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THE STEREOSPECIFIC POLYMERIZATION OF 1-PENTENE

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ABSTRACT

A study has been made of the polymerization of 1-pentene using a titanium trichloride-triethyl aluminum catalyst and n-heptane as the solvent. The polymerizations were run in glass reaction vessels at pressures near atmospheric and over a temperature range from 0° to 85°C. The monomer concentration was varied from 5 to 95 volume percent; the titanium trichloride concentration was varied from 5 to 50 grams per liter; and the triethyl aluminum concentration was varied from 0.4 to 12 moles per liter. The rate of polymerization, intrinsic viscosity, and polymer density were measured as a function of these reaction conditions.

The rate of polymerization was found to be first order with respect to monomer concentration and titanium trichloride concentration and independent of the aluminum alkyl concentration. The temperature dependence of the rate was found to be of the Arrhenius form with an activation energy of 7.5 kcal/mol. It was found also that the specific rates for two different grades of titanium trichloride were not directly proportional to the specific surface area of the titanium trichloride

as measured by nitrogen adsorption. At higher temperatures the catalyst activity was found to decrease with time according to a process which appeared to be first order with respect to the titanium trichloride concentration.

The intrinsic viscosity of the polymer was found to increase with increasing monomer concentration, to decrease with increasing aluminum alkyl concentration, to be independent of the titanium trichloride concentration, and to decrease with increasing temperature. In order to correlate these molecular weight data satisfactorily with these reaction variables it was necessary to assume an empirical relationship between the intrinsic viscosity and the number average degree of polymerization. This relationship indicated that the ratio of viscosity average to number average molecular weight increased with increasing molecular weight. Some support for this empirical form was obtained from a few osmotic pressure determinations.

Little variation in polymer density was observed with reaction conditions. However, the nature of the catalyst used did affect the density.

These results have been interpreted according to the mechanism proposed by Natta and others whereby the aluminum alkyl is strongly adsorbed on the surface of the titanium trichloride forming an active catalyst site. The polymer grows out from this site with each addition of monomer occuring at the same site. Termination of the growth of the polymer molecule can occur by several processes; (a) spontaneous monomolecular termination; (b) transfer with monomer; and (c) transfer with the aluminum alkyl.

I. INTRODUCTION

A. Objectives of the Study

The most general objective of this study is to contribute to a better understanding of the processes involved in the synthesis of stereoregular polymers. One method of approach to this subject would be a study of the effect of reaction conditions on the rate of polymerization as well as on the molecular properties of the resulting polymer.

The important molecular properties of any polymer molecule would include its chemical composition, molecular weight, degree and type of branching or crosslinking, and the steric order of the individual repeating units within the polymer chain. Since, in general, one must deal with a polymer aggregate composed of many molecules which may vary in size and structure, it is necessary to characterize the properties of the polymer either in terms of a distribution of the property or in terms of an average property.

The particular polymer properties which were selected for study in this research are the intrinsic viscosity and osmotic pressure as measures of the average molecular weight, and the density and x-ray diffraction pattern as a measure of the average crystallinity of the polymer molecules. These properties, then, together with the rate of polymerization were studied as a function of reaction conditions.

The reaction variables which were chosen for investigation are the concentrations of the monomer and the two catalyst components, the reaction temperature, and the surface area of the catalyst.

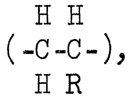
A system consisting of 1-pentene as the monomer, titanium trichloride in conjunction with aluminum triethyl as the catalyst, and n-heptane as the solvent was selected and is felt to be representative of this type of stereospecific polymerization.

B. Stereoregularity in High Polymers

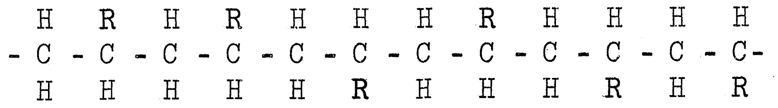
The discovery of catalysts which would produce high molecular weight, linear polyethylene under surprisingly mild conditions was followed rapidly by the development of the concepts of stereoregular polymers and stereospecific polymerization. Although some previous work had been done along these lines, it was largely through the efforts of Prof. Natta and his coworkers that these concepts were developed and publicized.

Natta's early work dealt mainly with the synthesis of high molecular weight polymers from hydrocarbon olefins and diolefins using catalysts prepared from aluminum alkyls and titanium chlorides. It was found that not only could new polymers be synthesized but that fractions of these polymers exhibited crystalline x-ray patterns. Furthermore, when some of the standard monomers were polymerized with these catalysts the polymers obtained had properties considerably different from those of the typical "free radical" polymers, and these differences in physical properties were found to be due to differences in the crystallinity of the two types of polymer.

Several features of the new polymers appear to account for the large increase in crystallinity. First, these polymers are essentially linear. Thus, short chain branching reactions, common in the high pressure polymerization of ethylene, apparently do not occur. Second, whereas in the free radical polymerization of many monomers some 1 - 3 percent of the growth steps are "head-to-head", the structural units in these crystalline polymers seem to be alligned "head-to-tail" exclusively. Finally, there appears to be some regularity of the steric configuration of the assymetric carbon atoms along the polymer chain in these crystalline polymers.

Although the first two of these features are essential in stereoregular polymers, it is the third condition which allows the polymer chains to become part of a crystal structure. In an addition polymer whose repeating structural unit is  $(-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{R}{C}}-)$, where R is any group other than hydrogen, the carbon atom to which the R group is attached will be assymetric. Thus every other carbon atom along the backbone of the polymer chain will be assymetric and it is the order of the steric configurations of these carbon atoms which plays such an important part in determining the properties of the polymer.

