



DEPOSITED BY THE FACULTY OF
GRADUATE STUDIES AND RESEARCH



NOTES ON THE HISTORY OF THE
CITY OF BOSTON

KINETIC STUDIES OF A REDOX
POLYMERIZATION

by

Robert M. Brown B.Sc.

A thesis presented to the Faculty
of Graduate Studies and Research
of McGill University in partial
fulfilment of the requirements for
the Degree of Doctor of Philosophy

From the Physical Chemistry Laboratory under
the supervision of Dr. C. A. Winkler

McGill University,
Montreal, Canada.

April 1951

ACKNOWLEDGEMENTS

The writer wishes to acknowledge gratefully the awards of a Fellowship from the Spruce Falls Pulp and Paper Company, a Studentship and a Fellowship from the National Research Council of Canada, and financial assistance from the Department of Veterans Affairs.

TABLE OF CONTENTS

<u>INTRODUCTION</u>	1
THE EMULSION SYSTEM	1
FREE RADICAL POLYMERIZATION	7
Initiation, Propagation and Termination Reactions	7
Chain Transfer Reaction	10
Branching and Cross-linking Reactions,.....	12
REACTION LOCI IN EMULSION POLYMERIZATION	17
DILUTE SOLUTION VISCOSITY BEHAVIOUR OF HIGH POLYMERS	22
THE PRESENT INVESTIGATION	27
<u>EXPERIMENTAL</u>	30
TECHNIQUES	30
Polymerization Recipe	30
Materials	31
Preparation of Emulsifier Solution	32
Preparation of Activator Solution	32
Preparation of Shortstopping Suspension	33
Charging Procedure	34
Shortstopping and Sampling Procedures	35
THE POLYMERIZATION REACTION	37
Reproducibility	37
Overall Rate of Polymerization	41

TABLE OF CONTENTS (cont.)

Initial Surge of Polymerization	44
Zero Order Polymerization	50
Reaction at High Conversions	55
THE MERCAPTAN CHAIN TRANSFER REACTION	60
Mercaptan Analysis	60
Rate of Mercaptan Consumption	62
MONOMER-POLYMER RATIO IN THE LATEX PARTICLE	78
Method	78
Effect of Polymerization Rate	81
Effect of Polymerization Temperature	84
VARIABLES INFLUENCING POLYMER VISCOSITY AND THE GEL POINT	89
Determination of Intrinsic Flow Times	89
Effect of Mercaptan Concentration and Polymerization Temperature	90
Effect of Activator Concentration	98
Effect of the Nature of the Emulsifier	99
<u>DISCUSSION</u>	103
THE POLYMERIZATION REACTION	103
THE CROSS-LINKING REACTION	111
TERMINATION REACTIONS	119
<u>APPENDIX</u>	127
COAGULATION PROCEDURE	127
DRYING PROCEDURE AND POLYMER SOLUBILITY	127

TABLE OF CONTENTS (cont.)

SUMMARY AND CONTRIBUTION TO KNOWLEDGE135

REFERENCES140

INTRODUCTION

The development of emulsion polymerization has been one of the most important steps in the evolution of a commercial synthetic rubber. The main advantage of this type of system lies in the degree of control over the polymerization reaction which it affords. In the emulsion system, polymerization proceeds by a free radical chain reaction at numerous more or less isolated sites in close contact with an aqueous phase. The relative isolation of free radicals from one another permits a high concentration of relatively long-lived free radicals by preventing their interaction with each other. This allows polymerization to occur rapidly and to high molecular weights. The presence of the aqueous phase affords an efficient means of controlling temperature at the site of reaction and allows the continuous transfer of reactants to the site of reaction by diffusion.

THE EMULSION SYSTEM

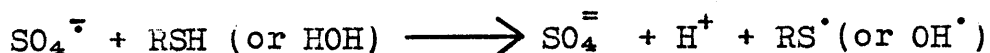
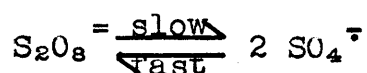
The emulsion polymerization system consists of four essential components: 1) Water 2) Monomer 3) Emulsifier 4) Initiating System. Electrolytes to increase the emulsion fluidity, and chain transfer agents to control the polymer molecular weight are often added to these four basic components. The addition of an antifreeze agent, generally an alcohol, permits the use of an emulsion system at sub-

freezing temperatures.

Polymerizations may be conducted in the absence of an emulsifier, e.g., the "bead" polymerization of styrene (1), but this is no longer a true emulsion system, the separated compartments of reaction being much larger, the reaction slower, and macroscopic "beads" of polymer rather than a latex being the product. The emulsifier plays a dual role in the emulsion system; it serves to keep fine monomer droplets and polymer particles in suspension in the latex and to establish numerous polymerization sites during the early stages of reaction. Of the various types of emulsifiers that have been used, the most important are fatty acid soaps, disproportionated rosin acid soaps, and synthetic detergents (2 - 9). The rosin acid soaps have come into favour in the commercial production of synthetic rubber owing to a desirable "tackiness" they impart to the resulting polymer (10).

The initiating system of the polymerization emulsion has undergone extensive development in the last few years. The function of the initiator is to supply a steady concentration of free radicals which can attach a monomer molecule to initiate a free radical chain reaction. In the region of 50°C., the decomposition of potassium persulphate has been found to provide a source of free radicals at a concentration suitable for initiation of polymerization in emulsion systems.

The persulphate decomposes slowly enough that a relatively small fraction of the initial amount is consumed during the course of the polymerization, hence a practically constant concentration of free radicals is maintained. In the Mutual Recipe for GR-S it has been found (11) that traces of a mercaptan greatly accelerate the rate of polymerization, and it is believed that the mercaptan acts as a reducing agent, facilitating the decomposition of the potassium persulphate, hence increasing the concentration of initiating free radicals. The decomposition of potassium persulphate in the presence of mercaptan has been investigated (12) and the following reactions postulated for the production of free radicals from this decomposition:



In this case $\text{SO}_4^{\cdot -}$, RS^{\cdot} or OH^{\cdot} radicals are available for initiating purposes. The reaction producing free radicals takes place in the aqueous phase of the emulsion, after which the free radicals diffuse into a source of monomer to initiate the polymerization reaction. The polymerization of styrene is rapid in the absence of mercaptan, and the kinetics of the reaction suggest that this monomer is itself involved in the decomposition of the persulphate.

Soon after the persulphate initiation had attained widespread commercial application in the production of synthetic rubber (GR-S), other initiating systems were developed simultaneously in the United States (6)(13 - 16), Germany (17 - 19), and England (20 - 22). These systems were much more active than persulphate and permitted investigations of emulsion polymerization at temperatures down to -40°C . Polymer produced at these lower temperatures showed improved physical properties (23 - 25) and activated initiating systems became of great importance.

The activated initiating systems are thought to act merely as a more prolific source of free radicals, the actual steps involved in the overall polymerization being essentially unchanged. In most activated initiator systems, free radicals are produced from the decomposition of an organic peroxide (15, 16) under the influence of a more powerful reducing agent than the mercaptan of the Mutual Recipe. The most widely used reducing agent at the present time is ferrous iron in the form of an organic or inorganic complex (26). The complexing agent retards the action of the iron, and confers upon it a more uniform behaviour which is prolonged throughout the course of the polymerization. A recent development is the use of polyamine reducing agents (27) to avoid the presence of traces

of iron in the resulting polymer. The addition of reducing sugars, particularly sorbose, levulose, and invert sugar, has been found to increase the efficiency of most of the iron-containing activators, and to be essential to the polyamine activator (6, 27, 28).

The actual mechanisms involved in the decomposition of these activated initiator systems have not yet been elucidated. The use of an organic peroxide in these systems suggests that the decomposition and production of free radicals occur in the monomer phase of the emulsion in contrast to the aqueous reactions of persulphate. Early work tended to confirm this (29) but more recent evidence seems to support the production of free radicals in the aqueous phase. Fordham and Williams have studied the catalyzed decomposition of cumene hydroperoxide in styrene (30) and concluded that the reaction was of an ionic nature, in contrast to the free radical kinetics of emulsion polymerizations employing cumene hydroperoxide and ferrous iron. The same workers have investigated the reaction of ferrous iron and cumene hydroperoxide in dilute acid in the presence of oxygen (31) and concluded the primary free radical producing step in the early stages of reaction to be bimolecular:



Further studies in the absence of oxygen (32) have supported

this conclusion. This reaction is therefore different stoichiometrically from the corresponding reaction between Fe^{++} and hydrogen peroxide in which the molar ratio of Fe^{++} to peroxide reacting has been found to be 2:1 in acid medium (21).

Since the emulsion system is alkaline, the relative dependence of free radical production on ferrous iron and cumene hydroperoxide in such a medium is of the most interest. However, this reaction is difficult to study, owing to its very high rate and exceeding sensitivity to traces of oxygen. Fordham and Williams hope to be able, eventually, to study the reaction of ferrous iron and cumene hydroperoxide in alkaline medium.

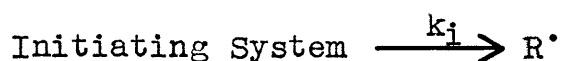
Most olefinic and -diene monomers have been successfully polymerized in an emulsion system. Investigations of the physical nature of the latex as it forms have generally been made with styrene in a persulphate recipe. The extension of these investigations to the butadiene-styrene comonomer system, and to the activated low temperature recipes is of particular interest in that these systems have become of great practical importance. However, the low boiling point of butadiene (-3°C) makes many of the important investigations difficult on latex containing this monomer.

FREE RADICAL POLYMERIZATION

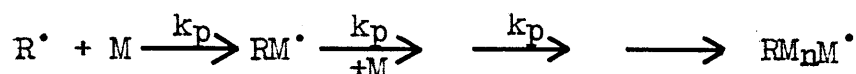
The Initiation, Propagation and Termination Reactions

In emulsion polymerization, as in all free radical polymerizations, reaction consists of three main steps which, for kinetic considerations, may be represented simply as:

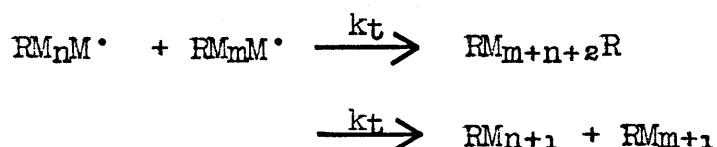
- 1) Production of the primary free radical by decomposition of an initiating system.



- 2) Propagation of the free radical by successive addition of monomer molecules.



- 3) Termination of the growing free radical by addition to or disproportionation with another free radical.



where R^\bullet , RM^\bullet , RM_mM^\bullet , RM_nM^\bullet are free radicals all henceforth represented as ΣR

k_i , k_p , k_t are the specific rate constants for initiation, propagation and termination respectively.

The rate equations for the production and destruction of free radicals, and the consumption of monomer may be expressed:

$$\frac{d\Sigma R}{dt} = k_i [\text{Init. System}] + k_p[M][\Sigma R]$$

$$- \frac{dR}{dt} = k_t [\Sigma R]^2 + k_p[M][\Sigma R]$$

$$- \frac{dM}{dt} = k_p [\Sigma R][M]$$

Under steady state conditions, the production and destruction of free radicals will proceed at equivalent rates, whence

$$k_t[\Sigma R]^2 + k_p[M][\Sigma R] = k_i [\text{Init. System}] + k_p[M][\Sigma R]$$

$$[\Sigma R] = \left(\frac{k_i}{k_t} \right)^{1/2} [\text{Init. System}]^{1/2}$$

$$\text{and } - \frac{dM}{dt} = k_p \left(\frac{k_i}{k_t} \right)^{1/2} [\text{Init. System}]^{1/2} [M] \quad \dots\dots(1)$$

This equation indicates that the rate of consumption of monomer, hence the rate of production of polymer, should be proportional to the square root of the concentration of initiator, and directly proportional to the monomer concentration. The copolymerization of 75:25 butadiene-styrene in homogeneous solution, using diazo-amino benzene as initiating agent, has been reported to behave in this manner (19). However, the rate of solution polymerization of styrene has been found to be proportional to the three-halves power of the monomer concentration (34), which suggests

that the monomer is involved in the initiating system in this case.

In the emulsion polymerization system, the initiator usually operates in the aqueous phase, producing free radicals which then migrate to a site of monomer concentration. As will be discussed later, this site may be a soap micelle containing solubilized monomer, or alternatively a minute monomer-polymer particle suspended in the aqueous phase. The initiating system is present in such an excess as not to be appreciably depleted during the course of a polymerization, and supplies free radicals at an essentially constant rate. A balance between the production and consumption of free radicals is soon set up which results in a steady state concentration of free radicals in the system. Then

$$\frac{d\Sigma R}{dt} = 0 = k_i [\text{Init. System}] + k_p [M][\Sigma R]$$

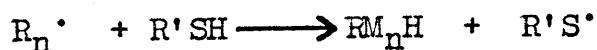
$$k_i [\text{Init. System}] = -k_p [M][\Sigma R] = \frac{dM}{dt}$$

and the rate of polymerization becomes a relative measure of the rate of decomposition of the initiator to give primary free radicals, provided the addition of monomer to free radicals is rapid enough to prevent loss of free radicals by side reactions. During the first 60 - 70% conversion of monomer to polymer, the monomer concentration at

the site of polymerization is maintained sufficiently high by diffusion from the oil phase to render the rate independent of monomer concentration. Beyond this conversion, the propagation rate becomes dependent on monomer concentration and the overall polymerization rate is first order in respect of monomer, if the monomer is not involved in the preliminary reactions of the initiating system.

The Chain Transfer Reaction

When certain agents are present in the polymerization system, the progress of a particular polymerization reaction between initiation by a free radical and final termination by another free radical may be interrupted numerous times by a "chain transfer" reaction. P. J. Flory (35) first suggested the existence of this reaction to explain the effect of certain solvents on polymer molecular weight in solution polymerization. Since that time, the reaction has received wide application as a means of controlling polymer molecular weight. In this reaction, the growing free radical attacks a molecule of the chain transfer agent rather than a molecule of the monomer. The free radical stabilizes itself by extracting an atom from the chain transfer agent, but in so doing leaves the residue of the transfer agent in the form of a free radical.



Thus, although a particular growing chain is stopped, the free radical concentration is not reduced and the newly formed free radical continues the addition of monomer. The net effect of such reactions of the propagating free radical is to cut the "kinetic chain", i.e. that chain which would be formed between initiation and final termination by another free radical, into a number of shorter chains. The frequency of these chain transfer reactions, and hence the length of polymer chains formed, can be controlled by varying the concentration and nature of the chain transfer agent.

Most transfer agents disappear from the polymerization emulsion in a first order manner since the concentration of free radicals is constant. The solubility and rate of diffusion of the transfer agent in the aqueous phase play a large part in determining the rate of reaction. Aliphatic mercaptans are particularly effective chain transfer agents and when present in sufficient concentration are the terminating agent for the majority of polymer chains formed in the system. This fact has been confirmed by analyses of polymers prepared in the presence of mercaptans, which have indicated that approximately one sulphur atom is present per polymer molecule (36, 37).

Bardwell and Winkler (38) have demonstrated how

the number and weight average degrees of polymerization of a polymer may be calculated from kinetic data on the mercaptan consumption during polymerization.

Their calculations yield

$$\bar{y}_{n\alpha} = \frac{\alpha}{R_0(1 - e^{-r\alpha})} \quad \dots\dots(2)$$

and

$$\bar{y}_{w\alpha} = \frac{2}{r^2\alpha R_0} (e^{r\alpha} - 1) \quad \dots\dots(3)$$

where α = fractional extent of conversion of monomer to polymer.

\bar{y} = average degree of polymerization, i.e. average number of structural units per polymer chain

$\bar{y}_{n\alpha}$ = number average degree of polymerization at conversion α

$\bar{y}_{w\alpha}$ = weight average degree of polymerization at conversion α

R_0 = initial mercaptan concentration (as moles per mole of initial monomer)

r = regulating index (39) = $-\frac{d \ln R}{d\alpha}$

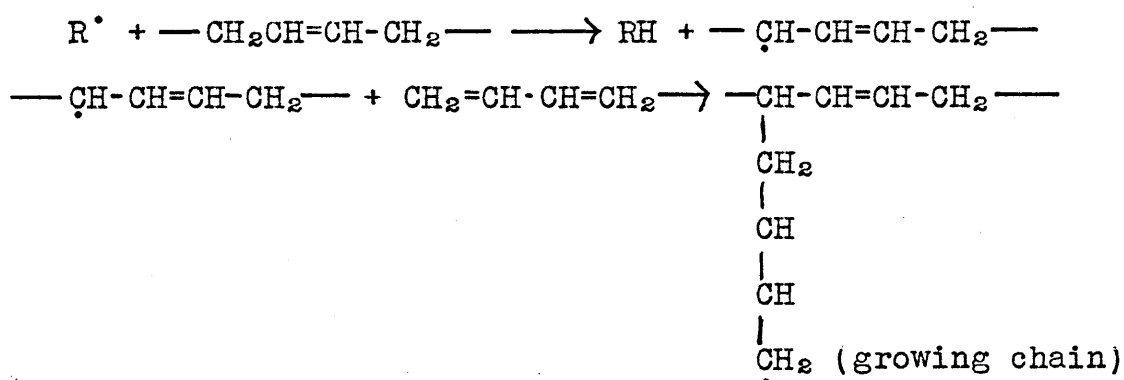
Such calculations give information about the average chain length of the polymer provided the majority of the chains are terminated by chain transfer with the mercaptan, and there is no interaction between growing radicals and segments of previously formed polymer chains.

Branching and Cross-linking Reactions

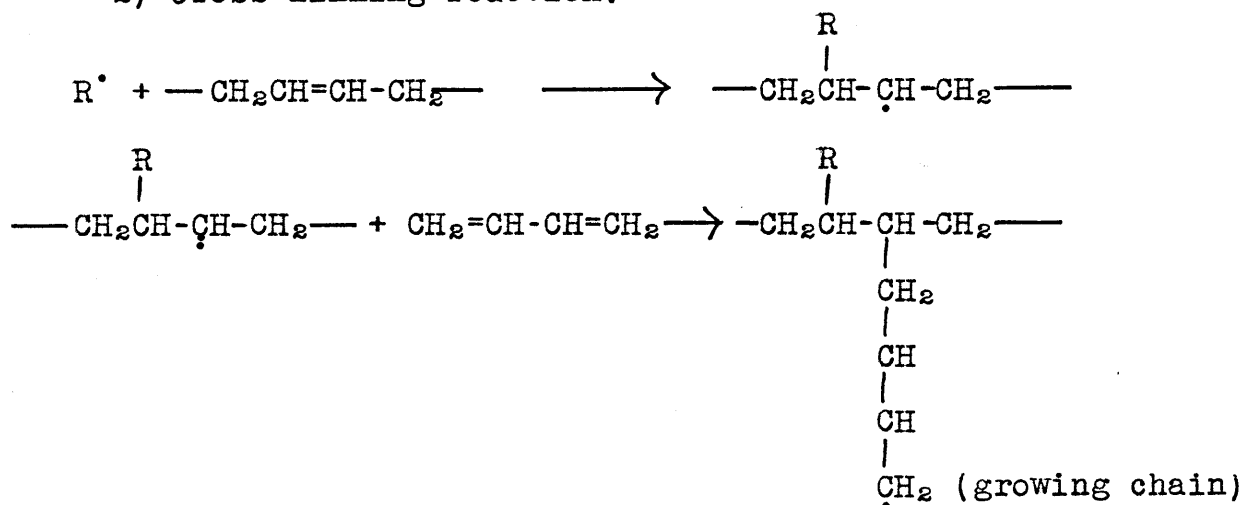
In addition to the three basic steps of free

radical polymerization, side reactions may occur in the polymerization of polyfunctional monomers with production of branched chains and cross-links. Flory (40) has proposed mechanisms for the formation of side chains and cross links by interactions of growing free radicals and the methylenic hydrogens or the residual double bonds of polymer chains.

1) Side chain formation:



2) Cross-linking reaction:

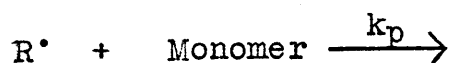


where R^{\bullet} represents a growing free radical chain. This

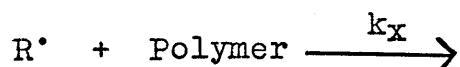
cross-linking reaction also may proceed with vinyl side groups on the chain which have resulted from 1,2 addition of butadiene units during formation of the polymer.

The occurrence of branching and cross-linking during polymerization results in a heterogeneous polymer with undesirable physical properties as an elastomer. Cross-linking ties linear polymer chains into three dimensional networks which are insoluble in the usual polymer solvents and which make the polymer difficult to process for commercial use. The extent of network formation can be controlled by decreasing the chain length of the original linear chains with the aid of chain transfer agents, but this practice sacrifices the desirable properties associated with high molecular weight, such as tensile strength. Hence, these side reactions of branching and cross-linking merit study in an effort to find a means of restricting their occurrence.

Flory (40) has suggested a means of determining the relative velocity constants of the cross-linking and propagation reactions in a polymerization where the majority of the termination is by a chain transfer reaction of which the kinetics may be readily studied. The rates of the propagation reaction



and the cross-linking reaction



may be represented by

$$\frac{d\alpha}{dt} = k_p [R^{\cdot}] [M] \quad \text{and} \quad \frac{d\gamma}{dt} = 2 k_x [R^{\cdot}] [P]$$

where α = fractional extent of conversion.

k_x = cross-linking velocity constant.

k_p = propagation velocity constant.

R^{\cdot} = concentration of free radicals at the site of polymerization.

M = concentration of monomer at the site of polymerization.

P = concentration of polymer at the site of polymerization.

γ = moles of cross-linked units/mole of initial monomer.

Every cross-linking reaction involves two structural units, hence the factor of two in the cross-linking rate equation. These specific rate constants are the average of the rate constants for 1,2 and 1,4 reaction in each case, but the ratio of 1,2 to 1,4 addition has been found to be relatively constant for a given system of polymerization (41).

The ratio of these rates is

$$\frac{d\gamma}{d\alpha} = 2 \frac{k_x}{k_p} \frac{[R^{\cdot}] [P]}{[R^{\cdot}] [M]} = 2 K \frac{P}{M}$$

$$d\gamma = 2 K \frac{P}{M} d\alpha \quad \dots\dots(4)$$

and the constant K is a measure of the relative rates of the two reactions. For bulk polymerization, the ratio P/M is given by the extent of reaction

$$P/M = \frac{\alpha}{1-\alpha}$$

Integration of (4) and division by α gives the density of cross-linked units, ρ , in the polymerized portion of the mixture

$$\rho = \frac{\nu}{\alpha} = -2K + \frac{1}{\alpha} \ln(1 - \alpha)$$

According to statistical theory (42) the formation of insoluble polymer, i.e. "gelation", will occur when ρ exceeds the reciprocal of the weight average degree of polymerization of the primary molecules, i.e. the weight average degree of polymerization which would have existed if no cross-linkages had been formed. Hence, at the first appearance of insoluble polymer, i.e. at the "gel point".

$$\rho = \frac{1}{\bar{y}_w}$$

If termination were predominantly by a chain transfer agent, \bar{y}_w may be calculated from kinetic data of the consumption of this agent, Equation (3). Hence, a knowledge of the gel point α_g and the kinetics of the consumption of the transfer agent involved should allow an evaluation of K, the relative rates of cross-linking to propagation.

Morton and Salatiello (43) have emphasized the importance of the site of reaction in applying such considerations to the emulsion system. It has been shown that 99% of the polymer is formed in the monomer-polymer particle of the latex (44). Herzefeld, Roginsky, Corrin and Harkins (45) have reported that the ratio of monomer to polymer in this particle drops with increasing conversion for styrene polymerization and similar behaviour has been reported for isoprene (46). However, for the emulsion polymerization of polybutadiene, Meehan (47) has found the M/P ratio to remain constant at 0.92 up to 50% conversion.

Morton and Salatiello (43) have investigated the cross-linking reaction in the polymerization of polybutadiene in a Mutual recipe, and, using Meehan's value for the M/P ratio, have found $K = 1.36 \times 10^{-4}$ at 50°C. with a difference in activation energy $E_x - E_p = 7.5 \pm 0.6$ Kcal/mole. On the basis of these results they calculate that a 50°C. drop in polymerization temperature should suppress the cross-linking reaction to such an extent as to allow a ten fold increase in weight average chain length without change in degree of cross-linking.

REACTION LOCI IN EMULSION POLYMERIZATION

Studies on the styrene-persulphate emulsion system have given considerable information about the physical pro-

cesses which take place in the course of an emulsion polymerization. Harkins (44, 48) has coordinated much of this evidence into a comprehensive theory of the mechanisms of these processes and their sequence of occurrence during polymerization.

In the early stages of polymerization, the soap of the emulsion is present mainly in the form of micelles, the polar groups of the soap molecules oriented towards the water and the hydrocarbon groups oriented towards one another. Such micelles may be associated in laminar aggregates, with intervening layers of water, depending on their concentration. The soap micelles absorb styrene within their hydrocarbon interior, providing regions of high styrene concentration dispersed throughout the aqueous phase. As the true solubility of styrene in the aqueous phase is very low, these styrene-swollen micelles have a much greater probability of encountering initiating free radicals than the dissolved styrene molecules. Once a micelle has captured a free radical, the concentration of monomer immediately surrounding the radical is very high, and polymerization can proceed extensively before termination is brought about by another free radical.

When polymerization has been initiated in a micelle, the monomer which is removed by reaction is replaced by

diffusion into the activated micelle from other micelles or from dispersed monomer droplets of the emulsion. Since this diffusion can proceed at a faster rate than the rate of polymerization within the micelle, the extent of polymerization is not limited by the micellar size or its original capacity for absorbing styrene. Polymer formed in the micelle can absorb styrene and the original micelle develops into a monomer-polymer particle of increasing dimensions. The particle has the soap of the original micelle adsorbed on its surface, and as it increases its surface area, it adsorbs more soap which is acquired from micelles still existing in the aqueous phase. Thus, a number of the original micelles have polymerization initiated within them and grow into monomer-polymer particles, and in so doing consume the soap and absorbed styrene of the remaining micelles.

When all micellar soap has disappeared as such very few additional sites of polymerization can be created. A small amount of initiation may be brought about by encounters of free radicals and dissolved monomer molecules in the aqueous phase, but this is a small fraction of that previously occurring in micelles. Thus, the number of polymer particles in the latex should remain practically constant after the micellar soap has disappeared, and is found experimentally to do so.

W. V. Smith (49) has extended Harkins' theory by considering quantitatively the number of soap micelles originally present, the rate of free radical production from the catalyst, the number of polymer particles finally formed in the latex, and the rate of mutual termination in bulk polymerization. On the basis of these considerations, he concludes that mutual termination within the polymer particle is very rapid, hence only one free radical can grow within a polymer particle at one time. The entrance of a second radical brings about mutual termination and a period of inactivity until another free radical enters the particle. Such a situation would imply that on the average each particle in the latex polymerizes one half the time. From the rate of production of free radicals and the number of particles, a time of 10 - 100 seconds is indicated for the alternate intervals of activity and inactivity in a persulphate-styrene system at 50°C. For the overall rate of polymerization this mechanism gives:

$$\frac{d\alpha}{dt} = \frac{1}{2}(\text{number of polymer particles})(\text{Rate of propagation in each particle})$$

where α = the fractional extent of conversion of monomer to polymer.

