6.5688 \times 10^{13}$	With Carbon Tetrachloride		1.65×10^{-4} (EX-73)	1.15×10^{-4} (EX-71)	0 (EX-71)
$\left(\frac{l}{cc-water}\right)$	With Xylene		5.6×10^{-4}	1.55×10^{-4} (EX-72)	1.5×10^{-5} (EX-72)
$d_0 = 801^\circ$	Without Chain Transfer Agent	2.0×10^{-4} (EX-77)	6.6×10^{-5} (EX-76)	1.8×10^{-5} (EX-76)	1.27×10^{-4} (EX-75)
$N_T = 5.799 \times 10^{12}$	With Carbon Tetrachloride		1.8×10^{-4} (EX-81)	7.6×10^{-5} (EX-81)	0.107^{**} 1.2×10^{-4} (EX-78)
				0.213^{**} 5.0×10^{-5} (EX-80)	0.213^{**} 0 (EX-80)
$\left(\frac{l}{cc-water}\right)$	With Xylene		4.8×10^{-4} (EX-82)	5.3×10^{-5} (EX-79)	0 (EX-79)
$d_0 = 1153^\circ$	Without Chain Transfer Agent	3.0×10^{-4} (EX-85)	2.4×10^{-4} (EX-84)	3.15×10^{-5} (EX-84)	8.6×10^{-5} (EX-79)
$N_T = 5.497 \times 10^{12}$	With Carbon Tetrachloride		2.8×10^{-4} (EX-88)	1.33×10^{-4} (EX-86)	0 (EX-86)
$\left(\frac{l}{cc-water}\right)$	With Xylene		7.0×10^{-4} (EX-89)	1.9×10^{-4} (EX-87)	3.15×10^{-5} (EX-87)

*: $\frac{\text{Initiator}}{\text{Monomer}}$ weight ratio in the recipe. **: $\frac{CCl_4}{\text{Monomer}}$ weight ratio in the recipe.

temperature because these higher temperatures lead to faster reactions and higher conversions.

Chain Transfer Agent Effect on k_d

The chain transfer agents used were carbon tetrachloride and xylene. The effect of chain transfer agents was clearly observed for both the styrene and MMA systems as predicted before. The value of k_d is increased by addition of chain transfer agents. There are two possible reasons for the effect of the chain transfer agents.

- (1) The chain transfer reaction produces a small, mobile free radical which can desorb from the polymer particle.
- (2) The chain transfer agents used were essentially insoluble in the water, but very miscible with styrene and MMA. Thus they may have functioned as a diluent to decrease the viscosity at the polymerization locus. As mentioned before, the lower the viscosity of the system, the higher the mobility of free radicals. The approximate weight ratios of chain transfer agent/monomer used are listed below:

	Carbon Tetrachloride	Xylene
Styrene system:	0.06 ~ 0.36	0.25
MMA system:	0.11	0.11

In our experiments, when the amount of chain

transfer agent (carbon tetrachloride) was changed, the value of k_d was effected as shown in Figure 48 and Figure 49. In the styrene system, the value of k_d increased as the amount of carbon tetrachloride increased; however, it tended to decrease in the MMA system. The discrepancy seems to result from the difference of transfer constants, C_s , of styrene and MMA as shown below:

$C_s \times 10^4$ for polymerization of	
Styrene	MMA
CCl_4 87.0 [60]	2.40 [61]

Particle Size Effect on k_d

Ugelstad et al. [52] published an empirical expression for k_d in the emulsion polymerization of vinyl chloride which is:

$$k_d = kv_p^{-2/3} = k' \cdot d_p^{-2} \quad (66)$$

Also, Nomura [5,23] and Ugelstad [3] derived theoretical expressions independently which were of the following form:

$$k_d = k'' \frac{1}{r^2} \left(\frac{k_{mct}}{k_p} \right) \quad (67)$$

In both of the above equations, k_d is proportional to d_p^{-2} . However, our results show that k_d increases as the particle size increases although we observed a few exceptions to this general trend. The exceptions are most pronounced in

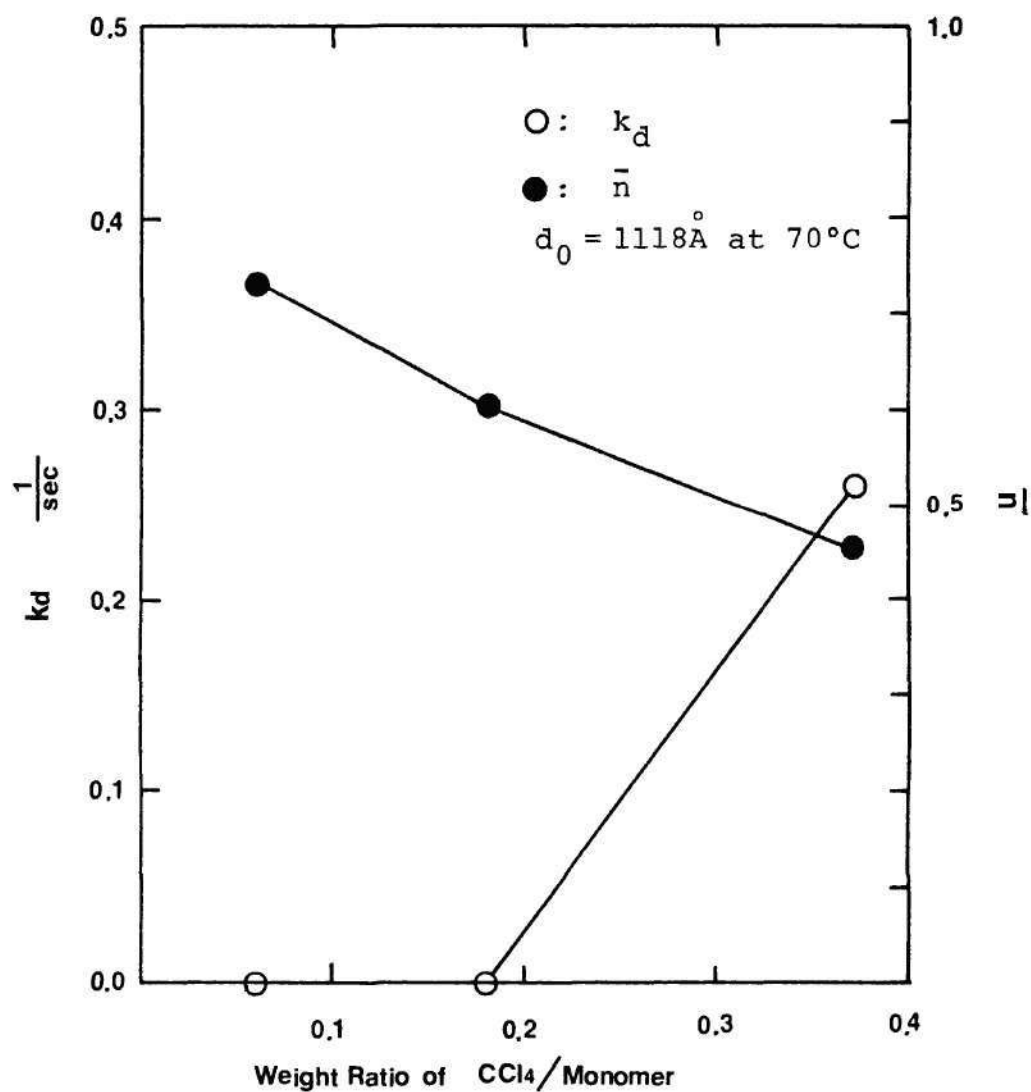


Figure 48. Effect of Amount of Carbon Tetrachloride on k_d and \bar{n} (Styrene).

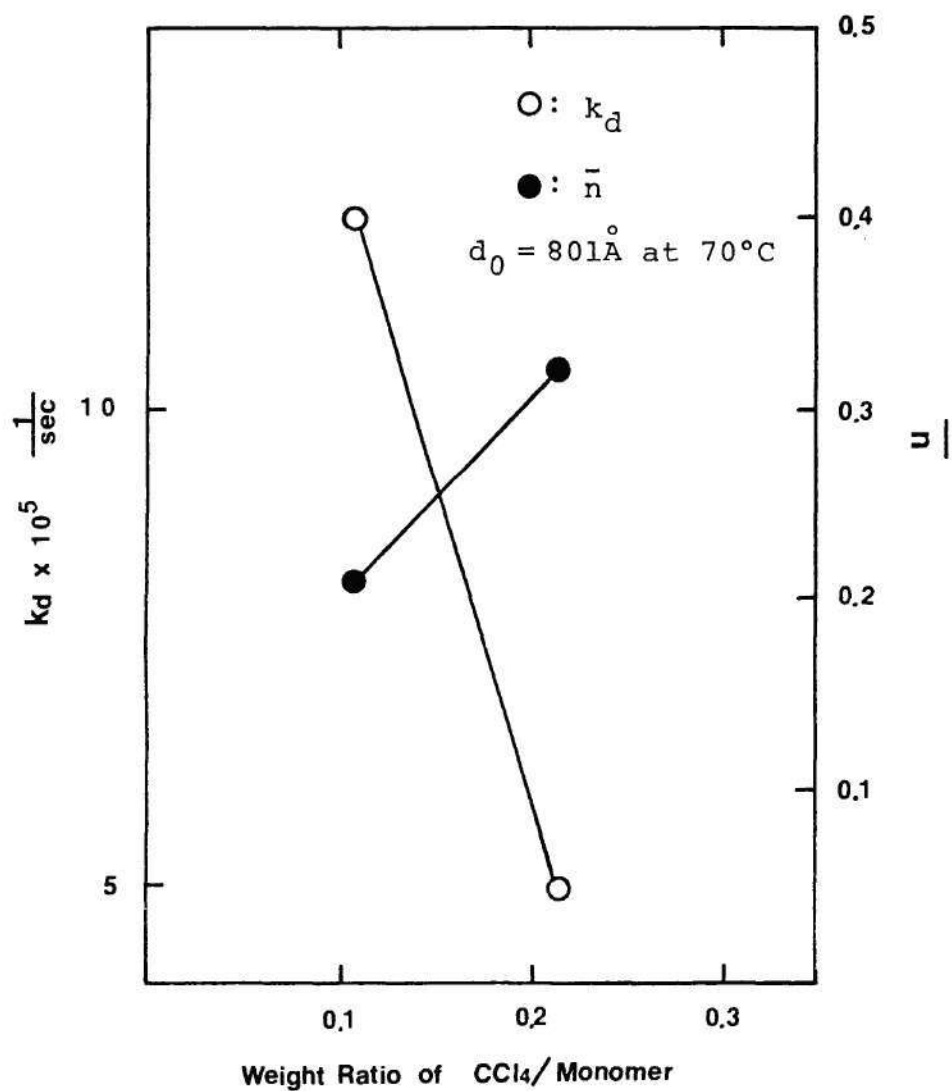


Figure 49. Effect of Amount of Carbon Tetrachloride on k_d and \bar{n} (MMA).

the styrene system.

Napper and Gilbert [33] reported experimental results which demonstrated that the value of k_d varied with the inverse square of the swollen particle radius, as expected for the diffusion controlled desorption of free radicals from the polymer particles.

Nomura and Ugelstad used the molecular diffusion theory to obtain their theoretical expression of k_d . They assumed that the mean diffusion path of a free radical was equal to the radius of the polymer particle. As mentioned before, free radicals can not penetrate easily into the particles because of their high interior viscosity in a seed polymerization. Therefore, the polymerization locus is assumed to be the swollen monomer layer on the polymer particle. Under this condition, the theoretical expression of k_d was derived by using molecular diffusion theory.

The diffusion rate of a free radical from the interior of swollen monomer layer on the polymer particle to the surface is given by

$$\begin{aligned} \frac{dm_2}{dt} &= - 4\pi \left(\frac{d_{ps}}{2} \right)^2 \cdot D_m \cdot \frac{C_a - C}{\frac{d_{ps} - d_p}{2}} \\ &= - \frac{2\pi \cdot d_{ps}^2 \cdot D_m \cdot (C_a - C)}{d_{ps} - d_p} \end{aligned} \quad (68)$$

where $\frac{dm_2}{dt}$: the diffusion rate of a free radical
 D_m : the diffusion constant in the monomer layer
 C_a : the concentration of free radicals at the inside surface
 C : the mean free radical concentration in the middle of the monomer layer

The diffusion rate from the outer surface of swollen monomer layer on the polymer particle to the bulk of the water is

$$\frac{dm_2}{dt} = 4\pi \left(\frac{d_{ps}}{2} \right)^2 \cdot \frac{D_w \cdot C'_a}{\frac{d_{ps} - d_p}{2}} = \frac{2\pi d_{ps}^2 \cdot D_w \cdot C'_a}{d_{ps} - d_p} \quad (69)$$

where D_w : the diffusion constant in the water phase
 C'_a : the free radical concentration at the outside surface of swollen monomer layer

The free radical concentration in the water phase is assumed to be equal to zero. The concentrations are expected to be in equilibrium with each other at the surface with an equilibrium constant.

$$a = \frac{C_a}{C'_a} \quad (70)$$

At the steady state,

$$D_w \cdot C'_a = - D_m (C_a - C) \quad (71)$$

Combining Eq. (70) with Eq. (71) yields

$$C_a = \frac{D_m \cdot C}{D_w + D_m \cdot a} \quad (72)$$

Substituting Eq. (72) into Eq. (69) gives

$$\frac{dm_2}{dt} = \frac{2\pi \cdot d_{ps}^2 \cdot D_w}{(d_{ps}^3 - d_p^3)} \cdot \frac{D_m \cdot C}{D_w + D_m \cdot a} \quad (73)$$

and since $C = \frac{n}{V} = \frac{n}{\frac{\pi}{6} (d_{ps}^3 - d_p^3)}$ we finally obtain

$$\frac{\frac{dm_2}{dt}}{n} = k_d = \frac{12 \cdot D_w \cdot D_m}{D_w + D_m \cdot a} \cdot \frac{d_{ps}^2}{(d_{ps}^3 - d_p^3) (d_{ps}^3 - d_p^3)} \quad (74)$$

At the early stage of the seed polymerization, $(d_{ps} - d_p)$ and $(d_{ps}^3 - d_p^3)$ are nearly constant. Thus Eq. (74) becomes:

$$k_d = k''' \cdot d_{ps}^2 \quad (75)$$

The value of k_d obtained experimentally was plotted against d_{ps}^2 as shown in Figures 50 through 52. These results show that the value of k_d is proportional to d_{ps}^2 . Therefore,

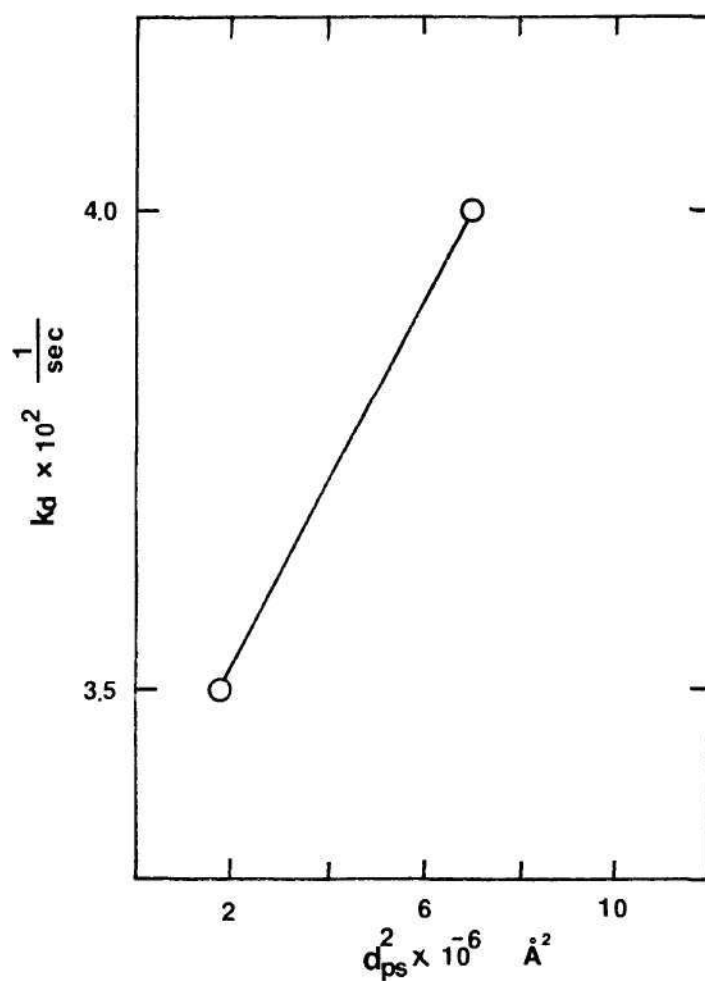


Figure 50. Desorption Rate Constant, k_d as a Function of d_{ps}^2 . Styrene at 50°C.