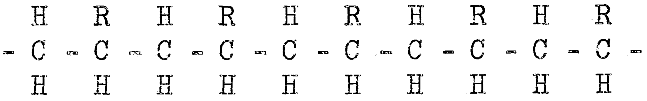
In polymerizations initiated by the normal free radical initiators the addition step appears to be completely random insofar as the configuration of the assymetric carbon atoms is concerned. These polymers, with random distribution of configurations along the chain, have been termed "atactic" by Natta (36). A section of such a polymer chain could be represented in two dimensions in the following way:



$$-\overset{H}{\underset{H}{C}}-\overset{R}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{R}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{R}{C}}-\overset{H}{\underset{H}{C}}-\overset{R}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{R}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{R}{C}}-$$

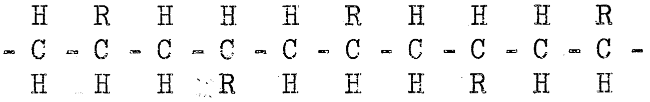
where the R group above the line represents one configuration and the R group below the line represents the other.

In polymerizations employing the new stereospecific catalysts, polymers have been obtained with at least two types of regular structure. In the first of these, termed "isotactic", the configuration of the assymetric carbon atoms remains the same for long sections of the polymer:



$$\begin{array}{ccccccccccccccccccccc} & H & & R & & H & & R & & H & & R & & H & & R & & H & & R & \\ - & C & - & C & - & C & - & C & - & C & - & C & - & C & - & C & - & C & - & C & - \\ & H & & H & & H & & H & & H & & H & & H & & H & & H & & H & \end{array}$$

In the second, termed "syndyotactic," there is a regular alternation of the two configurations along the polymer chain:



$$\begin{array}{ccccccccccccccccccccc} & H & & R & & H & & H & & H & & R & & H & & H & & H & & R & \\ - & C & - & C & - & C & - & C & - & C & - & C & - & C & - & C & - & C & - & C & - \\ & H & & H & & H & & R & & H & & H & & H & & R & & H & & H & \end{array}$$

Although these planar representations are useful in representing the various types of polymer, they are oversimplifications of the actual situation. X-ray data indicate that many of these stereoregular polymers form helical crystal structures with three or more monomer units in each turn of the helix. It is these helices then which line up with one another to form the crystalline material.

II. SURVEY OF RELATED LITERATURE

A. General

Several excellent books and reviews on the subject of stereospecific polymerization have been published in the last two years. The most recent, and probably the most complete, is the book by Gaylord and Mark, Linear and Stereoregular Addition Polymers. (24). While this book presents a good discussion of the polymerization mechanisms described in the literature, perhaps its most useful feature is an excellent tabulation of the data contained in the many foreign patents. A slightly different mechanistic viewpoint is expressed in an article by Friedlander (22) which also serves as an excellent introduction to, and review of the subject.

Schildknecht (79) and Tobolsky (85) have presented general reviews of the literature in this field while Stille (82) has reviewed the uses of complex metal catalysts including their use in this field of stereospecific polymerization.

A sizeable portion of the published work in this field is due to Dr. G. Natta and his coworkers at the Polytechnic Institute in Milan. Several of Natta's early articles provide a good introduction to the field as well as a discussion of the new concepts involved (37,38). More recently he has discussed the nomenclature relating to this field of stereospecific polymerization (36).

B. Catalyst Systems

Since Ziegler's discovery that titanium tetrachloride together with aluminum triethyl would catalyze the polymerization of ethylene (92) a large number of catalyst systems have been reported which will effect the polymerization of one or more monomers. The major differences which are found between one catalyst system and another are the type of monomer which can be polymerized, the relative activity of the catalyst, and the stereoregularity of the resulting polymer.

The type of catalyst system which seems to have received the greatest amount of attention thus far is the Ziegler type catalyst which is one produced by combining a titanium halide with an aluminum alkyl. Natta, using both titanium tetrachloride and titanium trichloride together with various aluminum alkyls, was able to polymerize numerous α - olefins including styrene, propylene, 1 - butene, 1 - pentene, 1 - hexene, 4 - methyl-1-pentene, 4 - methyl - 1 - hexene, and 5 - methyl - 1 - hexene (67-70). This system has also been reported to produce cis 1-4 polyisoprene (26,39), 1-2, polybutadiene (43,57) and cis 1-4 polybutadiene (39). The trichlorides of titanium, vanadium and chromium in conjunction with aluminum triethyl are reported to produce trans 1-4-polybutadiene (58).

Variations of this system also form active catalysts. For example, titanium dichloride, titanium tetrafluoride, titanium tetrabromide, titanium tetraiodide, titanium tetra-alcoholates will all catalyze the polymerization of propylene when combined with aluminum alkyls (71)

In general either the tetrachloride or the trichloride of titanium in conjunction with aluminum triethyl has been found to be the most active catalyst of this type while the titanium trichloride - aluminum triethyl system appears to give polymers with the highest degree of stereoregularity.

A number of other compounds have been found to be active catalysts in stereospecific polymerization. Isoprene can be polymerized to give specific isomers using n-butyl lithium (87) or dispersed lithium metal (81). Sodium alkyls (28), the Alfin catalysts (90), and potassium alkyls (91) will all produce crystalline polystyrene. In addition, a large number of compounds will catalyze the polymerization of ethylene giving a high density product (19,75); but since polyethylene contains no assymetric carbon atoms it is not a true stereoregular polymer. Nevertheless it seems probable that many of these catalysts could produce stereoregular polymers from a monomer such as propylene.