The polymerization rate should be independent of free radical production once all the polymer particles have been formed, since any change in free radical concentration should change

the interval of activity and inactivity equally. Using a reaction mixture seeded with a known number of polymer particles, Smith determined the rate of polymerization per particle and took this to be a measure of the rate of addition of monomer molecules to the growing free radicals, i.e. the rate of propagation, k_p . On this basis he calculated an activation energy of 11.7 Kcal/mole for the propagation reaction, which is considerably higher than the value of about 6.5 Kcal/mole determined by Bamford and Dewar (50). It seems doubtful that Smith measured the actual rate of propagation since it was necessary for him to include persulphate in the reaction mixture in spite of the fact that active free radicals presumably were present in half of the seed polymer particles.

An experiment reported by Harkins (44) makes it doubtful also that only one free radical grows in a polymer particle at one time. Polystyrene was polymerized in a persulphate recipe to 32% conversion by which time all the soap micelles were consumed and the constant number of polymer particles attained. When ferrous sulphate was added to this reaction mixture, the rate of polymerization was doubled, in spite of the fact that no new polymer particles could be formed. According to Smith's mechanism this would imply that the ferrous sulphate had affected the rate of propagation of the free radicals. This is very unlikely,

and Harkins suggests that a number of free radicals must be polymerizing simultaneously in each particle. This would more closely parallel bulk phase polymerization conditions, and the rate of polymerization would be controlled by the rate of production of initiator free radicals throughout the reaction. The zero order nature of the polymerization rate, which, on this basis, implies a constant rate of production of free radicals, would be explained by the limited reduction in initiator concentration in the course of a polymerization, as discussed in the previous section on free radical polymerization.

DILUTE SOLUTION VISCOSITY BEHAVIOUR OF HIGH POLYMERS

Staudinger in 1932 (51) demonstrated the dependence of dilute solution viscosity of high polymers on their molecular weight and expressed this relation in the form:

$$\frac{\eta_{sp}}{C} = KM$$

where $\eta_{sp} = \eta_r - 1 = \frac{\text{Viscosity of solution}}{\text{Viscosity of solvent}} - 1 = \text{specific viscosity}$

C = concentration of the solution in gms/100 ml. solution

M = the average molecular weight

K = a constant characteristic of the polymer-solvent system.

On the basis of theoretical considerations by Kuhn (52) and Huggins (53, 54) and practical experience of

Mark (55) and others, Staudinger's equation has been modified to

$$[\eta] = \left[\frac{\eta_{sp}}{c} \right]_{c \rightarrow 0} = KM^a \quad \dots\dots(5)$$

where a is a constant of value between zero and unity related to the shape and flexibility of the polymer chains. As the value η_{sp}/c was found to be dependent on concentration, the "reduced" value is used. This reduced specific viscosity, the "intrinsic" viscosity, has been shown (56) to be equivalent to the reduced inherent viscosity:

$$[\eta] = \left[\frac{\eta_{sp}}{c} \right]_{c \rightarrow 0} = \left[\frac{\ln \eta_r}{c} \right]_{c \rightarrow 0}$$

Equation (5) has been found to hold for a large number of polymer-solvent pairs and provides one of the most convenient methods for estimating polymer molecular weight once the empirical constants, K and a, have been evaluated by the use of some absolute molecular weight method such as osmometry or light scattering. For 75/25 butadiene-styrene copolymer prepared at 50°C, the molecular weight-intrinsic viscosity relation has been found to be:

$$[\eta] = 5.25 \times 10^{-4} M^{0.67} \quad \dots\dots(6)$$

for the determination of $[\eta]$ in toluene at 30°C. (57).

Viscosity measurements yield a "viscosity" average

molecular weight which may be related to weight and number average molecular weights if the distribution in molecular size is known. If no branching or cross-linking occurs, this distribution is the statistical result of the random occurrence of termination steps during chain growth. Such a distribution has been treated by several workers (58 - 61) who have shown the following relations to exist:

$$\frac{\bar{M}_w}{\bar{M}_n} = 1 + p \doteq 2 \quad \dots\dots(7)$$

$$\frac{\bar{M}_v}{\bar{M}_n} = \left\{ \Gamma(2 + a) \right\}^{1/a} \doteq 1.85 \text{ for } a = 0.67 \dots(8)$$

where \bar{M}_w = Weight average molecular weight = $\frac{\sum M_y w_y}{\sum w_y}$

\bar{M}_n = Number average molecular weight = $\frac{\sum M_y n_y}{\sum n_y}$

w_y and n_y being the weight and number fractions respectively of molecules containing y structural units and having a molecular weight M_y .

p = probability that propagation rather than termination will occur. This must be close to unity for a high polymer to result.

a = the constant in the viscosity-molecular weight equation (5).

Cross-linking of diene polymer molecules results in an increase in the average molecular weight of the polymer, and this is reflected in an increase in the polymer viscosity as reaction proceeds. Since the cross-linking

reactions occur in a practically random manner (40) the larger molecules are cross-linked preferentially, having a larger number of residual double bonds per molecule. Once cross-linking has progressed to such an extent that insoluble polymer is formed, this preferential incorporation of larger molecules in the cross-linked network is reflected in a drop in the viscosity of the soluble polymer. Thus, a maximum in the viscosity-conversion curve should occur at the point where insoluble polymer is first formed, i.e. the "gel point", and in practice this has been found to be true (62).

In the last few years, the "vistex" method (63) has been developed for the determination of the dilute solution viscosity of polymer dissolved directly from the latex. A mixture of hydrophobic and hydrophilic solvents, such as xylene and pyridine (63) or benzene and isopropanol (64) is used to dissolve the latex sample. All early work with this procedure was limited to the determination of inherent vistex viscosities since these were suitable for comparative purposes and there seemed to be no method of calculating viscosity average molecular weights from intrinsic vistex viscosity data. Baker (63) postulated that the maximum observed in the intrinsic viscosity-conversion curve at the gel point should exist in the inherent vistex viscosity-conversion curve also, and it has been found experimentally

(63, 64, 65) that the maximum occurs at the same conversion for both vistex and intrinsic viscosity data.

In a further investigation of the vistex method, Henderson and Legge (66) found the intrinsic vistex viscosity of a polymer to be related to its intrinsic viscosity in the pure hydrophobic component of the vistex solvent. At the same time they found it possible to dilute a vistex solution with the pure hydrophobic solvent to obtain the several levels of concentration required for the determination of intrinsic viscosity. An extrapolation of the values of the inherent viscosity of these solutions to zero polymer concentration yielded a value which corresponded exactly with the intrinsic viscosity of the dried polymer in the pure hydrophobic solvent. Thus, by using pure toluene as diluent, the intrinsic viscosity of a polymer in toluene can be determined from a solution of its latex in 80/20 toluene-isopropanol.

Solubility measurements on emulsion produced polymer have proven difficult owing to the occurrence of microgel (67) and the sensitivity of the polymer to drying conditions. Since the vistex method avoids the introduction of unknown variables in the polymer structure by coagulation and drying treatments, and eliminates the necessity of removing microgel, the determination of the maximum in the

viscosity-conversion curve has become the preferred method for determining the gel point in emulsion systems.

THE PRESENT INVESTIGATION

The particular advantage of redox polymerization systems over the original GR-S system is that significant improvements in physical properties of synthetic elastomers have been achieved by the use of these systems at lower polymerization temperatures (23, 24, 25). This development has been largely empirical and it was some time before there was any reliable indication about the specific changes in the polymer structure that might be responsible for the improvement. However, investigations over a wide range of polymerization temperatures - 50°C. to -20°C - have shown that the low temperature systems produce polymer chains which are much more regular in several respects. The overall improvement in molecular regularity is demonstrated by the more defined X-ray diffraction patterns produced by low temperature polymer (68, 69, 70). Also, infra-red spectroscopic methods have indicated the configuration about the internal double bonds to be predominantly trans in low temperature polymers (41, 71), while the much lower mercaptan requirements to maintain equivalent polymer solubility (41) in such systems suggests that the tendency for cross-linking is reduced.

Since each polymerization recipe is generally

suitable only over a limited temperature range, it has been difficult, but important to distinguish between effects resulting from temperature changes and effects resulting from changes in recipe. To accomplish this, it is necessary to study the kinetics of polymerization systems with overlapping temperature ranges and to observe which characteristics may be attributed to the nature of the system and which are a result of temperature differences independent of the system.

The purpose of the present investigation was to study the kinetics of a system for which the upper temperature limit overlapped the temperature range of the Mutual recipe while the lower limit extended down to temperatures at which commercial low temperature polymers were being prepared. Such a system should presumably allow comparison of the characteristics of the system with those of the thoroughly investigated Mutual system while still allowing investigation of polymerization kinetics at temperatures which produced significant improvement in the physical properties of 75/25 butadiene-styrene copolymer.

The evidence that the cross-linking reaction was suppressed by lower polymerization temperatures made an investigation of the cross-linking reaction in such a system of especial interest. The fact that temperature seemed to be the important variable suggested that the relative

activation energies of the cross-linking and propagation reactions were controlling factors, and Flory (40) has outlined a method for investigating these. The only experimental application that has yet been made of Flory's approach to the kinetics of cross-linking is the very recent work of Morton and Salatiello (43) on the formation of polybutadiene. It was obviously of interest and importance to attempt an extension of the treatment to a copolymerization system more closely paralleling those of present commercial interest.

With the ultimate objective of elucidating the kinetics of the cross-linking reaction in such a system, a study of the characteristics of a redox emulsion polymerization system was undertaken.

EXPERIMENTAL

TECHNIQUES

The polymerization reaction has been studied using the standard bottle technique for emulsion polymerization (72). One ounce, round-form bottles with metal screw caps were used. Each cap was punctured and fitted with an inner gasket of self-sealing Butyl rubber and a covering circle of oil-resistant Koroseal to allow repeated insertion of a hypodermic needle for sampling purposes (73). Throughout the polymerization, the charged bottles were clamped to a horizontal shaft and rotated end over end through a circle of about five inches diameter at 35 r.p.m. in a water bath controlled to $\pm 0.02^{\circ}\text{C}$.

Polymerization Recipe

The polymerization recipe was essentially the X-435-Kalex formula recommended by Mitchell, Spolsky and Williams (26).

TABLE I

POLYMERIZATION RECIPE

<u>Component</u>	<u>Parts by weight</u>
Butadiene	75.00
Styrene	25.00
Cumene hydroperoxide (68%)	0.24
Dresinate 731 (dry weight)	4.70
NaOH	0.11
Mixed tertiary mercaptan (MTM-4)	Variable (0.00 - 0.20)
Kalex Na (dry weight)	0.15
Dextrose	0.50
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	0.028
$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$	0.34
Distilled water	180.0
di-t-butyl hydroquinone (shortstop)	0.40

Each bottle was charged with $\frac{1}{12}$ of the above recipe, which occupied 27 ml., leaving a free space of 4 ml. to facilitate mixing of the emulsion during rotation of the bottles.

Materials

The following chemicals were kindly donated by the Polymer Corporation Limited, Sarnia, Ontario.

Butadiene 1,3	Purified by bubbling through 2N KOH solution to remove the inhibitor (300 p.p.m. p-tertiary butyl catechol), dried over calcium chloride and condensed in a dry ice-acetone trap.
Styrene	Purified by distillation at reduced pressure.
Cumene hydroperoxide	Used as received - a 68% solution of hydroperoxide in cumene.
Dresinate 731	A sodium soap of a mixture of hydrogenated and dehydrogenated rosin acids (5). It was used as received in a water paste of 65.6% solids.
MTM-4	A blend of tertiary mercaptans having the approximate composition, 60% C ₁₂ , 20% C ₁₄ , 20% C ₁₆ , and average molecular weight 220. It was used as received.
Kalex Na	Tetrasodium ethylene dinitrilotetracetate. It was used as received in a water solution of 34% solids.
Di-t-butyl hydroquinone	"Santovar 0". Used as received.

The Polymer Corporation Ltd., also supplied gasket material for the caps of the polymerization bottles. The

self-sealing gaskets consisted of undercured Butyl stock produced by the Polymer Corporation, while the oil-resistant gaskets were cut from Koroseal sheeting, a polyvinyl chloride product of B. F. Goodrich Co., Ltd. The Koroseal gaskets were soaked in styrene overnight before use to extract antioxidants and plasticize the material.

Other chemicals used were of reagent grade.

Preparation of Emulsifier Solution

A stock solution sufficient for 40 bottles was prepared at one time and volumetric aliquots used for each charge. The Dresinate 731 and sodium hydroxide were dissolved in 45 parts of the water charge, the solution boiled exactly 10 minutes and allowed to cool to room temperature. The evaporated water was then replaced, the solution filtered and stored in a screw cap bottle.

Preparation of Activator Solution

The activator consisted of an organic complex of ferrous iron which was sensitive to oxygen, and hence had to be stored under oxygen-free nitrogen. The trisodium phosphate, ferrous sulphate, dextrose and "Kalex Na" were dissolved in about 20 parts of the water charge in an Erlenmeyer flask. The solution was quickly heated to boiling and boiled exactly ten minutes. As boiling proceeded the

colour became yellow at first, then deeper and deeper wine coloured. The evaporated water was replaced with boiled air-free water and the solution cooled under a sweep of purified nitrogen admitted to the flask by a stopcock arrangement that allowed subsequent sampling of the activator solution with a pipette filled by positive nitrogen pressure inside the flask. An activator solution sufficient for 30 bottles was prepared at one time, and could be kept indefinitely without change in effectiveness as long as it was protected from oxygen. On contact with the air, the solution became an opaque brown colour. It was never used if it had changed colour at all.

Preparation of Shortstopping Suspension

As di-t-butyl hydroquinone is sparingly soluble in both water and styrene, it must be prepared as a suspension using the emulsifying agent present in the latex. The use of a different emulsifying agent, or the presence of too large solid particles will cause coagulation of polymer from the latex.

A portion of the above emulsifier solution was placed in a 4 oz. screw cap bottle, 8.2% by weight of finely ground di-t-butyl hydroquinone and a number of glass beads added, the bottle swept out with nitrogen, capped and rotated in the thermostat overnight. The di-t-butyl hydroquinone in this suspension settled out on standing several

hours, but could be redispersed by shaking. The shortstop turned yellow on prolonged contact with air but since this seemed to have little effect on its shortstopping powers, no precautions were taken to protect it from air on removing a sample.

Charging Procedure

Small pipettes were calibrated to deliver the required weights of the different liquid components of the charge. It was found convenient to operate these pipettes with a hypodermic syringe. In this way the loading procedure could be accomplished quickly with minimum mixing of the components prior to commencement of the polymerization by formation of the emulsion on shaking.

The water charge was first measured into the polymerization bottles from a 10 ml. burette. The required amount of emulsifier solution was then added to each bottle from a pipette and the bottles capped and cooled in ice water. From this point the charge of each bottle was completed before the next bottle had any further components added to it, to minimize the time the activator, peroxide, mercaptan and monomers were in contact before the emulsion was formed. The rest of the charging procedure was usually accomplished within 5 - 8 minutes.

The activator solution was charged from a small

pipette. Part of the styrene, containing the total mercaptan charge, was added immediately, followed by the remaining amount of styrene containing the cumene hydroperoxide, after which the bottle was capped and weighed. Excess butadiene was added and the cap replaced loosely on the bottle to allow butadiene to evaporate to the correct weight, thus eliminating air from the free space of the bottle. The bottle was then tightly capped, shaken vigorously and placed in the thermostat, this being taken as the starting time of the reaction.

Shortstopping and Sampling Procedures

After the desired polymerization time, the bottle was removed from the bath and 0.45 ml. of di-t-butyl hydroquinone suspension injected using a hypodermic syringe and needle inserted through the self-sealing gasket of the bottle cap. The bottle was shaken vigorously and replaced in the bath for $1/4$ - 1 hour to allow thorough mixing and reaction of the shortstopping agent.

The latex was sampled using the hypodermic syringe technique (74). If the bottle was at or below room temperature, it was advantageous to increase the pressure in it by admitting tank nitrogen through a hypodermic needle. After this, the bottle was shaken vigorously, and a sample of latex withdrawn using a No.20 needle and a syringe of approximate-

ly twice the sample volume. The syringe was of the Luer-Lok type equipped with a stopcock and a retaining device on the piston to withstand the pressure of the butadiene in the latex sample. The syringe assembly was weighed on an analytical balance, emptied into the desired vessel, and reweighed to determine the weight of sample obtained.

The extent of polymerization was determined on the basis of solids content of the latex (74). A one ml. weighed sample of latex was placed in a tared aluminum weighing dish, coagulated with 10 - 15 ml. of ethanol, evaporated to dryness, and finally dried in the vacuum oven. By correcting the total solids content of the latex for the known non-polymer solids charged, the percentage conversion of initial monomer to polymer could be calculated. When solids determinations were conducted on latices which had not been shortstopped, a drop of the shortstop suspension diluted with 1 - 2 ml. of water was placed in the evaporating dish before addition of the latex sample. Determinations were made on latices at zero polymerization time to check the calculated amount of non-polymer solids. These also showed that no polymerization occurred during evaporation to dryness in the presence of the shortstopping agent used. Duplicate determinations on the same bottle of latex gave values within 0.2% solids, i.e.

approximately 0.6% conversion. This error was due mainly to the difficulty of maintaining a uniform dispersion of the oil phase throughout the latex while sampling.

THE POLYMERIZATION REACTION

Reproducibility

Persistent difficulty in obtaining a reproducible rate of reaction was encountered throughout the work with this polymerization system. In the early work, the rates in individual bottles of each experiment varied so widely that it was virtually impossible to study the kinetics of the reaction. In later work reproducibility between individual bottles of a particular experiment was achieved, but the rate of polymerization was frequently not reproducible from experiment to experiment.

Numerous variables of the system were investigated in a search for the underlying cause of this erratic behaviour. While only negative results were obtained from this work, it is worthwhile to record here some of the possible influencing factors which have been considered.

The most obvious factor which suggests itself is variation in purity or concentration of the components of the polymerization system. This is largely ruled out by the fact that the same stock of materials was used for all

experiments, and the same master-batch solutions for all bottles of any one experiment. Thus, the water, emulsifier, activator, cumene hydroperoxide-styrene solution, mercaptan-styrene solution, and butadiene were all charged into the individual bottles as aliquots, using the same volumetric or gravimetric measuring devices for each charge. The mercaptan and styrene solutions were prepared just before being required. The butadiene was purified within a few hours of use and stored at $-78^{\circ}\text{C}.$; the styrene was distilled under reduced pressure and kept at $5^{\circ}\text{C}.$ for periods of not more than 10 days. Use of undistilled, freshly distilled or distilled and stored styrene made no difference to the results obtained. The presence or absence of mercaptan had no influence on reproducibility. Variation in age of the emulsifier or activator solutions showed no correlation with variation in rates observed, although traces of a filmy solid were deposited from some emulsifier solutions after a week's aging. While the Dresinate 731 emulsifier is certainly not chemically pure, it was prepared as a filtered solution, which should distribute impurities uniformly. Replacement of it by potassium laurate effected no marked improvement in reproducibility.

Oxygen can both inhibit and catalyze free radical reactions of the type involved in such a polymerization system, and hence can cause very erratic behaviour. In all emulsion polymerizations, oxygen is presumably eliminated

from the free space of the system by flushing with nitrogen or with excess butadiene. In the present investigation, the time allowed for butadiene evaporation prior to capping was varied from 2 to 5 minutes without affecting the reproducibility. Longer flushing times seemed to affect the reproducibility adversely, perhaps due to the more prolonged period during which the various components of the system were in contact before formation of the emulsion.

The aqueous portions of the charge might introduce enough dissolved oxygen to cause trouble, but the use of oxygen-free water, and air-saturated water showed no difference in behaviour. In subsequent work, air-saturated water was used in all experiments.

Very often the reaction vessel may influence a chemical reaction, especially a free radical reaction which may be sensitive to traces of impurities and to surface catalytic effects. The polymerization vessel consisted of a glass bottle closed by a metal screw cap with an inner liner of Koroseal or, in some cases, Neoprene. The Neoprene gaskets were extracted with hot acetone and dried in a vacuum oven before use, while the Koroseal gaskets were soaked in styrene for several days, the surface wiped dry of styrene, and used without being allowed to dry out. The omission of these treatments in either case made no difference

to the polymerization behaviour. The gaskets made gas-tight seals with the glass bottles, since no bubbles of escaping butadiene were observed when the charged bottles were submerged in the water of the thermostat.

The glass bottles themselves might cause irreproducible results either through a surface catalytic effect, or by carry-over of contamination from a previous experiment or from cleaning. In an effort to vary the glass surface exposed to the reaction mixture, one bottle was coated on the inside with a paraffin-polyethylene mixture, while glass wool was added to a second bottle. Good checks between the rates in the two bottles were obtained, which would seem to eliminate surface catalysis as a variable.

At this point, the cleaning procedure for the bottles was changed from the use of hot chromic acid to a hot nitric-sulphuric acid mixture. This seemed to give some improvement in reproducibility and it was felt that the cause of the trouble had been found. However, in an experiment using a series of new bottles, poor checks were again obtained, indicating that the erratic behaviour could not be attributed to contamination from a previous experiment or from the cleaning process used between experiments.

During the latter part of the above work, it was

noted that the reproducibility gradually improved with successive experiments. This obscured the effects of the particular variables being investigated, but by the time the above work was completed, the reproducibility was such as to allow rate studies to be made, with the majority of the individual points lying within $\pm 1.5\%$ conversion of the average rate. These limits were quite acceptable for study of the system. Approximately this accuracy within each individual experiment was obtainable throughout the remainder of the work except for an occasional lapse. Thus, although no changes had been introduced in materials, experimental procedures or techniques, the early erratic behaviour had largely disappeared. In view of all the possibilities which have been cleared of responsibility for this behaviour, it does not seem possible to specify the difficulty inherent in obtaining reproducible results -- unless it be sheer experience of the operator.

The Overall Rate of Polymerization

Figure 1 is a plot of typical rate curves for the polymerization reaction at various temperatures from the data of Table II. The rates of these experiments approximate the average rate of all experiments at each temperature. The reproducibility obtainable in any one experiment is illustrated by the deviation of individual

TABLE II

THE RATE OF POLYMERIZATION AT FIVE TEMPERATURES

Experiment No.116 0.05 parts MTM-4 charged Poly'n Temp.= 45.0°C.		Experiment No.90 0.05 parts MTM-4 charged Poly'n Temp.= 35.0°C.		Experiment No.91 0.05 parts MTM-4 charged Poly'n Temp.= 25.0°C.		Experiment No.96 0.05 parts MTM-4 charged Poly'n Temp.= 15.0°C.		Experiment No.63 0.10 parts MTM-4 charged Poly'n Temp.= 5.0°C.	
Poly'n Time (hrs.)	% Conver- sion	Poly'n Time (hrs.)	% Conver- sion	Poly'n Time (hrs.)	% Conver- sion	Poly'n Time (hrs.)	% Conver- sion	Poly'n Time (hrs.)	% Conver- sion
0.50	17.9	0.67	7.6	1.00	14.9	2.2	22.5	4.0	17.4
0.75	22.4	1.00	23.2	2.00	23.4	4.0	34.6	8.0	28.6
1.00	28.2	1.33	28.2	2.50	29.2	5.0	37.0	10.1	36.8
1.25	36.6	1.67	34.8	3.00	32.8	6.0	40.8	12.0	39.2
1.50	42.5	2.00	38.0	3.50	37.4	7.0	45.5	14.0	40.5
1.75	49.5	2.33	45.3	4.00	41.1	8.0	52.1	16.0	50.8
2.00	55.5	2.67	50.6	4.50	47.0	9.0	55.9	18.3	56.1
2.25	61.0	3.00	55.9	5.00	50.4	10.0	65.5	20.0	64.6
2.50	69.8	3.33	59.4	5.50	57.5	11.0	66.1	22.0	69.4
2.75	75.5			6.00	65.0	12.0	71.4	24.0	72.4
								26.0	76.6
Zero order rate of polymerization = 26.7%/hr.		Zero order rate of polymerization = 16.4%/hr.		Zero order rate of polymerization = 9.00%/hr.		Zero order rate of polymerization = 4.96%/hr.		Zero order rate of polymerization = 2.72%/hr.	

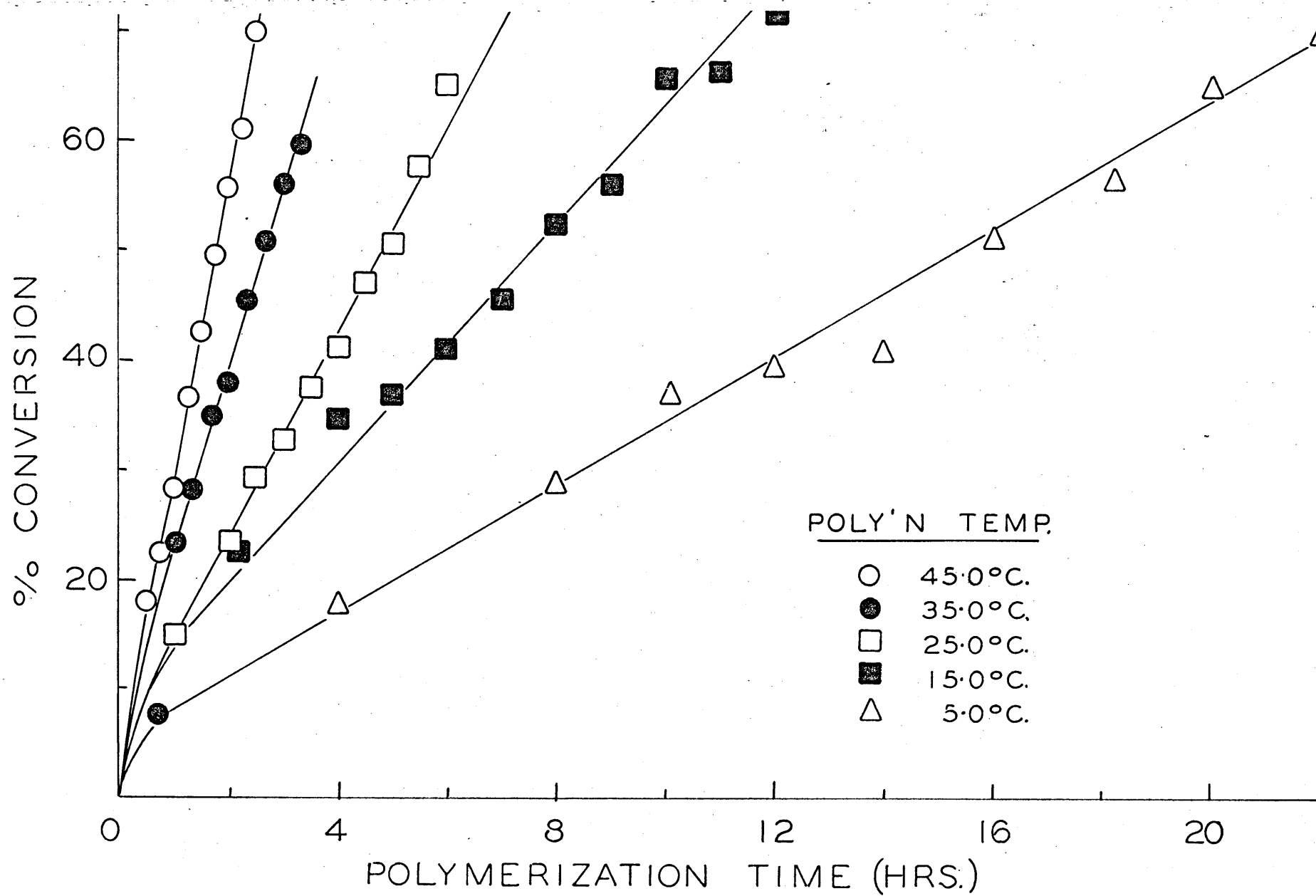


Figure 1. The rate of polymerization at various temperatures.

points from the curve. The first 8 - 10% of reaction is seen to have occurred at a fast rate almost independent of temperature, followed by a zero order reaction to 65 - 70% conversion. When the reaction was carried beyond this point, it gradually slowed down. The slope of the linear portion of the curve is taken as the zero order rate in the steady state condition of the emulsion. Presumably, in this region the rate of reaction was controlled by the rate of initiation, which, in turn, was constant owing to a constant supply of free radicals from the initiator.