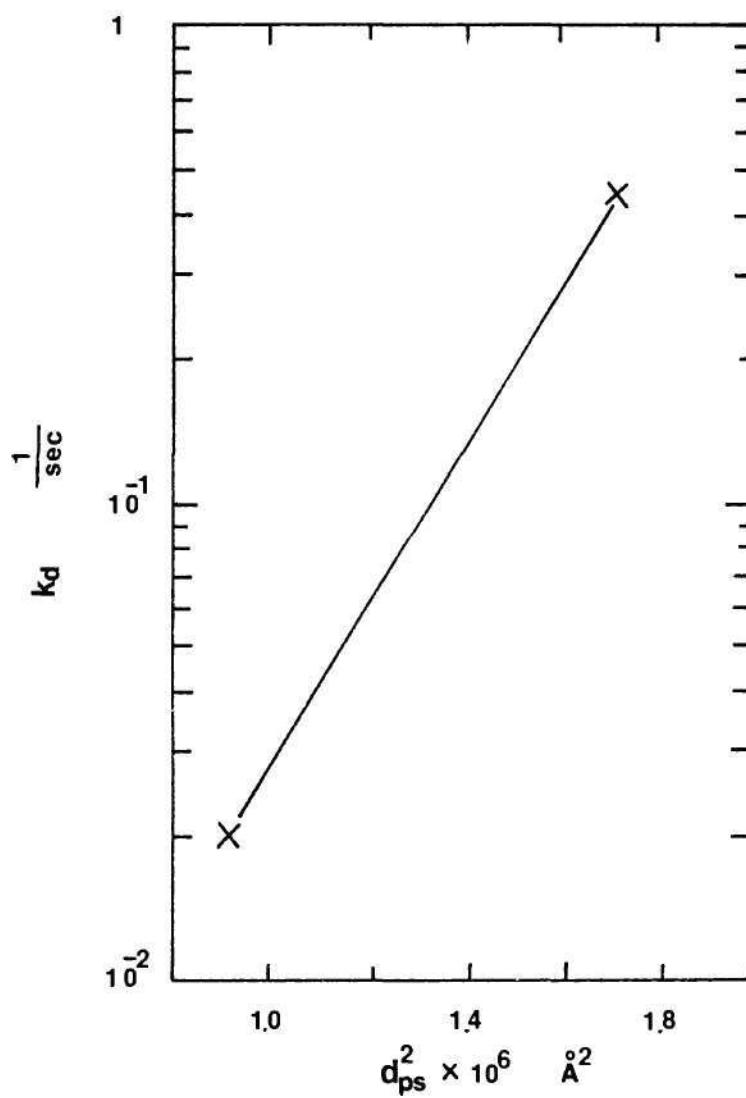


Figure 51. Desorption Rate Constant, k_d as a Function of d_{ps}^2 . Styrene at 60°C .

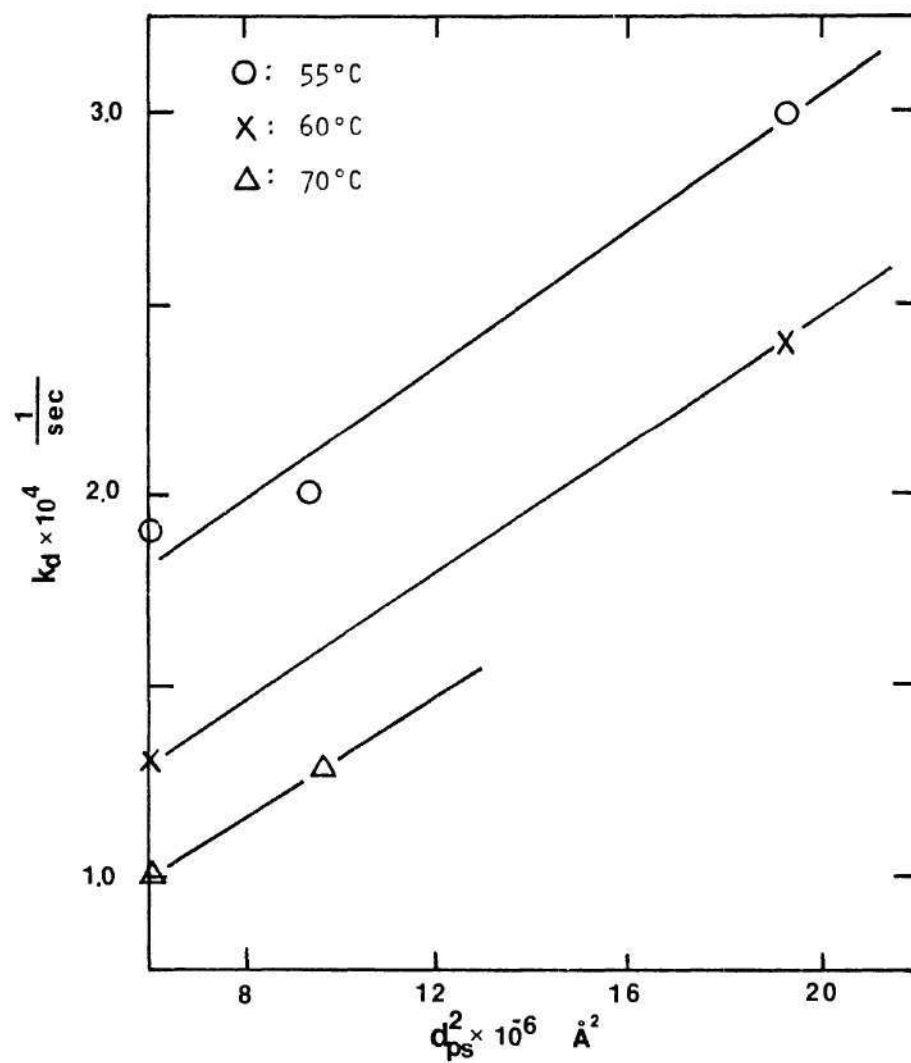


Figure 52. Desorption Rate Constant, k_d as a Function of d_{ps}^2 , MMA at 50°C, 60°C and 70°C.

the polymerization locus in a seed polymerization seems to be in the swollen monomer layer on the polymer particle.

Desorption of Free Radicals in Styrene Systems

Let us consider first, "What is the physical meaning of the free radical desorption process from the polymer particle?" The desorption process is a diffusion process and is also very complex. A variety of free radical types could be desorbed. These include the primary initiator radical, a monomer radical, an oligomeric radical or a low molecular weight radical which is generated by the reaction with a chain transfer agent. Oligomeric radicals of modest to high molecular weight cannot diffuse from the polymer particles into the water phase because of low mobility and molecular entanglements. Therefore, in the desorption process, the small molecule which is generated by the chain transfer reaction, the initiator free radical and the monomer radical may be desorbed. Our results (Table 10) show that desorption of free radicals from the polymer particles occurs in the styrene system. Usually, styrene emulsion polymerization is modeled by Smith-Ewart Case II theory by assuming that the free radical desorption from particles does not occur because of the low-rate of the monomer chain transfer reaction. However, the desorption of free radicals cannot be ignored in the styrene system under certain conditions which are expressed later in

Table 12 and Figure 53.

Napper and Gilbert [33] showed that the styrene emulsion polymerization kinetics followed Smith-Ewart Case I theory because of radical desorption under suitable conditions (e.g., low initiator concentrations and/or small particle diameter).

Comparison of k_d Values Determined

Napper and Gilbert [33] determined a value of k_d for a seed emulsion polymerization of styrene. The unswollen diameter of their seed particles was 720\AA . The average k_d value determined at 50°C was 1.1×10^{-3} (1/sec).

Nomura et al. [5] calculated values of k_d using the following theoretical relationship:

$$k_d = \left\{ \bar{n} + \frac{k_p \cdot [M]_p \cdot C_d \cdot r^2}{3 \cdot \delta \cdot D_w} \right\}^{-1} \left\{ \frac{k_{mct}}{k_p} + \frac{k_{cct} \cdot [CT]}{k_p \cdot [M]_p} + \frac{\rho_i (1 - \bar{n})}{N_T \cdot k_p \cdot [M]_p \cdot \bar{n}} \right\} (k_p \cdot [M]_p) \quad (36)$$

The values of k_d were used to show the relationship between \bar{n} and $\beta = \frac{\rho_i}{k_d \cdot N_T}$ (dimensionless parameter). The author calculated k_d values from Nomura's graph of \bar{n} vs. β because Nomura did not publish any k_d values. The k_d value was 6.38×10^{-3} (1/sec) for styrene at 50°C . The value of k_d for MMA at 30°C varied from 5.6×10^{-4} (1/sec) to 2.8 (1/sec).

The values obtained in this work for styrene are

Table 12. Comparison of k_d , α and m Values of This Work with Those of Napper.

	This Work				Napper & Gilbert	Nomura
	50°C		60°C		$d_0 = 720\text{\AA}$ 50°C (average value)	50°C
	814\AA	1118\AA	2250\AA	814\AA	1118\AA	
$k_d \left(\frac{1}{\text{sec}} \right)$	7.44	2.856×10^{-2}	3.505×10^{-2}	2.0×10^{-2}	4.4×10^{-1}	6.38×10^{-3}
$\alpha = \frac{\rho_i \cdot v_s}{N_T \cdot k_{\text{ntp}}}$	1.779×10^{-4}	5.844×10^{-4}	1.652×10^{-2}	5.372×10^{-4}	1.791×10^{-3}	1.241×10^{-5}
$m = \frac{k_d \cdot v_s}{k_{\text{ntp}}}$	3×10^{-2}	3×10^{-4}	3×10^{-3}	1×10^{-4}	1×10^{-3}	---

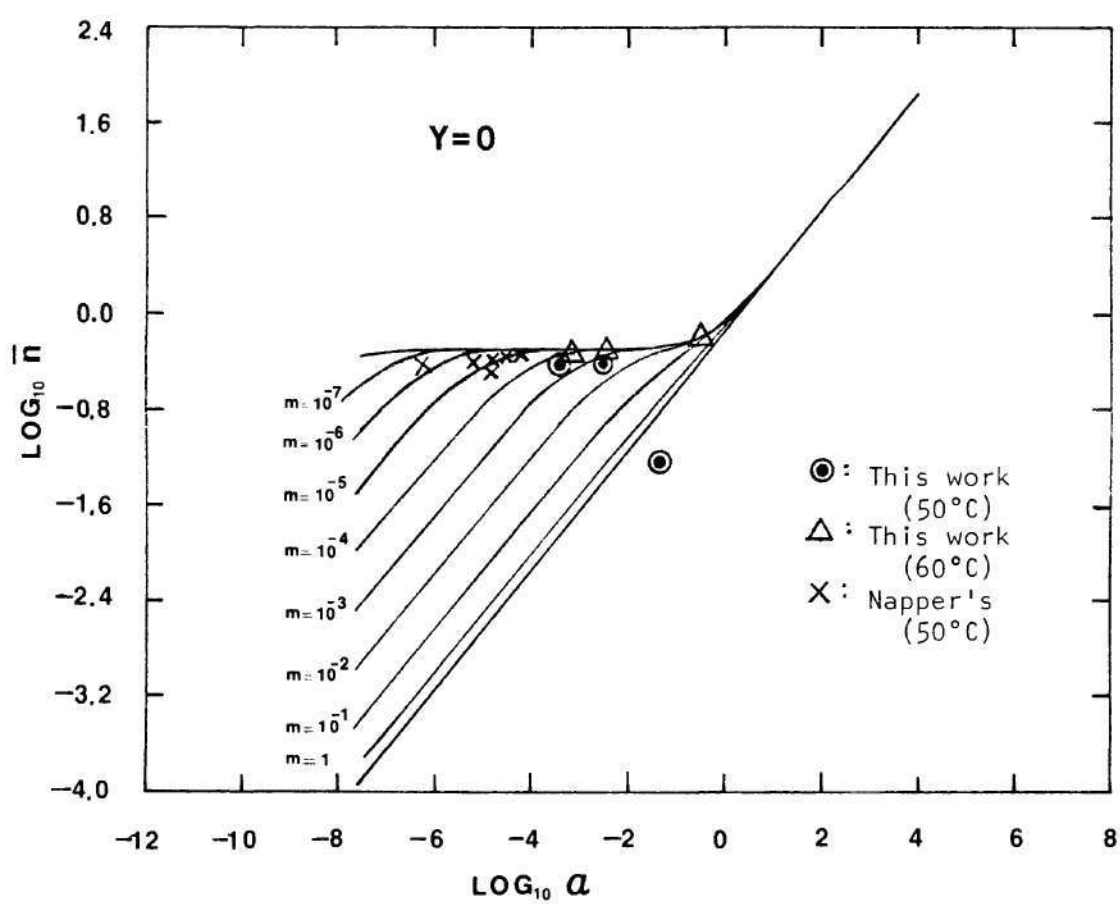


Figure 53. Experiment Range Differences Between This Work and Napper's.

higher for both the results listed above. A comparison is shown in Table 12. The experimental differences between this work and Napper's is indicated by Ugelstad's dimensionless numbers, α and m , and also by the range difference in $\log \bar{n}$ vs. $\log \alpha$ curve as shown in Figure 53. Values for α were not calculated from Normura's paper because his experimental data on the number of polymer particles could not be related to individual experiments. The difference in k_d values between this work and Napper's may be based on the difference of experimental conditions as shown in Figure 53.

k_d Values for Styrene and MMA Latexes

The value of k_d of styrene (2.0×10^{-2} to 5.7×10^{-1}) was considerably larger than that of MMA (3.15×10^{-5} to 7.4×10^{-4}). When the difference of the monomer chain transfer constant, C_M between styrene and MMA is considered, the higher k_d value in the styrene system may be explained clearly. The monomer chain transfer constants are listed below [53]:

	$C_M(-) \times 10^{-4}$
Methylmethacrylate	0.07 ~ 0.18
Styrene	0.6 ~ 1.1
Vinyl acetate	1.75 ~ 2.8
Vinyl chloride	6.25

The small free radicals which are generated by the monomer chain transfer reaction in the polymer particle may desorb

from the polymer particles. When the generation of small free radicals is increased, the value of k_d may be increased. Therefore, the system of monomer which has the larger value of the monomer chain transfer constants shows the higher value of k_d . Since the C_M value for styrene is ten times higher than the C_M of MMA, the value of k_d of styrene is higher than that of MMA.

Comparison Between k_d Values Determined by Ugelstad's Model with Those Determined by the Model in This Work

Ugelstad et al. [22] developed a kinetic model which permits the average number of free radicals in the polymer particle, \bar{n} , to be calculated as a function of three parameters; α , m and Y . The Ugelstad model accounts for reabsorption of free radicals into polymer particles and for the contribution of termination in the water phase. Ugelstad assumed that the polymerization occurs only in the polymer particle.

The k_d values calculated by Ugelstad model are listed in Table 13 and Table 14. The mutual termination of free radicals in the water phase was neglected ($Y = 0$). k_d values for the styrene system are of the same order and show the same tendencies as those determined by the model developed in this work. However, k_d values determined by Ugelstad's model for the MMA system are very different from those of the new model and they are higher than those of styrene. The model used in this work considered the

Table 13. k_d Values Calculated by Ugelstad Model (Styrene).

	With/Without Chain Transfer Agent	k_d (1/sec)		
		50°C	60°C	70°C
$d_0 = 814\text{\AA}$	Without Chain Transfer Agent	7.44 (EX-28)	4.014×10^{-2} (EX-29)	0 (EX-30)
$N_T = 1.332 \times 10^{13}$	With Carbon Tetrachloride		0 (EX-37)	0 (EX-38)
$\left(\frac{1}{\text{cc-water}}\right)$	With Xylene			1.916×10^{-1} (EX-51)
$d_0 = 1118\text{\AA}$	Without Chain Transfer Agent	2.856×10^{-2} (EX-31)	1.541×10^{-1} (EX-32)	0 (EX-33)
$N_T = 1.0758 \times 10^{13}$	With Carbon Tetrachloride			0.06* (EX-39)
				0.181* (EX-40)
				0.373* (EX-41)
$\left(\frac{1}{\text{cc-water}}\right)$	With Xylene	28.575 (EX-50)	3.082×10^{-1} (EX-49)	0 (EX-48)
$d_0 = 2250\text{\AA}$	Without Chain Transfer Agent	3.505×10^{-2} (EX-34)	0 (EX-35)	0 (EX-36)
$N_T = 3.058 \times 10^{13}$	With Carbon Tetrachloride			0 (EX-42)
$\left(\frac{1}{\text{cc-water}}\right)$	With Xylene		0 (EX-45)	0 (EX-43)

*: CCl_4 monomer weight ratio in the recipe

Table 14. k_d Values Calculated by Ugelstad Model (MMA).

		k_d (l/sec)			
		55°C		70°C	
		First Slope	Second Slope	First Slope	Second Slope
With/Without Chain Transfer Agent					
$d_0 = 645^\circ$	Without Chain Transfer Agent	2.194 (EX-70)	4.536×10^{-1} (EX-69)	$2.733 \times 10^{-4*}$ (EX-68)	$2.733 \times 10^{-4*}$ (EX-68)
	With Carbon Tetrachloride			$6.766 \times 10^{-4*}$ (EX-69)	$6.766 \times 10^{-4*}$ (EX-67)
$N_T = 6.5688 \times 10^{13}$			9.072×10^{-1} (EX-73)	3.182×10^{-1} (EX-71)	0 (EX-71)
$\left(\frac{1}{cc-water}\right)$			4.536 (EX-74)	3.818×10^{-1} (EX-72)	1.273×10^{-2} (EX-72)
$d_0 = 801^\circ$	Without Chain Transfer Agent	76.35 (EX-77)	4.737 (EX-76)	9.968 (EX-75)	0 (EX-75)
	With Carbon Tetrachloride		23.680 (EX-81)	0.107** (EX-81)	0.107** (EX-78)
$N_T = 5.799 \times 10^{12}$				0.213** (EX-80)	0.213** (EX-80)
$\left(\frac{1}{cc-water}\right)$					
With Xylene			473.7 (EX-82)	2.658 (EX-79)	0 (EX-79)
$d_0 = 1153^\circ$	Without Chain Transfer Agent	\odot (EX-85)	\odot (EX-84)	22.282 (EX-83)	0 (EX-83)
	With Carbon Tetrachloride		\odot (EX-88)	33.423 (EX-86)	0 (EX-86)
$N_T = 5.497 \times 10^{12}$			\odot (EX-89)	55.703 (EX-87)	1.114 (EX-87)
$\left(\frac{1}{cc-water}\right)$					

\odot : $m = \frac{k_d \cdot v}{k_{mtp}}$ could not be obtained from Ugelstad's graph. *: $\frac{\text{Initiator}}{\text{Monomer}}$ weight ratio in the recipe.