Although this brief review of stereospecific catalysts is by no means complete, it is hoped that it will indicate that a variety of materials can serve as active catalysts in these polymerizations. More complete tabulations of these catalysts and the appropriate polymerization conditions can be found in the review articles mentioned above. (22,24,79,85)

C. Polymerization Kinetics and Mechanism

The kinetics of polymerization reactions involving these complex metal catalysts has received considerable attention in the past two years. The majority of this kinetic work has dealt with catalysts formed from the titanium chlorides and metal alkyls. Ethylene, propylene, styrene and isoprene have all been studied under a variety of reaction conditions and the kinetic behavior apparently varies considerably with the particular catalyst system.

The system of propylene, titanium trichloride and aluminum triethyl has probably been subjected to the most thorough study and, again, this is due to the work of Natta and his colleagues. The most complete presentation of these data was in a series of six articles (61-66) while summaries or condensations have appeared in several places (40, 56, 64, 65). In general, the results of this work show that the rate of polymerization is first order with respect to propylene and titanium trichloride concentrations and independent of the aluminum alkyl concentration. An overall activation energy of about 10 kcal/mol is obtained. The reciprocal degree of polymerization is found to be proportional to the half power of both the aluminum triethyl conc. and the titanium trichloride conc., and proportional to the reciprocal of the propylene concentration.

Natta and Danusso have reported a similar study on the kinetics of styrene polymerization using both the tri- and tetra-chlorides of titanium together with aluminum alkyls. Again these results have been presented in a series of articles (13-16,53). Using titanium trichloride with aluminum triethyl, the rate of polymerization is found to be first order with respect to the concentrations of both monomer and titanium trichloride. However, more complicated behavior with regard to catalyst aging and activity was noted. An overall activation energy of 10.5 kcal/mol was found. Using titanium tetrachloride and aluminum triethyl the rates were found to be a strong function of the ratio of Al/Ti.

Burnett and Tait (7), in a short note, described similar results with styrene, titanium trichloride and aluminum triethyl obtaining the same first order dependence and an activation energy of about 8 kcal/mol.

Saltman (83) has reported on the kinetics of isoprene polymerization using titantium tetrachloride and aluminum triisobutyl. A marked dependence of both the rate and the nature of the products on the ratio of Al/Ti is found. The rate is reported to be first order with respect to monomer, titanium tetrachloride and aluminum trialkyl concentrations and an activation energy of 14.4 kcal/mol is found over the range from 0° to 20°C.

A number of people have studied the polymerization of ethylene using a catalyst of titanium tetrachloride together with various metal alkyls. Friedlander (21) studied the reactions between titanium tetrachloride and both n-butyl lithium and triisobutyl aluminum as well as the activity of these catalysts in ethylene polymerization. Orzechowski (72) studied the titanium tetrachloride/triisobutyl aluminum system with more emphasis on experimental procedure. Both found effects of Al/Ti ratio and order of catalyst addition, which apparently involved reduction of the titanium tetrachloride as well as adsorption phenomena. Ludlum (33), studying the same system, found the polymerization rate to be first order in monomer concentration and titanium tetrachloride concentration and the usual complicated effect of Al/Ti ratio.

McGowan and Ford (34) investigated both n-butyl lithium and dibutyl zinc together with titanium tetrachloride in the polymerization of ethylene. They found that the polymerization was second order in monomer concentration, first order in titanium tetrachloride concentration and essentially independent of the amount and nature of the alkyl. Gilchrist (25), studying the same system (with di-butyl zinc) found an involved dependence on the rate of both the titanium and alkyl concentrations as well as the second order dependence on the monomer concentration.

In general, then, the systems involving titanium trichloride appear to be first order in monomer in titanium concentrations, independent of the alkyl concentration, and they have overall activation energies in the range of 10 kcal/mol. Systems involving titanium tetrachloride are not readily amenable to generalization due probably to complications arising in the reduction of the titanium tetrachloride by the alkyl.

In addition to these articles, each of which includes some discussion of the mechanism as applied to the specific system, several theoretical papers have been presented which discuss the reaction mechanism. The majority of these deal with the nature of the catalyst sites.

Eirich and Mark (17,18) have discussed possible mechanisms for stereospecific polymerization including the nature of the catalyst sites. Assuming reversible adsorption of both the co-catalyst and monomer on the catalyst, rate and molecular weight relationships were derived. These relationships have been adopted to the system studied in this research and are discussed more fully in a later section(pg. 17).

Uelzmann (89), Patat (76), and Natta (41) have discussed the nature of the catalyst complex active in Ziegler type polymerizations. Agreement is reached only in that a bimetallic complex is formed, that the propagation step takes place at the complex, and that the configuration of the adding monomer unit is influenced by the complex.

Mussa (35) has considered the problem of the molecular weight distribution of the product obtained in these polymerizations. Data indicating that this distribution is unusually broad are discussed and mechanisms are presented which might rationalize these data.

Bailey and Lundberg (5) have treated the variations in polymer crystallinity on the basis of a single type of catalyst site. A relationship between the polymer crystallinity and the "degree of stereospecificity" of the catalyst is derived and the effect of temperature on the degree of stereospecificity is discussed.