The Initial Surge of Polymerization

These rate curves, like all that have been obtained with this system, are of particular interest in that they show short periods of very rapid reaction at the beginning of the polymerization before the steady zero order rate was established. This initial surge of reaction was very rapid even at the lowest temperature, as seen in Table III, Figure 2 and an investigation of its temperature dependence is not possible at the temperatures feasible with this system, i.e. above 0°C. The amount of this initial surge was not very reproducible, but usually amounted to an intercept of 6 - 10% conversion when the zero order rate was extrapolated back to zero time. The amount of the fast initial reaction, as measured by this intercept, showed no correlation with polymerization temperature.

TABLE III

THE RATE OF POLYMERIZATION AT LOW CONVERSION

Polymerization Temperature = 5.0°C
No Mercaptan charged
Zero order rate of polymerization =
2.33%/hr.

<u>Experiment No.</u>	<u>Polymerization Time (hrs.)</u>	<u>% Conversion</u>
113	0.25	5.14
	0.50	7.51
112	1.20	10.79
	2.40	13.86
	3.60	16.46
	4.80	20.22
	6.00	21.93
	7.20	23.98

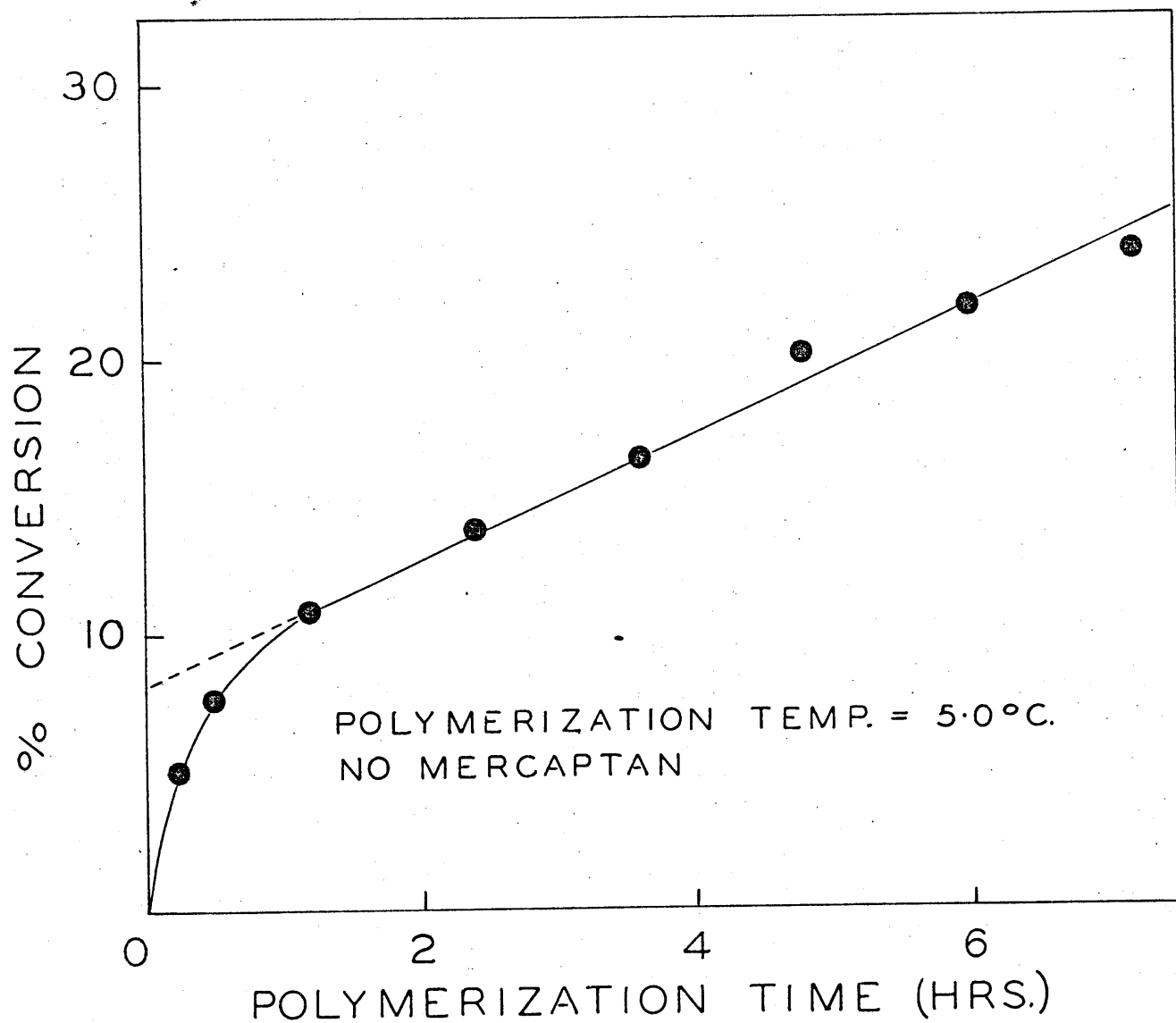


Figure 2. The rate of polymerization at low conversion.

This fast reaction appears to be dependent upon the initiator system as a whole, since when either the peroxide or the activator, or both, were omitted from the charge, no polymerization took place at all. If these components were then added to the emulsified charge by syringe, the usual polymerization curve was obtained. This behaviour could be caused by an abnormally fast production of free radicals arising from interaction of the initiating system and an impurity in the emulsion.

Possible sources of such an impurity were investigated by varying the components of the system wherever possible. The elimination of mercaptan from the charge was without effect, while the polymerization of pure butadiene and pure styrene in the system at 5°C. gave yields of 16.2% and 39.2% respectively after the first hour compared with the zero order rate of 2.5%/hour for 75/25 butadiene-styrene mixture. The commercial Dresinate emulsifier could be a source of numerous impurities but substitution of potassium laurate in the recipe did not alter the form of the rate curve as shown in Figure 3, Table IV. This is in agreement with the fact that this behaviour is not observed when Dresinate is used in a persulphate recipe at higher temperatures (3).

TABLE IV

THE RATE OF POLYMERIZATION USING POTASSIUM

LAURATE AND KALEX K

Experiment No. 122
Polymerization Temperature = 25.0°C
MTM-4 charged = 0.05 parts

<u>Polymerization Time</u> <u>(hrs.)</u>	<u>% Conversion</u>
1.10	10.1
2.00	22.6
3.00	26.2
3.67	36.8
4.33	43.1
5.00	46.7
5.67	50.4
6.33	51.8
7.00	65.6
8.00	65.0

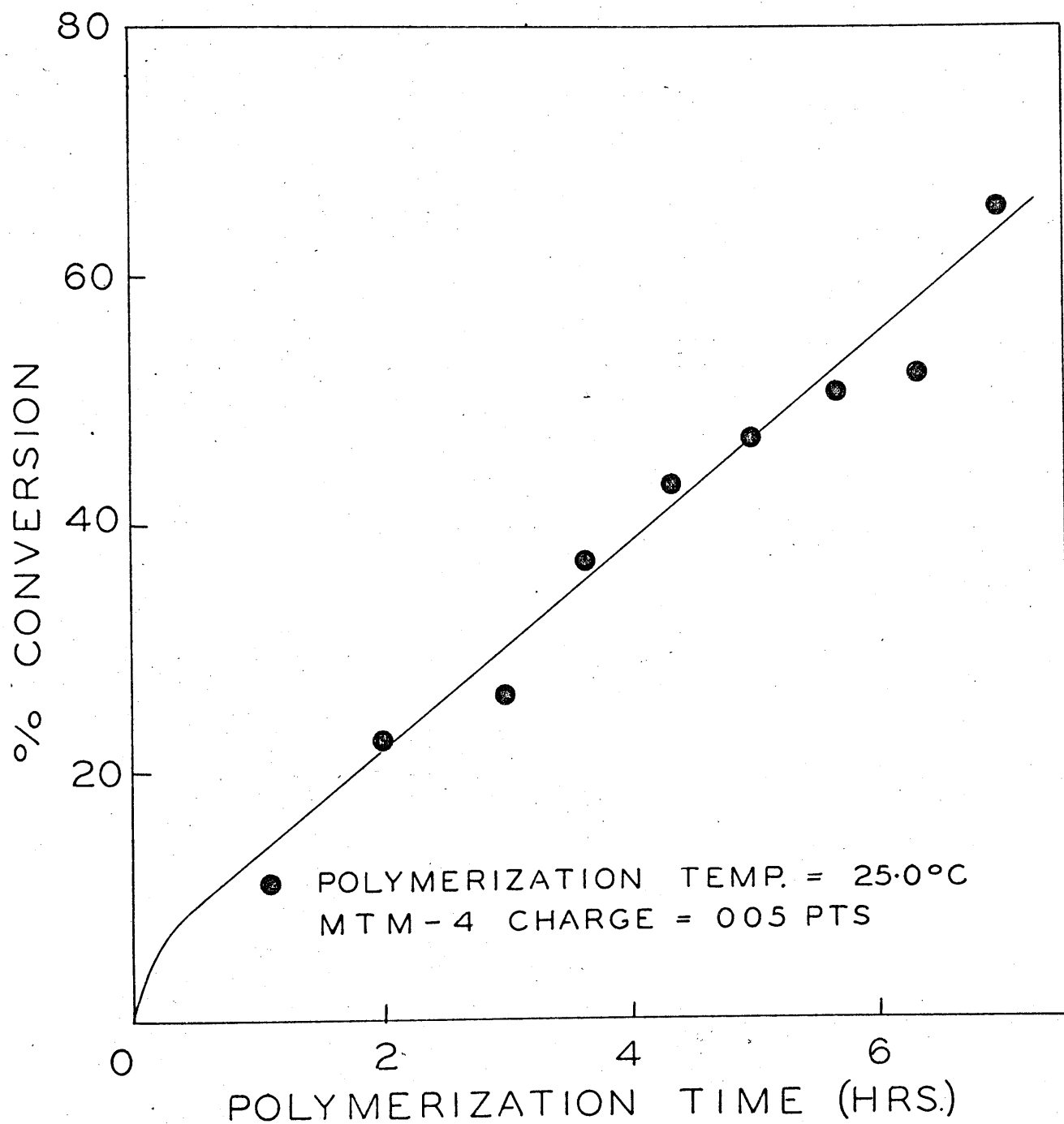


Figure 3. The rate of polymerization using Kalex K and potassium laurate.

These observations lead to the conclusion that the cause of this early polymerization behaviour lies solely with the initiating system. Since the fast rate is restricted to the very early portion of polymerization it must be involved with reactions which occur when the oil-soluble and water-soluble components of the initiator, oxidant and reducer, first come together in the emulsion. This initial contact must produce a flood of free radicals which is then followed by the slow reaction which supplies the steady concentration of free radicals during the major part of the polymerization.

If this abnormally fast reaction were more extensive in a particular experiment it might reduce the concentration of the initiating system to such an extent that the subsequent zero order rate would be lower than usual. However, no general relation was found to hold between the extent of the initial surge and the subsequent rate of polymerization. The side reactions of the initiator apparently do not vary sufficiently to cause a noticeable effect on the free radical production during the remainder of the polymerization.

The Zero Order Polymerization

The dependence of polymerization rate on activator concentration was investigated by comparing the extent of polymerization in 5 1/2 hours at 25°C. when various fractions

of the normal amount of activator solution were charged. The total charge weight and electrolyte concentration were maintained essentially constant by addition of water containing trisodium phosphate of the same concentration as the activator solution. The results are recorded in Table V. It is seen that the polymerization rate is very dependent on activator concentration at low concentrations, but above a concentration of about one half of the normal charge, the rate tends to become independent of activator concentration. Since the normal charge corresponds to an optimum recipe developed by Mitchell et al (26), it is to be expected that the rate should decrease for higher concentrations of activator.

For the normal activator charge, it is seen from Table V that a relatively large portion of the activator may be consumed during polymerization without appreciably reducing the rate or disturbing its zero order character. At one quarter the normal charge, the rate would presumably be much more sensitive to activator consumption, but a good zero order rate curve was still obtained at this concentration, Table VI, Figure 4, indicating that the actual consumption of activator during polymerization was slight.

In spite of the good reproducibility of individual points within each experiment as shown in Figure 1, it was not possible to duplicate accurately the slope of the zero order portion of the polymerization rate curve.

TABLE V

THE DEPENDENCE OF POLYMERIZATION RATE ON ACTIVATOR
CONCENTRATION

Polymerization Temperature = 25.0°C.
Polymerization Time = 5.50 hours
No mercaptan charged

<u>Experiment No.</u>	<u>Activator Charge</u>	<u>% Conversion in 5.5 hrs.</u>
117	0.25 of normal charge	33.8
	0.50 " "	50.5
	0.75 " "	55.0
91	1.00 " "	55.5

TABLE VI

THE RATE OF POLYMERIZATION USING 1/4 OF THE NORMAL
ACTIVATOR CHARGE

Experiment No. 120
Polymerization Temperature = 25.0°C.
MTM-4 charged = 0.05 parts

<u>Polymerization Time</u> <u>(hrs.)</u>	<u>% Conversion</u>
2.0	18.7
4.0	28.0
6.0	36.6
8.0	47.2
12.0	63.8
16.0	73.1
20.0	74.2
24.0	85.9
28.0	83.7

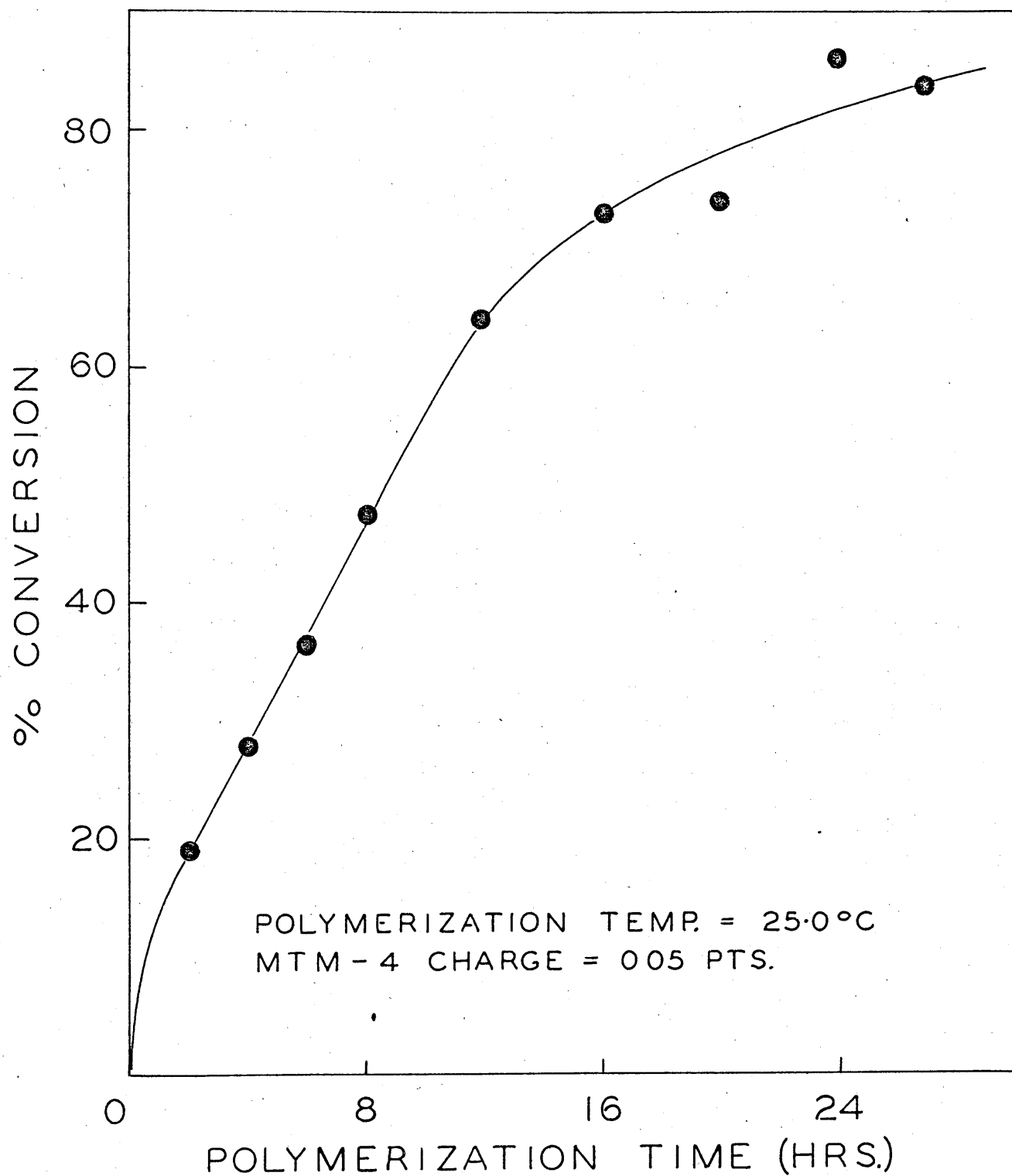


Figure 4. The rate of polymerization using 1/4 normal activator charge.

Table VII is a summary of the zero order rates for all comparable experiments done with this system. The variability of the reaction in duplicate experiments is apparent. However, when the logarithms of the average rates are plotted against the reciprocal of the absolute temperature, Figure 5, a surprisingly good straight line is obtained. Using the slope of this line in an integrated Arrhenius equation:

$$E = 2.303 R \frac{\log k_2 - \log k_1}{\frac{1}{T_1} - \frac{1}{T_2}}$$

an activation energy of 9700 cal/mole is found for the process which is rate controlling during the zero order portion of polymerization.

Reaction at High Conversions

Equation (1) indicates that the rate of disappearance of monomer should become first order in respect of monomer once the monomer concentration at the site of polymerization drops low enough to influence the rate. Figure 6 is a first order plot, from the data of Table VIII, of the monomer concentration in the portion of the polymerization curve beyond the region where the rate is zero order, i.e. beyond the point of disappearance of a free monomer phase when all the monomer in the system is at the site of polymerization. The monomer disappearance

TABLE VII

THE ZERO ORDER RATES OF POLYMERIZATION

Polymerization Temperature	5.0°C.	15.0°C.	25.0°C.	35.0°C.	45.0°C.
Zero order rates of polymerization	2.40%/hr.	5.47%/hr.	8.74%/hr.	14.6%/hr.	26.7%/hr.
	2.72	4.96	9.18	16.9	
	2.34	4.60	10.38	16.4	
	2.58	6.05	7.69	13.9	
	3.48	4.73	8.87	17.1	
	3.22	4.10	10.80		
	3.17		9.00		
	2.33		8.70		
			9.70		
			8.20		
			9.00		
			10.15		
			6.90		
Arithmetic Mean Rates	2.78%/hr.	4.93%/hr.	9.02%/hr.	15.8%/hr.	26.7%/hr.
Probable Error of the Mean Rates	0.11	0.17	0.20	0.43	
Reciprocal of the Absolute Temperature	3.600×10^{-3}	3.472×10^{-3}	3.358×10^{-3}	3.240×10^{-3}	3.140×10^{-3}

Activation Energy for the Zero Order Reaction from Figure 5
= 9700 cal./mole from Figure 5.

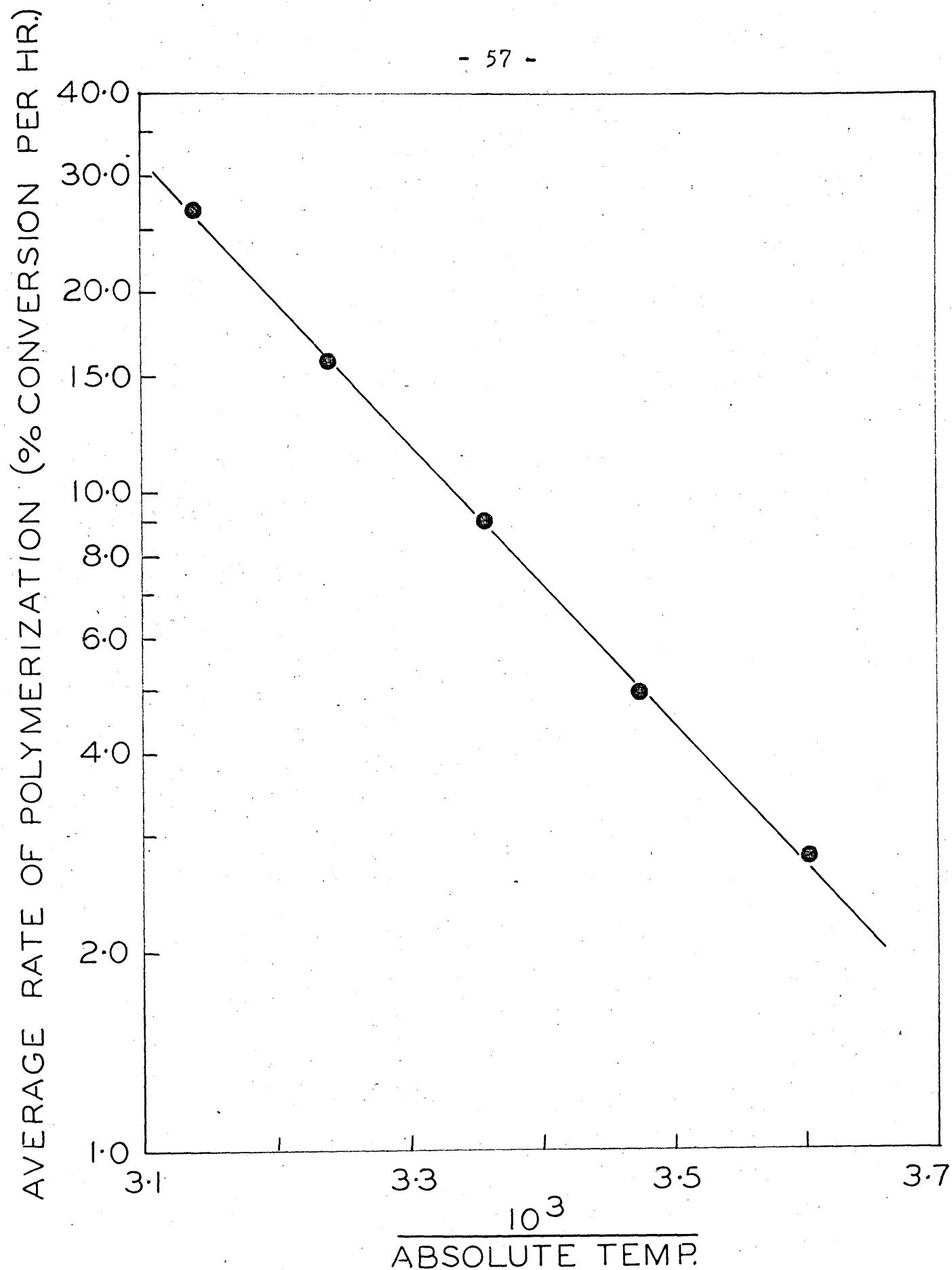


Figure 5. Arrhenius plot for the polymerization reaction.

TABLE VIII

THE RATE OF MONOMER DISAPPEARANCE AT
HIGH CONVERSION

<u>Experiment No.</u>	<u>Poly'n Temp.</u>	<u>MTM-4 charged</u>	<u>Poly'n Time (hrs.)</u>	<u>% Conversion</u>	<u>Monomer Conc. (gms/gm polymer)</u>
55	25.0°C.	0.20 parts	9.00	78.5	0.274
			10.00	82.0	0.220
			11.00	84.6	0.182
			12.00	88.6	0.129
99	5.0°C.	0.03 parts	18.25	63.0	0.588
			20.25	68.5	0.460
			22.20	72.4	0.381
			24.00	77.1	0.297

First order rate constant at 25.0°C. = $10.1 \times 10^{-2} \text{ hr}^{-1}$

First order rate constant at 5.0°C. = $5.0 \times 10^{-2} \text{ hr}^{-1}$

ACTIVATION ENERGY = 5700 cal/mole.