**: $\frac{CCl_4}{\text{Monomer}}$ weight ratio in the recipe.

disappearance of free radicals from the water phase by the water-phase polymerization. The rate of disappearance was expressed as follows:

$$r_{wp} = k_{pw} \cdot [M]_w \cdot [R\cdot]_w$$

The above term was neglected in the styrene system because $[M]_w$ of styrene monomer (0.005 gmole/l) is extremely low. But, it was included in the MMA model due to the high value of $[M]_w$ (0.15 gmole/l).

When the computation of k_d was carried out eliminating the term of the water-phase polymerization in the case of MMA, the relationship between \bar{n} and k_d obtained are shown in Figures 54 through 56. The values of k_d obtained from those figures by using experimental \bar{n} values is shown in Table 15. These k_d values agreed with the results obtained with Ugelstad's model.

Ugelstad and Nomura demonstrated theoretically that k_d was proportional to k_{mct} (monomer chain transfer constant) as shown in Eq. (26) and Eq. (30). When the model including the water phase polymerization is used to obtain k_d , the results agree with the above theoretical expression. However, they do not agree when Ugelstad's model is used to obtain k_d values for MMA. Since Ugelstad's model does not account for the consumption of free radicals in the water

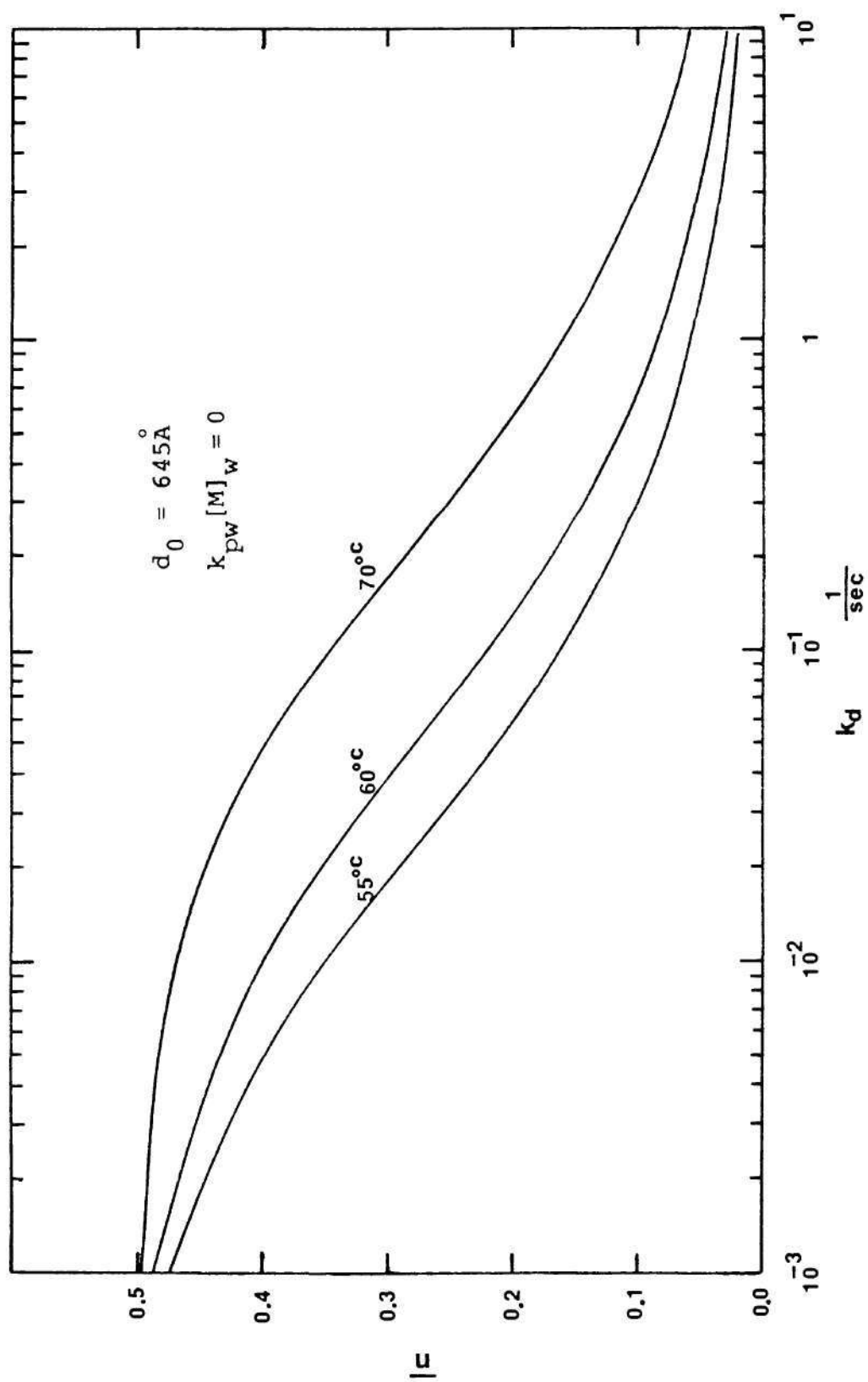


Figure 54. Relationship of \bar{n} vs. k_d (MMA) at 55°C , 60°C and 70°C .

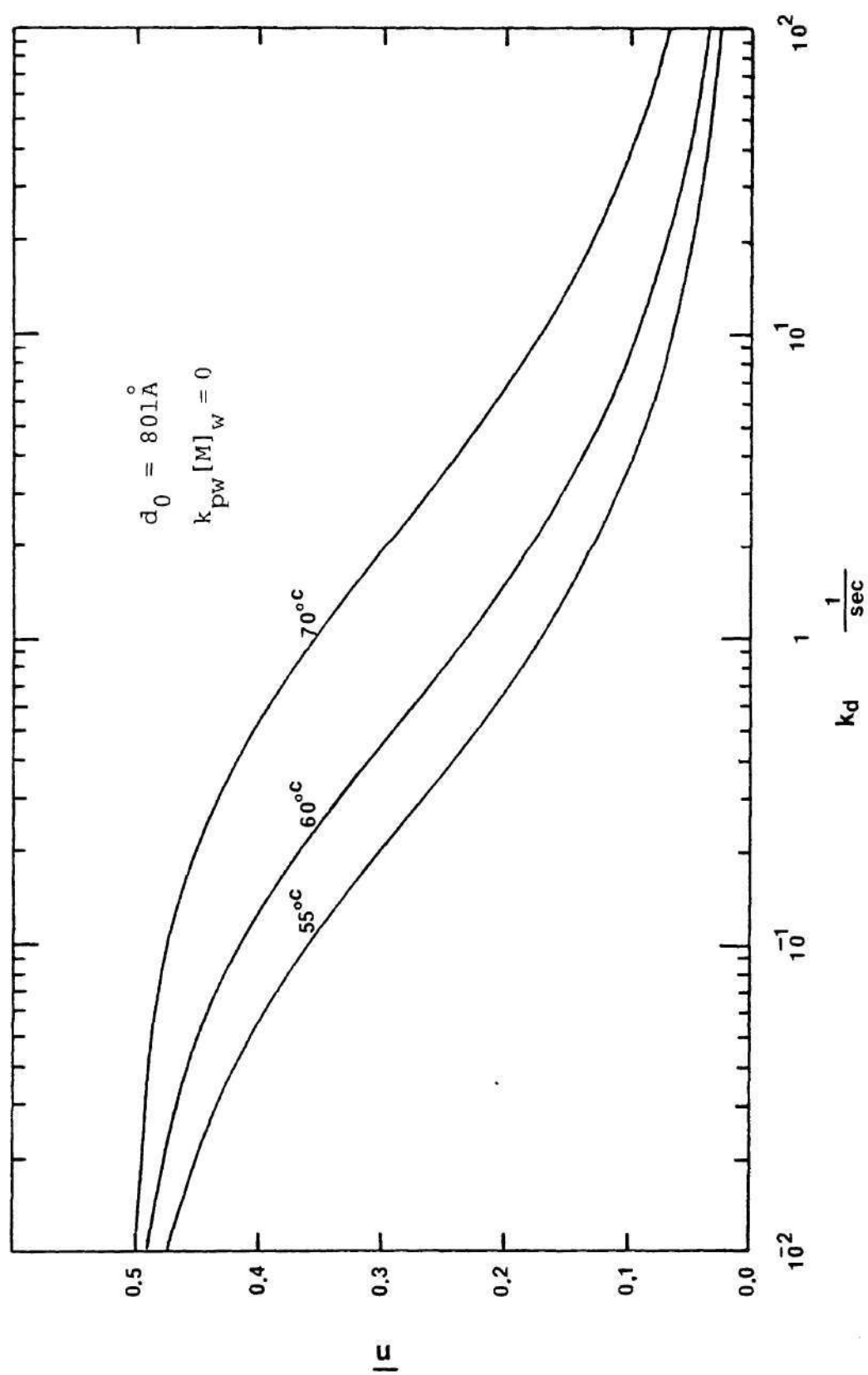


Figure 55. Relationship of \bar{n} vs. k_d (MMA) at 55°C , 60°C and 70°C .

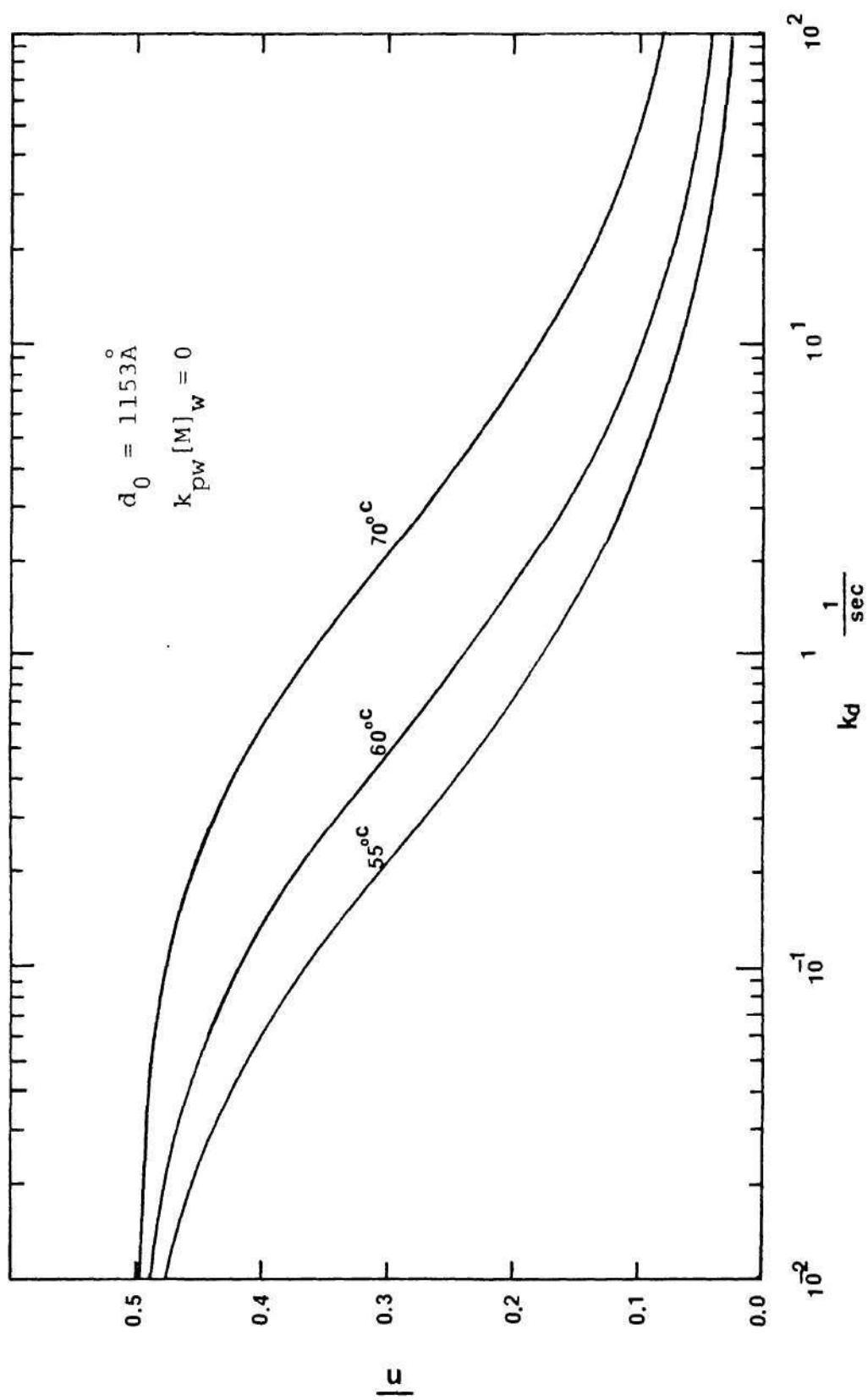


Figure 56. Relationship of \bar{n} vs. k_d (MMA) at 55°C, 60°C and 70°C.

phase, the above differences are noted. When the average number of free radicals per particle, \bar{n} , was calculated, the contribution of the water-phase polymerization was neglected.

The actual polymerization rate must be expressed as follows:

$$R_p = k_p \cdot [M]_p \cdot \left(\frac{\bar{n} \cdot N_T}{N_A} \right) + k_{pw} \cdot [M]_w \cdot [R\cdot]_w \quad (77)$$

In the MMA system, R_p for Experiment-69 (60°C) was $5.362 \times 10^{-8} \left(\frac{\text{gmole}}{\text{cc-water} \cdot \text{sec}} \right)$. In this calculation, k_{pw} was set equal to $175.35 \left(\frac{\text{l}}{\text{gmole} \cdot \text{sec}} \right)$, $[M]_w$ to $0.15 \left(\frac{\text{gmole}}{\text{l}} \right)$, $[R\cdot]_w$ to $10^8 \left(\frac{\text{radicals}}{\text{cc-water}} \right)$ [Ref. 50]. Therefore, the term of water-phase polymerization can be neglected because it is very small compared with the total R_p value. However, when the material balance of free radicals in the water-phase is considered, the effect of disappearance of free radicals due to the water-phase polymerization cannot be ignored because such a reaction would cause a change in \bar{n} .

Change of Polymer Particle During the Polymerization

Equation (65), which was used to calculate the values N_1 and N_2 , includes the time-variable parameter v_{ps} . Gardon [54] pointed out that there is no steady state in the Smith-Ewart recursion formula Eq. (7) because of the above reason. When the value of k_d was calculated, v_{ps} was treated as a constant and \bar{n} was obtained assuming a steady state condition.

The change of the particle diameter (unswollen) was calculated by using the conversion data as shown in Tables 16 and 17. The relationship between \bar{n} and k_d as a function of the unswollen particle diameter is shown in Figures 57 and 58. These results show that there is no big difference in the order of the k_d value even if the particle diameter is changed at the rate observed in these experiments. A kinetic model which accounts for the time dependence of v_{ps} will be needed to obtain more accurate k_d values.

Table 16. Change of Polymer Particle Diameter (Unswollen) in the Steady State for Styrene.

		Temperature (°C)	Steady State Length (hr)	Polymer Particle Diameter (Å) at Final Steady State
814Å Latex	EX-28	50	4	879
	EX-29	60	5	1430
	EX-30	70	4.5	1686
1118Å Latex	EX-31	50	5	1435
	EX-32	60	4.5	1443
	EX-30	70	4	1783
2250Å Latex	EX-34	50	5	2364
	EX-35	60	5	2784
	EX-36	70	4.5	2978

Table 17. Change of Polymer Particle Diameter (Unswollen) in the Steady State for MMA.