D. Polymer Properties

In addition to the general properties of stereoregular polymers, two specific areas of property determination have received particular attention. The first of these areas concerns the relationships between the solution properties of these polymers, especially those concerned with molecular weight determination. The second concerns the determination of polymer crystallinity and the factors which influence this crystallinity.

The solution property studies were generally concerned with relationships between intrinsic viscosities and osmotic pressure or light scattering molecular weight. Danusso and Moraglio (54,12) studied the relationships between intrinsic viscosities in toluene and osmotic pressure molecular weights with a series of fractionated samples of polystyrene. Both atactic and isotactic polymer samples were studied and the intrinsic viscosity-molecular weight relationships were found to be essentially the same for the two types of polymer. Differences between the isotactic and atactic polymer were found in the second virial coefficients from osmotic pressure.

Similar studies on polystyrene in toluene have been made by Ang (3,4), Peaker (74), and Trosssarelli (86), all of whom used light scattering to determine molecular weights. Their results were essentially the same as those of Danusso and Moraglio.

Krigbaum, Carpenter and Newman (29) have reported on intrinsic viscosity, light scattering, and osmotic pressure measurements of isotactic polystyrene in o-dichlorobenzene and p-chlorotoluene. They found the distribution of unfractionated samples to be quite broad, with $\bar{M}_v/\bar{M}_n$ in the range of 10.

Chaing (8) and Ang (4) have determined the intrinsic viscosity-molecular weight relationship for isotactic polypropylene using fractionated samples and the light scattering technique. Ciampi (11) has reported similar results with osmotic pressure measurements on fractionated samples of isotactic polypropylene. Again these studies showed that the intrinsic viscosity-molecular weight relationship was independent of the polymer tacticity whereas interaction coefficients were affected by the structure.

Natta has described the crystal structure, as determined by x-ray diffraction patterns, of several crystalline polymers (44-50, 52, 59). In particular, rather complete structure determination has been made for isotactic polypropylene (50) and syndiotactic 1, 2-polybutadiene (46). Natta has also presented methods for determining the degree of crystallinity of isotactic polypropylene (51) and isotactic polystyrene (55) on the basis of specific volume.

The thermodynamics of crystallization in linear polyethylene has been studied by Quinn and Mandelkern (77) while Tung and Buckser (84) have investigated the effect of molecular weight on crystallinity in polyethylene. In both of these cases specific volume was used as a measure of the polymer crystallinity.

Methods of obtaining absolute crystallinities using x-ray diffraction have been described by Krimm and Tobolsky (30,31) and Ohlberg and Alexander (2,73).

III. THEORETICAL CONSIDERATIONS

A. Rate of Polymerization

1. General Kinetics of Double Bond Polymerization - The kinetics of homogeneous free radical polymerization of olefins has been studied quite thoroughly and summarized by several authors (20,23,24). The assumptions which are made and the relationships which are derived do an excellent job of explaining polymerization data over wide ranges of conditions. Thus it would seem appropriate to present here a brief summary of these relationships.

As in other chain reactions several processes are involved in the conversion of monomer to polymer. These processes can be considered to fall into three groups: chain initiation, chain propagation, and chain termination.

The initiation of polymerizations is considered to include two separate steps: (1) the formation of active free radicals, and (2) the addition of a monomer unit to an active free radical. In the first step an organic initiator (I) such as benzoyl peroxide decomposes to form two "primary" free radicals (I•)

$$I \xrightarrow{k_d} 2\,I\bullet \qquad (1)$$

Secondly, a monomer unit (M) adds to an active free radical to form a "chain" radical ($M_1\bullet$)

$$I\bullet + M \xrightarrow{k_a} M_1\bullet \qquad (2)$$

The growth, or propagation, steps in the polymerization reaction can be represented in a similar manner

$$M_1\cdot + M \xrightarrow{k_p} M_2\cdot$$

$$M_2\cdot + M \xrightarrow{k_p} M_3\cdot$$

or in general

$$M_x\cdot + M \xrightarrow{k_p} M_{x+1}\cdot \tag{3}$$

One of the most important assumptions involved in the development of these kinetic relationships is that the reactivity of the various chain radicals ($M_x\cdot$) is independent of the size of the chain. Thus the same rate constant, k_p, is applicable at each step.

Termination of the growing chain can occur in several ways. In the first, by "coupling", two growing chains combine to form one dead polymer molecule

$$M_x\cdot + M_y\cdot \xrightarrow{k_{tc}} M_{x+y} \tag{4a}$$

In the second, the two growing chains "disproportionate" to form two dead molecules

$$M_x\cdot + M_y\cdot \xrightarrow{k_{td}} M_x + M_y \tag{4b}$$

Finally, a growing chain radical may terminate by removing a hydrogen atom (or some free radical group) from a molecule, or "transfer agent". This process is called termination by transfer and can be generally represented as follows:

$$M_x\cdot + SH \xrightarrow{k_{ts}} M_xH + S\cdot \tag{4c}$$

where SH is any transfer agent and S· is a free radical which may or may not be capable of further initiation of polymer chains.

These equations, then, describe the mechanism of an initiated free radical polymerization and from them, together with several assumptions, general kinetic relationships can be derived.