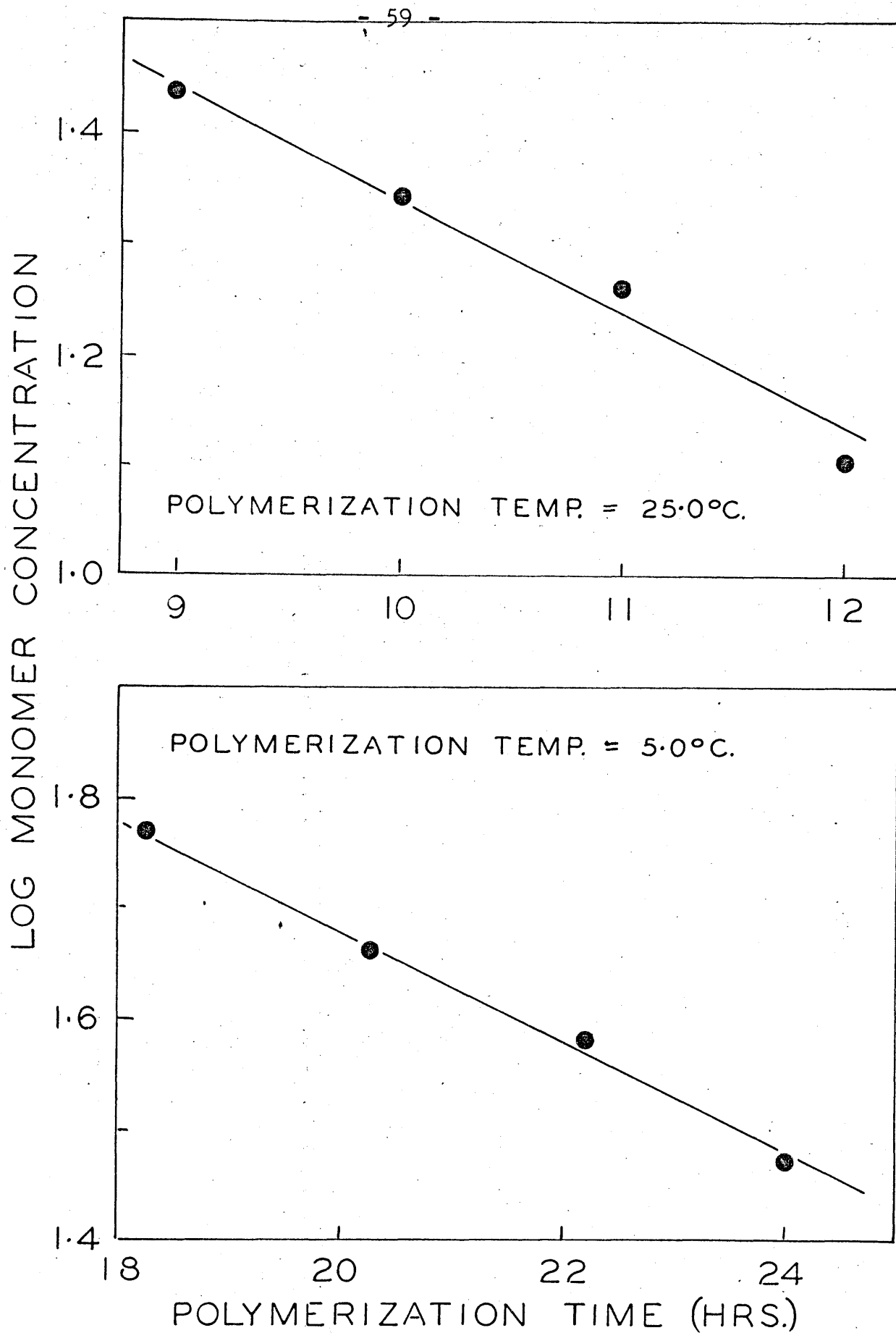


Figure 6. First order plot of monomer disappearance at high conversions.

is seen to follow first order behaviour in this region of reaction. Since the previous data have shown that in the zero order region the initiator system is depleted to a relatively insignificant extent during a polymerization, the deviation from zero order behaviour beyond 65% conversion can scarcely be attributed to a decrease in the concentration of initiating free radicals and it seems reasonable to infer that the monomer concentration becomes the rate controlling factor during this phase of polymerization. If this is true, the activation energy measured in these later stages of polymerization should be that for the disappearance of monomer, i.e. it should be the activation energy of propagation. An activation energy of 5700 cal/mole is obtained from the two experiments in Figure 6. This value is doubtless inaccurate since the first order reaction can be followed only over a short range.

THE MERCAPTAN CHAIN TRANSFER REACTION

The kinetics of the mercaptan chain transfer reaction were studied by measuring the disappearance of mercaptan from the emulsion system during the course of the polymerization reaction.

Mercaptan Analysis

The residual mercaptan in the latex was determined by amperometric titration with silver nitrate according to

the method of Kolthoff and Harris (75). A number of these analyses were made on 5 ml. samples of latex obtained by syringe sampling and coagulated in rapidly stirred ethanol. The results were unsatisfactory, however, since it was not only very difficult to get uniform samples of the latex in this way, but the polymer tended to roll up into compact lumps on coagulation. Satisfactory results were finally obtained when the following procedure was used. Without shortstopping the polymerization, a one ml. sample of latex was removed from the bottle for determination of percentage conversion. A No. 20 needle connected to a closed stopcock was inserted in the bottle, the bottle inverted over a beaker containing 400 ml. of rapidly stirred ethanol, and the stopcock partially opened, allowing only a very fine stream of latex to escape. The whole contents of the bottle were coagulated in this manner, one ml. of 0.1N ferrous sulphate in 1.0N sulphuric acid immediately added and stirring continued 1 to 2 minutes. The mixture was allowed to stand at least 5 minutes, and then concentrated ammonium hydroxide was added to an excess of 0.25N. The solution was titrated amperometrically with 0.0025N silver nitrate. By this method, sampling error appeared to be largely eliminated and a well dispersed coagulum obtained.

Rate of Mercaptan Consumption

Typical analytical data for the disappearance of mercaptan during the course of the polymerization at various temperatures are presented in Table IX. The reaction of mercaptan as a chain transfer agent in an emulsion system has generally been found to be first order up to about 60% conversion, after which the reaction falls off due to changes in the condition of the emulsion. The first order plots of Figure 7 follow this pattern except for deviations during the early stages of reaction. These early portions of the mercaptan disappearance curves correspond to the initial fast polymerization reactions. It may be observed that at different temperatures there is a distinct difference in behaviour of the mercaptan disappearance curves in this region. At 35°C. the rate of disappearance is slightly slower than first order during the first few minutes of reaction. At 25°C. the reaction seems to be first order from zero time. At 15° and 5°C., the disappearance rate in the initial stages of reaction is seen to be increasingly faster than the first order rate of subsequent reaction.

When the mercaptan disappearance is correlated with the extent of the polymerization reaction, Figure 8, it is found in all cases that the rate of mercaptan disappearance does not keep up with the rate of polymerization

TABLE IX

THE RATE OF MERCAPTAN DISAPPEARANCE DURING
POLYMERIZATION AT FOUR TEMPERATURES

Experiment No. 107
Polymerization Temperature = 35.0°C.
MTM-4 charged = 0.05 parts

<u>Polymerization Time</u> <u>(hrs.)</u>	<u>% Conversion</u>	<u>% Mercaptan</u> <u>Unreacted</u>
0.60	16.6	84.4
1.10	24.5	67.5
1.65	34.1	56.4
2.20	42.7	46.2
2.75	53.3	37.0
3.30	63.8	28.0
3.85	75.0	19.0

First order rate constant = 0.376 hr⁻¹

TABLE IX (cont.)

Experiment No. 108
Polymerization Temperature = 25.0°C.
MTM-4 charged = 0.05 parts

<u>Polymerization Time</u> <u>(hrs.)</u>	<u>% Conversion</u>	<u>% Mercaptan</u> <u>Unreacted</u>
1.10	16.2	80.3
2.10	25.2	65.4
3.10	30.4	57.4
4.05	40.9	47.1
5.10	44.2	43.5
6.05	51.5	40.2

First order rate constant = 0.187 hr⁻¹

TABLE IX (cont.)

Experiment No. 109
Polymerization Temperature = 15.0°C.
MTM-4 charged = 0.05 parts

<u>Polymerization Time</u> <u>(hrs.)</u>	<u>% Conversion</u>	<u>% Mercaptan</u> <u>Unreacted</u>
1.15	18.3	84.1
2.60	22.5	71.5
4.05	29.1	61.9
5.55	34.1	53.9
7.10	41.0	47.3
8.55	50.8	40.8
10.15	59.7	31.4

First order rate constant = 0.114 hr^{-1}

TABLE IX (cont.)

Experiment No. 111
Polymerization Temperature = 5.0°C.
MTM-4 charged = 0.03 parts

<u>Polymerization Time (hrs.)</u>	<u>% Conversion</u>	<u>% Mercaptan Unreacted</u>
3.10	20.1	70.5
6.10	26.1	58.1
9.10	33.3	48.8
12.40	38.3	41.6
14.85	44.6	38.0
18.20	55.1	31.2

First order rate constant = 0.0558 hr⁻¹

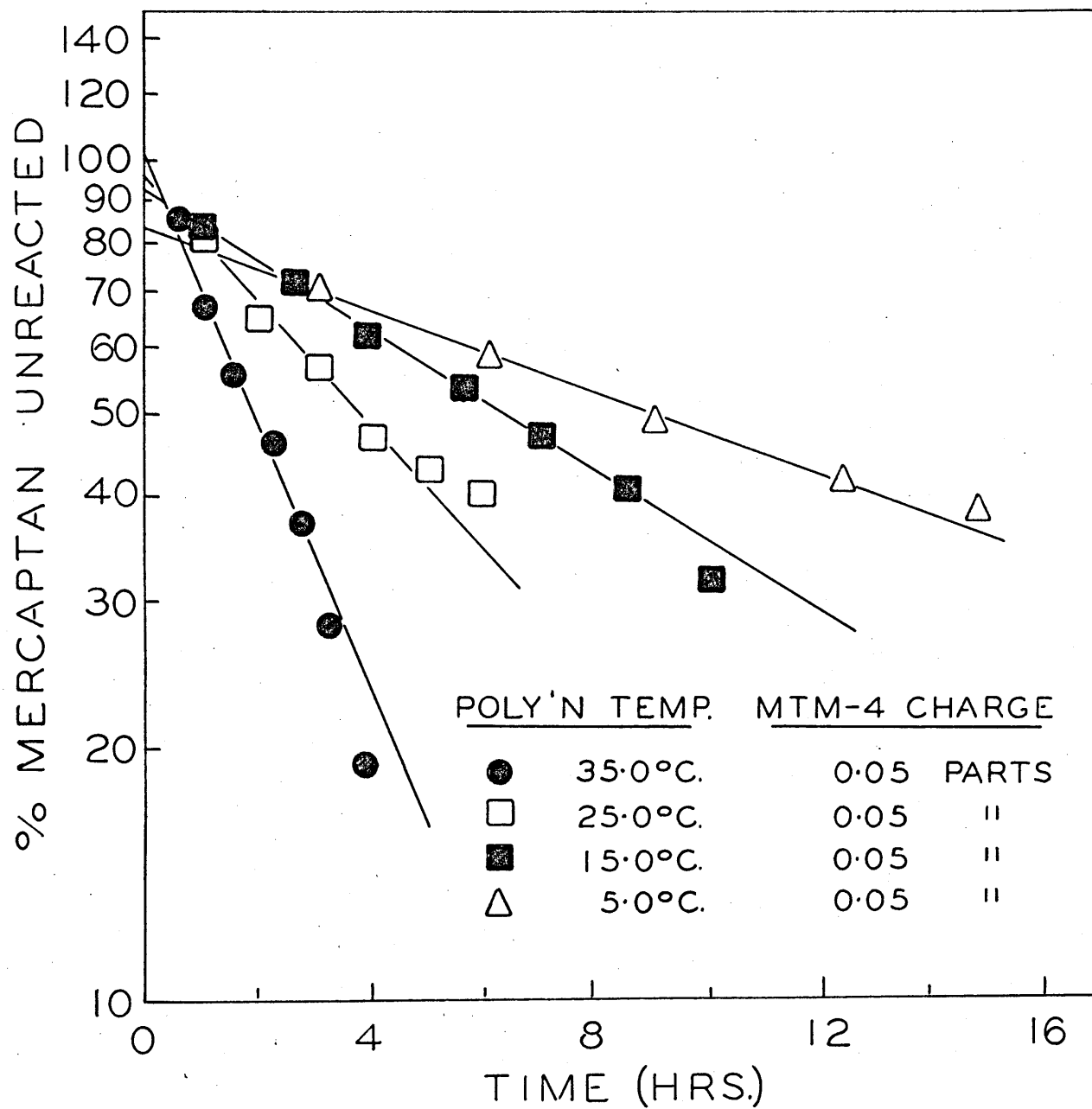


Figure 7. The rate of mercaptan disappearance at various temperatures.

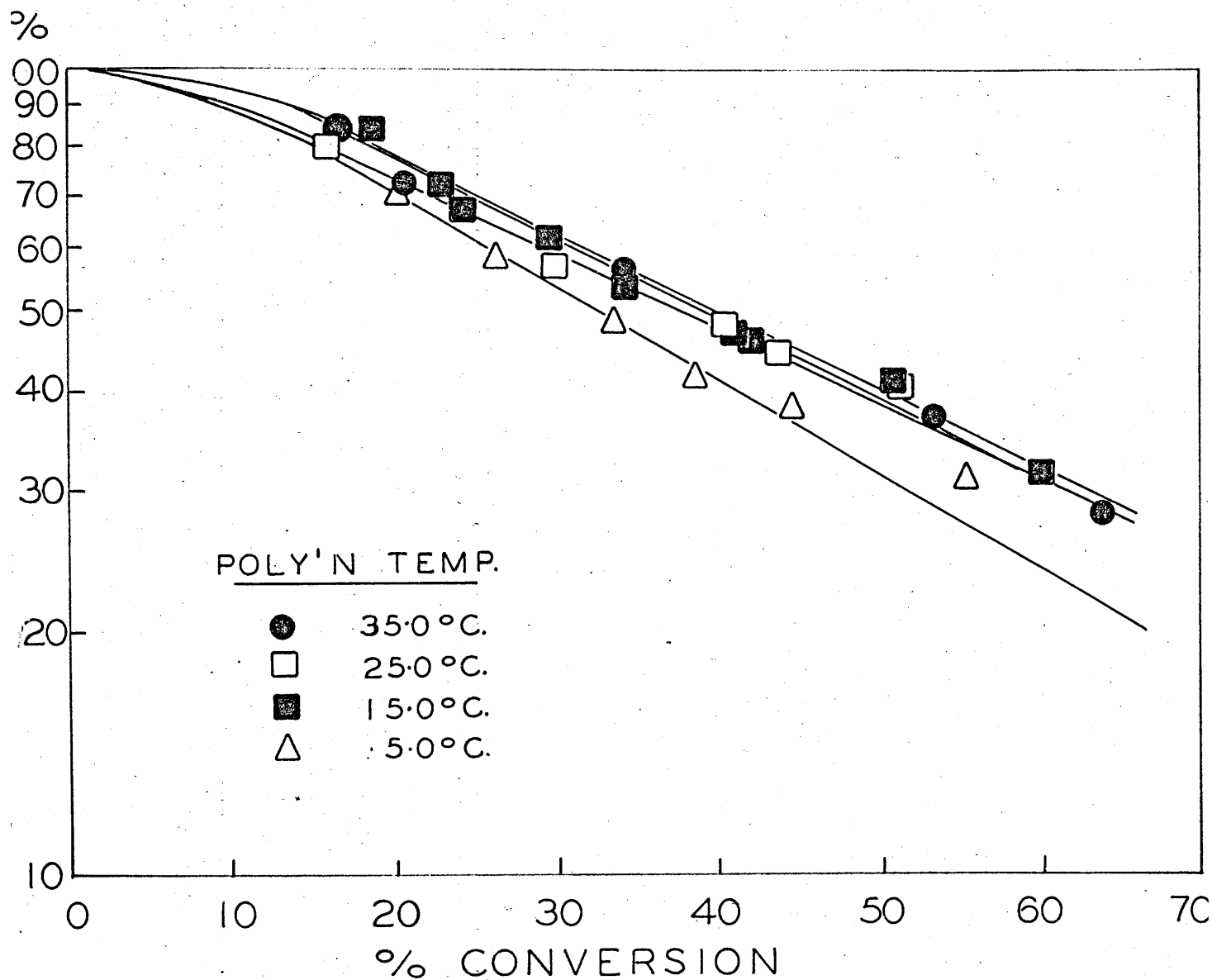


Figure 8. Mercaptan disappearance during the course of polymerization.

during the fast initial reaction. This implies either that abnormally long polymer chains are formed, or that a terminating or chain transfer agent other than mercaptan is present and capable of terminating the abnormally large number of chains initiated. Viscosity measurements on polymer of 5 - 20% conversion, Table X, Figure 9, indicate that this polymer is of low molecular weight rather than high. Hence, a mode of termination other than by mercaptan would appear to play a major role in the initial stages of polymerization.

The higher mercaptan consumption during the initial surge of polymerization at low temperatures suggests that the reaction involving the non-mercaptan terminating agent becomes less effective, relative to the reaction with mercaptan, as the temperature is lowered, and therefore has a higher activation energy. If the first order curves are extrapolated back to zero time, it seems reasonable to consider variation of the intercepts so obtained as a measure of the relative effect of temperature on the reactions with mercaptan and with the other terminating agent. If this be true, a plot of the logarithm of this intercept against the reciprocal of the absolute temperature should correspond to the difference in activation energy for the two types of termination. The experiment at 5°C. cannot be included in these considerations, since the initial charge of mercaptan

TABLE X

THE VISCOSITY OF LOW CONVERSION POLYMER

Experiments Nos. 112 and 115
Polymerization Temperature = 5.0°C.
MTM-4 charged = 0.20 parts

<u>Polymerization Time</u> <u>(hrs.)</u>	<u>% Conversion</u>	<u>Intrinsic Flow</u> <u>Time t</u>
0.25	6.27	0.490
0.50	7.09	0.635
0.75	6.74	0.748
1.20	12.63	0.812
2.40	15.17	0.990
3.60	17.01	1.130
4.80	18.69	1.189

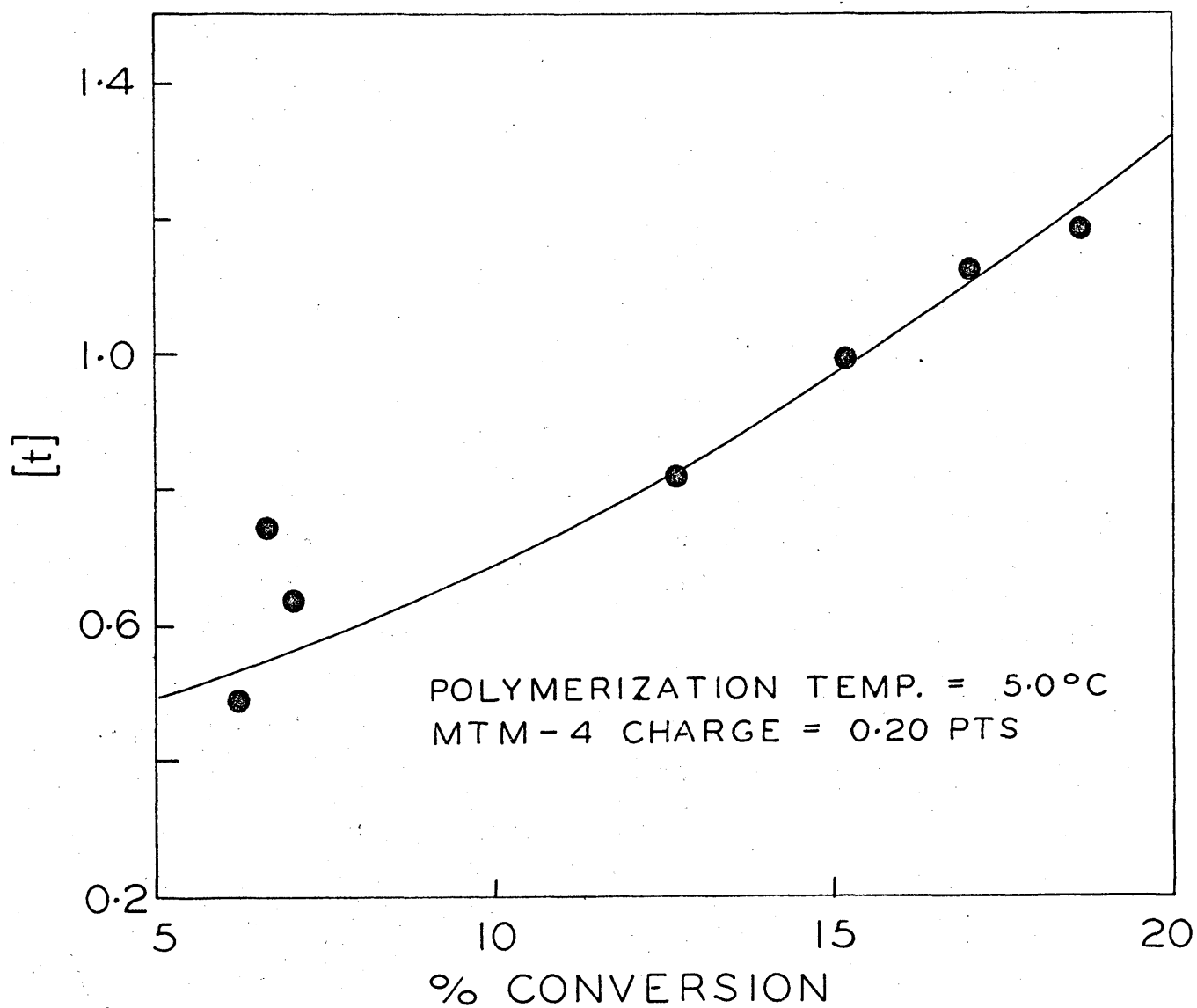


Figure 9. Intrinsic flow time of low conversion polymer.

was less than in the other three experiments, and the ratio of mercaptan to other termination would be lower.

The intercepts of the mercaptan disappearance rate curves were obtained from large scale plots of the curves of Figure 7, Table IX, and are reported in Table XI. Figure 10 is an Arrhenius plot of these intercepts and gives a value of about 900 cal/mole for the activation energy difference of the two terminating processes. If now the activation energy for the mercaptan reaction can be determined, an activation energy may be evaluated for the other mode of termination operating during the initial fast polymerization.

The mercaptan chain transfer reaction is directly affected by the rate of formation of the polymer free radical chains, hence is subject to the same irregularities between duplicate experiments as the polymerization reaction. A number of rate experiments at each temperature were therefore made to evaluate the corresponding mercaptan disappearance rates. Table XII is a summary of data for a number of experiments at each temperature. Most of these data were obtained from analyses on 5 ml. samples of latex. This method did not yield very consistent analytical data, but a reasonable estimate of the average rate of mercaptan disappearance was possible at each temperature. Figure 11 is

TABLE XI

INTERCEPTS OBTAINED BY EXTRAPOLATING THE FIRST ORDER
PORTION OF THE MERCAPTAN DISAPPEARANCE
CURVES TO ZERO TIME

Obtained from large scale plots of the curves of Figure 7

<u>Polymerization</u> <u>Temperature</u>	<u>Recip. Absolute</u> <u>Temperature</u>	<u>Intercept</u>	<u>Log</u> <u>Intercept</u>
35.0°C.	3.240×10^{-3}	102% Conversion	2.009
25.0°C.	3.358×10^{-3}	96% "	1.982
15.0°C.	3.472×10^{-3}	92% "	1.964

Activation Energy Difference indicated by the Arrhenius plot,
Figure 10 = 890 cal/mole.

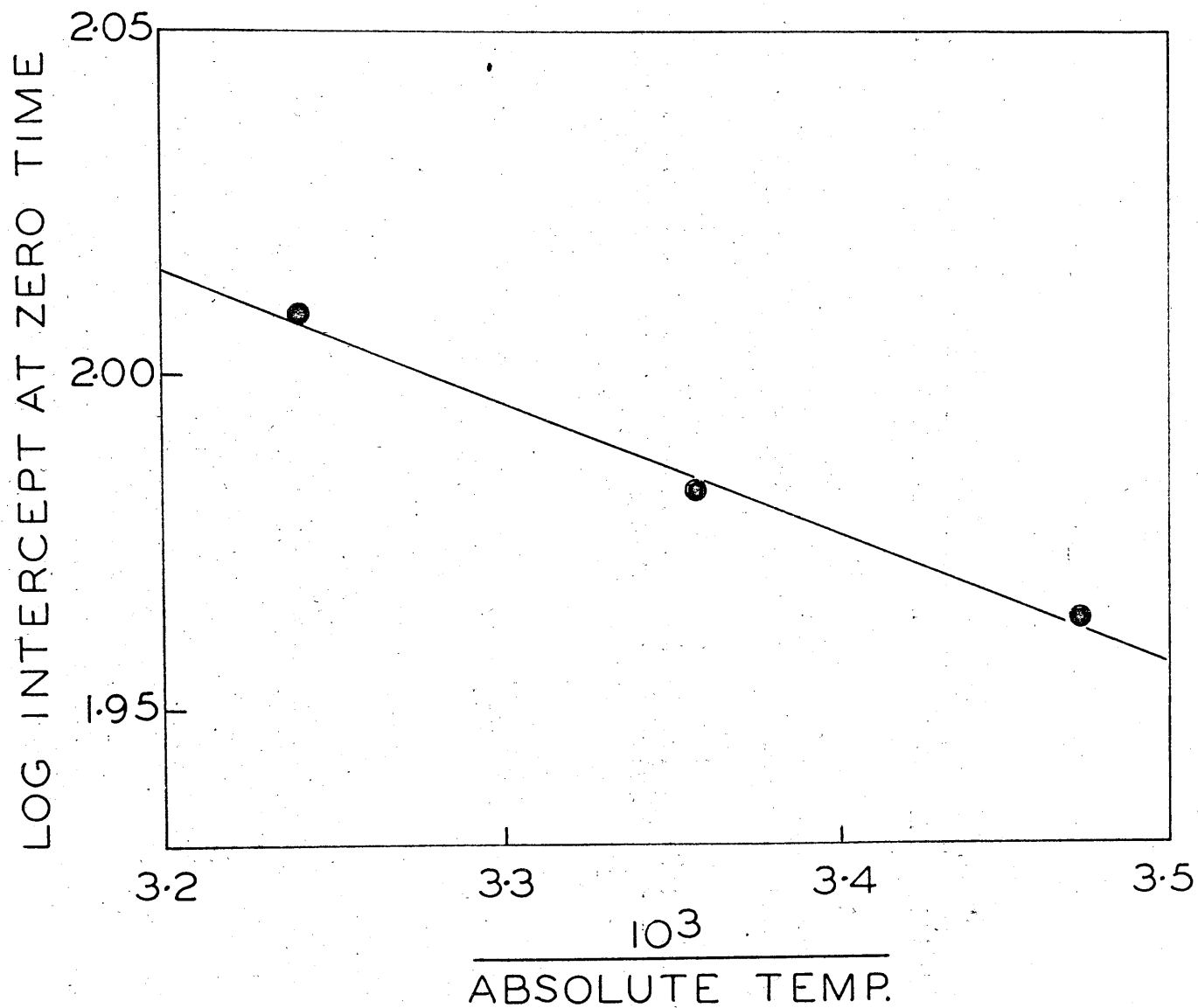


Figure 10. Arrhenius plot for the intercepts of the mercaptan disappearance rate curve.

TABLE XII

FIRST ORDER RATE CONSTANTS FOR THE
CONSUMPTION OF MERCAPTAN

<u>Polymerization</u> <u>Temperature</u>	35.0°C.	25.0°C.	15.0°C.	5.0°C.
<u>1/T°A</u>	3.240x10 ⁻³	3.358x10 ⁻³	3.472x10 ⁻³	3.600x10 ⁻³
<u>First order</u> <u>rate constants</u>	0.327	0.257	0.112	0.0562
	0.258	0.193	0.128	0.0744
	0.376	0.212	0.102	0.0558
		0.187		
<u>Arithmetic</u> <u>Mean Rate</u> <u>Constants</u>	0.320	0.212	0.114	0.0621

Activation Energy indicated by the Arrhenius plot, Figure 11
= 9,000 cal/mole.