	Temperature (°C)	Steady State Length (min)	Polymer Particle Diameter (Å) at Final Steady State
645Å Latex	EX-70	55	90
	EX-69	60	90
	EX-68	70	60
801Å Latex	EX-77	55	130
	EX-76	60	110
	EX-75	70	60
1153Å Latex	EX-85	55	130
	EX-84	60	140
	EX-83	70	60

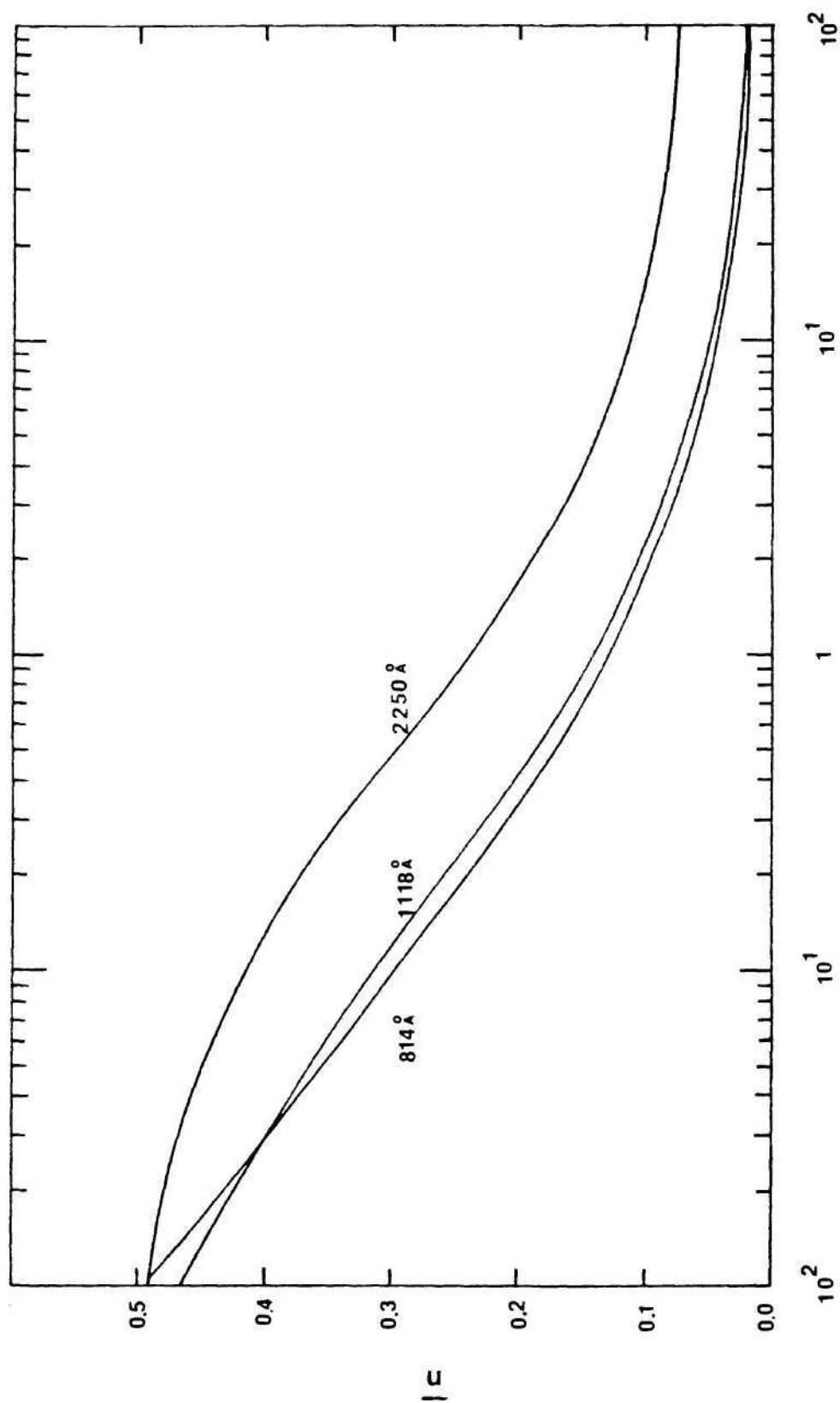


Figure 57. Relationship of \bar{n} vs. k_d Depending on d_p at 50°C (Styrene).

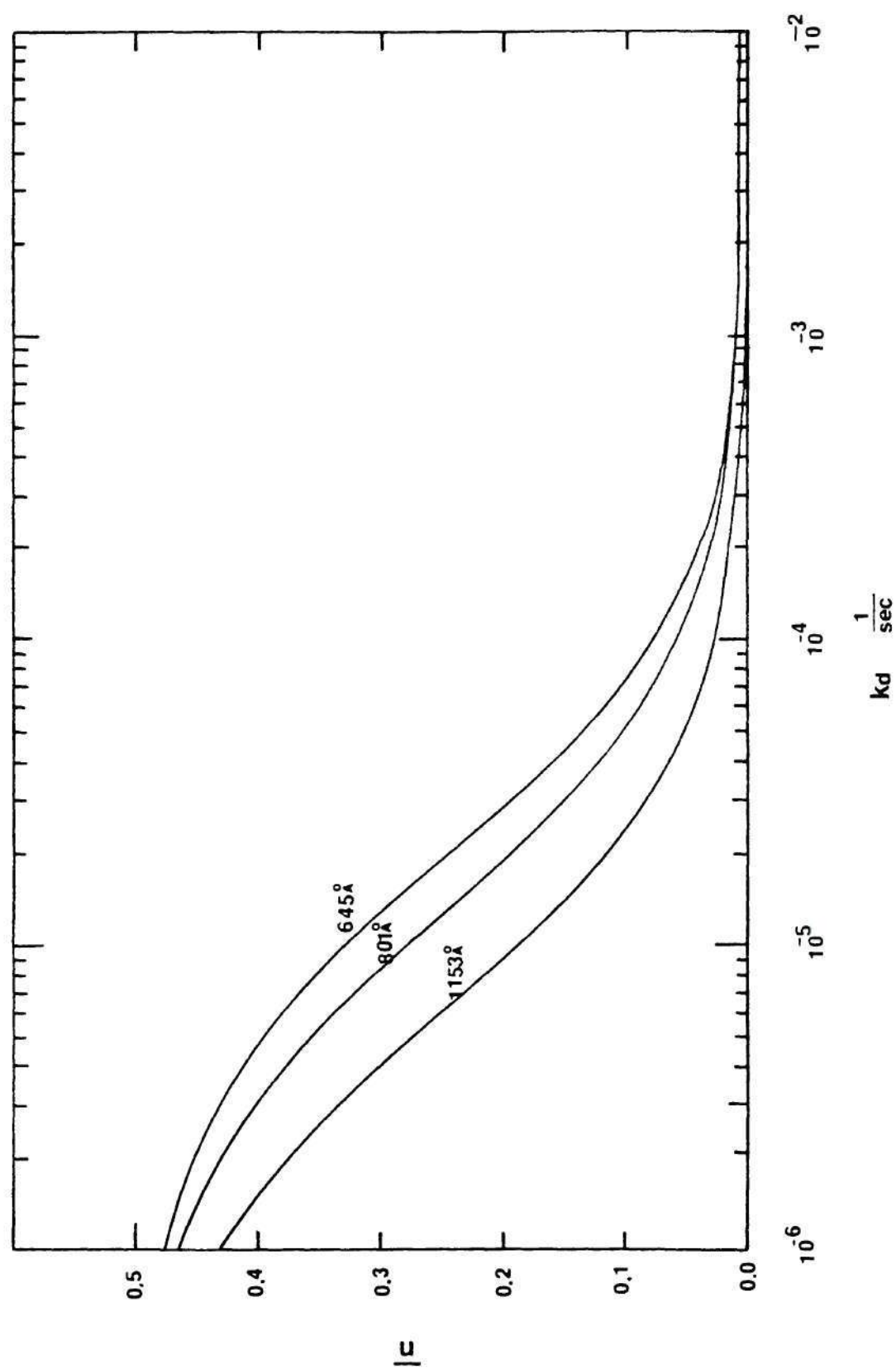


Figure 58. Relationship of \bar{n} vs. k_d Depending on d_p at 50°C (MMA).

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

The competitive growth experiment for the styrene system was carried out to determine a value for C in $\frac{dv}{dt} = k \cdot d_p^C$. If the system obeys Smith-Ewart Case II theory, that is if $k_d = 0$, the value of C must be zero. However, our results show the value of C to be about 2.0. This result is consistent with our assumption that the surface area of the polymer particle influences the volumetric growth rate.

The value of k_d was not zero even in the styrene system. The value of k_d for the styrene system was higher than that of MMA. Since styrene has the higher value of the monomer chain transfer constant, small molecules which can be easily desorbed are generated faster than in the MMA system.

The value of k_d tended to decrease with increases in the polymerization temperature for styrene and MMA. When chain transfer agents were added, k_d increased.

The effect of chain transfer agent on k_d was investigated by using carbon tetrachloride and xylene as the chain transfer agents. The addition of carbon

tetrachloride and xylene increased the value of k_d , and decreased the polymerization rate. These chain transfer agents would not effect the polymerization rate in bulk or solution polymerization.

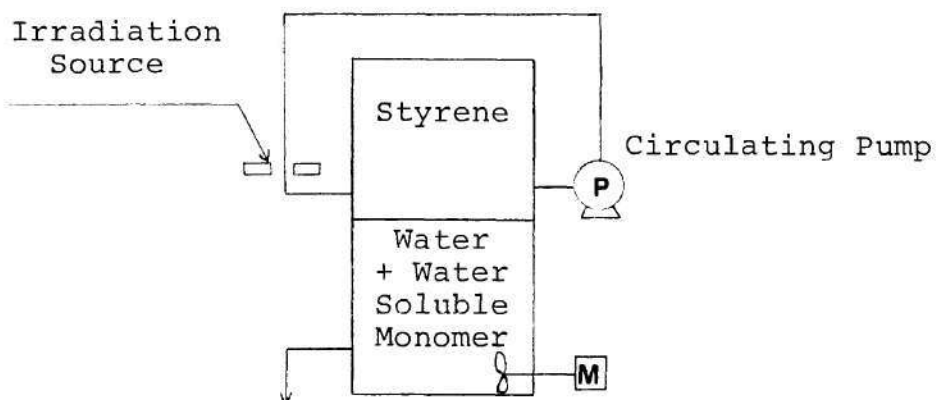
The desorption rate constant, k_d was shown to be a function of d_{ps}^2 for the case where free radicals were assumed to be desorbed from a swollen monomer layer, not from the center of the polymer particle. k_d was also found experimentally to be proportional to d_{ps}^2 .

Values of k_d calculated by Ugelstad's model in the MMA system were higher than those calculated by the model used in this work. The deviation seems to be based on whether water-phase deactivation of free radicals due to polymerization is considered or not.

Recommendations

1) The indirect determination of the desorption rate constant, k_d was demonstrated in the styrene and MMA systems. However, no one has demonstrated directly the transformation of the free radicals from the bulk phase to the water phase. Hence, an experiment to determine the desorption of free radicals is recommended. It can be studied by using the irradiation apparatus shown in the diagram on page 139.

First, the interface of styrene and water containing the water soluble monomer (i.e., acrylamide) is



prepared by the natural decanting. The water solution is stirred and styrene monomer is circulated by the circulation pump at constant temperature. The styrene monomer is irradiated to generate monomer radicals at the end of circulating path. The irradiation source is set up so that it does not effect the initiation in the water solution. At the specified time, the water solution is taken out and characterized by the viscosity measurement and IR or NMR. If existence of polymer or oligomer is demonstrated, direct evidence would be obtained for the desorption of free radicals from the styrene phase to the water phase.

2) The value of k_d as determined for the styrene and MMA systems was effected by the monomer chain transfer constant, C_M . Therefore, the vinyl acetate system, which has a high value of the monomer chain transfer constant, might yield a higher value of k_d . Hence, the same kind of experiments are recommended for vinyl acetate emulsion polymerization.

3) v_{ps} in Eq. (65), as mentioned before, is a time variable parameter. The value of v_{ps} is not constant even if a steady state is achieved with the polymerization rate. Thus, a new kinetic model which accounts for the change of v_{ps} should be derived.

APPENDICES

APPENDIX 1

LIST OF CONSTANTS

Molecular weight of styrene monomer = 104.15 (gram/gmole)

Molecular weight of methylmethacrylate = 100.12 (gram/gmole)

Molecular weight of potassium persulfate = 270.33 (gram/
gmole)

Molecular weight of sodium lauryl sulfate = 288 (gram/gmole)

Density of styrene monomer (20°C) = 0.906 (gram/cm³)

Density of polystyrene (20°C) = 1.05 (gram/cm³)

Density of Methylmethacrylate (25°C) = 0.939 (gram/cm³)

Density of Polymethylmethacrylate (20°C) = 1.19 (gram/cm³)

Rate Constant of Radical Entry into

Polymer Particle (k_2)

$$k_2 = 2\pi \cdot D_w \cdot d_{ps} \left(\frac{\text{cm}^3}{\text{sec} \cdot \text{gmole}} \right)$$

Radical Diffusion Coefficient in Water Phase (D_w)

$$D_w = 7.4 \times 10^{-8} \times \frac{(x \cdot M_w)^{1/2} \cdot T}{\eta \cdot V^{0.6}} \quad [\text{Ref. 55}]$$

where x : association parameter, 2.6 for water

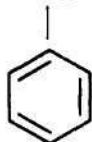
M_w : molecular weight of solvent, 18.0 $\frac{\text{g}}{\text{gmole}}$ for
water

T : temperature (°K)

η : viscosity of solution (C_p), 1.0 C_p for water

V: Molal volume of solute at normal boiling point $\frac{\text{cm}^3}{\text{gmole}}$

Styrene [56]: $\text{CH}=\text{CH}_2$



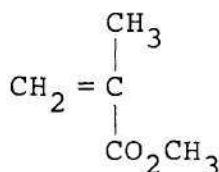
$$\text{C} \times 8 = 14.8 \times 8 = 118.4 \text{ cm}^3/\text{gatom}$$

$$\text{H} \times 8 = 3.7 \times 8 = 29.6$$

$$148.0 \text{ cm}^3/\text{gmole}$$

$$^*V_{\text{styrene}} = 148.0 - 15.0 = 133.0 \text{ cm}^3/\text{gmole}$$

MMA:



$$\text{C} \times 5 = 14.8 \times 5 = 74.0 \text{ cm}^3/\text{gatom}$$

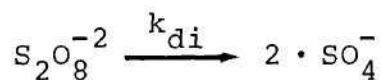
$$\text{O} \times 2 = 12.0 \times 2 = 24.0$$

$$\text{H} \times 8 = 3.7 \times 8 = 29.6$$

$$127.6 \text{ cm}^3/\text{gmole}$$

$$^*V_{\text{MMA}} = 127.6 \text{ cm}^3/\text{gmole}$$

Decomposition Rate Constant of Initiator (k_{di})



* These data were used.

$$\begin{aligned}
 k_{di} &= 2.18 \times 10^{20} \cdot \exp\left(-\frac{33500}{RT}\right) && \text{1/hour} \\
 &= 6.055 \times 10^{16} \cdot \exp\left(-\frac{33500}{RT}\right) && \text{1/sec [Ref. 51]}
 \end{aligned}$$

R: gas constant 1.9872

The estimation of k_{di} is a very difficult problem. According to Parts [57] the value of k_{di} can be altered by the presence of monomer or emulsifier.

Mutual Termination Reaction Rate Constant (k_{mtp})

The data which are listed in the Polymer Handbook [58] were plotted as shown in Figures 59 and 60. k_{mtp} values were picked up from the linear line which approximated the wide-range data.

Propagation Rate Constant in the Water Phase (k_{pw}) [59]

The propagation rate constant in the water phase, k_{pw} , for MMA was calculated by the following relationship:

$$k_{pw} = 2.1306 \times 10^5 \cdot \exp\left(-\frac{4700}{RT}\right)$$

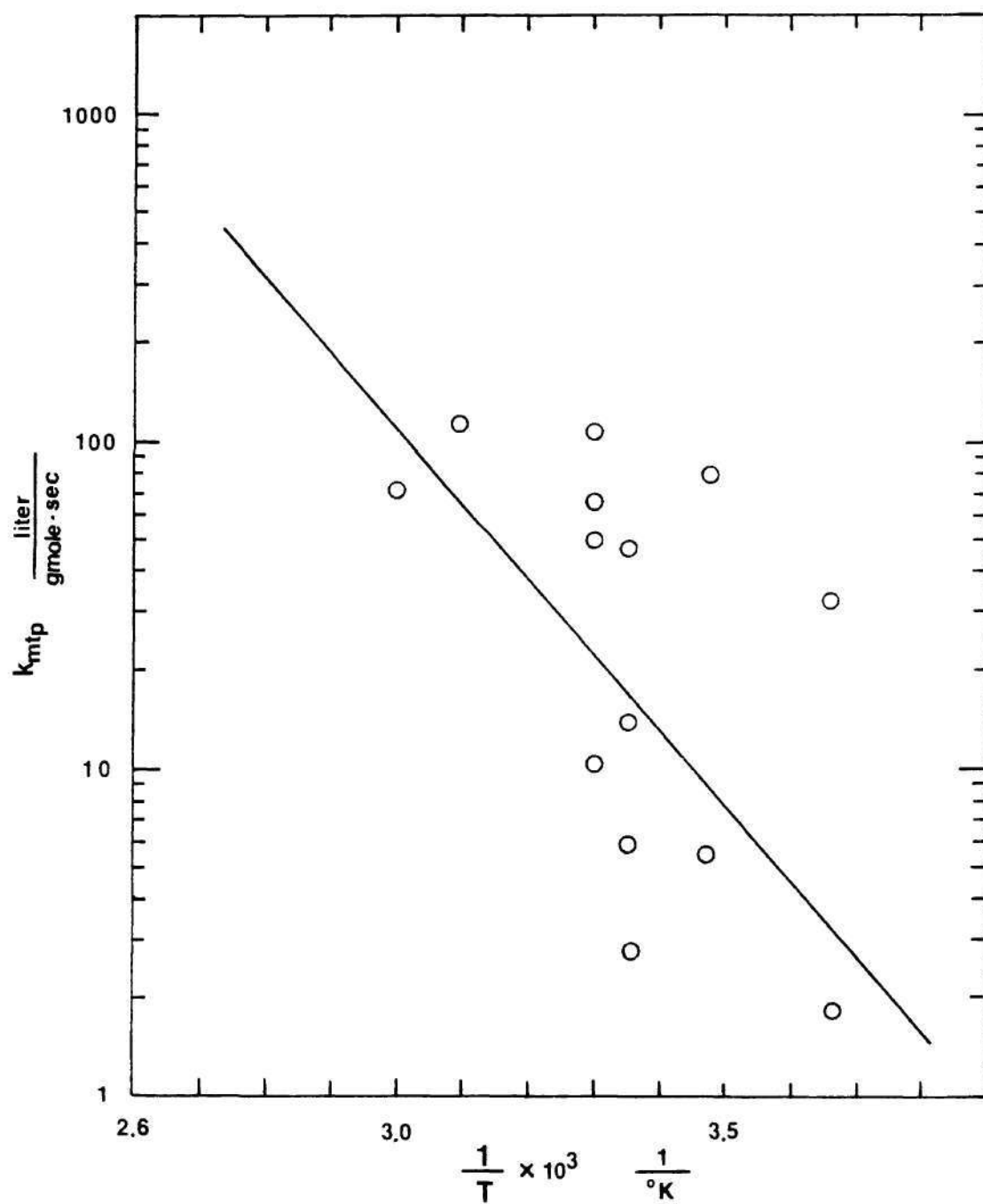
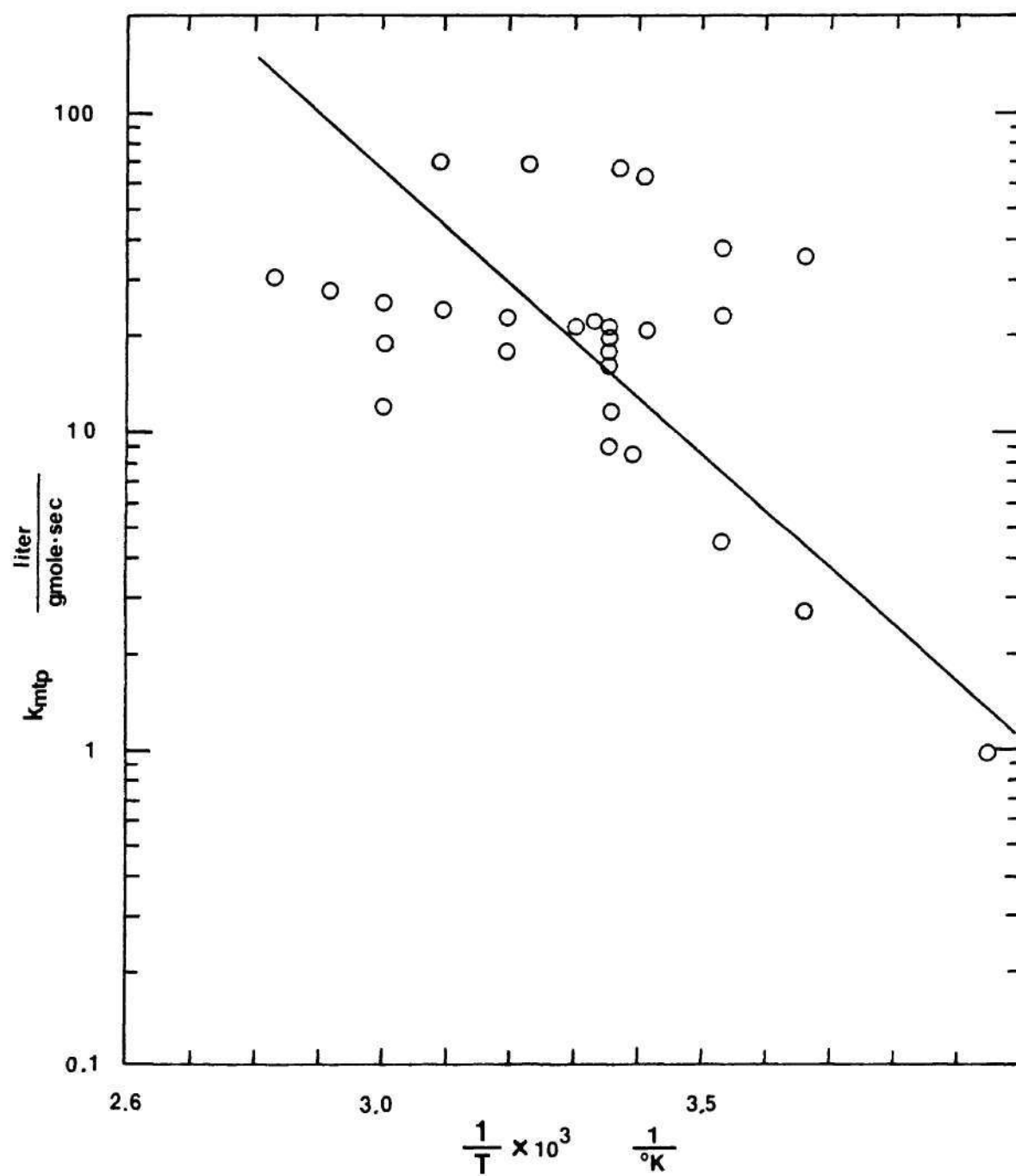


Figure 59. Relationship of k_{mtp} vs. $\frac{1}{T}$ (Styrene).



APPENDIX 2

PREPARATION OF MONODISPERSED LATEX

(A) Latex-8 (Styrene)	unit: gram
Recipe Styrene monomer	4.9940
Potassium persulfate	0.0135
Sodium lauryl sulfate	0.1440
Water	<u>1000.0000</u>
	1005.1515
Reaction temperature	70°C
Reaction time	44 hours
Average conversion	70.03 %
Seed latex data	

Calculation of average diameter

$$\sum n_i d_{pi} = 13.999 \mu$$

$$n_i = 175$$

$$d_{pn} = \frac{\sum n_i \cdot d_i}{n_i} = \frac{13.999}{175} = 0.0800 \mu$$

$$\sum n_i d_{pi}^6 = 4816.872 \times 10^{-8} \mu^6$$

$$d_{pw} = \left(\frac{\sum n_i \cdot d_i^6}{\sum n_i \cdot d_i^3} \right)^{1/3} = 0.08106 = 810.6 \text{ \AA}$$

$$U (\text{latex dispersity}) = \frac{d_w}{d_n} = 1.013$$

Calculation of number of particles

M_0 : monomer concentration

$$4.994 \left(\frac{\text{g}}{\text{l-water}} \right) = 0.004994 \left(\frac{\text{gram}}{\text{cc-water}} \right)$$

X_M : conversion 70.03% = 0.7003

$$d_p: 810.60 \text{ \AA} = 0.08106 \mu$$

$$= 0.08106 \times 10^{-4} \text{ cm}$$

A_s : surface area occupied by an emulsifier molecule $37 \times 10^{-6} \text{ cm}^2/\text{molecule}$ for sodium lauryl sulfate

ρ_{poly} : polymer density 1.05 g/cm^3 for polystyrene

$$N_T = \frac{M_0 \cdot X_M}{\frac{\pi}{6} \cdot d_p^3 \cdot \rho_{\text{poly}}}$$

$$= \frac{0.004994 \times 0.7003 \times 6}{3.14 \times (0.08106 \times 10^{-4})^3 \times 1.05}$$

$$= 1.1945 \times 10^{13} \left(\frac{\text{particle}}{\text{cc-water}} \right)$$

(B)	Latex-9 (Styrene)	unit: gram
Recipe	Styrene monomer	9.9808
	Potassium persulfate	0.0131
	Sodium lauryl sulfate	0.0573
	Water	<u>1000.0000</u>
		1010.0512
	Reaction temperature	70°C
	Reaction time	43 hours

Average conversion 83.35%

Seed latex data

$$d_{pn} = 0.1156 = 1156\overset{\circ}{\text{\AA}}$$

$$d_{pw} = 0.1161 = 1161$$

$$U = 1.005$$

$$N_T = 0.9677 \times 10^{13} \left(\frac{\text{particle}}{\text{cc-water}} \right)$$

(C) Latex-22 (Styrene) unit: gram

Recipe Styrene monomer 5.1861

Potassium persulfate 0.0141

Sodium lauryl sulfate 0.1442

Water 1000.0000
1005.3444

Reaction temperature 70°C

Reaction time 40 hours

Average conversion 76.12 %

Seed latex data

$$d_{pn} = 0.0814 \mu = 814\overset{\circ}{\text{\AA}}$$

$$d_w = 0.0821 \mu = 821\overset{\circ}{\text{\AA}}$$

$$U = 1.009$$

$$N_T = 1.3320 \times 10^{13} \left(\frac{\text{particle}}{\text{cc-water}} \right)$$

(D) Latex-24 (Styrene) unit: gram

Recipe Styrene monomer 9.7161

Potassium persulfate 0.0149

Sodium lauryl sulfate 0.0577

Water 1000.0000
1009.7887

Reaction temperature 70°C

Reaction time 25 hours

Average conversion 85.02%

Seed latex data

$$d_{pn} = 0.1118 \mu = 1118 \overset{\circ}{\text{Å}}$$

$$d_{pw} = 0.1123 \mu = 1123 \overset{\circ}{\text{Å}}$$

$$U = 1.004$$

$$N_T = 1.0758 \times 10^{13} \left(\frac{\text{particle}}{\text{cc-water}} \right)$$

(E) Latex-1 (Styrene) unit: gram

Recipe Styrene monomer 20.7359

Potassium persulfate 0.0824

Water 1000.0000

1020.8183

Reaction temperature 70°C

Reaction time 34 hours, 50 min.

Average conversion 92.31 %

Seed latex data

$$dp_n = 0.2250 \mu = 2250 \overset{\circ}{\text{Å}}$$

$$d_{pw} = 0.2250 \mu = 2250 \overset{\circ}{\text{Å}}$$

$$U = 1.000$$

$$N_T = 3.058 \times 10^{12} \left(\frac{\text{particle}}{\text{cc-water}} \right)$$

(F) Latex-47 (MMA) unit: gram

Recipe Methylmethacrylate monomer 45.4540

Potassium persulfate 0.0540

Sodium lauryl sulfate 0.2956

Water	<u>4000.0000</u>
	4045.8036
Reaction temperature	70°C
Reaction time	30 hours
Average conversion	96.63%
Seed latex data	

$$d_{pn} = 0.0645 \mu = 645\overset{\circ}{\text{A}}$$

$$d_{pw} = 0.0659 \mu = 659\overset{\circ}{\text{A}}$$

$$U = 1.022$$

$$N_T = 6.5688 \times 10^{13} \left(\frac{\text{particle}}{\text{cc-water}} \right)$$

(G) Latex-56 (MMA) unit: gram

Recipe Methylmethacrylate monomer	10.0089
Potassium persulfate	0.0505
Water	<u>4000.0000</u>
	4010.0594

Reaction temperature	70°C
Reaction time	33 hours
Average conversion	74.18%
Seed latex data	

$$d_{pn} = 0.0801 \mu = 801\overset{\circ}{\text{A}}$$

$$d_{pw} = 0.0825 \mu = 825\overset{\circ}{\text{A}}$$

$$U = 1.030$$

$$N_T = 5.799 \times 10^{12} \left(\frac{\text{particle}}{\text{cc-water}} \right)$$

(H) Latex-53 (MMA) unit: gram

Recipe Methylmethacrylate monomer	22.5124
Potassium persulfate	0.0580

Water	<u>4000.0000</u>
	4022.5704
Reaction temperature	70°C
Reaction time	30 hours
Average conversion	93.29%
Seed latex data	
	$d_{pn} = 0.1153 \mu = 1153 \overset{\circ}{\text{A}}$
	$d_{pw} = 0.1157 \mu = 1157 \overset{\circ}{\text{A}}$
	$U = 1.003$
	$N_T = 5.497 \times 10^{12} \left(\frac{\text{particle}}{\text{cc-water}} \right)$

APPENDIX 3

CALCULATION OF C BY VANDERHOFF'S METHOD

Since $v = (\pi/6) \cdot d_p^3$, Eq. (77) can be obtained from Eq. (40)

$$\left(\frac{1}{d_p}\right) \left(\frac{d \cdot d_p}{dt}\right) = \left(\frac{2k}{\pi}\right) \cdot d_p^{c-3} \quad (77)$$

k is assumed to be the same for particles of all sizes at any one instant in a particular emulsion polymerization.

Integrate Eq. (77):

$$d_p^{3-c} - d_p^{3-c} = \frac{2(3-c)}{\pi} \int_0^t k(t) \cdot dt \quad (78)$$

If two different growing particles are considered with the initial sizes, d_{a0} , d_{b0} and the final sizes d_a , d_b .

$$d_a^{3-c} - d_{a0}^{3-c} = d_b^{3-c} - d_{b0}^{3-c} = \frac{2(3-c)}{\pi} \int_0^t k(t) \cdot dt \quad (79)$$

Define $\alpha = \frac{d_{a0}}{d_{b0}}$ $\gamma = \frac{d_b}{d_{b0}}$

Solve Eq. (79) for the final ratio of diameters, $\frac{d_a}{d_b}$:

$$\frac{d_a}{d_b} = \frac{1}{\gamma} [\gamma^3 + \alpha^3 - 1]^{1/3} \quad (80)$$

Eq. (80) for various integral values of

$$c = 0:$$

$$\frac{d_a}{d_b} = \left(1 + \frac{\alpha^3 - 1}{\gamma^3} \right)^{1/3} \quad (81)$$

$$c = 1:$$

$$\frac{d_a}{d_b} = \left(1 + \frac{\alpha^2 - 1}{\gamma^2} \right)^{1/2} \quad (82)$$

$$c = 2:$$

$$\frac{d_a}{d_b} = \left(1 + \frac{\alpha - 1}{\gamma} \right) \quad (83)$$

$$c = 2.5:$$

$$\frac{d_a}{d_b} = \frac{1}{\gamma} (\gamma^{0.5} + \alpha^{0.5} - 1)^2 \quad (84)$$

$$c = 3:$$

$$\frac{d_a}{d_b} = \alpha \quad (85)$$

Theoretical variation of $\frac{d_a}{d_b}$ with γ at integral values of m in this seed competitive polymerization was based on the calculation data in Table 18. This data was used to draw theoretical solid lines in Figures 10 and 11.

Table 18. Theoretical Variation of d_{pa}/d_{pb} with γ
when $\alpha = 1.445$.

γ	$c = 0.0$	$c = 1.0$	$c = 2.0$	$c = 2.5$	$c = 3.0$
1.00	1.445	1.445	1.445	1.445	1.445
1.10	1.3600	1.3781	1.4045	1.4225	↓
1.20	1.2941	1.3250	1.3708	1.4029	
1.30	1.2425	1.2821	1.3423	1.3860	
1.40	1.2016	1.2470	1.3179	1.3708	
1.50	1.1690	1.2180	1.2967	1.3572	
1.60	1.1428	1.1937	1.2781	1.3451	
1.70	1.1215	1.1732	1.2618	1.3340	
1.80	1.1041	1.1558	1.2472	1.3239	
1.90	1.0897	1.1408	1.2342	1.3147	
2.00	1.0778	1.1278	1.2225	1.3062	

APPENDIX 4

RECIPE AND CONVERSION DATA
FOR POLYMERIZATION RATE EXPERIMENTS

(1) In Figures 18, 19 and 20

			Time	Conversion
EX-28 (50°C)	unit: gram		(hr)	[P] $\left(\frac{\text{gmole}}{\text{cc-water}}\right)$
Recipe Latex-22	100.0034		0.5	4.52×10^{-5}
Potassium persulfate	0.0101		1.0	4.27×10^{-5}
			1.5	4.39×10^{-5}
Styrene	<u>10.0049</u>		2.0	4.37×10^{-5}
	110.0184		2.5	4.34×10^{-5}
			3.0	4.57×10^{-5}
			3.5	4.73×10^{-5}
			4.0	4.77×10^{-5}
EX-29 (60°C)	unit:gram			
Recipe Latex-22	110.0011		0.5	4.86×10^{-5}
Potassium persulfate	0.0103		1.0	6.17×10^{-5}
			1.5	7.60×10^{-5}
Styrene	<u>10.0061</u>		2.0	9.51×10^{-5}
	110.0175		2.5	11.61×10^{-5}
			3.0	13.51×10^{-5}
			3.5	15.21×10^{-5}
			4.0	17.23×10^{-5}
			4.5	18.73×10^{-5}
			5.0	20.53×10^{-5}