The steady state treatment is applied to the total concentration of free radical species present [M·] in that it is assumed that this concentration does not change with time. This is equivalent to the assumption that the rate of initiation is equal to the rate of termination under steady state conditions. Noting that Equations (2), (3), and (4c) do not affect the chain radical concentration we can obtain an expression for the rate of change in radical concentration and set it equal to zero:

$$\frac{d[M\cdot]}{dt} = 0 = 2k_d\ [I] - k_{tc}\ [M\cdot]^2 - k_{td}\ [M\cdot]^2 \qquad (5)$$

Combining the two termination steps and solving for the radical concentration we obtain

$$[M\cdot] = \left(\frac{2k_d\ [I]}{k_t}\right)^{1/2} \qquad (6)$$

From Equation (3) we can write an expression for the rate of propagation (R_p)

$$R_p = k_p\ [M]\ [M\cdot] \qquad (7)$$

and combining Equations (6) and (7) we can express this rate in terms of measureable quantities

$$R_p = k_p\left(\frac{2\ k_d}{k_t}\ [I]\right)^{1/2}[M] \qquad (8)$$

Since the amount of monomer reacting according to Equation (2) is negligible compared to that reacting according to Equation (3) if the degree of polymerization is large, the rate of propagation is essentially equal to the rate of polymerization.

$$R_p = \frac{-d\,[M]}{d_t} \qquad (9)$$

Several comments should be made concerning this derivation. First, the expression for the rate of initiation (included in Equation 5) is usually modified to include an efficiency factor to allow for primary radicals which are formed but do not initiate chains. Second, when termination according to chain transfer (Equation 4c) yields radicals which are unreactive (inhibition) or less reactive (retardation) the expression for the rate of polymerization will be appropriately altered. However, it is not felt that a discussion of these factors is appropriate at this point.

2. Heterogeneous Catalysis - Having discussed briefly some of the methods used in treating homogeneous polymerization reactions we shall now proceed to discuss relationships applicable in stereospecific polymerizations.

One of the characteristics of many of these polymerizations is the presence of a solid catalytic species. Thus, the problems of heterogeneous catalysis and adsorption become important, and again these have been adequately treated by many authors (32,80). The application of these principles to heterogeneous polymerization has been treated by Eirich and Mark (17,18).

A reaction which takes place at a surface can be considered to occur in five consecutive steps:

1. Diffusion of the reactants to the surface
2. Adsorption of the reactants
3. Chemical reaction
4. Desorption of the products
5. Diffusion of the products from the surface.

In bulk polymerizations, where the viscostiy of the media becomes high, it is likely that the diffusion steps 1 and 5 could become important. However, at low conversions such as were attained in this study the viscosities remain low and the diffusion processes are most probably quite rapid as compared with the other steps in the process.

The desorption of the products (step 4) is often difficult to separate from the reaction step. It is therefore usual to consider the two steps together. This is not a convenient concept in polymerization reactions because many propagation steps occur before termination of the chain and the subsequent desorption. However, this very fact reduces the importance of the desorption step in rate considerations and it is generally neglected.

This, then, leaves two important steps in the surface reaction: the adsorption of the reactants and the subsequent chemical reaction. Applying the Langmuir-Hinshelwood mechanism to the propagation step of a surface catalyzed polymerization gives the following scheme:

$$M + S - \overset{\substack{P\\|}}{S} \rightarrow -\overset{\substack{M\\ \cdot}}{S} - \overset{\substack{P\\|}}{S} - \rightarrow -S - \overset{\substack{\;\;\diagup P\\ M\\|}}{S} -$$

where S represents the solid surface, M the monomer unit, and P the polymer chain of n monomer units.

If we now consider a unit area of catalyst surface having a concentration of active sites c^*_s (sites per cm.^{2}) and having a fraction θ of these sites covered with adsorbed monomer, then the rate of chemical reaction per unit area of surface (r) can be written

$$r = k_p c^*_s \theta \tag{10}$$

where k_p is the reaction rate constant. It then remains to relate the concentration of adsorbed monomer to the concentration of the reactant in the bulk liquid.

This relationship has been derived by Langmuir by assuming that at equilibrium the rate of adsorption of a reactant on the solid surface will equal its rate of desorption. These rates can be expressed in terms of the bulk concentration of the reactant (C_R), the concentration of surface sites, and the fraction of the surface sites covered by the reactant:

$$r_a = k_1 C_R c^*_s (1 - \theta) \tag{11}$$

$$r_d = k_{-1} c^*_s \theta \tag{12}$$

Equating these two rates and solving for the fraction of surface covered one obtains:

$$\theta = \frac{k_1 C_R}{k_{-1} + k_1 C_R} \tag{13}$$

Using the form of Equation (13) to relate the concentration of adsorbed monomer ($c^*_s\theta$) to the bulk monomer concentration (C_M), we can obtain an expression for the rate of polymerization (R_p):

$$R_p = \frac{k_p\ k_1\ \ s\ c^*_s\ C_M}{k_{-1} + k_1 C_M} \tag{14}$$

where s is the specific surace of the catalyst ($cm^2/g.$) and the rate is expressed in terms of g. per hr. per g. of catalyst.

Two special cases occur which are of interest. In the first, the monomer concentration is small or it is not readily adsorbed so that $k_{-1} \gg k_1 C_M$. The reaction rate then becomes first order with respect to the monomer concentration. In the second case the monomer concentration is large or it is very easily adsorbed such that $k_1 C_M \gg k_{-1}$. The rate then becomes independent of the monomer concentration.

3. Ziegler Type Catalysts - At this point it seems appropriate to consider briefly some of the features of Ziegler type catalysts. In particular, this system of titanium trichloride with an aluminum alkyl will be considered since it consists of a preformed solid catalyst and a liquid cocatalyst which can be considered to be adsorbed on the surface of the solid. Systems based on titanium tetrachloride can be related to this system by assuming that the aluminum alkyl first reduces the tetrachloride to the solid tri- (or di-) chloride after which it is adsorbed on the surface to provide active catalyst sites.