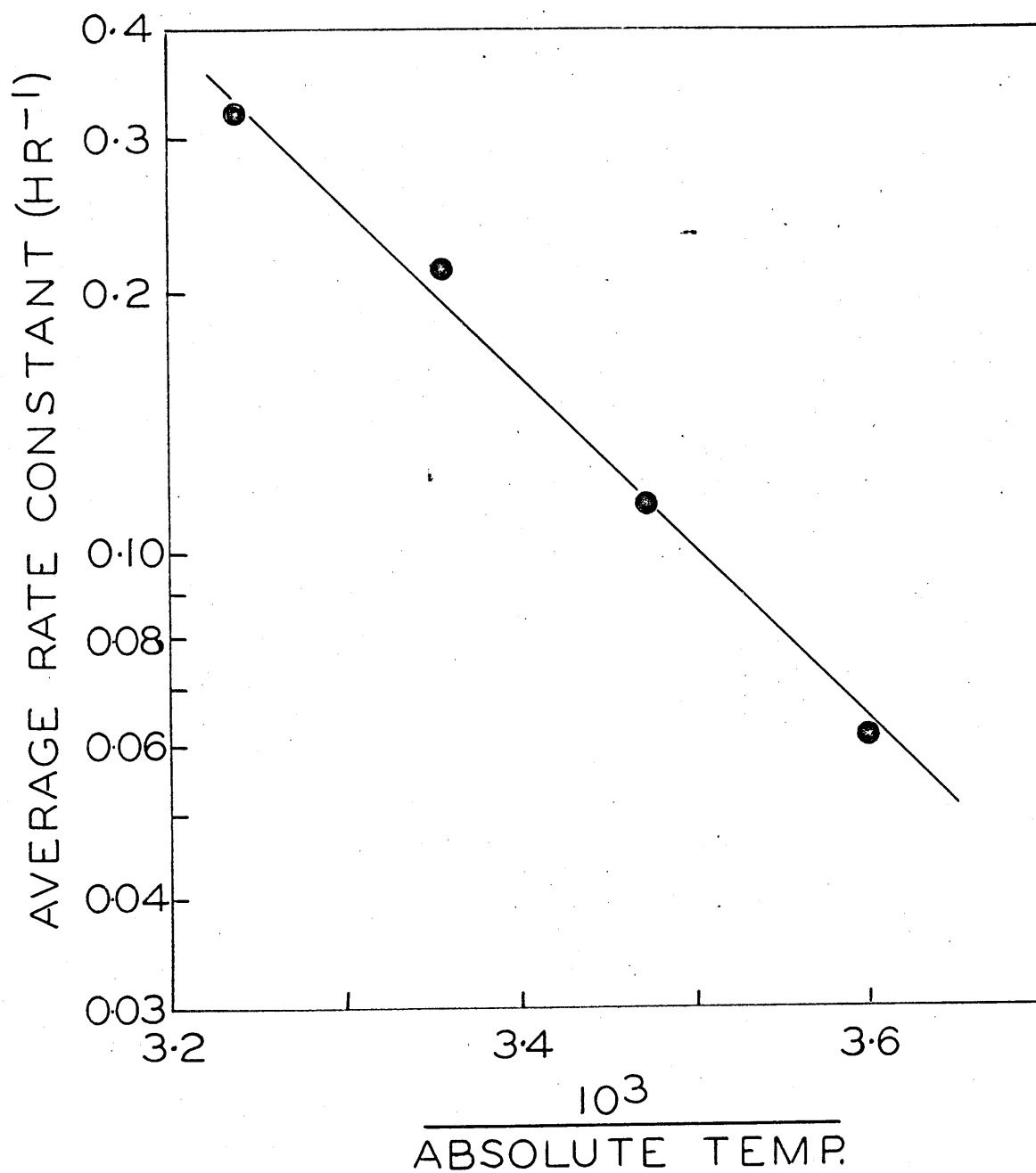


Figure 11. Arrhenius plot for the mercaptan chain transfer reaction.

an Arrhenius plot for the rate of mercaptan disappearance at the different temperatures, from Table XII. The average rates give a satisfactory straight line from which the activation energy for the disappearance of mercaptan may be assessed as about 9000 cal/mole in this system.

From this value and the difference in activation energy of the two terminating processes, the activation energy for the second terminating process is estimated to be about 9900 cal/mole. This is in good agreement with the value of 9700 cal/mole obtained for the production of free radicals, as indicated by the polymerization reaction. This suggests that the non-mercaptan termination is the result of mutual termination of free radicals. This does not imply that the activation energy for a radical-radical reaction is of the order of 10 Kcal/mole, but that the mutual termination reaction is controlled by the concentration, hence rate of production, of free radicals in the same sense as the rate of the polymerization reaction itself. The existence of an appreciable amount of mutual termination during the fast initial polymerization is to be expected when it is considered that this fast reaction indicates an abnormally high concentration of initiating and growing free radicals.

MONOMER-POLYMER RATIO IN THE LATEX PARTICLE

Method

A gravimetric method (45) for determining the ratio of monomer to polymer in the latex particle during polymerization was used to study the present butadiene-styrene system.

After a bottle of latex had been in the polymerization bath the desired length of time, it was removed and tank nitrogen admitted to it through a hypodermic needle to facilitate syringe sampling. The bottle was then vigorously shaken and a one ml. sample removed by syringe. The bottle was immediately placed top down in a centrifuge cup and centrifuged exactly 4 minutes at 2000 r.p.m. During this time the one ml. sample was weighed and coagulated in a tared evaporating dish containing a small amount of shortstopping agent. Centrifugation of the polymerization mixture separated it into two layers, a lighter oil phase and an "aqueous phase". The oil phase consisted of that portion of the unreacted monomers and monomer-soluble constituents which had been dispersed as discrete oil droplets throughout the emulsion during polymerization. The "aqueous phase" was not a true aqueous phase, but consisted of a suspension of latex particles, i.e. polymer particles containing dissolved monomer, in the water of the polymerization mixture. The centrifuged

bottle was carefully removed from the centrifuge without disturbing the separated phases and the lower aqueous layer of latex quickly sampled. This sample was weighed and coagulated in approximately the same time required for the sample taken before centrifugation. A correction to the percentage conversion was made for the amount of polymerization that occurred during centrifugation.

The ratio of monomer to polymer in the aqueous phase of the emulsion was calculated from the above measurements. From a consideration of the percentage solids in the total latex and the percentage of the aqueous phase to which these solids correspond the weight of the aqueous phase of the latex was calculated. The weight of monomer in this phase is the difference between the weight of the phase and its solids and water content. The weight of polymer in this phase is the same as the weight of polymer in the total latex.

$$\frac{\text{Monomer in aqueous phase}}{\text{Polymer in aqueous phase}} = \frac{\text{Wt. of aqueous phase} - \text{Total Solids} - \text{Wt. of Water}}{\text{Total Wt. of Solids} - \text{Wt. of non-polymer Solid}}$$

If the monomer is soluble only in the polymer portion of the aqueous phase, the above ratio will be the ratio of monomer to polymer in the polymer particle. However, soap micelles of the emulsifier render the monomer soluble in the water of the aqueous phase to a considerable extent,

which results in high values of the above ratio at low conversions where most of the soap is present as micelles. After polymerization passes a certain point, the soap concentration drops below the critical value for micelle formation as it becomes dispersed over the growing surface of polymer particles. The solubility of the monomer in the water of the aqueous phase then becomes small and the above ratio may be taken to represent the ratio of monomer to polymer in the polymer particle.

As Herzefeld et al (45) point out, it is not certain that this type of measurement gives a dynamic value of the monomer-polymer ratio, since the diffusion processes involved may be of such a rate as to disrupt the dynamic conditions during the time required to perform the necessary operations. To maintain dynamic conditions as long as possible, the polymerization reaction was not short-stopped in the procedure used in this investigation. Of course, as soon as monomer begins to separate from the aqueous portion of the emulsion, the dynamic diffusion conditions are disrupted.

Since calculations of M/P from gravimetric data involve a difference calculation, experimental errors are greatly magnified below 20 - 30% conversion and this region cannot be satisfactorily investigated. The values obtained

in this region are also in error by the amount of monomer solubilized by the soap micelles.

Effect of Polymerization Rate

The monomer-polymer ratio is determined by the ratio of diffusion of monomer into the polymer particle, relative to the rate of its polymerization within the particle. Measurements of the M/P ratio have been found sensitive to irregularities in polymerization rate which have been observed with this system in duplicate experiments. Figure 12, Table XIII, is an illustration of the effect of polymerization rate on the M/P curve at 25°C. The faster rate of polymerization results in lower values of M/P at corresponding conversions due to a faster disappearance of monomer by polymerization with no corresponding increase in the rate of diffusion of monomer into the particle. The average of the two polymerization rates of the experiments in Figure 12 is close to the overall average rate for 25°C. (Table II), and the M/P-conversion curve corresponding to the overall average rate may therefore be estimated roughly by drawing a curve intermediate between the two experimental curves of Figure 12.

When $\log \frac{M}{M+P}$ (i.e. log of the fraction of the total particle consisting of monomer) is plotted against $\log \alpha$ (i.e. log of the fractional extent of conversion)

TABLE XIII

THE EFFECT OF POLYMERIZATION RATE ON THE RATIO OF
MONOMER TO POLYMER IN THE LATEX PARTICLE

Polymerization Temperature = 25.0°C.
MTM-4 charged = 0.05 parts

Experiment No.	Zero order rate of Polymerization	Polymerization Time (hrs.)	% Conversion	M/ P
85	9.7%/hr.	1.90	22.2	1.99
		2.47	27.4	1.12
		3.00	36.4	1.38
		3.70	40.0	0.80
		4.40	45.8	0.73
		5.00	51.6	0.66
86	8.2%/hr.	2.05	27.0	1.60
		2.50	31.2	1.97
		3.00	34.4	1.05
		3.50	39.1	0.90
		4.00	44.3	0.89
		4.50	47.3	0.77
		5.00	51.6	0.65
		5.50	55.5	0.62
		6.00	63.8	0.54
		6.50	66.2	0.48

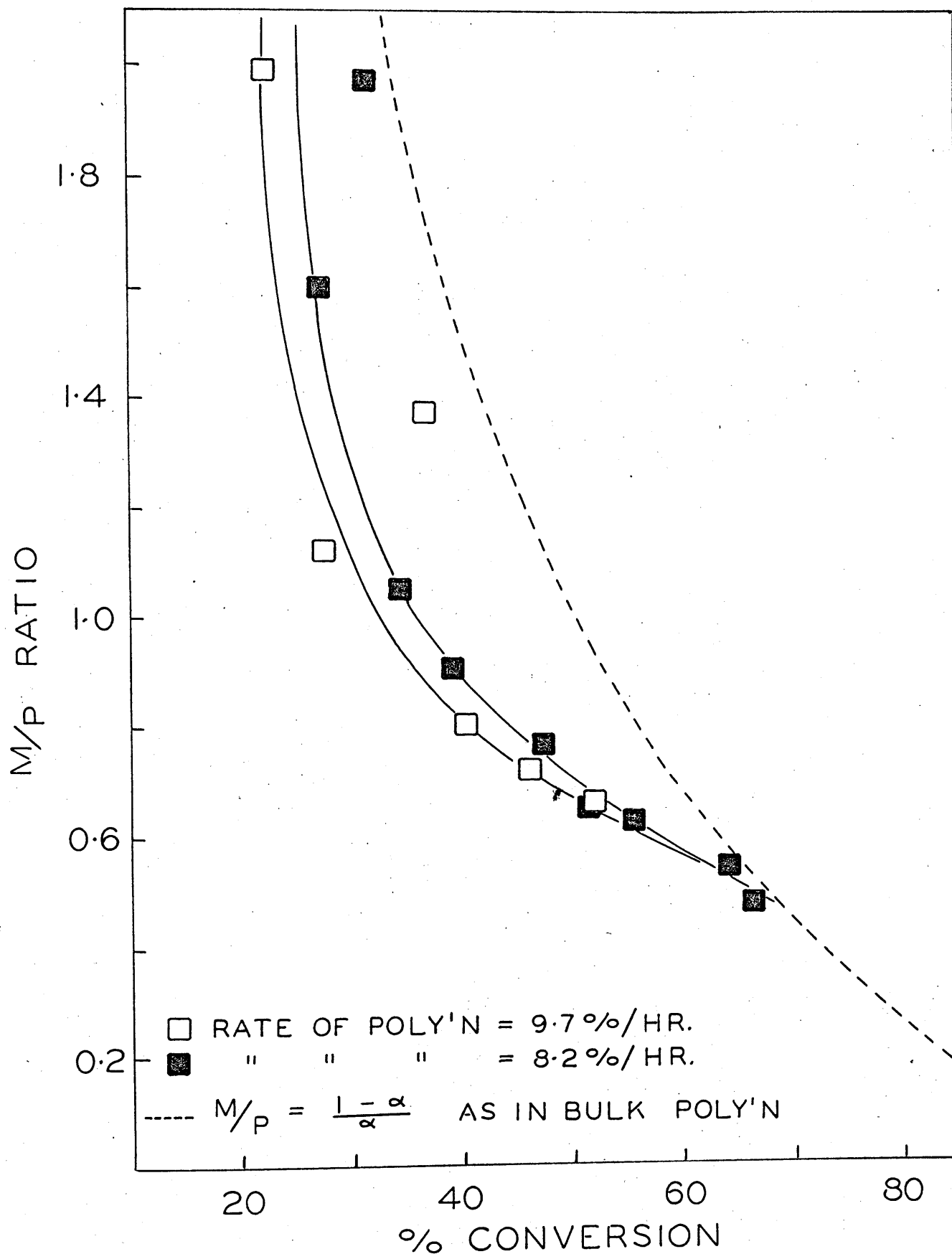


Figure 12. The effect of rate of polymerization at 25.0°C. on the M/P - conversion relationship.

a straight line is obtained, Figure 13, Table XIV.

The equation

$$\frac{M}{M+P} = a\alpha^{-b} \quad \text{.....(9)}$$

is found to relate $\frac{M}{M+P}$ and α , the constants a and b both being influenced by polymerization rate. As an approximation, $\frac{M}{M+P}$ is proportioned to $\alpha^{-1/2}$.

Effect of Polymerization Temperature

No simple correlation of the M/P-conversion curves with polymerization temperature was found, Figure 14, Table XV. This is perhaps not surprising when it is realized that there are a number of influencing factors, all of which are temperature dependent. In the present system, the presence of two monomers complicates both diffusion and polymerization, the two factors which determine the M/P ratio. The relative rates of diffusion, and the relative rates of polymerization of the two monomers will probably change with polymerization temperature (76), and with extent of reaction as the relative concentrations of the remaining monomer change. These several variables must be influenced by temperature changes in such a manner as to compensate for one another since as is seen in Figure 14 the temperature effect on the overall behaviour is relatively small. The fact that the temperature effect is only of the same magnitude as that observed for the variation in

TABLE XIV

THE LINEAR RELATION OF $\log \frac{M}{M+P}$ AND $\log \alpha$

Experiment No.	Poly'n Temp.	Poly'n Rate	Fractional Extent of Conversion (α)	$\log \alpha$	$\frac{M}{M+P}$	$\log \frac{M}{M+P}$
85	25.0°C.	9.7%/hr.	0.274	$\bar{1}.438$	0.528	$\bar{1}.723$
			0.364	$\bar{1}.561$	0.580	$\bar{1}.763$
			0.400	$\bar{1}.602$	0.445	$\bar{1}.648$
			0.458	$\bar{1}.661$	0.420	$\bar{1}.623$
			0.516	$\bar{1}.713$	0.396	$\bar{1}.598$
86	25.0°C.	8.2%/hr.	0.270	$\bar{1}.431$	0.615	$\bar{1}.789$
			0.312	$\bar{1}.494$	0.664	$\bar{1}.822$
			0.344	$\bar{1}.537$	0.522	$\bar{1}.718$
			0.391	$\bar{1}.592$	0.473	$\bar{1}.675$
			0.443	$\bar{1}.646$	0.470	$\bar{1}.672$
			0.473	$\bar{1}.675$	0.434	$\bar{1}.638$
			0.516	$\bar{1}.713$	0.393	$\bar{1}.594$
			0.555	$\bar{1}.744$	0.382	$\bar{1}.582$
			0.638	$\bar{1}.805$	0.351	$\bar{1}.545$
98	5.0°C.	3.48%/hr.	0.662	$\bar{1}.821$	0.322	$\bar{1}.508$
			0.336	$\bar{1}.526$	0.519	$\bar{1}.715$
			0.424	$\bar{1}.627$	0.457	$\bar{1}.660$
			0.511	$\bar{1}.708$	0.429	$\bar{1}.633$
			0.564	$\bar{1}.751$	0.400	$\bar{1}.602$
			0.609	$\bar{1}.785$	0.376	$\bar{1}.575$
			0.668	$\bar{1}.825$	0.362	$\bar{1}.559$
			0.696	$\bar{1}.843$	0.340	$\bar{1}.532$
			0.701	$\bar{1}.846$	0.301	$\bar{1}.479$
			0.721	$\bar{1}.858$	0.293	$\bar{1}.467$

From Figure 13:

For a poly'n rate of 9.7%/hr. at 25.0°C., $\log \frac{M}{M+P} = \log 0.294 - 0.453 \log \alpha$
 " " " " 8.2%/hr. at 25.0°C., $\log \frac{M}{M+P} = \log 0.265 - 0.646 \log \alpha$
 " " " " 3.5%/hr. at 5.0°C., $\log \frac{M}{M+P} = \log 0.295 - 0.524 \log \alpha$

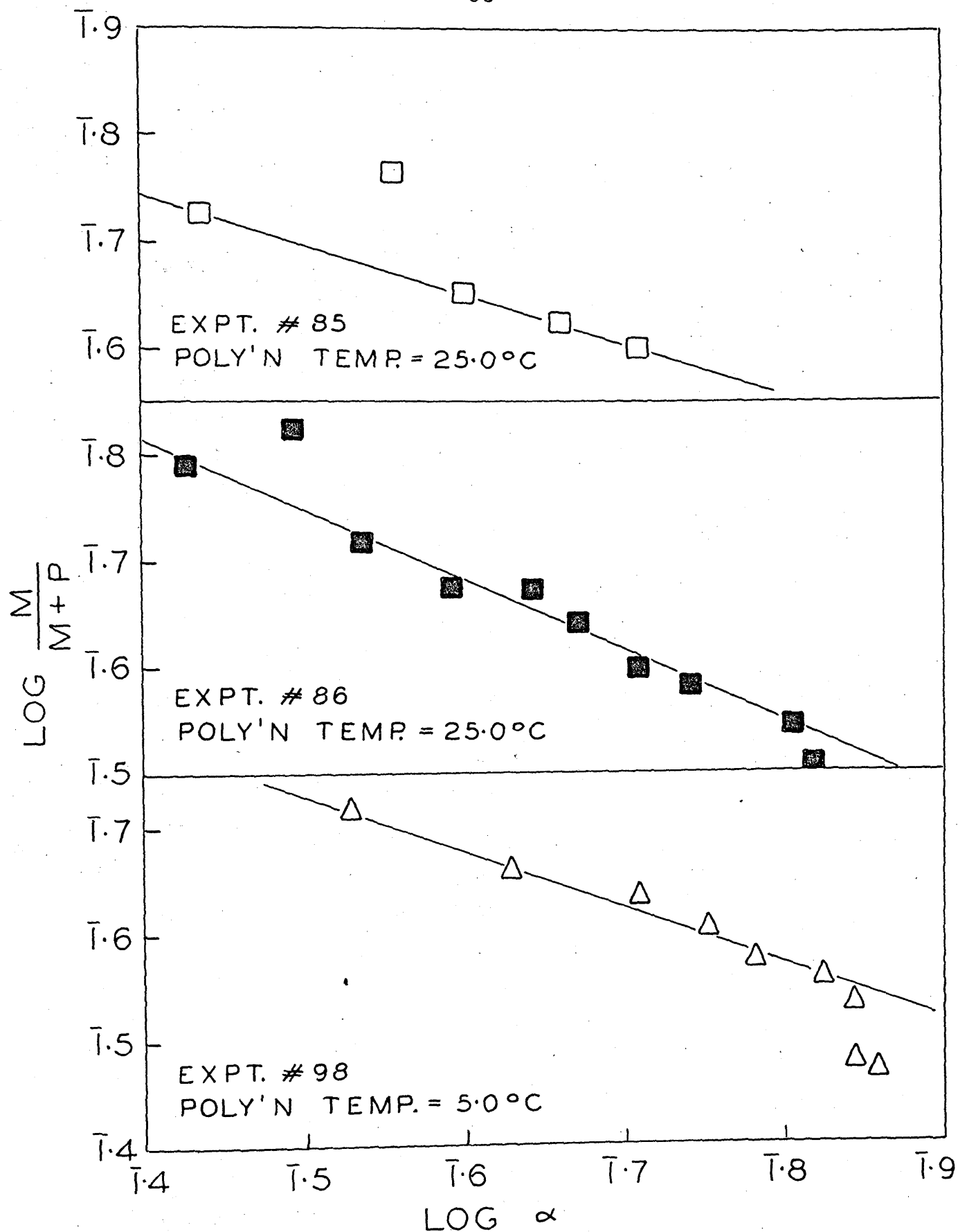


Figure 13. The linear relation of $\log \frac{M}{M+P}$ and $\log \alpha$.

TABLE XV

THE EFFECT OF POLYMERIZATION TEMPERATURE ON THE
MONOMER-POLYMER RATIO

<u>Experiment No.</u>	<u>Polymerization Temperature</u>	<u>Polymerization Time (hrs.)</u>	<u>% Conversion</u>	<u>M/P</u>
87	35.0°C.	1.1	22.8	1.38
		1.5	28.6	1.42
		2.0	36.4	1.10
		2.5	43.0	0.92
		3.0	49.3	0.69
		3.5	58.0	0.57
		4.0	66.1	0.50
		4.5	71.9	0.40
		5.0	78.1	0.31
85	25.0°C.	1.9	22.2	1.99
		2.5	27.4	1.12
		3.0	36.4	1.38
		3.7	40.0	0.80
		4.4	45.8	0.73
		5.0	51.6	0.66
96	15.0°C.	2.2	22.5	1.82
		4.0	34.6	1.27
		5.0	37.0	1.11
		6.0	40.8	0.74
		7.0	45.5	0.73
		8.0	52.1	0.71
		9.0	55.9	0.65
		11.0	66.1	0.50
		12.0	71.4	0.43
98	5.0°C.	10.0	33.6	1.08
		12.0	42.4	0.85
		14.0	51.1	0.75
		16.0	56.4	0.67
		18.0	60.9	0.61
		20.1	66.8	0.57
		22.0	69.6	0.52
		24.0	70.1	0.43
		26.0	72.1	0.42

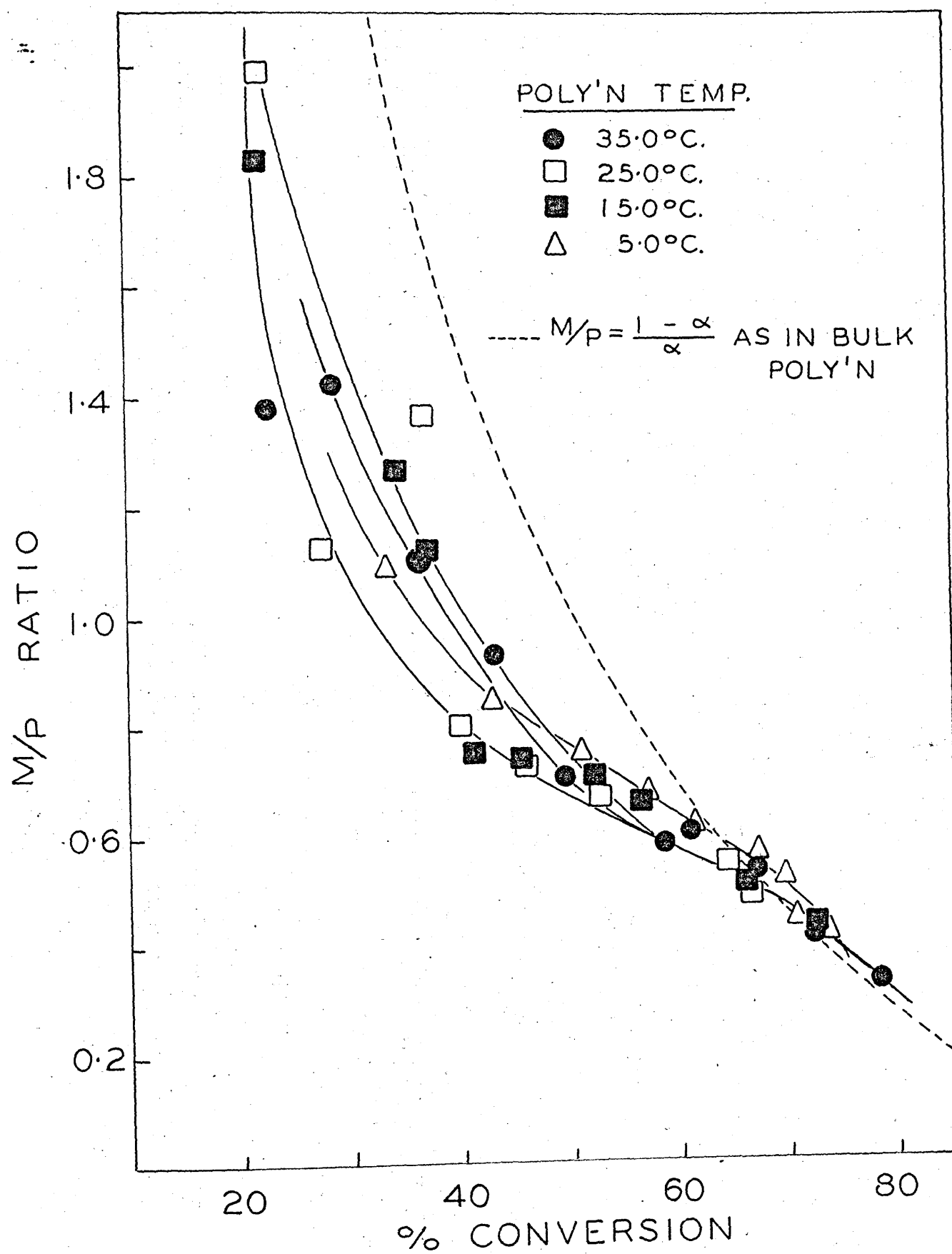


Figure 14. The effect of polymerization temperature on the M/P vs conversion relationship.

polymerization rates, Figure 12, makes it impossible to obtain significant information without a large number of experiments.

VARIABLES INFLUENCING POLYMER VISCOSITY AND THE GEL POINT

Determination of Intrinsic Flow Times

Flow times of polymer solutions at 24.8°C. were determined in modified Ubbelohde viscometers having large solution reservoirs to allow measurements at several concentrations by successive dilutions in the viscometer. The vistex method of Henderson and Legge (66) was followed using 80/20 (by volume) toluene-isopropanol as solvent and pure toluene as diluent to obtain the several solutions required for the determination of the intrinsic viscosity in pure toluene. Calibration curves were established for solvent flow time at each toluene concentration in the presence of various water contents for each new batch of mixed solvent used.

A known weight of latex, approximately one ml. in volume, was dissolved in the vistex solvent and diluted to 100 ml. at 25°C. The solution was filtered through a sintered glass disk, porosity M, and the flow time of a 20 ml. aliquot taken. Flow times were then determined for three successive dilutions with 10 mls. of pure toluene. A similar aliquot of the solution was evaporated to dryness

to determine the polymer concentration, suitable allowance being made for the non-polymer solids known to be in the latex. The water content of the solution was calculated from the water content of the latex used in preparing the solution and solvent flow times obtained from the calibration curves. A plot of the four values of $\frac{\ln t_r}{C}$ vs C extrapolated to zero concentration was used to obtain the intrinsic flow time of the polymer in toluene. Since the viscometers were designed with reasonably long flow times, 124.5 and 113.0 seconds for toluene at 24.8°C., kinetic energy corrections were neglected and the results recorded as intrinsic flow times, $[t]$.