			Time	Conversion
EX-30 (70°C)			(hr)	[P] $\left(\frac{\text{gmole}}{\text{cc-water}}\right)$
Recipe	Latex-22	100.0006	0.5	7.06×10^{-5}
	Potassium		1.0	10.35×10^{-5}
	persulfate	10.0068	1.5	14.00×10^{-5}
	Styrene	<u>0.0103</u>	2.0	17.35×10^{-5}
		110.0177	2.5	20.95×10^{-5}
			3.0	24.43×10^{-5}
			3.5	26.64×10^{-5}
			4.0	30.07×10^{-5}
			4.5	33.67×10^{-5}
			5.0	37.81×10^{-5}
EX-38 (70°C)				
Recipe	Latex-22	100.0001	0.5	8.02×10^{-5}
	Potassium	0.0100	1.0	11.19×10^{-5}
	persulfate		1.5	14.63×10^{-5}
	Styrene	10.0032	2.0	18.22×10^{-5}
	Carbon	0.6111	2.5	21.85×10^{-5}
	tetrachloride	<u></u>	3.0	25.44×10^{-5}
		110.6244	3.5	29.11×10^{-5}
			4.0	32.75×10^{-5}
			4.5	36.47×10^{-5}
			5.0	42.71×10^{-5}
EX-51 (70°C)				
Recipe	Latex-22	100.0050	0.5	7.48×10^{-5}
	Potassium	0.0102	1.0	9.60×10^{-5}
	persulfate		1.5	12.12×10^{-5}
	Styrene	10.0059	2.0	14.67×10^{-5}
	Xylene	<u>2.5001</u>	2.5	16.94×10^{-5}
		112.5212	3.0	19.48×10^{-5}
			3.5	21.82×10^{-5}

unit: gram			Time (hr)	Conversion [P] $\left(\frac{\text{gmole}}{\text{cc-water}}\right)$
EX-51 (cont'd)			4.0	24.13×10^{-5}
			4.5	26.27×10^{-5}
			5.0	28.52×10^{-5}
EX-37 (60°C)				
Recipe	Latex-22	100.0011	0.5	6.48×10^{-5}
	Potassium	0.0098	1.0	9.33×10^{-5}
	persulfate		1.5	10.31×10^{-5}
	Styrene	10.0049	2.0	11.06×10^{-5}
	Carbon	0.2211	2.5	14.45×10^{-5}
	tetrachloride		3.0	16.96×10^{-5}
		110.2369	3.5	18.54×10^{-5}
			4.0	20.54×10^{-5}
			4.5	22.96×10^{-5}
			5.0	24.53×10^{-5}

(2) In Figures 21 and 22

EX-31 (50°C)				
Recipe	Latex-24	100.0001	0.5	9.39×10^{-5}
	Potassium	0.0102	1.0	10.00×10^{-5}
	persulfate		1.5	10.92×10^{-5}
	Styrene	9.9995	2.0	11.49×10^{-5}
		110.0098	2.5	12.35×10^{-5}
			3.0	13.13×10^{-5}
			3.5	13.89×10^{-5}
			4.0	14.98×10^{-5}
			4.5	15.88×10^{-5}
			5.0	16.78×10^{-5}

EX-32 (60°C)				
Recipe	Latex-24	100.0015	0.5	8.96×10^{-5}
	Potassium	0.0106	1.0	10.00×10^{-5}
	persulfate			

EX-32 (cont'd)		unit: gram	Time (hr)	Conversion [P] $\left(\frac{\text{gmole}}{\text{cc-water}}\right)$
Styrene	<u>9.9990</u>		1.5	11.08×10^{-5}
	110.0111		2.0	12.42×10^{-5}
			2.5	13.56×10^{-5}
			3.0	14.38×10^{-5}
			3.5	15.33×10^{-5}
			4.0	16.61×10^{-5}
			4.5	17.06×10^{-5}
			5.0	17.74×10^{-5}

EX-33 (70°C)

Recipe	Latex-24	100.0013	0.5	11.10×10^{-5}
	Potassium	0.0103	1.0	13.78×10^{-5}
	persulfate		1.5	16.21×10^{-5}
	Styrene	<u>10.0007</u>	2.5	22.14×10^{-5}
		110.0123	3.0	25.42×10^{-5}
			3.5	28.70×10^{-5}
			4.0	32.17×10^{-5}
			4.5	35.95×10^{-5}
			5.0	38.85×10^{-5}

EX-39 (70°C)

Recipe	Latex-24	100.0014	0.5	12.30×10^{-5}
	Potassium	0.0102	1.0	15.11×10^{-5}
	persulfate		1.5	17.89×10^{-5}
	Styrene	10.0042	2.0	21.28×10^{-5}
	Carbon	0.6015	2.5	24.46×10^{-5}
	tetrachloride	<u> </u>	3.0	27.81×10^{-5}
		110.6173	3.5	31.18×10^{-5}
			4.0	34.92×10^{-5}
			4.5	38.13×10^{-5}
			5.0	42.02×10^{-5}

			unit: gram	Time (hr)	Conversion [P] $\left(\frac{\text{gmole}}{\text{cc-water}}\right)$
EX-40 (70°C)					
Recipe	Latex-24	100.0050		0.5	11.64×10^{-5}
	Potassium persulfate	0.0104		1.0	14.40×10^{-5}
				1.5	16.82×10^{-5}
	Styrene	10.0000		2.0	19.47×10^{-5}
	Carbon tetra-chloride	1.8079		2.5	22.00×10^{-5}
		<hr/>		3.0	24.50×10^{-5}
		111.8233		3.5	27.09×10^{-5}
				4.0	29.53×10^{-5}
				4.5	31.38×10^{-5}
				5.0	33.66×10^{-5}
EX-41 (70°C)					
Recipe	Latex-24	100.0058		0.5	12.12×10^{-5}
	Potassium persulfate	0.0100		1.0	15.01×10^{-5}
				1.5	17.54×10^{-5}
	Styrene	10.0024		2.0	19.80×10^{-5}
	Carbon tetra-chloride	3.7270		2.5	21.81×10^{-5}
		<hr/>		3.0	23.91×10^{-5}
		113.7452		3.5	25.76×10^{-5}
				4.0	27.65×10^{-5}
				4.5	29.37×10^{-5}
				5.0	30.84×10^{-5}
EX-48 (70°C)					
Recipe	Latex-24	100.0707		0.5	11.05×10^{-5}
	Potassium persulfate	0.0105		1.0	13.36×10^{-5}
				1.5	15.41×10^{-5}
	Styrene	10.0166		2.0	17.80×10^{-5}
	Xylene	2.5825		2.5	19.93×10^{-5}
		<hr/>		3.0	22.22×10^{-5}
		112.6803		3.5	24.82×10^{-5}

			unit: gram	Time (hr)	Conversion [P] $\left(\frac{\text{gmole}}{\text{cc-water}}\right)$
EX-48 (cont'd)				4.0	27.73×10^{-5}
				4.5	29.41×10^{-5}
				5.0	31.18×10^{-5}
(3) In Figure 23					
EX-49 (60°C)					
Recipe	Latex-24	110.0271		0.5	9.47×10^{-5}
	Potassium	0.0112		1.5	10.57×10^{-5}
	persulfate			2.0	11.47×10^{-5}
	Styrene	10.0147		2.5	12.29×10^{-5}
	Xylene	2.5025		3.0	13.43×10^{-5}
		<hr/>		3.5	14.23×10^{-5}
		112.5555		4.0	15.14×10^{-5}
				4.5	16.45×10^{-5}
				5.0	17.77×10^{-5}
(4) In Figure 24					
EX-50 (50°C)					
Recipe	Latex-24	100.0082		0.5	9.34×10^{-5}
	Potassium	0.0100		1.0	8.98×10^{-5}
	persulfate			1.5	9.01×10^{-5}
	Styrene	10.0088		2.0	9.09×10^{-5}
	Xylene	2.5767		2.5	8.92×10^{-5}
		<hr/>		3.0	9.62×10^{-5}
		112.6037		3.5	9.59×10^{-5}
				4.0	10.06×10^{-5}
				4.5	9.37×10^{-5}
				5.0	9.27×10^{-5}

			unit: gram	Time (hr)	Conversion [P] $\left(\frac{\text{gmole}}{\text{cc-water}} \right)$
(5) In Figure 25					
EX-34 (50°C)					
Recipe	Latex-1	99.9997		0.5	20.08×10^{-5}
	Potassium	0.0100		1.0	19.67×10^{-5}
	persulfate			1.5	19.72×10^{-5}
	Styrene	<u>10.0000</u>		2.0	19.66×10^{-5}
		110.0097		2.5	19.84×10^{-5}
				3.0	20.09×10^{-5}
				3.5	20.35×10^{-5}
				4.0	20.69×10^{-5}
				4.5	20.97×10^{-5}
				5.0	21.28×10^{-5}
EX-35 (60°C)					
Recipe	Latex-1	100.0000		0.5	22.07×10^{-5}
	Potassium	0.0100		1.0	23.46×10^{-5}
	persulfate			1.5	24.81×10^{-5}
	Styrene	<u>10.0019</u>		2.0	26.19×10^{-5}
		110.0119		2.5	27.23×10^{-5}
				3.0	28.14×10^{-5}
				3.5	30.42×10^{-5}
				4.0	31.75×10^{-5}
				4.5	33.22×10^{-5}
				5.0	34.81×10^{-5}
EX-36 (70°C)					
Recipe	Latex-1	100.0022		0.5	21.69×10^{-5}
	Potassium	0.0100		1.0	24.09×10^{-5}
	persulfate			1.5	25.55×10^{-5}
	Styrene	<u>10.0024</u>		2.5	31.22×10^{-5}
		110.0146		3.0	33.62×10^{-5}

	unit: gram	Time (hr)	Conversion [P] $\left(\frac{\text{gmole}}{\text{cc-water}}\right)$
EX-36 (cont'd)		3.5	36.57×10^{-5}
		4.0	39.87×10^{-5}
		4.5	42.62×10^{-5}
		5.0	46.08×10^{-5}

(6) In Figure 26

EX-42 (70°C)

Recipe	Latex-1	100.0037	0.75	18.06×10^{-5}
	Potassium	0.0100	1.25	18.53×10^{-5}
	persulfate		1.75	19.82×10^{-5}
	Styrene	10.0129	2.25	20.92×10^{-5}
	Carbon tetra-	3.6014	2.75	22.84×10^{-5}
	chloride		3.25	24.51×10^{-5}
		<u>113.6280</u>	3.75	26.27×10^{-5}
			4.25	27.31×10^{-5}
			4.75	28.76×10^{-5}

EX-43 (70°C)

Recipe	Latex-1	100.0078	0.5	21.67×10^{-5}
	Potassium	0.0107	1.0	22.72×10^{-5}
	persulfate		1.5	23.55×10^{-5}
	Styrene	10.0071	2.0	25.32×10^{-5}
	Xylene	2.5017	2.5	26.62×10^{-5}
		<u>112.5273</u>	3.0	28.58×10^{-5}
			3.5	30.51×10^{-5}
			4.0	32.54×10^{-5}
			4.5	33.88×10^{-5}
			5.0	36.11×10^{-5}

unit: gram			Time (hr)	Conversion [P] $\left(\frac{\text{gmole}}{\text{cc-water}}\right)$
(7) In Figure 27				
EX-45 (60°C)				
Recipe	Latex-1	100.0038	0.5	21.09 x 10 ⁻⁵
	Potassium	0.0100	1.0	20.89 x 10 ⁻⁵
	persulfate		1.5	21.71 x 10 ⁻⁵
	Styrene	10.0177	2.0	22.43 x 10 ⁻⁵
	Xylene	<u>2.5098</u>	2.5	23.36 x 10 ⁻⁵
		112.5413	3.0	23.91 x 10 ⁻⁵
			3.5	24.79 x 10 ⁻⁵
			4.0	25.70 x 10 ⁻⁵
			4.5	26.47 x 10 ⁻⁵
			5.0	27.12 x 10 ⁻⁵
(8) In Figure 28				
EX-67 (70°C)			Time (min)	
Recipe	Latex-47	100.0068	0	1.314 x 10 ⁻⁴
	Potassium	0.0101	10	2.219 x 10 ⁻⁴
	persulfate		20	3.646 x 10 ⁻⁴
	MMA	<u>14.9272</u>	30	5.834 x 10 ⁻⁴
		114.9441	40	10.076 x 10 ⁻⁴
			50	15.170 x 10 ⁻⁴
EX-68 (70°C)				
Recipe	Latex-47	100.0061	0	1.262 x 10 ⁻⁴
	Potassium	0.0041	10	2.271 x 10 ⁻⁴
	persulfate		20	3.369 x 10 ⁻⁴
	MMA	<u>15.0009</u>	30	4.648 x 10 ⁻⁴
		115.0111	40	6.326 x 10 ⁻⁴
			50	9.091 x 10 ⁻⁴
			60	14.529 x 10 ⁻⁴

			Time (min)	Conversion [P] $\left(\frac{\text{gmole}}{\text{cc-water}}\right)$
EX-69 (60°C)				
Recipe	Latex-47	100.0037	0	1.268×10^{-4}
	Potassium persulfate	0.0040	10	1.504×10^{-4}
			20	1.748×10^{-4}
	MMA	<u>15.0052</u>	30	2.064×10^{-4}
		115.0129	40	2.354×10^{-4}
			50	2.691×10^{-4}
			60	3.012×10^{-4}
			70	3.378×10^{-4}
			80	3.731×10^{-4}
			90	4.175×10^{-4}

EX-70 (55°C)				
Recipe	Latex-47	100.0023	0	1.253×10^{-4}
	Potassium persulfate	0.0040	10	1.295×10^{-4}
			20	1.273×10^{-4}
	MMA	<u>15.0110</u>	30	1.487×10^{-4}
		115.0173	40	1.580×10^{-4}
			50	1.747×10^{-4}
			60	1.843×10^{-4}
			70	1.990×10^{-4}
			80	2.021×10^{-4}
			90	2.211×10^{-4}

(9) In Figure 29

EX-71 (70°C)			0	1.257×10^{-4}
Recipe	Latex-47	100.0029	10	2.114×10^{-4}
	Potassium persulfate	0.040	20	3.152×10^{-4}
			30	4.437×10^{-4}
	MMA	15.0064	40	6.087×10^{-4}
	Carbon tetra-chloride	<u>1.6000</u>	50	8.463×10^{-4}
		116.6133		

			Time	Conversion
unit: gram			(min)	[P] $\left(\frac{\text{gmole}}{\text{cc-water}}\right)$
EX-72 (70°C)				
Recipe	Latex-47	100.0130	0	1.250×10^{-4}
	Potassium persulfate	0.0042	10	1.990×10^{-4}
			20	2.874×10^{-4}
	MMA	15.0005	30	3.973×10^{-4}
	Xylene	<u>1.5801</u>	40	5.184×10^{-4}
		116.5978	50	6.622×10^{-4}
			60	8.356×10^{-4}
			70	11.016×10^{-4}

(10) In Figure 30

EX-73 (60°C)

Recipe	Latex-47	100.0021	0	1.306×10^{-4}
	Potassium persulfate	0.0044	10	1.360×10^{-4}
			20	1.656×10^{-4}
	MMA	15.0000	30	1.920×10^{-4}
	Carbon tetra-chloride	<u>1.6037</u>	40	2.211×10^{-4}
		116.6102	50	2.528×10^{-4}
			60	2.734×10^{-4}
			70	3.009×10^{-4}
			80	3.270×10^{-4}
			90	3.608×10^{-4}

EX-74 (60°C)

Recipe	Latex-47	100.0026	0	1.240×10^{-4}
	Potassium persulfate	0.0042	10	1.260×10^{-4}
			20	1.273×10^{-4}
	MMA	15.0055	30	1.368×10^{-4}
	Xylene	<u>1.5995</u>	40	1.499×10^{-4}
		116.6118	50	1.611×10^{-4}
			60	1.703×10^{-4}

	unit: gram	Time (min)	Conversion [P] $\left(\frac{\text{gmole}}{\text{cc-water}}\right)$
EX-74 (cont'd)		70	1.824×10^{-4}
		80	1.874×10^{-4}
		90	1.979×10^{-4}

(11) In Figure 31

EX-77 (55°C)

Recipe Latex-56	100.0052	0	1.67×10^{-5}
Potassium persulfate	0.0040	20	2.29×10^{-5}
		30	2.17×10^{-5}
MMA	<u>15.0000</u>	40	2.33×10^{-5}
	115.0092	50	2.20×10^{-5}
		60	2.72×10^{-5}
		70	2.46×10^{-5}
		80	2.50×10^{-5}
		90	2.70×10^{-5}
		100	2.71×10^{-5}
		110	2.62×10^{-5}
		120	2.82×10^{-5}
		130	2.75×10^{-5}
		150	2.78×10^{-5}

EX-76 (60°C)

Recipe Latex-56	100.0021	0	2.01×10^{-5}
Potassium persulfate	0.0041	20	2.77×10^{-5}
		30	2.80×10^{-5}
MMA	<u>15.0029</u>	40	3.07×10^{-5}
	115.0091	50	3.42×10^{-5}
		60	3.71×10^{-5}
		70	4.05×10^{-5}
		80	4.45×10^{-5}
		90	4.99×10^{-5}
		100	5.34×10^{-5}

unit: gram		Time (mins)	Conversion [P] $\left(\frac{\text{gmole}}{\text{cc-water}}\right)$
EX-76 (cont'd)		110	5.80×10^{-5}
		120	6.65×10^{-5}
		130	7.27×10^{-5}
		140	8.58×10^{-5}
		160	9.29×10^{-5}
EX-75 (70°C)			
Recipe Latex-56	101.0100	0	1.76×10^{-5}
Potassium	0.0041	20	1.89×10^{-5}
persulfate		30	2.77×10^{-5}
MMA	<u>15.0018</u>	40	3.34×10^{-5}
	116.0159	50	3.94×10^{-5}
		60	4.77×10^{-5}
		70	6.43×10^{-5}
		80	9.38×10^{-5}
		90	11.78×10^{-5}
		100	16.08×10^{-5}
		110	20.90×10^{-5}
		120	26.10×10^{-5}
		130	32.86×10^{-5}
		140	44.52×10^{-5}

(12) In Figure 32

EX-78 (70°C)