The nature of the titanium trichloride - aluminum alkyl system indicates that the active sites are formed by the adsorption of the alkyl on the titanium trichloride surface. However, as was indicated previously, the precise nature of the bonding between these compounds has not been determined. It seems probable that a coordination complex between the Al and Ti atoms exists thereby giving an assymetric nature to the catalyst site which would help to explain the stereospecificity of the propagation step in the polymerization reaction.

The kinetics of the polymerization for a given catalyst system are essentially independent of these considerations and, for the same reasons, little information concerning the nature of the catalyst can be obtained from kinetic data.

If we consider the most general case of reversible adsorption of the alkyl of the titanium trichloride surface we can obtain an expression for the concentration of active sites as a function of the alkyl concentration, C_A, by applying the Langmuir relationship derived previously (Equation (13)) and letting c_s represent the concentration of sites available for alkyl adsorption:

$$c^*_s = c_s\theta = \frac{c_s\, k_1\, C_A}{k_{-1} + k_1 C_A} \qquad (15)$$

where c^*_s represents the concentration of sites (sites/cm^2) on which the alkyl is adsorbed (therefore active sites for polymerization), c_s the total concentration of sites available for alkyl adsorption, C_A the bulk alkyl concentration, k_1 and k_{-1} rate constants.

Again, in the limiting cases, the concentration of active sites can be either directly proportional to, or independent of the bulk concentration of the aluminum alkyl.

4. <u>The Overall Rate Equation</u> - We can now obtain an expression for the overall rate of polymerization in terms of measureable quantities and constants of the system. Combining Equations (14) and (15) and distinguishing between the adsorption rate constants for the monomer and alkyl we obtain:

$$R_p = \frac{k_p\, s\, c_s\, K_M\, K_A\, C_M\, C_A}{(1 + K_M C_M)(1 + K_A C_A)} \qquad (16)$$

where $K = k_1/k_{-1}$, the reciprocal of the equilibrium dissociation constant, for the monomer (K_M) and the aluminum alkyl (K_A). R_p, the rate of propagation, is numerically equal to the rate of polymerization:

$$R_p = \frac{1}{G_{Ti}}\frac{dP}{dt} = -\frac{1}{G_{Ti}}\frac{dM}{dt} \tag{17}$$

where G_{Ti} is the weight of $TiCl_3$, P the weight of polymer, and M the weight of monomer. From Equation (16) we can see that the polymerization rate can vary from first order to zero order dependence on both the monomer and the alkyl concentrations.

Analysis of the overall rate equation with regard to temperature effects results in a rather complicated expression since the dissociation constants as well as the rate constant are temperature dependent. This dependence is usually expressed in the Arrhenius form:

$$k_p = A_p\, e^{\frac{-E_p}{RT}} \tag{18a}$$

$$K_M = A_M\, e^{\frac{+D_M}{RT}} \tag{18b}$$

$$K_A = A_A\, e^{\frac{+D_A}{RT}} \tag{18c}$$

where A_p, A_M, and A_A are the classical frequency factors, E_p the activation energy for the chemical reaction, and D_M and D_A are dissociation energies for the dissociation equilibrium of the monomer and alkyl on the solid titanium trichloride.

We can, however, get a good idea of the relative magnitudes of the temperature effect by considering the limiting cases of Equation (16).

The largest temperature effect will be found for the case in which both the monomer and the aluminum alkyl are strongly adsorbed and present in excess. In this case the rate will be independent of both concentrations:

$$R_p = k_p \; s \; c_s \qquad (19)$$

and the temperature dependence will be expressed by,

$$R_p = A_p \; s \; c_s \; e^{\frac{-E_p}{RT}} \qquad (20)$$

If the monomer is weakly adsorbed but the alkyl strongly complexed the temperature dependence will be of the form:

$$R_p = A_p \; A_M \; s \; c_s \; C_M \; e^{\frac{-E_p + D_M}{RT}} \qquad (21)$$

The lowest overall activation energy will be obtained for the case of weak monomer adsorption and weak alkyl complexing (or low alkyl concentration):

$$R_p = A_p \; A_M \; A_A \; s \; c_s \; C_M \; C_A \; e^{\frac{-(E_p - D_M - D_A)}{RT}} \qquad (22)$$

These equations, then, predict the rate behavior for heterogeneous polymerization on the basis of classical adsorption and reaction rate theory with the tacit assumption that active catalyst sites are of a uniform nature.

5. Non-uniform Reaction Sites - The most significant factor in stereospecific polymerization is the fact that the polymer produced has a certain steric order. While the causes for the presence of order in the polymer are connected with the nature of the catalyst, the fraction of polymer possessing this order can be considered from a kinetic viewpoint.

Experimentally it has been found that catalytic systems which produce stereoregular polymer simultaneously produce a certain amount of polymer with no steric order or at least little steric order. One explanation that has been put forth for this behavior is that more than one type of catalyst site is present. In particular it has been suggested that two types of site are present, one giving ordered polymer and the other giving non-ordered polymer.

Another explanation is that a single type of catalyst site is present but that these sites produce polymer with a distribution of structures ranging from complete steric order to disorder.

It seems probable that in the actual situation catalyst sites with a distribution of stereospecificities are present each of which produces polymer with a distribution of structures. The analysis of a system according to such a model would be far too complicated to be useful. It is, however, instructive to consider briefly one of the simpler models.