The Effect of Mercaptan Concentration and Polymerization Temperature

Since the cross-linking reaction was to be investigated, it was desired to adjust the amount of mercaptan to yield a gel point at a percentage conversion where the steady state conditions of the emulsion still existed, i.e., where a separate monomer phase was still present and the mercaptan still disappeared in a first order manner. Investigations of the mercaptan disappearance and of the M/P ratio in the latex particle have shown these conditions to persist up to 60 - 65% conversion in the present system. Tables XVI and XVII, Figures 15 and 16 present the effect of mercaptan concentration on the viscosity-conversion curve at 25° and

TABLE XVI

THE EFFECT OF MERCAPTAN CONCENTRATION ON THE VISCOSITY-
CONVERSION RELATIONSHIP IN A 25.0°C. POLYMERIZATION

<u>Experiment No.</u>	<u>Mercaptan Charge (parts)</u>	<u>Polymerization Time (hrs.)</u>	<u>% Conversion</u>	<u>[η]</u>
82	0.10	1.0	16.3	1.130
		2.0	25.9	1.980
		3.0	36.1	2.782
		4.0	45.8	3.250
		5.0	58.1	3.870
		6.0	69.0	3.901
		7.0	75.4	3.525
91	0.05	2.5	29.2	3.250
		3.0	32.8	3.590
		3.5	37.4	4.136
		4.0	41.1	3.998
		4.5	47.0	4.021
		5.0	50.4	4.047
		5.5	57.5	3.789
		6.0	65.0	3.483

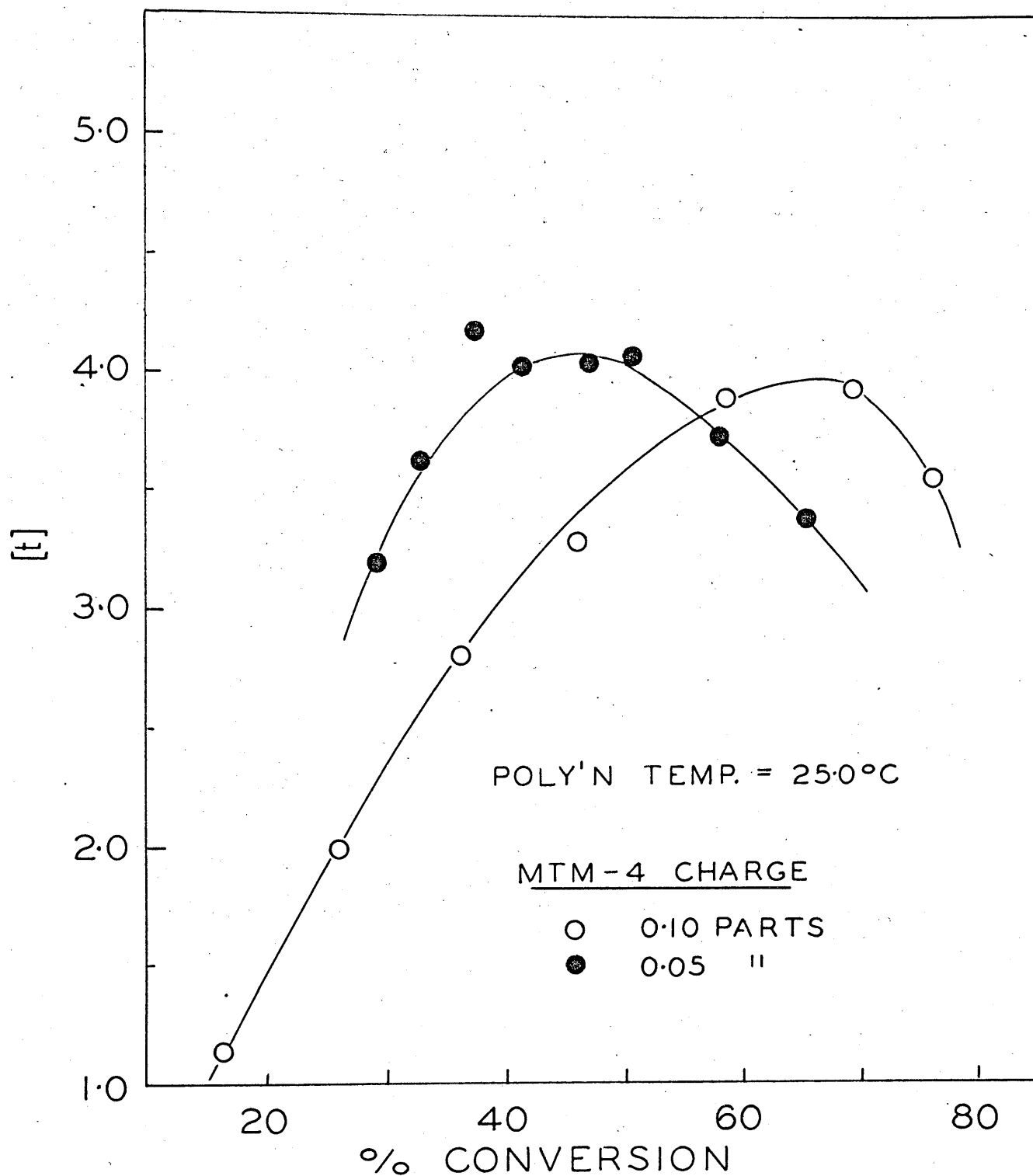


Figure 15. The effect of mercaptan concentration on the viscosity - conversion relationship of polymer produced at 25.0°C.

TABLE XVII

THE EFFECT OF MERCAPTAN CONCENTRATION ON THE VISCOSITY-
CONVERSION RELATIONSHIP IN A 5.0°C. POLYMERIZATION

<u>Experiment No.</u>	<u>Mercaptan Charge (parts)</u>	<u>Polymerization (Time (hrs.))</u>	<u>% Conversion</u>	<u>[η]</u>
98	0.05	11.0	36.2	3.450
		13.0	45.4	4.238
		15.0	51.4	4.372
		17.0	59.8	4.725
		19.0	64.0	4.810
		21.0	63.3	4.854
		23.0	69.6	4.784
		25.0	72.0	4.571
99	0.03	10.2	38.9	4.264
		14.2	51.7	4.972
		16.2	57.9	5.085
		18.3	63.2	5.125
		20.3	68.6	4.548
		22.2	72.5	4.310
102	0.00	6.1	21.9	4.090
		8.2	28.0	5.013
		10.1	33.2	4.783
		12.2	45.1	4.814
		14.2	48.7	4.802
		16.1	54.3	4.703
		18.0	49.1	4.639
		20.0	59.5	4.290

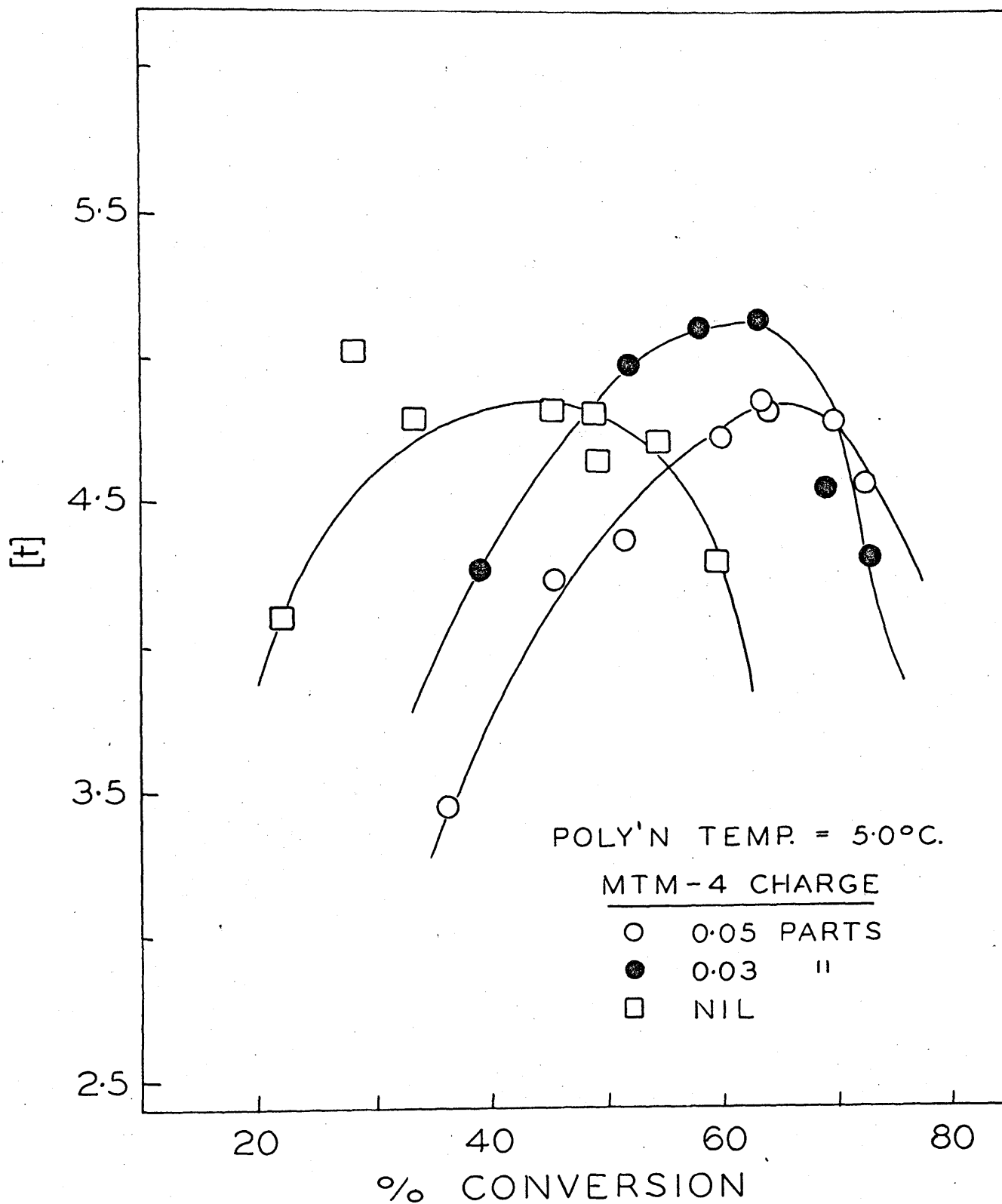


Figure 16. The effect of mercaptan concentration on the viscosity - conversion relationship of polymer produced at 5.0°C.

5°C. It is seen that higher mercaptan concentrations raise the gel point but result in lower viscosities, hence shorter polymer chains, at comparable conversions below the gel point. These results indicate that a concentration of 0.05 parts MTM-4 per 100 parts monomer is the maximum that may be charged in the present system and still maintain the gel point below the upper limit of 65% conversion for polymerization temperatures down to 5°C. Figure 17, Table XVIII, demonstrates the effect of polymerization temperature on the viscosity-conversion curve for such a concentration of mercaptan. The maximum, representing the gel point, is seen to be raised and shifted to higher conversions with decreasing temperature. Thus, low temperatures permit the growth of longer soluble polymer chains and suppress the cross-linking reaction to such an extent that formation of insoluble polymer occurs much later in the course of the polymerization reaction. Although the polymerizations represented in the figure occurred in the presence of the same initial concentration of mercaptan, the amount of mercaptan chain transfer in the various experiments was not strictly comparable since the polymerization and chain transfer reactions were affected to different extents by temperature changes, as indicated by their different activation energies. The variation of gel point with polymerization temperature was quite regular except for polymerization at 35°C., where the gel point

TABLE XVIII

THE EFFECT OF POLYMERIZATION TEMPERATURE ON THE
VISCOSITY-CONVERSION RELATIONSHIP

MTM-4 charge = 0.05 parts

<u>Experiment No.</u>	<u>Polymerization Temperature</u>	<u>Polymerization Time (hrs.)</u>	<u>% Conversion</u>	<u>[η]</u>
116	45.0°C.	0.75	22.4	2.280
		1.00	28.2	2.638
		1.25	36.6	2.840
		1.50	42.5	2.753
		1.75	49.5	2.580
		2.00	55.5	2.510
		2.25	61.0	2.430
88	35.0°C.	0.67	17.7	1.810
		1.00	24.8	2.415
		1.33	27.6	2.780
		1.67	36.2	3.313
		2.00	39.0	3.520
		2.33	45.5	3.667
		2.67	48.5	3.602
		3.00	57.9	3.182
		3.33	65.3	2.988
91	25.0°C.	2.5	29.2	3.250
		3.0	32.8	3.590
		3.5	37.4	4.136
		4.0	41.1	3.998
		4.5	47.0	4.021
		5.0	50.4	4.047
		5.5	57.5	3.789
		6.0	65.0	3.483
97	15.0°C.	5.0	29.5	3.730
		6.0	35.9	3.850
		7.0	41.9	4.210
		8.0	44.5	4.355
		9.0	48.2	4.650
		10.0	53.4	4.561
		11.0	66.1	4.220
98	5.0°C.	11.0	36.2	3.450
		13.0	45.4	4.238
		15.0	51.4	4.372
		17.0	59.8	4.725
		19.0	64.0	4.810
		21.0	63.3	4.854
		23.0	69.6	4.784
		25.0	72.0	4.571

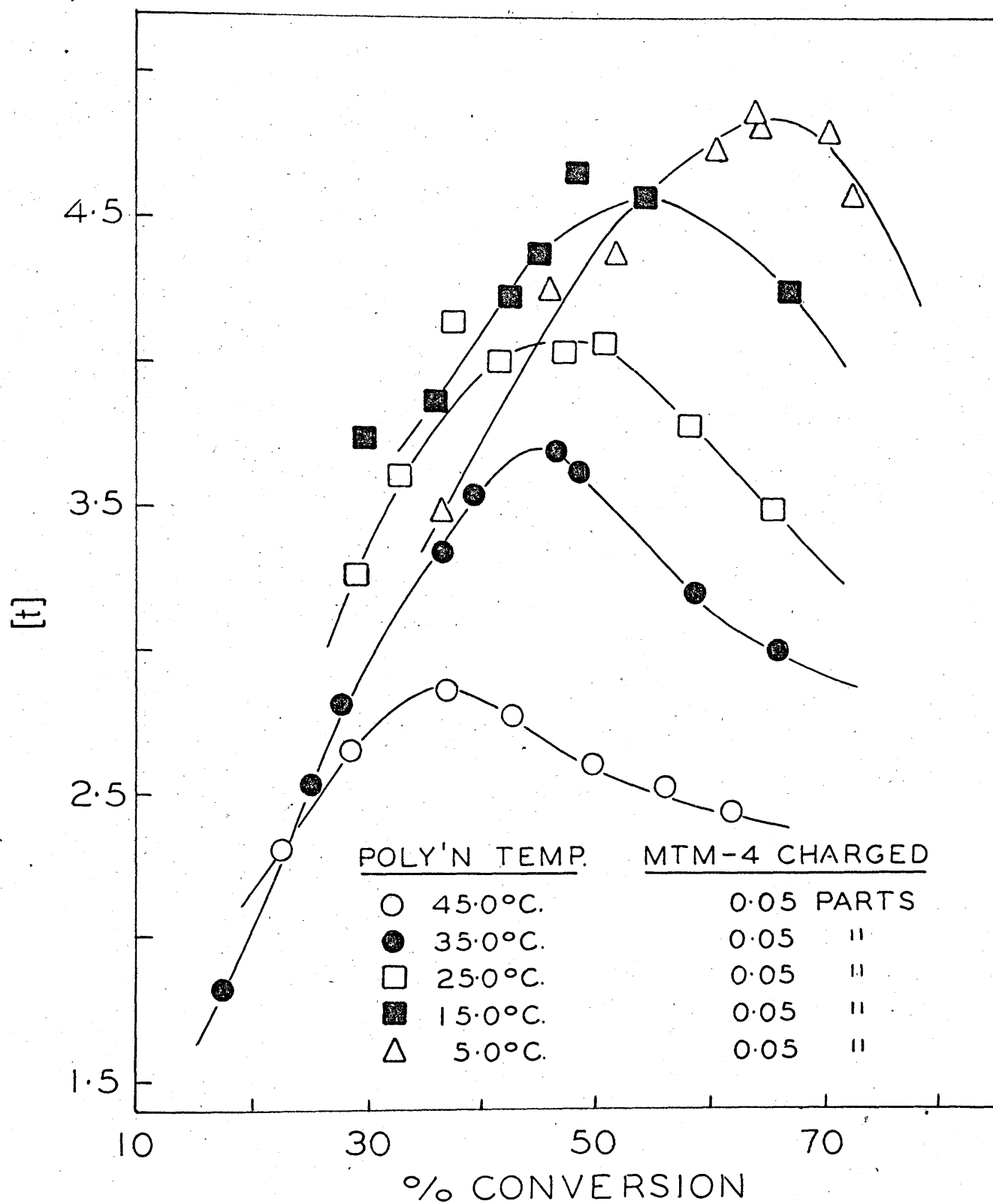


Figure 17. The effect of polymerization temperature on the viscosity - conversion relationship.

differed only slightly from that at 25°C. The viscosity-conversion curves for both these temperatures were confirmed in duplicate experiments.

The relatively high gel point observed for a mercaptan-free system at 5°C., Figure 16, indicates that at this temperature the cross linking reaction was retarded to an extent such that termination by means other than mercaptan permitted gel-free polymer to be formed up to 35 - 40% conversion. As a consequence of this, only a small amount of mercaptan is required to maintain the gel point within desirable limits of conversion, i.e. below 60 - 65%. It is likely that non-mercaptan termination was quite prominent in all the reactions represented in Figure 17. If this is true, primary molecular weights can no longer be inferred from mercaptan consumption data since termination of many primary chains would not be by mercaptan.

The Effect of Activator Concentration

The kinetic studies of the mercaptan chain transfer reaction demonstrated the presence of detectable amounts of mutual termination in the polymerization reaction, but gave no indication as to whether such termination was extensive enough to affect the molecular weight appreciably. If the free radical concentration in the polymerization system is decreased, the rate of mutual termination relative

to the rate of polymerization should be decreased since the former depends on $[R\cdot]^2$ whereas the latter depends on $[R\cdot]$. Such a decrease should result in an increase in average length of the polymer chains if mutual termination constitutes a significant part of the total termination, and should cause a shift in the gel point similar to that caused by a decrease in mercaptan concentration. Decreasing the activator charge should decrease the rate of polymerization and effect a decrease in production of free radicals. When the activator charge was reduced to 1/4 the normal charge, a significant shift in the gel point was observed, Figure 18, Table XIX. Thus, mutual termination does occur in the system to an extent sufficient to affect molecular weight.

The Effect of the Nature of the Emulsifier

When it became apparent that termination in the present system was not overwhelmingly by mercaptan chain transfer reaction, it was realized that chain transfer reactions involving the Dresinate 731 emulsifier might be of importance. Dresinate 731 is a commercial mixture of sodium soaps of hydro and dehydro abietic and pimaric acids. These soaps have been found to have a retarding effect on the polymerization rate in the Mutual persulphate recipe (9) indicating their susceptibility to reaction with the free

TABLE XIX

THE EFFECT OF THE NATURE OF THE EMULSIFIER AND THE
CONCENTRATION OF THE ACTIVATOR ON THE
VISCOSITY-CONVERSION RELATIONSHIP

Polymerization Temperature = 25.0°C.
 MTM-4 charged = 0.05 parts

<u>Experiment</u> <u>No.</u>	<u>Activator</u> <u>Charge</u>	<u>Emulsifier</u>	<u>Polymerization</u> <u>Time (hrs.)</u>	<u>%</u> <u>Conversion</u>	<u>[η]</u>
91	Normal	Dresinate 731	1.0	14.9	-
			2.0	23.4	-
			2.5	29.2	3.250
			3.0	32.8	3.590
			3.5	37.4	4.136
			4.0	41.1	3.998
			4.5	47.0	4.021
			5.0	50.4	4.047
			5.5	57.5	3.789
			6.0	65.0	3.483
120	1/4 Normal	Dresinate 731	2.0	18.7	2.940
			4.0	28.0	4.440
			6.0	36.6	4.540
			8.0	47.2	4.402
122	Normal	Potassium Laurate	2.0	22.6	4.555
			3.0	26.2	5.228
			3.7	36.8	4.828
			4.3	43.1	4.370
			5.0	46.7	4.040
			5.7	50.4	4.135

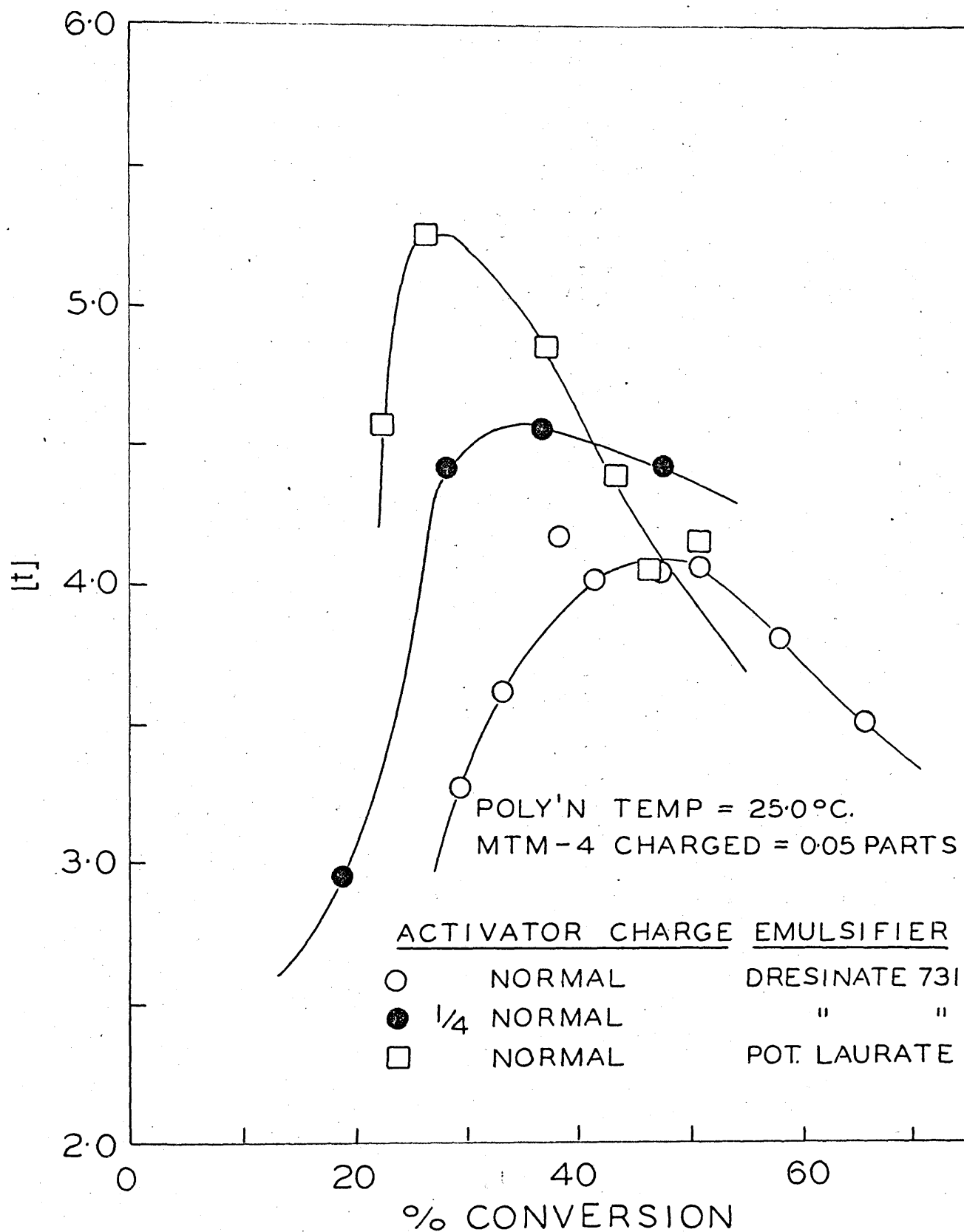


Figure 18. The effect of the nature of the emulsifier and the concentration of the activator on the viscosity - conversion relationship.

radicals in the system. It is quite likely that some of these Dresinate-free radical reactions could bring about chain transfer. The occurrence of such reactions by the emulsifier was investigated by substituting a laurate soap for the Dresinate in the polymerization recipe. As sodium fatty acid soaps gel at low temperatures, potassium laurate was used and this necessitated the substitution of potassium chloride and potassium Kalex for the sodium phosphate and sodium Kalex of the original recipe. A zero order polymerization rate of 8.1%/hr. was obtained at 25°C., with an initial fast reaction corresponding to an intercept of 6.5% conversion, Figure 3. Thus, the changes in recipe did little to affect the character of the polymerization reaction. However, Figure 18, Table XIX, indicates that there was a major change in gel point and molecular weight of soluble polymer. It is evident that changing the emulsifier eliminated some termination from the system which is strong evidence that the non-mercaptan termination is not solely mutual termination but may also be caused partly by the Dresinate 731 emulsifier.

DISCUSSION

THE POLYMERIZATION REACTION

In the present investigation, the shape of the polymerization rate curve has been found to differ from that of the Mutual recipe only in its initial portion, which would seem to indicate that the basic polymerization mechanisms are much the same in the two systems. This is supported by other characteristics of the activated polymerization system investigated in this study, e.g. the kinetics of mercaptan consumption, and variation of the M/P ratio in the latex particle with conversion. However, the two systems also appear to differ in important respects.

Perhaps the most obvious difference between the present system and the Mutual recipe system is the rate of initial polymerization. In persulphate-initiated emulsion polymerizations, induction periods of varying length have been encountered and found to be due to the inhibiting effect of oxygen on the reaction (77). With extreme precautions to exclude oxygen, it has been possible to eliminate this induction period almost completely, but the initial rate has never been increased beyond the subsequent zero order rate. In contrast to this, the present system displayed a very fast initial reaction in all experiments. Traces

of oxygen cause the rapid decomposition of ferrous iron in alkaline medium in the absence of hydroperoxide (78) and it is likely that any oxygen present in the freshly charged emulsion which would cause inhibition in the per-sulphate system, is rapidly removed from the present redox system by such reaction. Reaction of oxygen and ferrous iron in this manner may proceed by a free radical mechanism, but if any free radicals are produced in the present system by such means they are ineffective in initiating polymerization, since polymer is formed only when the peroxide as well as the activator is present.

The importance of this fast reaction lies in the fact that study of it might lead to new and much more active initiating systems for use either at very low temperatures, or in greatly reduced concentrations at more conventional temperatures. It has been established that the initial surge of polymerization is independent of any polymerization variables other than the activator and peroxide and involves the initiator system as a whole.

The possible effect of introducing additional activator to the present system after polymerization has proceeded far enough for all micellar soap to have disappeared is a point of considerable interest. If the initial activator charge were less than the optimum, the rate of

polymerization should be increased on the addition of more activator, in accordance with Harkins experience on adding ferrous sulphate to the Mutual recipe under similar circumstances (44). If such treatment resulted in a surge of reaction immediately on adding the extra activator, it should provide practically unassailable evidence that the fast initial reaction was an inherent characteristic of the initiating system. Presumably it could not be attributed to the interaction of some impurity in the emulsion with the initiating system, since reaction at the beginning of the polymerization would have removed any such impurity. Such experiments would perhaps allow a closer study of this fast reaction and give interesting information about the behaviour of the mercaptan chain transfer agent under such circumstances.