Recipe Latex-56	100.0048	0	2.02×10^{-5}
Potassium	0.0041	20	2.52×10^{-5}
persulfate		30	3.02×10^{-5}
MMA	15.0006	40	3.78×10^{-5}
Carbon tetra-	1.6062	50	4.68×10^{-5}
chloride	<u>116.6157</u>	60	6.23×10^{-5}
		70	6.60×10^{-5}

		unit: gram	Time (min)	Conversion [P] $\left(\frac{\text{gmole}}{\text{cc-water}} \right)$
EX-78 (cont'd)			80	8.42×10^{-5}
			90	10.95×10^{-5}
			100	13.29×10^{-5}
			110	16.28×10^{-5}
			120	18.39×10^{-5}
EX-79 (70°C)				
Recipe	Latex-56	100.0023	0	2.18×10^{-5}
	Potassium	0.0043	20	3.93×10^{-5}
	persulfate		30	5.37×10^{-5}
	MMA	15.0027	40	6.37×10^{-5}
	Xylene	<u>1.6093</u>	50	9.46×10^{-5}
		116.6186	60	12.41×10^{-5}
			70	16.35×10^{-5}
			80	20.90×10^{-5}
			90	22.63×10^{-5}
			110	33.99×10^{-5}
EX-80 (70°C)				
Recipe	Latex-56	100.0003	0	2.35×10^{-5}
	Potassium	0.0040	20	4.44×10^{-5}
	persulfate		30	5.90×10^{-5}
	MMA	15.0035	40	6.53×10^{-5}
	Carbon tetra-	3.2029	50	9.94×10^{-5}
	chloride	<u>118.2107</u>	60	14.88×10^{-5}
			70	19.02×10^{-5}
			80	24.47×10^{-5}
			90	26.80×10^{-5}

unit: gram Time (min) Conversion [P] $\left(\frac{\text{gmole}}{\text{cc-water}} \right)$

(13) In Figure 33

EX-81 (60°C)

Recipe	Latex-56	100.0105	0	2.23×10^{-5}
	Potassium persulfate	0.0039	10	2.46×10^{-5}
			20	2.32×10^{-5}
	MMA	15.0278	30	2.65×10^{-5}
	Carbon tetra-chloride	1.6037	40	2.77×10^{-5}
		<hr/>	50	2.97×10^{-5}
		116.6459	60	3.13×10^{-5}
			70	3.51×10^{-5}
			80	3.82×10^{-5}
			90	4.11×10^{-5}
			100	4.31×10^{-5}
			110	4.83×10^{-5}
			120	5.06×10^{-5}
			130	5.24×10^{-5}

EX-82 (60°C)

Recipe	Latex-56	100.0056	0	2.17×10^{-5}
	Potassium persulfate	0.0042	10	2.25×10^{-5}
			20	2.38×10^{-5}
	MMA	15.0013	30	2.46×10^{-5}
	Xylene	1.6011	40	2.52×10^{-5}
		<hr/>	50	2.52×10^{-5}
		116.6122	60	2.53×10^{-5}
			70	2.66×10^{-5}
			90	2.78×10^{-5}
			100	2.88×10^{-5}
			110	2.75×10^{-5}
			120	2.98×10^{-5}

(14) In Figure 34

EX-85 (55°C)

unit: gram			Time (min)	Conversion [P] $\left(\frac{\text{gmole}}{\text{cc-water}}\right)$
Recipe	Latex-53	100.0046	0	5.99×10^{-5}
	Potassium	0.0041	10	6.13×10^{-5}
	persulfate		30	6.22×10^{-5}
	MMA	<u>15.0078</u>	40	6.24×10^{-5}
		115.0165	50	6.33×10^{-5}
			60	6.03×10^{-5}
			70	6.39×10^{-5}
			80	6.05×10^{-5}
			90	6.37×10^{-5}
			100	6.23×10^{-5}
			110	6.36×10^{-5}
			130	6.41×10^{-5}

EX-84 (60°C)

Recipe	Latex-53	100.0081	0	6.00×10^{-5}
	Potassium	0.0043	10	6.27×10^{-5}
	persulfate		20	5.95×10^{-5}
	MMA	<u>15.0087</u>	30	6.10×10^{-5}
		115.0211	40	5.89×10^{-5}
			50	6.59×10^{-5}
			60	6.35×10^{-5}
			70	6.79×10^{-5}
			80	7.05×10^{-5}
			90	7.46×10^{-5}
			100	7.79×10^{-5}
			110	8.29×10^{-5}
			120	8.48×10^{-5}
			140	8.99×10^{-5}

			Time	Conversion
unit: gram			(min)	[P] $\left(\frac{\text{gmole}}{\text{cc-water}} \right)$
EX-83 (70°C)				
Recipe	Latex-53	100.0036	0	6.18×10^{-5}
	Potassium	0.0042	10	6.07×10^{-5}
	persulfate		20	7.41×10^{-5}
	MMA	<u>15.0025</u>	30	7.56×10^{-5}
		115.0103	40	9.97×10^{-5}
			50	13.53×10^{-5}
			60	16.36×10^{-5}
			80	25.81×10^{-5}

(15) In Figure 35

EX-86 (70°C)				
Recipe	Latex-53	100.0097	0	6.13×10^{-5}
	Potassium	0.0046	10	6.59×10^{-5}
	persulfate		20	6.42×10^{-5}
	MMA	15.0018	30	7.25×10^{-5}
	Carbon tetra-	1.6196	40	7.92×10^{-5}
	chloride	<u>116.6357</u>	50	9.46×10^{-5}
			60	10.76×10^{-5}
			70	13.09×10^{-5}
			80	15.07×10^{-5}
			90	17.72×10^{-5}
			100	18.42×10^{-5}

EX-87 (70°C)				
Recipe	Latex-53	100.0013	0	5.59×10^{-5}
	Potassium	0.0045	10	5.70×10^{-5}
	persulfate		20	6.33×10^{-5}
	MMA	15.0208	30	6.49×10^{-5}
	Xylene	<u>1.6095</u>	40	6.71×10^{-5}
		116.6361	50	7.58×10^{-5}

unit: gram			Time (min)	Conversion [P] $\left(\frac{\text{gmole}}{\text{cc-water}} \right)$
EX-87 (cont'd)			60	8.68×10^{-5}
			70	9.37×10^{-5}
			80	10.43×10^{-5}
			90	10.93×10^{-5}
			100	12.66×10^{-5}
EX-88 (60°C)				
Recipe	Latex-53	100.0134	0	5.59×10^{-5}
	Potassium	0.0040	10	5.73×10^{-5}
	persulfate		20	5.93×10^{-5}
	MMA	15.0088	30	6.06×10^{-5}
	Carbon tetra-	1.6067	40	5.87×10^{-5}
	chloride		50	6.18×10^{-5}
		<u>116.6329</u>	60	5.99×10^{-5}
			70	6.28×10^{-5}
			80	6.24×10^{-5}
			90	6.36×10^{-5}
			100	6.17×10^{-5}
			120	6.34×10^{-5}
			140	6.35×10^{-5}
EX-89 (60°C)				
Recipe	Latex-53	100.0044	0	5.95×10^{-5}
	Potassium	0.0041	10	5.82×10^{-5}
	persulfate		20	5.94×10^{-5}
	MMA	15.0044	30	6.13×10^{-5}
	Xylene	1.6065	40	5.96×10^{-5}
		<u>116.6194</u>	50	5.85×10^{-5}
			60	6.04×10^{-5}
			70	5.88×10^{-5}
			80	6.19×10^{-5}
			90	6.16×10^{-5}
			110	6.20×10^{-5}
			120	6.07×10^{-5}

APPENDIX 5

CALCULATION OF \bar{n}

All calculations were carried out as mentioned below:

EX-69 (60°C) for MMA $d_0 = 645\text{\AA}$
 $N_T = 6.5688 \times 10^{13} \left(\frac{\text{particle}}{\text{cc-water}} \right)$

	Time (seconds)	[P] $\frac{\text{gmole}}{\text{cc-water}}$
1.	0	1.268×10^{-4}
2.	600	1.504×10^{-4}
3.	1200	1.748×10^{-4}
4.	1800	2.064×10^{-4}
5.	2400	2.354×10^{-4}
6.	3000	2.691×10^{-4}
7.	3600	3.012×10^{-4}
8.	4200	3.378×10^{-4}
9.	4800	3.731×10^{-4}
10.	5400	4.175×10^{-4}

$$\text{Slope} = 5.362 \times 10^{-8} \left(\frac{\text{gmole}}{\text{cc-water} \cdot \text{sec}} \right)$$

$$(r^2 = 0.9969)$$

$$k_p = 616.163 \left(\frac{\text{l}}{\text{gmole} \cdot \text{sec}} \right) \text{ at } 60^\circ\text{C}$$

$$[M]_p = 7.0 \left(\frac{\text{gmole}}{\text{l}} \right)$$

$$n = \frac{R_p \times N_A}{k_p \times [M]_p \times N_T} = \frac{5.362 \times 10^{-8} \times 6.023 \times 10^{23}}{616.163 \times 7.0 \times 6.5688 \times 10^{13}}$$

$$= 0.114$$

Styrene

EX-28 (50°C)

$$\begin{aligned}\text{Slope} &= 8.06 \times 10^{-10} \left(\frac{\text{gmole}}{\text{cc-water} \cdot \text{sec}} \right) \\ (r^2 &= 0.959) \\ \bar{n} &= 0.0556\end{aligned}$$

EX-30 (70°C)

$$\begin{aligned}\text{Slope} &= 1.8575 \times 10^{-8} \left(\frac{\text{gmole}}{\text{cc-water} \cdot \text{sec}} \right) \\ (r^2 &= 0.999) \\ \bar{n} &= 0.634\end{aligned}$$

EX-38 (70°C)

$$\begin{aligned}\text{Slope} &= 1.9876 \times 10^{-8} \left(\frac{\text{gmole}}{\text{cc-water} \cdot \text{sec}} \right) \\ (r^2 &= 0.9998) \\ \bar{n} &= 0.678\end{aligned}$$

EX-31 (50°C)

$$\begin{aligned}\text{Slope} &= 4.577 \times 10^{-4} \left(\frac{\text{gmole}}{\text{cc-water} \cdot \text{sec}} \right) \\ (r^2 &= 0.998) \\ \bar{n} &= 0.390\end{aligned}$$

EX-33 (70°C)

$$\begin{aligned}\text{Slope} &= 17.338 \times 10^{-4} \left(\frac{\text{gmole}}{\text{cc-water} \cdot \text{sec}} \right) \\ (r^2 &= 0.9985) \\ \bar{n} &= 0.732\end{aligned}$$

EX-29 (60°C)

$$\begin{aligned}\text{Slope} &= 9.97 \times 10^{-9} \left(\frac{\text{gmole}}{\text{cc-water} \cdot \text{sec}} \right) \\ (r^2 &= 0.999) \\ \bar{n} &= 0.479\end{aligned}$$

EX-37 (60°C)

$$\begin{aligned}\text{Slope} &= 1.1244 \times 10^{-8} \left(\frac{\text{gmole}}{\text{cc-water} \cdot \text{sec}} \right) \\ (r^2 &= 0.9953) \\ \bar{n} &= 0.540\end{aligned}$$

EX-51 (60°C)

$$\begin{aligned}\text{Slope} &= 1.3134 \times 10^{-8} \left(\frac{\text{gmole}}{\text{cc-water} \cdot \text{sec}} \right) \\ (r^2 &= 0.9998) \\ \bar{n} &= 0.448\end{aligned}$$

EX-32 (60°C)

$$\begin{aligned}\text{Slope} &= 5.577 \times 10^{-4} \left(\frac{\text{gmole}}{\text{cc-water} \cdot \text{sec}} \right) \\ (r^2 &= 0.9956) \\ \bar{n} &= 0.331\end{aligned}$$

EX-50 (50°C)

$$\begin{aligned}\text{Slope} &= 3.22 \times 10^{-10} \left(\frac{\text{gmole}}{\text{cc-water} \cdot \text{sec}} \right) \\ (r^2 &= 0.4923) \\ \bar{n} &= 0.0275\end{aligned}$$

EX-49 (60°C)

$$\begin{aligned}\text{Slope} &= 5.167 \times 10^{-9} \left(\frac{\text{gmole}}{\text{cc-water} \cdot \text{sec}} \right) \\ (r^2 &= 0.992) \\ \bar{n} &= 0.307\end{aligned}$$

EX-40 (70°C)

$$\begin{aligned}\text{First Slope} &= 1.4328 \times 10^{-8} \left(\frac{\text{gmole}}{\text{cc-water} \cdot \text{sec}} \right) \\ (r^2 &= 0.9998) \\ \bar{n} &= 0.605\end{aligned}$$

$$\begin{aligned}\text{Second Slope} &= 1.2917 \times 10^{-8} \left(\frac{\text{gmole}}{\text{cc-water} \cdot \text{sec}} \right) \\ (r^2 &= 0.9986) \\ \bar{n} &= 0.545\end{aligned}$$

EX-48 (70°C)

$$\begin{aligned}\text{Slope} &= 1.2743 \times 10^{-8} \left(\frac{\text{gmole}}{\text{cc-water} \cdot \text{sec}} \right) \\ (r^2 &= 0.999) \\ \bar{n} &= 0.538\end{aligned}$$

EX-35 (60°C)

$$\begin{aligned}\text{Slope} &= 7.787 \times 10^{-9} \left(\frac{\text{gmole}}{\text{cc-water} \cdot \text{sec}} \right) \\ (r^2 &= 0.9974) \\ \bar{n} &= 1.628\end{aligned}$$

EX-39 (70°C)

$$\begin{aligned}\text{Slope} &= 1.7581 \times 10^{-8} \left(\frac{\text{gmole}}{\text{cc-water} \cdot \text{sec}} \right) \\ (r^2 &= 0.9993) \\ \bar{n} &= 0.742\end{aligned}$$

EX-41 (70°C)

$$\begin{aligned}\text{First Slope} &= 1.3428 \times 10^{-8} \left(\frac{\text{gmole}}{\text{cc-water} \cdot \text{sec}} \right) \\ (r^2 &= 0.9975) \\ \bar{n} &= 0.567\end{aligned}$$

$$\begin{aligned}\text{Second Slope} &= 1.0478 \times 10^{-8} \left(\frac{\text{gmole}}{\text{cc-water} \cdot \text{sec}} \right) \\ (r^2 &= 0.9994) \\ \bar{n} &= 0.454\end{aligned}$$

EX-34 (50°C)

$$\begin{aligned}\text{Slope} &= 1.532 \times 10^{-9} \left(\frac{\text{gmole}}{\text{cc-water} \cdot \text{sec}} \right) \\ (r^2 &= 0.9968) \\ \bar{n} &= 0.461\end{aligned}$$

EX-36 (70°C)

$$\begin{aligned}\text{Slope} &= 1.5017 \times 10^{-8} \left(\frac{\text{gmole}}{\text{cc-water} \cdot \text{sec}} \right) \\ (r^2 &= 0.9972) \\ \bar{n} &= 2.231\end{aligned}$$

EX-45 (60°C)

$$\begin{aligned}\text{Slope} &= 4.071 \times 10^{-9} \left(\frac{\text{gmole}}{\text{cc-water} \cdot \text{sec}} \right) \\ (r^2 &= 0.9925) \\ \bar{n} &= 0.851\end{aligned}$$

EX-42 (70°C)

$$\begin{aligned}\text{Slope} &= 7.929 \times 10^{-9} \left(\frac{\text{gmole}}{\text{cc-water} \cdot \text{sec}} \right) \\ (r^2 &= 0.9945) \\ \bar{n} &= 1.178\end{aligned}$$

EX-43 (70°C)

$$\begin{aligned}\text{Slope} &= 9.11 \times 10^{-9} \left(\frac{\text{gmole}}{\text{cc-water} \cdot \text{sec}} \right) \\ (r^2 &= 0.9947) \\ \bar{n} &= 1.353\end{aligned}$$

MMA

EX-67 (70°C)

$$\begin{aligned}\text{First Slope} &= 1.9433 \times 10^{-7} \left(\frac{\text{gmole}}{\text{cc-water} \cdot \text{sec}} \right) \\ (r^2 &= 0.9918) \\ \bar{n} &= 0.3056\end{aligned}$$

Second Slope

$$\begin{aligned}&= 6.469 \times 10^{-7} \left(\frac{\text{gmole}}{\text{cc-water} \cdot \text{sec}} \right) \\ (r^2 &= 0.9858) \\ \bar{n} &= 1.017\end{aligned}$$

EX-70 (55°C)

$$\begin{aligned}\text{First Slope} &= 1.871 \times 10^{-8} \left(\frac{\text{gmole}}{\text{cc-water} \cdot \text{sec}} \right) \\ (r^2 &= 0.9868) \\ \bar{n} &= 0.0466\end{aligned}$$

EX-68 (70°C)

$$\begin{aligned}\text{First Slope} &= 1.876 \times 10^{-7} \left(\frac{\text{gmole}}{\text{cc-water} \cdot \text{sec}} \right) \\ (r^2 &= 0.9985) \\ \bar{n} &= 0.295\end{aligned}$$

Second Slope

$$\begin{aligned}&= 5.4013 \times 10^{-7} \left(\frac{\text{gmole}}{\text{cc-water} \cdot \text{sec}} \right) \\ (r^2 &= 0.9669) \\ \bar{n} &= 0.8495\end{aligned}$$

EX-71 (70°C)

$$\begin{aligned}\text{First Slope} &= 1.763 \times 10^{-7} \left(\frac{\text{gmole}}{\text{cc-water} \cdot \text{sec}} \right) \\ (r^2 &= 0.9959) \\ \bar{n} &= 0.277\end{aligned}$$