If we assume that there are two types of catalyst site present, one producing stereoregular polymer and the other producing atactic polymer, the total rate of polymerization will be equal to the sum of the rates at each type of site. If we then consider the situation in which the monomer is weakly adsorbed but the alkyl strongly complexed such that Equation (21) is applicable, the following expression can be derived:

$$\left(\frac{dP}{dt}\right)_{tot} = A' C_M G_{Ti} e^{-\frac{\Delta E_1}{RT}} \left(1 + B e^{\frac{\delta E}{RT}}\right) \qquad (23)$$

where the rate is expressed in g. per hr., A' and B are constants, G_{Ti} is the weight of $TiCl_3$ present, ΔE_1 is the overall activation energy for the polymerization at one type of site, and δE is the difference between this activation energy and that for the other type of catalyst site.

Thus, it can be seen that for this case only the form of the temperature dependence of the rate is affected by assuming a "multiple site" model. Obviously, if the activation energies at the two types of site are nearly equal, Equation (23) will reduce to the usual Arrhenius representation.

Although it is possible to derive, in certain cases, expressions for the rate which will show a different dependence on monomer concentration (or alkyl concentration) when the "multiple site" model is used, the different form of temperature dependence as expressed in Equation (23) is probably the most significant. This arises from the fact that the difference in activation energies (δE) can be obtained independently from measurements of the temperature dependence of the polymer crystallinity.

We have seen, then, that theories which have been suggested to account for variations in the degree of crystallinity can also lead to variations in the form of the rate equations. In the next sections we will consider the effect of reaction conditions on the degree of crystallinity as predicted by these models.

B. Degree of Stereospecificity

1. Definition - The concept of the degree of stereospecificity, which appears to be a useful one, is related to the propagation step of a

polymerization process and to the regularity of the resulting polymer. A precise definition of the term has been proposed by Bailey and Lundberg (5) and much of the following derivation is due to them.

As a model for analysis they have chosen an infinitely long polymer molecule formed by the addition of an infinite number of monomer units. In a polymer such as a poly (α - olefin) each monomeric unit in the polymer contains an assymetric carbon atom and this carbon atom will have one of two steric configurations. The probability that a monomer unit enters the growing chain with a given configuration is defined as the "degree of stereospecificity" of the propagation step.

Using a slightly different model we can arrive at another definition. Consider a catalyst site of an assymetric nature and a polymer chain growing at that site. We define the degree of stereospecificity as the probability that the monomer unit enters the polymer chain with a given configuration relative to the catalyst site and therefore relative also to the growing polymer chain. This is the case of catalyst controlled propagation.

Using this same model we can also define the degree of stereospecificity as the probability that the monomer unit will add with the same configuration as that of the adjacent monomer unit. This might be termed polymer controlled propagation.

These three definitions yield relationships between the degree of stereospecificity and the crystalline fraction which are nearly equivalent. They differ, however, in one important aspect relating to the type of order in the polymer, that is, the prediction of syndyotactic polymer. For the situation in which the propagation step is "catalyst controlled" a degree of stereospecificity (p) of 0.5 corresponds to random polymerization while at p = 1.0 or p = 0 the resulting polymer will be completely isotactic. On the other hand, for "polymer controlled" propagation (or for the model of Bailey and Lundberg) the situation for which $p = 0$ corresponds to sydyotactic polymerization, $p = 0.5$ to random and $p = 1.0$ to isotactic polymerization.

2. Relation to Polymer Crystallinity - Bailey and Lundberg (5) have derived, on the basis of their definition of the degree of stereospecificity, a relationship between this degree of stereospecificity and the "maximum degree of crystallinity" in the polymer.

In this derivation they first obtained the probability of obtaining a sequence n units long of assymetric carbon atoms having the same configuration. Then, assuming that only sequences of length greater than n_o are capable of crystallization, the maximum degree of crystallinity (D_{max}) is equated to the fraction of material existing in sequences of length greater than n_o:

$$D_{max} = \frac{\sum_{n_o}^{\infty} np^{(n-1)} (1-p)^2}{\sum_{0}^{\infty} np^{(n-1)} (1-p)^2} = \left[\frac{p^{n_o - 1}}{(\ell np)^2} - \frac{n_o \, p^{n_o - 1}}{\ell np} \right] (1-p)^2 \qquad (24)$$

If this derivation is carried out on the basis of the kinetic model involving polymer control of the propagation step Equation (24) is readily obtained. If catalyst control is assumed, the relationship between D_{max} and p is identical to Equation (24) except for a second term which is negligible except for p close to 0.5.

The parameter n_o in this derivation should be regarded as an average value rather than an absolute length of theoretical significance. Bailey and Lundberg have estimated it to be about 10-20 for polypropylene. Fortunately, its absolute value is not particularly critical for the calculation of activation energy differences on the basis of these models.

Finally, let us consider the relationship between the degree of stereospecificity and the maximum degree of crystallinity for the situation in which two types of catalyst site are present. If we assume that one type of site produces essentially amorphous material ($p = 0.5$) while the other produces essentially isotactic material ($p = 1.0$) then we can define an "average degree of stereospecificity" which will be linearly related to the fraction of sites producing isotactic material (f_1):

$$p_{avg.} = \frac{1}{2}(1 + f_1) \tag{25}$$

The maximum degree of crystallinity can also be related to this fraction of sites and therefore to $p_{avg.}$:

$$p_{avg.} = \frac{1}{2}\left[\frac{b + (2 - b)\, D_{max}}{b + (1 - b)\, D_{max}}\right] \tag{26}$$

where b is ratio of the propagation rates at the "isotactic" and "amorphous" sites.