Further information about the cause of this initial behaviour may be obtained from kinetic studies of the interaction of the activator and the peroxide when they are first brought together. Work along this line has not progressed far enough as yet to allow a study of the complete initiator systems as they are used in polymerization systems.

The existence of the fast initial rate of polymerization followed by a much slower, but sustained, rate

is not consistent with W. V. Smith's proposed mechanism for emulsion polymerization (49). As discussed previously, Smith suggested that the initiator controls the polymerization rate only by determining the number of polymer particles that are formed during the very early stages of polymerization. Once the formation of new particles ceases owing to the disappearance of micellar soap, the rate is determined by the number of particles that have been formed and the rate of propagation within each particle. Thus, Smith's mechanism provides no means for changing the polymerization rate other than by final depletion of monomer once the steady number of particles has been established. If this mechanism were true for the system of the present investigation, the fast initial rate of polymerization would indicate that a large number of particles were formed, all of which should continue to grow with the specific velocity k_p regardless of any subsequent drop in initiator activity, and the initial fast rate should be sustained throughout the polymerization. The fact that this does not occur, together with Harkins' (44) evidence for the feasibility of increasing the rate of polymerization in circumstances where it is impossible for the number of polymer particles to increase, throws considerable doubt on Smith's proposal. The only explanation for these facts seems to be that more than one

free radical can grow in a polymer particle at one time, in spite of the evidence from termination in bulk polymerization on which Smith bases his mechanism. Apparently the frequency of mutual termination in bulk polymerization cannot be considered as the frequency of mutual termination within the polymer particle of emulsion polymerization.

The amount of initiator consumption during polymerization appears to be very small in this system, as it is also in the Mutual system where analysis has shown that less than 5% of the original persulphate initiator is consumed during the course of a polymerization (79). The rate equation derived from the three basic reactions of initiation, propagation and termination using steady state approximations has been shown to be:

$$-\frac{dM}{dt} = k_p \left(\frac{k_i}{k_t} \right)^{1/2} [\text{Initiating System}]^{1/2} [M] \dots\dots(1)$$

From about 10 to 65% conversion the polymerization rate has been found to be constant, which, according to equation (1) would mean that the concentration of the initiating system and the monomers remains essentially constant in this region of reaction. The rate of polymerization has been found to be much more sensitive to activator concentration at concentrations below one half the normal charge used in this system, but even with one quarter the normal activator

charge, the zero order rate curve was obtained. This indicates that little of this component of the initiating system is consumed during the course of the polymerization reaction.

A difference in activation energies for the overall polymerization in the redox and Mutual systems should be observed if the rate of production of free radicals by decomposition of the respective initiators, which differ widely in their activities, is the rate controlling process in each case. In the present investigation, an activation energy of 9.7 Kcal/mole has been found for the overall polymerization reaction as measured by the zero order rate between 10 and 65% conversion. This is of the same order of magnitude as the activation energy of 11.1 Kcal/mole found for the reaction of ferrous iron and cumene hydroperoxide in aqueous acid medium by Fordham and Williams (31). A value of 17 Kcal/mole has been reported for a Mutual polymerization system (80) which is in accord with the activation energy of 18.6 Kcal/mole found for the decomposition of potassium persulphate under emulsion conditions using the special RRC soap of the Mutual recipe (81). Thus, the activation energy for the overall polymerization in each system closely parallels the activation energy for the decomposition of the corresponding initiating system, and decomposition of the initiating system

is strongly indicated as the rate controlling process in the two systems within the limits of conversion specified.

The polymerization becomes first order in respect of monomer when reaction has proceeded to such an extent that the concentration of monomer becomes the rate controlling factor in the emulsion system.

The data in Table VIII for this region of reaction permit an estimate of about 6 Kcal/mole for the activation energy for propagation, which compares favourably with activation energies of 6 - 7 Kcal/mole found for the propagation of styrene (50), methyl methacrylate (82) and vinyl acetate (83) by photochemical investigations. These values contrast with the activation energy of 11 kcal/mole calculated for styrene propagation by Smith (49) on the basis of his suggested mechanism for emulsion polymerization.

The activation energy for the reaction of ferrous iron with a peroxide (21) or hydroperoxide (31) has been determined as 10 - 12 Kcal/mole. For high polymer to be formed in a polymerizing system, propagation must occur much more frequently than initiation, hence the initiation step must have a higher activation energy than the propagation step. In the Mutual system, the activation energy

of initiation is much higher than any suggested values for that of propagation, but in redox systems the activation energy of initiation is of the same order of magnitude as that proposed by Smith for propagation. Since the activation energy of propagation should be independent of the nature of the initiating system, the fact that high polymer can be obtained using an initiating system of such low activation energy is an indication that the value of 11.7 Kcal/mole proposed by Smith for the propagation reaction is too high. The value of 6 Kcal/mole obtained in the present investigation is in line with values obtained by other methods and is sufficiently lower than the activation energy for initiation to allow formation of high polymer.

As a consequence of the fact that the activation energy for initiation is much closer to that of propagation in redox than in Mutual recipe systems, the frequency of mutual free radical termination relative to the frequency of propagation is much greater in the redox system. Hence, the "kinetic chain length" of the polymer, i.e. the average length of the polymer chains that would be formed by uninterrupted polymerization between initiation and termination by another free radical, is much shorter. As a result, less additional termination by chain transfer agents is required to produce the equivalent polymer chain

length. This characteristic of the present system has become evident in the investigation of the cross-linking and termination reactions.

THE CROSS-LINKING REACTION

An experimental application of Flory's kinetics of cross-linking (40) depends on simple means of measuring the gel point of the system, the relation of the monomer-polymer ratio at the site of reaction to the extent of conversion and \bar{y}_w , the weight average degree of polymerization of the primary polymer chains. It was originally hoped to be able to elucidate the kinetics of the cross-linking reaction in a quantitative manner by measurement of these variables in the present system. However, this investigation has shown there to be no adequate means of determining \bar{y}_w in the present system owing to the complex nature of the termination reactions.

Investigation of the gel point has given qualitative information of importance on the cross-linking reaction. Since gelation occurs when there is, on the average, one cross-link per primary chain, the gel point depends on the number of primary chains, hence on the average primary chain length, as well as on the total number of cross-links in a system. This is reflected in the fact that the gel point may be varied by changing the amount of chain transfer reaction in the system, which affects the

primary chain length. In considering gel point data it is necessary to distinguish between effects arising from variation of the amount of cross-linking, and effects arising from variation of the primary chain length. The intrinsic viscosity of the polymer before and at the gel point is helpful in drawing this distinction.

The viscosity characteristics of the polymer formed in the present experiments have been found to be markedly affected by polymerization temperature. Low temperatures allow production of soluble polymer up to higher conversions where the kinetics of the termination reactions result in higher primary molecular weights. (See, for example, the plot of conversion vs the degree of polymerization as calculated from mercaptan disappearance data, Figure 19) Below the gel points, the small differences in polymer viscosities at the same conversion suggest that the size of the primary polymer chains is practically the same for different polymerization temperatures. A comparison of these viscosities gives only a rough indication of the relative primary chain lengths, since varying amounts of branching and cross-linking are present in the different polymers, especially close to the gel point.

When the gel point is raised by using a larger

amount of chain transfer agent instead of a decrease of temperature, the polymer viscosities below the gel point indicate that much shorter polymer chains are formed at the same conversion. The reduction in chain length produced by the additional chain transfer agent is usually sufficient to counteract the effect of increased conversion on the chain length, with the result that the peak of the viscosity-conversion curve is usually lower in spite of the fact that it occurs at higher conversions.

This contrast between the effect of polymerization temperature and chain transfer agent on the polymer viscosity is evidence that the reduction in gelation achieved by lowering temperature is a result of a reduction in the amount of cross-linking and not a result of a decrease in polymer chain length. The fact that Morton and Salatiello (43) have observed a similar dependence of gel point on polymerization temperature in the polymerization of butadiene at 40°, 50° and 60°C. in a Mutual recipe indicates the effect to be independent of the polymerization system.

The ratio of monomer to polymer in the latex particle necessary for quantitative treatment of the gel point data by Flory's approach has been shown to be very dependent on conversion in the present experiments in somewhat the manner found for the polymerization of styrene in

a Mutual recipe (45) and in contrast to its reported independence from conversion in butadiene emulsion polymerization (47). In both styrene and butadiene polymerization, the separate monomer phase was reported to exist only up to 50% conversion, but in the present polymerizations the conversion at which the M/P ratio in the latex particle becomes equal to that in the total emulsion indicates a separate monomer phase to exist up to 65% conversion. Higher polymerization temperatures did not lower this conversion, which suggests that it is a characteristic of the present system, perhaps a result of the Dresinate emulsifier or the higher electrolyte concentration than in the Mutual recipe.

Over the conversion range investigated, the equation

$$\frac{M}{M+P} = a\alpha^{-b} \quad \dots(9)$$

was found to describe the variation of the monomer concentration in the latex particle with conversion, α , reasonably well up to the point where all remaining monomer was in the latex particles. The dependence of P/M on conversion may be deduced from this:

$$P/M = \frac{P/M+P}{M/M+P} = \left(1 - \frac{M}{M+P}\right) \frac{M+P}{M} = \frac{M+P}{M} - 1 = \frac{1}{a} \alpha^b - 1 \quad \dots(10)$$

Insertion of this expression in Flory's equation (4) for the relative rates of cross-linking and propagation allows integration:

$$\begin{aligned} d\nu &= 2K \frac{P}{M} d\alpha & \dots\dots(4) \\ &= 2K \left(\frac{1}{a} \alpha^b - 1 \right) d\alpha \\ \nu &= 2K \left(\frac{\alpha^{b+1}}{a(b+1)} - \alpha \right) = 2K\alpha(A\alpha^b - 1) \end{aligned}$$

where $A = \frac{1}{a(b+1)}$

Division by α gives the density of cross-linked units, , in the polymerized portion of the mixture.

$$\begin{aligned} \rho &= \frac{\nu}{\alpha} = 2K(A\alpha^b - 1) \\ K &= \frac{\rho}{2(A\alpha^b - 1)} & \dots\dots(11) \end{aligned}$$

At the gel point

$$\rho = \frac{1}{\bar{y}_w}$$

If the major portion of the total termination in the system is by chain transfer with a mercaptan, the average degree of polymerization of the primary chains, \bar{y}_w , may be calculated from mercaptan consumption data using the relation:

$$\bar{y}_w = \frac{2(e^{R_0} - 1)}{aR_0^2} \dots\dots(3)$$

End group analysis (36, 37) has shown chain transfer reaction with mercaptan to be the main mode of termination in the Mutual system and it was hoped that the same would be true in the system of this investigation. From the curves of Figures 1 and 7 it is possible to calculate average values for the regulating index of the mercaptan, r , at various temperatures:

$$r = - \frac{d \ln R}{d\alpha} = \frac{k_{\text{chain transfer}}}{k_{\text{polymerization}}}$$

where $k_{\text{polymerization}}$ = rate of change of fractional extent of conversion.

The molar amount of mercaptan initially present, R_0 , is known from analytical data. However, utilization of mercaptan consumption data as representing total termination in calculating \bar{y}_w leads to results which cast doubt on the predominant character of mercaptan termination in the present system.

If mercaptan consumption data are used to calculate \bar{y}_w , the ratio of the velocity constants of the cross-linking and the propagation reactions, K , may be expressed as:

$$K = \frac{a g r^2 R_0}{4(e^{r a g} - 1)(A a^b - 1)} \quad \dots\dots(12)$$

Table XX is a presentation of the calculated values of K for two mercaptan concentrations at 25.0°C. and 5.0°C.

The value of K obtained in this investigation is of the same order of magnitude as that reported by Morton and Salatiello (43) for butadiene polymerization (1.02×10^{-4} at 40°C.; 1.36×10^{-4} at 50°C.) but it has been found to vary with mercaptan concentration. This suggests that mercaptan consumption data give erroneous values for \bar{y}_w , for which other evidence has also been obtained.

In the present polymerization system, it has been found necessary to reduce the mercaptan concentration to a very low level to obtain gel points within the acceptable range of conversion, i.e. in the region where monomer still exists as a separate phase and mercaptan consumption is first order. In fact, at 5.0°C. it has been necessary to eliminate mercaptan entirely to obtain a gel point below 45% conversion. This suggests a high frequency of termination by means other than mercaptan and, presumably, this non-mercaptan termination must be present even in systems containing mercaptan. As the mercaptan concentration is reduced, a point should be reached where this non-mercaptan termination begins to represent an appreciable fraction of the total termination. After this point, kinetic data for the mercaptan chain transfer reaction can no longer be considered to represent the kinetic behaviour of the whole ter-

TABLE XX

VARIATION OF k_x/k_p WITH TEMPERATURE AND
MERCAPTAN CONCENTRATION

Polymerization Temp.	A*	b*	r**	R ₀ (moles per mole initial monomer)	α_g^{***}	K = k_x/k_p
25.0°C.	2.38	0.65	2.06	2.78×10^{-4}	0.65	0.853×10^{-4}
25.0°C.	2.38	0.65	2.06	1.39×10^{-4}	0.47	0.915×10^{-4}
5.0°C.	2.22	0.52	2.23	1.39×10^{-4}	0.65	0.449×10^{-4}
5.0°C.	2.22	0.52	2.23	1.835×10^{-4}	0.61	0.308×10^{-4}

* From Table XIV

** From Figure 1 and 7

*** From Figures 15 and 16

mination reaction, hence, can no longer give valid information as to the size of the primary polymer chains. Consideration of the termination reactions indicate that such is the case in the system under investigation in this study.

TERMINATION REACTIONS

Comparison of degrees of polymerization calculated from mercaptan consumption data and from intrinsic viscosity data gives support to the suggestion that the non-mercaptan termination operating in this system was appreciable. When mercaptan consumption data represent total termination, they indicate the molecular weight that would be attained in the total absence of cross-linking and branching reactions. On the other hand, viscosity measurements indicate the actual molecular weight of the soluble polymer, hence, reflect the sharp rise and subsequent drop in molecular weight of soluble polymer caused by such side reactions. At very low conversions, where the extent of cross-linking is small, the molecular weights calculated from viscosity data and from mercaptan consumption data should be of the same order, but the viscosity molecular weight should become rapidly larger than the molecular weight calculated from mercaptan disappearance as reaction proceeds to the gel point.

For Mutual recipe GR-S polymerized at 50.0°C.,

molecular weights may be derived from intrinsic viscosity values in toluene by the relation (57):

$$[\eta] = 5.25 \times 10^{-4} \times M_v^{0.67} \quad \text{.....(6)}$$

where M_v is the "viscosity average" molecular weight.

Structural heterogeneity of butadiene-styrene copolymer does not vary greatly with polymerization temperature (41) and this equation should be valid to calculate molecular weights of polymer formed at 35.0°C., only 15° below the temperature for which the equation was established. The average molecular weight of the structural unit in 75/25 butadiene-styrene copolymer produced at 50.0°C. is 59.4 at 40% conversion, based on a styrene content of 18.7% reported by Meehan (84). This value has been used to calculate average degrees of polymerization, \bar{y}_v , from the viscosity molecular weights.

Statistical mechanical considerations relate the various primary degrees of polymerization in the following manner (38):

$$\bar{y}_v = 1.85 \bar{y}_n = \frac{1.85}{2.00} \bar{y}_w \quad \text{.....(13)}$$

Equation (13) allows calculation of \bar{y}_w from mercaptan consumption data, hence \bar{y}_v for the primary polymer chains can be evaluated.

These calculations have been made for a polymerization at 35.0°C., Table XXI, taking $[t]$ to represent $[\eta]$, and the results plotted in Figure 19. It is immediately observed that, in spite of the existence of the extensive cross-linking that must be present in the polymer just prior to and at the gel point, the actual molecular weights indicated by viscosity measurements are much lower than the primary molecular weights suggested by mercaptan consumption data. Thus, the mercaptan consumption cannot be a true indication of the primary molecular weights, and extensive termination by other means must occur. Comparison of the molecular weights at low conversion, i.e. 20% conversion, suggests that mercaptan terminates only about one half of the polymer chains formed, since the average degree of polymerization calculated from mercaptan consumption data is about twice that indicated by viscosity measurements. Accurate comparisons of this type at low conversions to obtain quantitative information about the extent of non-mercaptan termination are precluded in the present system by the anomalous behaviour of the polymerization and mercaptan chain transfer reaction rates in this region.

The non-mercaptan termination appears to arise from at least two sources as indicated by investigation

TABLE XXI

COMPARISON OF AVERAGE CHAIN LENGTHS INDICATED BY VISCOSITY
MEASUREMENTS AND BY MERCAPTAN DISAPPEARANCE KINETICS

Polymerization Temperature = 35.0°C.
MTM-4 charged = 0.05 parts

<u>% Conversion</u>	<u>\bar{y}_v from viscosity measurements \times</u>	<u>\bar{y}_v from mercaptan disappearance kinetics $\times\times$</u>
17.7	3270	8080
24.8	5030	8740
27.6	6210	9040
36.2	8100	9830
39.0	8850	10180
45.5	9440	10900
48.5	9160	11240
57.9	7600	12500
65.3	6930	13600

\times Calculated from the data of Experiment No. 88, Table XVIII
using the equations: $[\eta] = 5.25 \times 10^{-4} M_v^{0.67}$
 $\bar{y}_v = \frac{M_v}{59.4}$

$\times\times$ Calculated from the equation:

$$\bar{y}_v = 0.92 \bar{y}_w = 0.92 \times \frac{2(e^{ra}-1)}{araR_0}$$

where $R_0 = 1.39 \times 10^{-4}$ moles mercaptan/mole initial monomer
 $r = 1.88$ for polymerization at 35.0°C. from Figures
1 and 7.

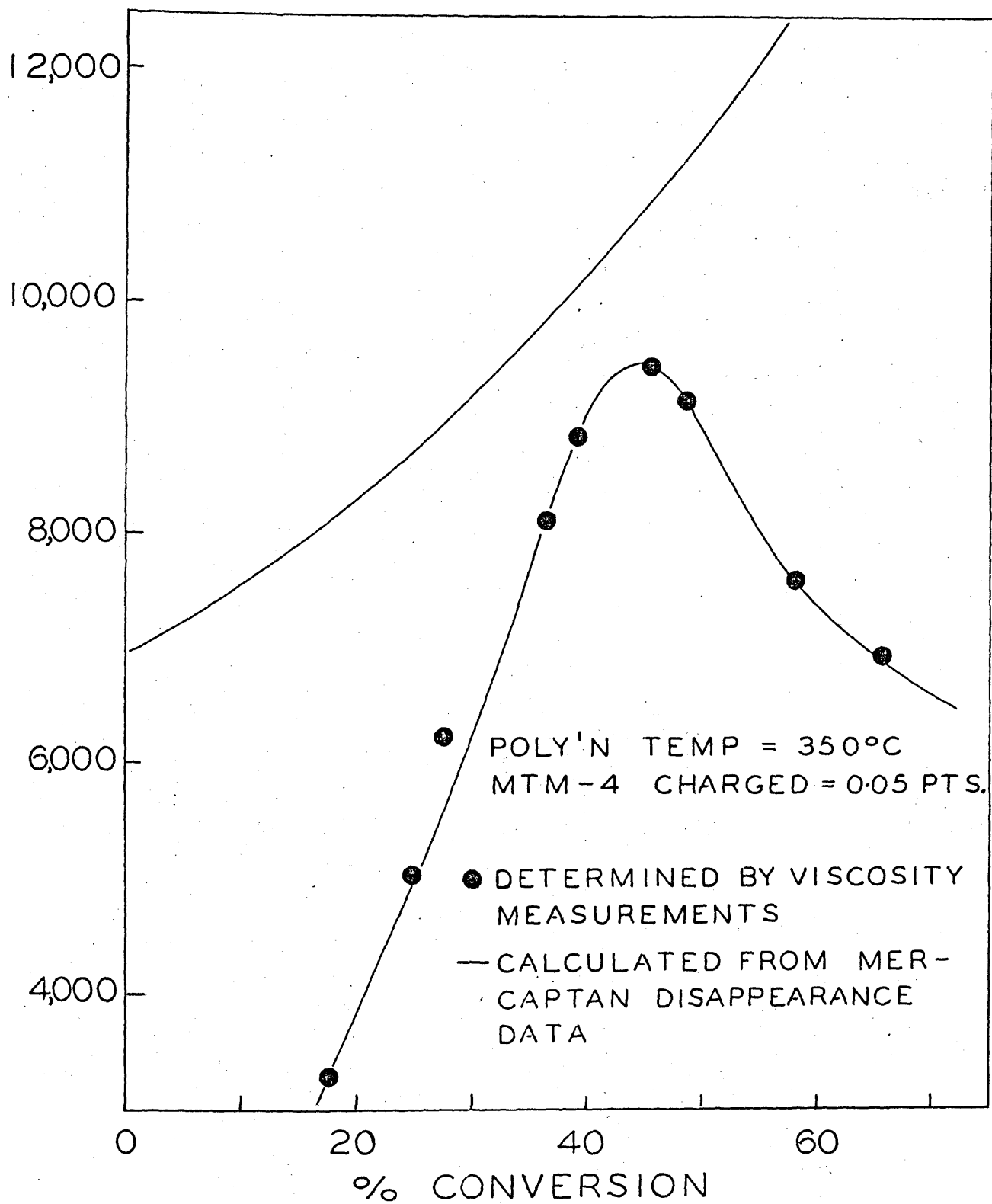


Figure 19. Comparison of the average degrees of polymerization determined by viscosity measurements with those calculated from kinetic data of the disappearance of mercaptan.

of the effect of recipe constituents on the gel point. The nature of the emulsifier and the concentration of the activator have both been found to affect the viscosity-conversion curve in such a way as to indicate clearly that they are responsible for considerable termination in the system. A reduction of the amount of this termination by changing the emulsifier and by reducing the concentration of the activator has resulted in lower gel points in a manner analogous to the effect of reduced mercaptan concentration.

The emulsifier probably terminates by a chain transfer mechanism similar to the reaction of mercaptan. The chemical nature of the emulsifier and the fact that polymerization proceeds at a fast rate support this suggestion. If the emulsifier were merely terminating without simultaneously initiating, it would drastically lower the free radical concentration, hence the rate of polymerization. Termination arising from the emulsifier might be eliminated or greatly reduced with some emulsifying agent other than that used in the present studies.

It is conceivable that some constituent of the activator could act as a chain transfer agent, but it is much more likely that the activator affects the polymer molecular weight by its effect on the free radical concentration in the polymerization system, i.e. through

influencing mutual termination. The presence of mutual termination has made itself apparent in the effect of temperature on the competition of mercaptan and mutual termination in the polymerizing system. Since mutual termination is dependent on the concentration of free radicals in the system, it is controlled by the initiating system in a manner similar to the polymerization reaction itself. Hence, its temperature dependence will be the same as that of the polymerization reaction and will indicate an activation energy of about 10 Kcal/mole. On the other hand, the activation energy for the mercaptan chain transfer reaction has been found to be approximately 9 Kcal/mole, so that lower polymerization temperatures allow a greater proportion of mercaptan termination. However, non-mercaptan termination still remains significant as is indicated by the lack of agreement of K values calculated for 5.0°C. polymerizations, and by the high gel point observed for the mercaptan-free polymerization at 5.0°C.

The fact that the mercaptan chain transfer reaction and the reaction which is rate controlling for mutual termination have an activation energy difference of only about one Kcal/mole explains the much greater amount of mutual termination in this system than in the persulphate-initiated system. Since these activation

energies allow the two termination reactions to compete on a practically equal basis, there will always be a relatively large proportion of mutual termination in this system, even in the presence of larger amounts of mercaptan. This makes the calculation of primary molecular weights from mercaptan consumption data a doubtful procedure under any conditions of mercaptan concentration.

The present investigation has provided information about the polymerization and termination processes in a low temperature system which suggests the approach that would obtain termination data required for study of the cross-linking reaction. Since mutual termination apparently cannot be eliminated from low temperature systems, it would be necessary to study a system in which termination is predominantly by the interaction of free radicals. The frequency of termination, and the polymer chain length, would then depend on the kinetics of the initiating system and could, perhaps, be deduced in a manner similar to that possible for bulk and solution polymerization. No doubt this would entail considerably more knowledge of the kinetics of the redox initiating system than is now available.

APPENDIX

SENSITIVITY OF POLYMER TO DRYING CONDITIONS

Coagulation Procedure

When solid polymer was desired for any analysis, the latex, diluted with twice its volume of distilled water, was poured in a thin stream into rapidly stirred n-butanol containing 1% phenyl- β -naphthylamine (PBNA) antioxidant. The coagulated polymer was removed from the butanol, washed several times with butanol or distilled water and pressed as dry as possible with the flattened end of a glass rod. This formed a mat approximately 1/8 inch thick which was transferred to a petri dish and dried in a vacuum oven.

Drying Procedure and Solubility

When solubility measurements are to be done on the polymer, drying conditions must be such as to bring about agglomeration of microgel to macrogel (67) without introducing any cross-linking of the soluble polymer molecules. The appearance of an insoluble fraction of polymer during the polymerization has been shown to be accompanied by a drop in the intrinsic viscosity-conversion curve. Since the vistex method avoids any heat treatment of the polymer, a comparison of the peak of the intrinsic vistex viscosity-conversion curve with the sharp rise of the gel-

conversion curve of the dried polymer should indicate the suitability of the drying treatment.

The static extraction principle developed by Baker (85), and used by Bardwell and Winkler (86), was employed for solubility measurements. A 0.06 to 0.10 gm. sample of polymer was torn into approximately 10 mg. fragments and weighed into a Harris cage (67) of about 15 ml. volume. It is important that the cage volume be greater than the volume of swollen gel or extraction will be retarded and erroneously high gel values obtained. The cage was immersed in 100 ml. of reagent grade toluene containing 0.05% PBNA. Extraction took place at room temperature in the dark, the solvent being renewed after 24 hours. After a total of 48 hours extraction, the cage was removed from the solvent, dried in a vacuum oven, and the weight of insoluble polymer determined.

Under drying conditions recommended by Kolthoff (63) and Bardwell and Winkler (86) for GR-S polymer, i.e. 12 hours at 80.0°C. in a vacuum oven, the polymer under investigation here was found to undergo extensive cross-linking as evidenced by the appearance of gel in the dried polymer at much lower conversions than indicated by the vistex viscosity-conversion curve, Table XXII, Figure 20.

TABLE XXII

VISTEX VISCOSITY AND GEL CONTENT OF POLYMER DRIED

12 HOURS AT 80.0°C. IN VACUO

Polymerization Temperature = 25.0°C.