Second Slope

$$= 3.355 \times 10^{-7} \left(\frac{\text{gmole}}{\text{cc-water} \cdot \text{sec}} \right)$$

$$(r^2 = 0.9946)$$

$$\bar{n} = 0.528$$

EX-72 (70°C)

First Slope

$$= 1.5088 \times 10^{-7} \left(\frac{\text{gmole}}{\text{cc-water} \cdot \text{sec}} \right)$$

$$(r^2 = 0.9961)$$

$$\bar{n} = 0.237$$

Second Slope

$$= 2.8763 \times 10^{-7} \left(\frac{\text{gmole}}{\text{cc-water} \cdot \text{sec}} \right)$$

$$(r^2 = 0.9871)$$

$$\bar{n} = 0.452$$

EX-74 (60°C)

First Slope

$$= 1.497 \times 10^{-8} \left(\frac{\text{gmole}}{\text{cc-water} \cdot \text{sec}} \right)$$

$$(r^2 = 0.9878)$$

$$\bar{n} = 0.0318$$

EX-73 (60°C)

First Slope

$$= 4.405 \times 10^{-8} \left(\frac{\text{gmole}}{\text{cc-water} \cdot \text{sec}} \right)$$

$$(r^2 = 0.9971)$$

$$\bar{n} = 0.0936$$

EX-75 (70°C)

First Slope

$$= 1.155 \times 10^{-8} \left(\frac{\text{gmole}}{\text{cc-water} \cdot \text{sec}} \right)$$

$$(r^2 = 0.9969)$$

$$\bar{n} = 0.206$$

Second Slope

$$= 5.225 \times 10^{-8} \left(\frac{\text{gmole}}{\text{cc-water} \cdot \text{sec}} \right)$$

$$(r^2 = 0.9924)$$

$$\bar{n} = 0.931$$

EX-76 (60°C)

First Slope

$$= 5.657 \times 10^{-9} \left(\frac{\text{gmole}}{\text{cc-water} \cdot \text{sec}} \right)$$

$$(r^2 = 0.9907)$$

$$\bar{n} = 0.136$$

Second Slope

$$= 1.2029 \times 10^{-8} \left(\frac{\text{gmole}}{\text{cc-water} \cdot \text{sec}} \right)$$

$$(r^2 = 0.9796)$$

$$\bar{n} = 0.290$$

EX-78 (70°C)

First Slope

$$= 1.1916 \times 10^{-8} \left(\frac{\text{gmole}}{\text{cc-water} \cdot \text{sec}} \right)$$

$$(r^2 = 0.9630)$$

$$\bar{n} = 0.212$$

Second Slope

$$= 4.172 \times 10^{-8} \left(\frac{\text{gmole}}{\text{cc-water} \cdot \text{sec}} \right)$$

$$(r^2 = 0.9981)$$

$$\bar{n} = 0.743$$

EX-80 (70°C)

First Slope

$$= 1.801 \times 10^{-8} \left(\frac{\text{gmole}}{\text{cc-water} \cdot \text{sec}} \right)$$

$$(r^2 = 0.9943)$$

$$\bar{n} = 0.321$$

EX-77 (55°C)

First Slope

$$= 1.048 \times 10^{-9} \left(\frac{\text{gmole}}{\text{cc-water} \cdot \text{sec}} \right)$$

$$(r^2 = 0.8657)$$

$$\bar{n} = 0.0295$$

EX-79 (70°C)

First Slope

$$= 1.769 \times 10^{-8} \left(\frac{\text{gmole}}{\text{cc-water} \cdot \text{sec}} \right)$$

$$(r^2 = 0.9951)$$

$$\bar{n} = 0.315$$

Second Slope

$$= 5.6933 \times 10^{-8} \left(\frac{\text{gmole}}{\text{cc-water} \cdot \text{sec}} \right)$$

$$(r^2 = 0.9953)$$

$$\bar{n} = 1.014$$

EX-81 (60°C)

First Slope

$$= 2.482 \times 10^{-9} \left(\frac{\text{gmole}}{\text{cc-water} \cdot \text{sec}} \right)$$

$$(r^2 = 0.9638)$$

$$\bar{n} = 0.0598$$

Second Slope
 $= 7.099 \times 10^{-8} \left(\frac{\text{gmole}}{\text{cc-water} \cdot \text{sec}} \right)$
 $(r^2 = 0.9963)$
 $\bar{n} = 1.265$

EX-82

First Slope
 $= 9.91 \times 10^{-10} \left(\frac{\text{gmole}}{\text{cc-water} \cdot \text{sec}} \right)$
 $(r^2 = 0.9715)$
 $\bar{n} = 0.0239$

EX-84 (60°C)

First Slope
 $= 9.70 \times 10^{-10} \left(\frac{\text{gmole}}{\text{cc-water} \cdot \text{sec}} \right)$
 $(r^2 = 0.5002)$
 $\bar{n} = 0.0246$

Second Slope
 $= 5.624 \times 10^{-9} \left(\frac{\text{gmole}}{\text{cc-water} \cdot \text{sec}} \right)$
 $(r^2 = 0.9947)$
 $\bar{n} = 0.143$

Second Slope
 $= 5.109 \times 10^{-9} \left(\frac{\text{gmole}}{\text{cc-water} \cdot \text{sec}} \right)$
 $(r^2 = 0.9955)$
 $\bar{n} = 0.123$

EX-83

First Slope
 $= 9.133 \times 10^{-9} \left(\frac{\text{gmole}}{\text{cc-water} \cdot \text{sec}} \right)$
 $(r^2 = 0.8968)$
 $\bar{n} = 0.172$

Second Slope
 $= 7.456 \times 10^{-8} \left(\frac{\text{gmole}}{\text{cc-water} \cdot \text{sec}} \right)$
 $(r^2 = 0.9339)$
 $\bar{n} = 1.401$

EX-85 (55°C)

First Slope
 $= 3.75 \times 10^{-10} \left(\frac{\text{gmole}}{\text{cc-water} \cdot \text{sec}} \right)$
 $(r^2 = 0.6055)$
 $\bar{n} = 0.0112$

EX-86 (70°C)

$$\begin{aligned} \text{First Slope} \\ &= 6.740 \times 10^{-9} \left(\frac{\text{gmole}}{\text{cc-water} \cdot \text{sec}} \right) \\ (r^2 &= 0.9395) \\ \bar{n} &= 0.127 \end{aligned}$$

$$\begin{aligned} \text{Second Slope} \\ &= 3.2457 \times 10^{-8} \left(\frac{\text{gmole}}{\text{cc-water} \cdot \text{sec}} \right) \\ (r^2 &= 0.9932) \\ \bar{n} &= 0.610 \end{aligned}$$

EX-88 (60°C)

$$\begin{aligned} \text{First Slope} \\ &= 0.84 \times 10^{-9} \left(\frac{\text{gmole}}{\text{cc-water} \cdot \text{sec}} \right) \\ (r^2 &= 0.8692) \\ \bar{n} &= 0.0213 \end{aligned}$$

EX-87 (70°C)

$$\begin{aligned} \text{First Slope} \\ &= 5.05 \times 10^{-9} \left(\frac{\text{gmole}}{\text{cc-water} \cdot \text{sec}} \right) \\ (r^2 &= 0.9695) \\ \bar{n} &= 0.095 \end{aligned}$$

$$\begin{aligned} \text{Second Slope} \\ &= 1.5655 \times 10^{-8} \left(\frac{\text{gmole}}{\text{cc-water} \cdot \text{sec}} \right) \\ (r^2 &= 0.9930) \\ \bar{n} &= 0.294 \end{aligned}$$

EX-89

$$\begin{aligned} \text{First Slope} \\ &= 0.355 \times 10^{-9} \left(\frac{\text{gmole}}{\text{cc-water} \cdot \text{sec}} \right) \\ (r^2 &= 0.6119) \\ \bar{n} &= 0.0090 \end{aligned}$$

APPENDIX 6

To solve a system of non-linear algebraic equations such as Eq. (64) and Eq. (65), a generalization of the secant method was used in a computer program. While the secant method uses the last iterate and a memory (the previous iterate) to perform an iteration by local linearization, for two equations a memory of two iterates is required to perform two local linearizations.

From Eq. (64) and Eq. (65), in the case of styrene system where, $[M]_w \approx 0$, the following equations are set up:

$$\begin{aligned}
 F(1) = & -2k_d \cdot k_2 \cdot N_1^2 - 4k_{di} \cdot k_2 \cdot f \cdot [I] \cdot N_A \cdot N_1 \\
 & - 5 \cdot k_d \cdot k_2 \cdot N_1 \cdot N_2 + (4k_d \cdot k_2 \cdot N_T - 2k_{di} \cdot k_2 \cdot f \\
 & \cdot [I] \cdot N_A) N_2 - 2k_d \cdot k_2 \cdot N_2^2 + 2k_{di} \cdot k_2 \cdot f \cdot [I] \\
 & \cdot N_T \cdot N_A = 0
 \end{aligned} \tag{86}$$

$$\begin{aligned}
 F(2) = & k_2 \cdot k_d \cdot N_1^2 + 2 \cdot k_2 \cdot k_d \cdot N_1 \cdot N_2 \\
 & + 2 \cdot k_2 \cdot k_{di} \cdot f \cdot [I] \cdot N_A \cdot N_1 - \frac{2 \cdot k_2 \cdot k_{mtp} \cdot N_T}{v_{ps} \cdot N_A} N_2 \\
 & - 2k_2 \cdot k_d \cdot N_T \cdot N_2 = 0
 \end{aligned} \tag{87}$$

In the case of MMA system that $[M]_w$ term cannot be neglected. $[M]_w \neq 0$ and the following equations are set up:

$$\begin{aligned}
 F(1) = & -2k_d \cdot k_2 \cdot N_1^2 - (4 \cdot k_{di} \cdot k_2 \cdot f \cdot [I] \cdot N_A \\
 & + k_d \cdot k_{pw} \cdot [M]_w \cdot N_A) N_1 - 5k_d \cdot k_2 \cdot N_1 \cdot N_2 \\
 & + (4k_d \cdot k_2 \cdot N_T - 2k_{di} \cdot k_2 \cdot f \cdot [I] \cdot N_A \\
 & + 2 \cdot k_d \cdot k_{pw} \cdot [M]_w \cdot N_A) N_2 - 2k_d \cdot k_2 \cdot N_2^2 \\
 & + 2k_{di} \cdot k_2 \cdot f \cdot [I] \cdot N_T \cdot N_A = 0
 \end{aligned} \tag{88}$$

$$\begin{aligned}
 F(2) = & k_2 \cdot k_d \cdot N_1^2 + 2 \cdot k_2 \cdot k_d \cdot N_1 \cdot N_2 \\
 & + 2 \cdot k_2 \cdot k_{di} \cdot f \cdot [I] N_A \cdot N_1 - \frac{2 \cdot k_2 \cdot k_{mtp} \cdot N_T}{v_{ps} \cdot N_A} N_2 \\
 & - 2k_2 \cdot k_d \cdot N_T \cdot N_2 - \frac{2k_{pw} \cdot k_{mtp} \cdot [M]_w \cdot N_2}{v_{ps}} \\
 & - 2k_{pw} \cdot k_d \cdot [M]_w \cdot N_A \cdot N_2 = 0
 \end{aligned} \tag{89}$$

The reference or experimental values of k_2 , k_{di} , N_T , $[I]$, k_{mtp} , v_{ps} , $[M]_w$, k_{pw} are substituted into Eq. (86) and (87) or Eq. (88) and (89). The values of N_1 and N_2 are calculated for fixed values of k_d so that $F(1)$ and

$F(2)$ are nearly equal to zero. The two cases of the styrene system ($d_0 = 1118\text{\AA}$, 60°C) and the MMA system ($d_0 = 801\text{\AA}$, 60°C) are shown below as examples:

Styrene system ($d_0 = 1118\text{\AA}$, 60°C)

$$F(1) = - 0.06262 \times k_d \times N_1^2 - 0.1859 \times N_1 - 0.1566 \times k_d \times N_1 \times N_2 \\ + (1.3474 \times k_d - 0.09294) \times N_2 - 0.06262 \times k_d \times N_2^2 + 1$$

$$F(2) = 0.1861 \times 10^{-3} \times k_d \times N_1^2 + 0.3722 \times 10^{-3} \times k_d \times N_1 \times N_2 \\ + 0.005524 \times 10^{-1} \times N_1 - N_2 - 0.4004 \times 10^{-2} \times k_d \times N_2$$

MMA system ($d_0 = 801\text{\AA}$, 60°C)

$$F(1) = - 30.252 \times 10^{-2} \times k_d \times N_1^2 - 0.3448 \times N_1 - 75.63 \times 10^{-2} \times k_d \\ \times N_1 \times N_2 + (350.86 \times 10^{-2} \times k_d - 0.1724) \times N(2) \\ - 30.252 \times 10^{-2} \times k_d \times N_2^2 + 1$$

$$F(2) = 2.0846 \times 10^{-4} \times k_d \times N_1^2 + 4.1693 \times 10^{-4} \times k_d \times N_1 \times N_2 \\ + 0.02376 \times 10^{-2} \times N_1 - N_2 - 24.1774 \times 10^{-4} \times k_d \times N_2$$

The above non algebraic equations were solved for fixed various values of k_d .

Styrene System, $d_0 = 1118\text{\AA}$ at 60°C

```

1      PROGRAM NONLIN ( INPUT, OUTPUT )
2      COMMON NEQ, TOL, MXITER, MXFAIL
3      DIMENSION BAD(50), FOUT(50), FVAL(51,50)
4      DIMENSION GNEW(50), GUESS(51,50), X(51,101)
5      READ*, NEQ, TOL, MXITER, MXFAIL
6      CALL GNONLIQ ( BAD, FOUT, FVAL, GNEW, GUESS, X )
7      STOP
8      END

1      SUBROUTINE GNONLIQ ( BAD, FOUT, FVAL, GNEW, GUESS, X )
2      COMMON NEQ, TOL, MXITER, MXFAIL
3      COMMON/RKD/RKD
4      DIMENSION BAD(NEQ+1), FOUT(NEQ), FVAL(NEQ+1,NEQ)
5      DIMENSION GNEW(NEQ), GUESS(NEQ+1,NEQ)
6      DIMENSION X(NEQ+1,2*NEQ+1)
7      EXTERNAL FCN
8      READ*, ( GUESS(1,I), I = 1, NEQ )
9      READ*, ( GUESS(2,I), I = 1, NEQ )
10     DO 300 J=1,10
11     RKD=0,1*J
12     CALL NONLIQ ( FCN, GUESS, FVAL, X, NEQ+1, NEQ, GNEW,
13     FOUT, BAD, TOL, ATOL, MXITER, IRR, MXFAIL)
14     IF( IRR, EQ, 0) THEN
15     PRINT*, 'SUCCESS'
16     DO 100 I = 1, NEQ
17     PRINT*, 'X', I, '=', GNEW(I)
18 100 CONTINUE
19     DO 200 I = 1, NEQ
20     PRINT*, 'FUNC', I, '=', FOUT(I)
21 200 CONTINUE
22     GO TO 300
23     ELSE IF ( IRR. EQ. 1) THEN
24     PRINT* 'MXITER ITERATIONS MEET'
25     ELSE IF ( IRR. EQ. -1 ) THEN
26     PRINT*, 'MXFAIL ITERATIONS MEET '
27     ELSE IF ( IRR. EQ. -2 ) THEN
28     PRINT*, 'PROBLEM ILL CONDITIONED '
29     ENDIF
30     PRINT*, 'ATOL = ', ATOL
31     DO 400 I = 1, NEQ
32     PRINT*, 'X', I, '=', GNEW(I)
33 400 CONTINUE
34     DO 500 T = 1, NEQ
35     PRINT*, 'FUNC', I, '=', FOUT(I)
36 500 CONTINUE

```

```

37      GO TO 300
38 300  CONTINUE
39      STOP
40      END

```

```

1      SUBROUTINE FCN ( G, N, F )
2      COMMON/RKD/RKD
3      DIMENSION G(6), F(6)
4      F(1)=-0.06262*RKD*G(1)*G(1)-0.1859*G(1)-0,
           1566*RKD*G(1)*G(2)
5      C +(1.3474*RKD-0.09294)*G(2)-0.06262*RKD*G(2)*G(2)+1
6      F(2)=0.1861E-3*RKD*G(1)*G(1)+0.3722E-3*RKD*G(1)*G(2)
7      C +0.005524E-1*G(1)-G(2)-0.4004E-2*RKD*G(2)
8      RETURN
9      END

```

MMA System, $d_0 = 801\text{\AA}$ at 60°C

The program before SUBROUTINE FCN is the same as the one in the styrene system.

```

1      SUBROUTINE FCN( G, N, F )
2      COMMON/RKD/RKD
3      DIMENSION G(6), F(6)
4      F(1)=-30.252E-2*RKD*G(1)*G(1)-0.3448*G(1)
5      C -75.63E-2*RKD*G(1)*G(2)+(350.86E-2*RKD-0.1724)*G(2)
6      C -30.252E-2*RKD*G(2)*G(2)+1
7      F(2)=2.0846E-4*RKD*G(1)*G(1)+4.1693E-4*RKD*G(1)*G(2)
8      C +0.02376E-2*G(1)-G(2)-24.1774E-4*RKD*G(2)
9      RETURN
10     END

```

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