MTM-4 charged = 0.10 parts

Experiment 82

<u>Polymerization Time (hrs.)</u>	<u>% Conversion</u>	<u>[η]</u>	<u>% Gel</u>
1.0	16.3	1.130	-
2.0	25.9	1.980	0.0
3.0	36.1	2.782	0.0
4.0	45.8	3.250	58.5
5.0	58.1	3.870	59.8
6.0	69.0	3.901	66.6
7.0	75.4	3.525	70.3

Experiment 83

3.5	37.0	11.8
4.0	36.4	36.1
4.5	48.4	65.3
5.0	38.8	51.7
5.6	51.5	64.2
6.0	56.9	64.5
6.5	58.0	68.5

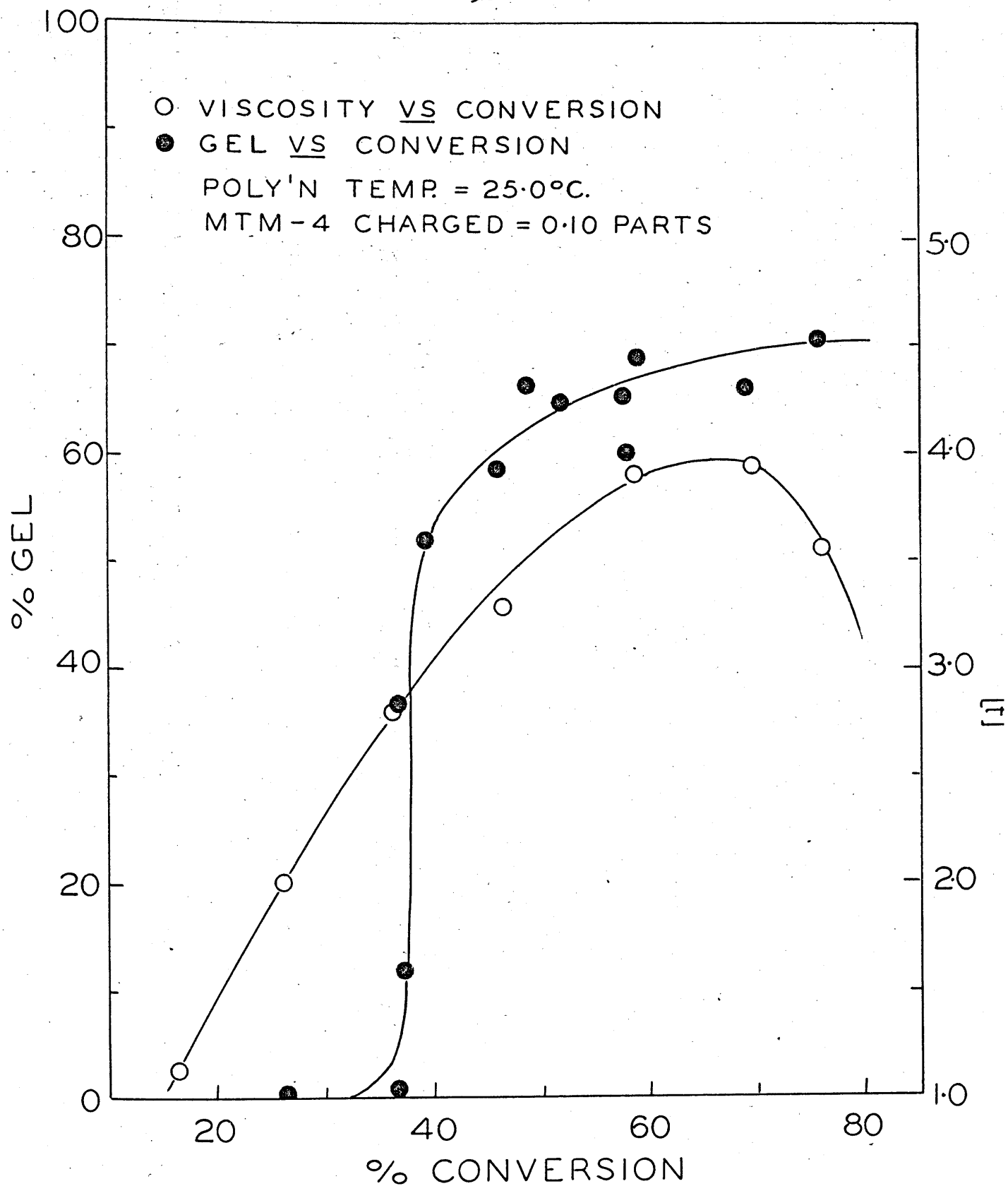


Figure 20. Discrepancy between vistex viscosity and gel content of polymer dried 12 hours at 80°C. in vacuo.

Apparently gel produced during this drying is quite weakly cross-linked, as it was found to become soluble on prolonged extraction with toluene, Table XXIII. Bardwell and Winkler (86) have shown GR-S gel to be stable under similar conditions of extraction for at least 25 days. In spite of the above effect, reproducible gel values were obtained when the standard extraction time was used.

With polymer produced in the system under study at 25.0°C., drying conditions of 12 hours at 50.0°C. in a vacuum oven proved satisfactory as shown in Table XXIV and Figure 21. Variation of drying time at this temperature from 6 to 60 hours had very little effect on the measured solubility of the polymer.

These conditions proved unsatisfactory when applied to polymer produced at 5.0°C. The correct conditions for this polymer were not investigated as it was evident that no general conditions could be established for polymer produced in this system at various temperatures. Previously it had been felt that these low temperature polymers were more sensitive to elevated drying temperatures than GR-S because of remnants of the more active initiating system remaining in them after coagulation. From the above results, polymerization temperature of the polymer is seen to be an influencing factor.

TABLE XXIII

BREAKDOWN OF GEL ON PROLONGED EXTRACTION AFTER DRYING

POLYMER 12 HOURS AT 80.0°C. IN VACUO

Polymerization Temperature = 25.0°C.
MTM-4 charged = 0.10 parts
Polymer Sample No. 82-3

<u>Time of Extraction</u>	<u>% Gel</u>
2 days	59.8; 57.5; New sample of latex coagulated and dried: 63.5
3 "	58.7
4 "	54.0
5 "	50.3

TABLE XXIV

VISTEX VISCOSITY AND GEL CONTENT OF POLYMER DRIED 12 HOURS

AT 50.0°C. IN VACUO

Polymerization Temperature = 25.0°C.
MTM-4 Charged = 0.05 parts

Experiment No. 91

<u>Polymerization Time (hrs.)</u>	<u>% Conversion</u>	<u>[η]</u>
1.0	14.9	-
2.0	23.4	-
2.5	29.2	3.250
3.0	32.8	3.590
3.5	37.4	4.136
4.0	41.1	3.998
4.5	47.0	4.021
5.0	50.4	4.047
5.5	57.5	3.789
6.0	65.0	3.483

Experiment No. 105

<u>Polymerization Time (hrs.)</u>	<u>% Conversion</u>	<u>% Gel</u>
0.4	10.2	-
1.0	17.7	-
2.0	25.1	-
3.0	34.0	0.0
3.5	40.8	0.0
4.0	46.0	4.3
4.5	52.3	41.2
5.0	56.9	54.5
5.6	62.4	67.1
6.1	67.9	77.7

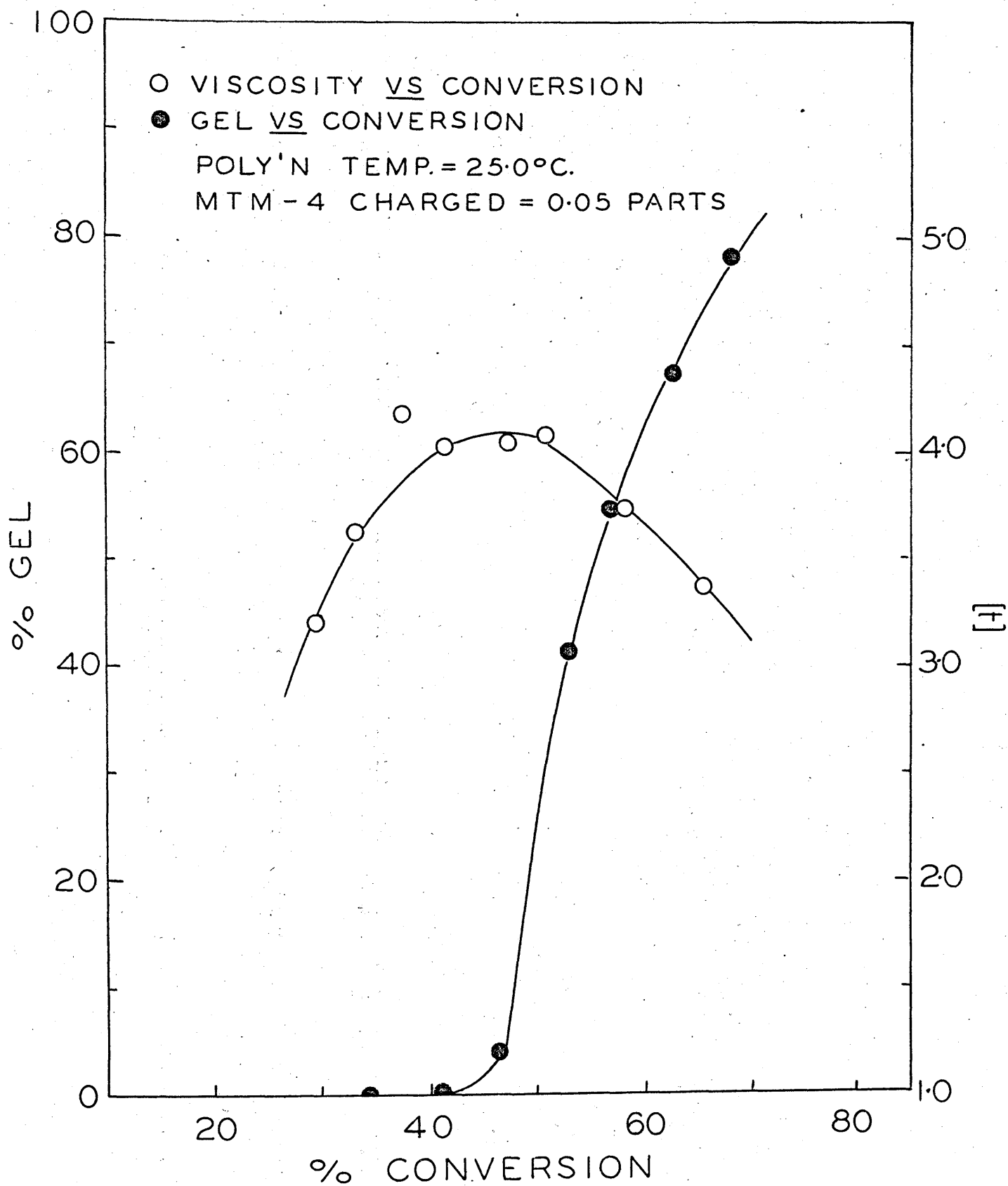


Figure 21. Correlation of vistex viscosity and gel content of polymer dried 12 hours at 50°C. in vacuo.

SUMMARY AND CONTRIBUTIONS TO KNOWLEDGE

The copolymerization of 75/25 butadiene-styrene in an emulsion system initiated by a cumene hydroperoxide-iron-Kalex combination has been studied over the temperature range 5.0°C. to 45.0°C. and the following characteristics observed:

1. An initial surge of reaction occurred which amounted to 6-10% conversion and was found to be dependent on the initiator system as a whole.
2. A zero order rate of polymerization occurred between 10 and 65% conversion. The temperature dependence of this rate indicated an activation energy of 9.7 Kcal/mole which was interpreted as the activation energy for the production of initiating free radicals by the initiator system.
3. An activation energy for propagation of 6 Kcal/mole was calculated from the temperature dependence of the first order polymerization rate observed beyond 65% conversion.
4. The ratio of monomer to polymer in the latex particle was found to decrease continuously with conversion.

The variation of the concentration of monomer in the particle with conversion could be represented by

$$\frac{M}{M+P} = a\alpha^{-b}$$

as long as a separate monomer phase was present.

The exponent, b , was approximately one half.

5. The separate monomer phase in the emulsion was completely consumed beyond about 65% conversion.
6. A slower polymerization rate, other variables being constant, was found to give higher values of the M/P ratio, as would be expected if the monomer content of the polymer particle were determined by the ratio of the rate of supply of monomer by diffusion from the oil phase and the rate of its removal by polymerization.
7. The M/P -conversion curve did not change markedly with polymerization temperature indicating that the rate of polymerization and the rate of diffusion of monomer into the polymer particle were affected to much the same extent by temperature.
8. The effect of temperature on the viscosity-conversion curve indicated that lower temperatures raised the

gel point without shortening the polymer chains. Hence, lower polymerization temperatures must decrease the proportion of the cross-linking reaction to the propagation reaction.

9. The ratio of the rates of cross-linking and propagation, Flory's $K = k_x/k_p$, was calculated for the present system using gelation, M/P-conversion and mercaptan consumption data and values of about 0.9×10^{-4} and 0.4×10^{-4} were found at 25.0°C. and 5.0°C. respectively. However, variation of K with mercaptan concentration indicated that this treatment was not valid for the data of this investigation and suggested that mercaptan was not the predominant terminating agent operating.
10. The consumption of MTM-4 in this system was found to occur in a first order manner in a reaction having an activation energy of 9.0 Kcal/mole.
11. The presence of a second terminating process having an apparent activation energy about 1 Kcal/mole greater than that of the mercaptan chain transfer reaction was detected. This apparent activation energy has been ascribed to the dependence of mutual termination on the concentration of free radicals, hence on their

rate of production by the initiator. The existence of mutual termination in appreciable amounts was confirmed by the effect on the viscosity-conversion curve of varying the rate of production of free radicals by varying the activator concentration.

12. The existence of termination by the emulsifier, Dresinate 731, was demonstrated by the change effected in the viscosity-conversion curve when the Dresinate 731 was replaced by potassium laurate, an emulsifier of a chemical nature much less prone to participate in chain transfer reaction.
13. Comparison of molecular weights calculated from mercaptan consumption data and from viscosity data suggested that only about one half of the polymer chains were terminated by mercaptan chain transfer reaction.
14. Lower polymerization temperatures were found to produce polymers which were much more sensitive to cross-linking during drying. Gel formed in this manner was very loosely cross-linked since it broke down gradually on prolonged extraction with a solvent, unlike gel formed during the polymerization reaction. Drying conditions of 12 hours at 50.0°C. in a vacuum

oven avoided cross-linking of polymer produced at 25.0°C, but were unsatisfactory for polymer produced at 5.0°C.

The results of this investigation suggest a study of the kinetics of the cross-linking reaction in a system in which only mutual termination is present.

REFERENCES

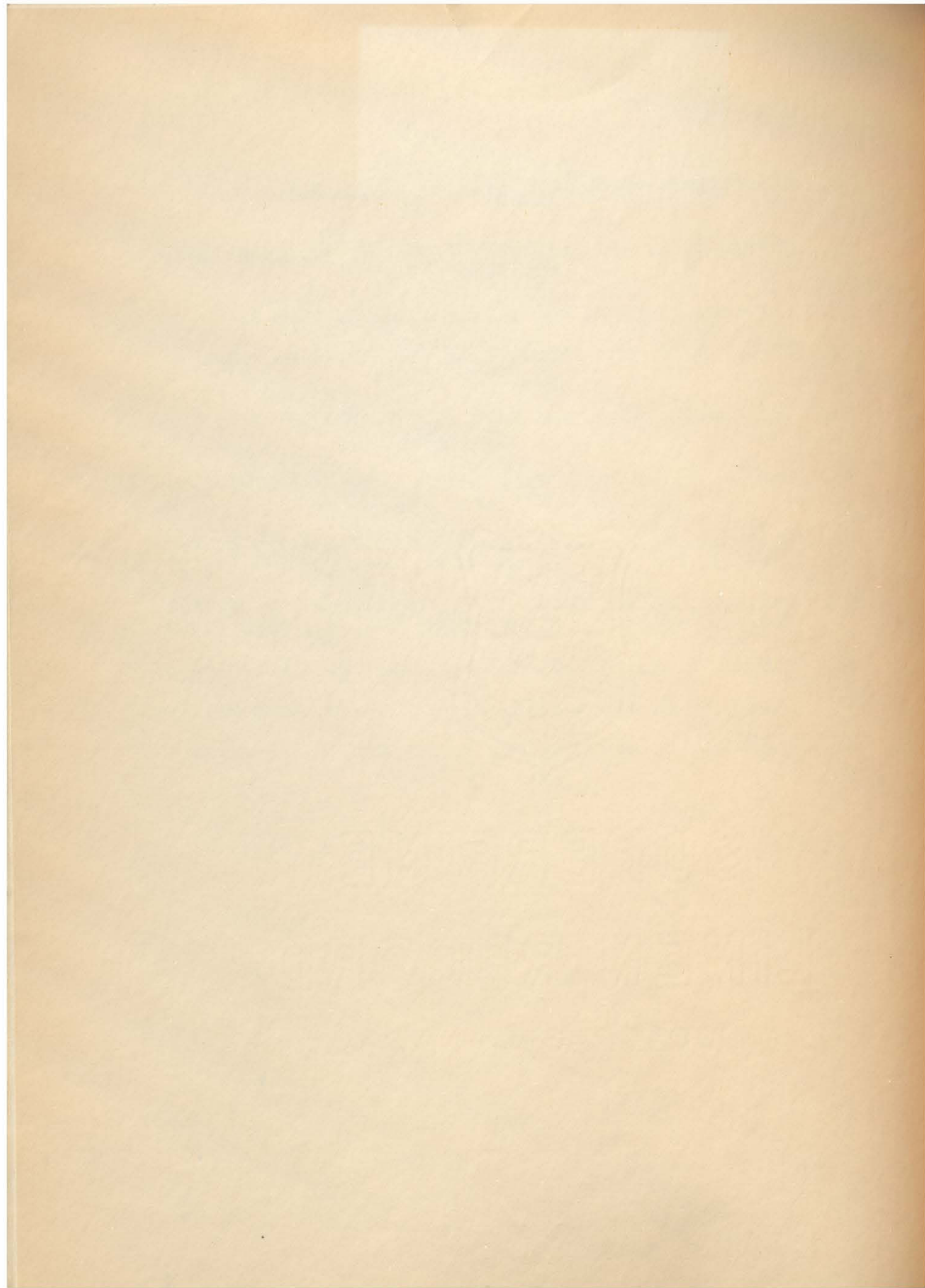
1. Hohenstein, W. P. and Mark, H. J. Polymer Sci. 1, 127 (1946)
2. Fryling, C. F., Landes, S. H., St. John, W. M. and Uранеck, C. A. Ind. Eng. Chem. 41, 986 (1949)
3. Azorlosa, J. L. Ind. Eng. Chem. 41, 1626 (1949)
4. Coe, W. S., Brady, J. L. and Cuthbertson, G. R. Ind. Eng. Chem. 38, 975 (1946)
5. Hays, J. T., Drake, A. E. and Pratt, Y. T. Ind. Eng. Chem. 39, 1129 (1947)
6. Marvel, C. S., Deanin, R., Overberger, G. G. and Kuhn, B. M. J. Polymer Sci. 3, 128 (1948)
7. Schulze, W. A., Tucker, C. M. and Crouch, W. W. Ind. Eng. Chem. 41, 1599 (1949)
8. Carr, C. W., Kolthoff, I. M., Meehan, E. J. and Stanberg, R. J. J. Polymer Sci. 5, 191 (1950)
9. Carr, C. W., Kolthoff, I. M., Meehan, E. J. and Williams, D. E. J. Polymer Sci. 5, 201 (1950)
10. Amberg, L. O. Ind. Eng. Chem. 41, 1626 (1949)
11. Kolthoff, I. M. and Harris, W. E. J. Polymer Sci. 2, 41 (1947)
12. Eager, R. L. and Winkler, C. A. Can. J. Research B.26, 527 (1948)
13. Johnson, P. H. and Bebb, R. L. J. Polymer Sci. 3, 389 (1948)
14. Starkweather, H. W., Bare, P. O., Carter, A. S., Hill, F. B. Jr., Hurka, V. R., Mighton, C. J., Saunders, P. A., Walker, H. W. and Yanker, M. A. Ind. Eng. Chem. 39, 210 (1947)
15. Marvel, C. S., Deanin, R., Kuhn, B. M. and Landes, S. H. J. Polymer Sci. 3, 433 (1948)
16. Vandenburg, E. J. and Hulse, G. E. Ind. Eng. Chem. 40, 932 (1948)

17. Kern, W. Die Makromolekulare Chem.
1, 199 (1948)
18. Weidlien, E. R. Jr. J. Chem. Eng. News 24, 771 (1946)
19. P.B. Item 5521 Office of Publications Board, Department
of Commerce, Washington, D.C.
20. Bacon, R. O. R. Trans. Faraday Soc. 42, 140 (1946)
21. Baxendale, J. H., Evans, M. G. and Park, G. S.
Trans. Faraday Soc. 42, 155 (1946)
22. Morgan, B. L. Trans. Faraday Soc. 42, 169 (1946)
23. White, L. M. Ind. Eng. Chem. 41, 1554 (1949)
24. Fielding, J. H. Ind. Eng. Chem. 41, 1560 (1949)
25. Sjothun, I. J. and Cole, O. D. Ind. Eng. Chem.
41, 1564 (1949)
26. Mitchell, J. M., Spolsky, R. and Williams, H. L.
Ind. Eng. Chem. 41, 1592 (1949)
27. Spolsky, R. and Williams, H. L. Ind. Eng. Chem.
42, 1847 (1950)
28. Kolthoff, I. M., Medalia, A. I. and Youse, M.
J. Polymer Sci. 6, 93 (1951)
29. Wall, F. T. and Swoboda, T. J. J. Am. Chem. Soc.
71, 919 (1949)
30. Fordham, J. W. L. and Williams, H. L. Can. J. Research
B.28, 551 (1950)
31. Fordham, J. W. L. and Williams, H. L. J. Am. Chem. Soc.
72, 4465 (1950)
32. Fordham, J. W. L. and Williams, H. L. SSR-154 Presented
before the Division of Physical and
Inorganic Chemistry, A.C.S. Sept. 1950.
Submitted to J. Am. Chem. Soc.
33. Walker, J. M. Ph.D. Thesis, McGill University,
September 1948
34. Schulz, G. V. and Huseman, E. Z. physik. Chem.
B.39, 246 (1938)

35. Flory, P. J. J. Am. Chem. Soc. 59, 241 (1937)
36. Snyder, H. R., Stewart, J. M., Allen, R. E. and Dearborn, R. J. J. Am. Chem. Soc. 68, 1422 (1946)
37. Wall, F. T., Banes, F. W. and Sands, G. D. J. Am. Chem. Soc. 68, 1429 (1946)
38. Bardwell, J. and Winkler, C. A. Can. J. Research B.27, 116 (1949)
39. Ewart, R. H., Smith, W. V. and Hulse, G. E. CR-73, June 16, 1943
40. Flory, P. J. J. Am. Chem. Soc. 69, 2893 (1947)
41. Meyer, A. W. Ind. Eng. Chem. 41, 1570 (1949)
42. Stockmayer, W. H. J. Chem. Phys. 12, 125 (1944)
43. Morton, M. and Salatiello, P. P. J. Polymer Sci. 5, S25 (1950)
44. Harkins, W. D. J. Polymer Sci. 5, 217 (1950)
45. Herzefeld, S. H., Roginsky, A., Corrin, M. L. and Harkins, W. D. J. Polymer Sci. 5, 207 (1950)
46. Herzefeld, S. H. and Harkins, W. D. CR-1825
47. Meehan, E. J. CR-1806
48. Harkins, W. D. J. Am. Chem. Soc. 69, 1428 (1947)
49. Smith, W. V. J. Am. Chem. Soc. 70, 3695 (1948)
50. Bamford, C. H. and Dewar, M. J. S. Proc. Roy. Soc. London. A 192, 309 (1948)
51. Staudinger, H. "Die Hockmolekularen organischen Verbindungen." Berlin, J. Springer (1932)
52. Kuhn, W. Z. physik. Chem. A161, 1 (1936)
53. Huggins, M. L. J. Phys. Chem. 42, 911 (1938)
54. Huggins, M. L. J. Phys. Chem. 43, 439 (1939)
55. Mark. H. "Die Feste Korper Hirzel" Leipzig, 1938

56. Huggins, M. L. Ind. Eng. Chem. 35, 980 (1943)
57. Scott, R. L., Carter, W. C. and Magat, M.
J. Am. Chem. Soc. 71, 220 (1949)
58. Flory, P. J. J. Am. Chem. Soc. 58, 1877 (1936)
59. Herrington, E. F. G. and Robertson, A. Trans Faraday
Soc. 38, 490 (1942)
60. Rehner, J. Ind. Eng. Chem. 36, 118 (1944)
61. Schulz, G. V. Z. physik. Chem. B 30, 379 (1935)
62. Yanko, J. A. and Pfau, E. S. CR-651, May 10, 1945
63. Baker, W. O., Mullen, J. W. II, and Heiss, J. H. Jr.
CR-247, January 21, 1944
64. Kolthoff, I. M. CR-609, June 7, 1945
65. B. F. Goodrich Company. CR-856, October 10, 1945
66. Henderson, D. A. and Legge, N. R. Can. J. Research
B27, 666 (1949)
67. Medalia, A. I. and Kolthoff, I. M. J. Polymer Sci.
5, S28 (1950)
68. Beu, K. E., Reynolds, W. B., Fryling, C. F. and
McMurray, H. L. J. Polymer Sci. 3, 465 (1948)
69. Hanson, E. E. and Halverson, G. J. Am. Chem. Soc.
70, 779 (1948)
70. Johnson, P. H. and Bebb, R. L. Ind. Eng. Chem.
41, 1577 (1949)
71. Hart, E. J. and Meyer, A. W. J. Am. Chem. Soc.
71, 1980 (1949)
72. Kolthoff, I. M. and Harris, W. E. J. Polymer Sci.
2, 41 (1947)
73. Harrison, S. A. and Meincke, E. R. Anal. Chem.
20, 47 (1948)
74. Houston, R. J. Anal. Chem. 20, 49 (1948)
75. Kolthoff, I. M. and Harris, W. E. J. Polymer Sci.
2, 49 (1947)

76. Goldfinger, G. and Seidlitz, M. J. Polymer Sci
3, 786 (1948)
77. Bovey, F. A. and Kolthoff, I. M. J. Am. Chem. Soc.
69, 2143 (1947)
78. Fordham, J. W. L. and Williams, H. L. SSR-146
79. Price, C. C. and Adams, C. E. J. Am. Chem. Soc.
67, 1674 (1945)
80. Hohenstein, W. P. and Mark, H. J. Polymer Sci.
1, 549 (1946)
81. Leslie, J. D. Ph.D. thesis, McGill University,
September 1948
82. Matheson, M. S., Auer, E. E., Bevilacqua, E. B. and
Hart, E. J. J. Am. Chem. Soc. 71, 497 (1949)
83. Matheson, M. S., Auer, E. E., Bevilacqua, E. B. and
Hart, E. J. J. Am. Chem. Soc. 71, 2610 (1949)
84. Meehan, E. J. J. Polymer Sci. 1, 318 (1946)
85. Baker, W. O. and Mullen, J. W. CR-70, June 24, 1943
86. Bardwell, J. and Winkler, C. A. Can. J. Research
B27, 128 (1949)



McGILL UNIVERSITY LIBRARY

I x M

.1B81.1951



UNACC.