3. Kinetic Considerations - If we consider the effect of reaction variables on the crystallinity in light of these models we find that the most important variable is that of temperature.

For the situation in which only one type of reaction site is considered it can be proposed that two different transition states exist corresponding to two configurations of the adding monomer unit. Thus, for polymer controlled propagation a unit adding with the same configuration as the adjacent unit will pass through one transition state while a unit adding with the opposite configuration will pass through the other transition state. For the case of catalyst control the two transition states will correspond to the two configurations of the monomer relative to the assymetric catalyst site. In either case rate constants corresponding to the two courses of reaction can be considered.

$$k_+ = A_+ \, e^{-E_+/RT} \tag{27a}$$

$$k_- = A_- \, e^{-E_-/RT} \tag{27b}$$

These rate constants can now be related to the degree of stereospecificity:

$$p = \frac{k_+}{k_+ + k_-} \tag{28}$$

If we rearrange Equation (27) and combine it with Equation (28) we obtain;

$$\frac{p}{1-p} = \frac{A_+}{A_-} \, e^{-\delta E/RT} \tag{29}$$

where δE is the difference in activation energies for the two processes.

Thus, if we obtain the maximum crystallinity of the polymer formed at several reaction temperatures we can relate this to the degree of stereospecificity through Equation (24). Then by plotting $\ln \left(\frac{p}{1-p}\right)$ *vs.* $\left(\frac{1}{T}\right)$ we can calculate the difference in activation energies for the two processes from the slope of this curve.

As we mentioned previously in connection with the polymerization rate, this energy difference is in the chemical rate activation energies. It should also be noted that the polymer crystallinity, according to this model, is completely independent of the concentrations of monomer, alkyl, and titanium trichloride as well as the dissociation energies of the monomer and alkyl.

For the case of two types of active site a similar dependence of crystallinity on temperature can be derived. Although the degree of stereospecificity can be used as a parameter, this relationship can be obtained more directly. Thus, the maximum degree of crystallinity is related to the rates of polymerization at the two types of site:

$$D_{max} \doteq \frac{(dP/dt)_1}{(dP/dt)_1 + (dP/dt)_2} \qquad (30)$$

Recognizing that $(dP/dt) = R_p f G_{Ti}$ and letting the ratio $(R_p)_1/(R_p)_2 = b$ we can rearrange Equation (38) to obtain:

$$\frac{D_{max}}{1-D_{max}} = \frac{f_1}{f_2}\, b \qquad (31)$$

If we take the most general form of the rate equation (Equation 16), the degree of crystallinity will be a slight function of monomer and alkyl concentration and the temperature dependence will be quite complicated. However, for any of the limiting cases of the rate equation (Equations 20,21,22), the ratio of the rates, b, can be expressed as a function of temperature only:

$$b = \frac{A_1\, e^{-\Delta E_1/RT}}{A_2\, e^{-\Delta E/RT}} \qquad (32)$$

Combining Equations (31) and (32) we obtain:

$$\frac{D_{max}}{1-D_{max}} = A\, e^{-\delta E/RT} \qquad (33)$$

where $\delta E = \Delta E_1 - \Delta E_2$ and A is a combination of constants. Equation (33) is very similar to Equation (29); the differences being that p is not a linear function of D_{max} and that the δE in Equation (33) includes the difference in the dissociation energies for the two types of process.

These two theories, then, can be tested by obtaining crystallinity data as a function of polymerization temperature. The linearity of an Arrhenius plot of the two functions of crystallinity would then indicate the applicability of the two theories.

4. Crystallinity Measurements - The two most widely used experimental methods for determining crystallinity are density and x-ray diffraction.

The use of density (or specific volume) measurements is based on the assumption that the specific volume of the crystalline and amorphous materials is not affected by the presence of the other phase. This assumption is probably not quite valid, but the accuracy possible in density measurements along with the ease of the measurement assures the continuing use of this method. The degree of crystallinity is given by:

$$D = \frac{\bar{v} - \bar{v}_a}{\bar{v}_c - \bar{v}_a} \qquad (34)$$

where $\bar{v}$ is the specific volume of the sample and $\bar{v}_c$ and $\bar{v}_a$ the specific volumes of the pure crystalline and pure amorphous materials respectively. Thus, if the crystallinities of two samples are known or can be calculated, the crystallinity of any other sample can be calculated from its density.

The x-ray diffraction method relies on the assumption that the scattering produced by a unit mass of amorphous material is independent of the presence of crystalline polymer. The amorphous fraction of the polymer is then obtained from the ratio of the normalized intensities at the peak of the amorphous halo of the sample to the amorphous polymer. A second method employs the total scattering of the amorphous fraction rather than just the peak intensity.

The advantage of this method is that only one sample of known crystallinity need be obtained (eg. totally amorphous). It has drawbacks in that the method requires expensive equipment and a fair amount of time, and that in many cases a crystalline peak occurs at the same angle as the major amorphous peak, resulting in poor accuracy and reproducibility.

C. Degree of Polymerization

1. Kinetic Considerations - In the treatment of free radical polymerization it is found that the degree of polymerization ($\bar{\bar{x}}_n$) is determined by the ratio of the rate of polymerization to the sum of the termination rates:

$$\bar{\bar{x}}_n = \frac{R_p}{\sum\limits_i (Rt)_i} \tag{35}$$

The major restrictions on this relationship are that branching and crosslinking reactions are unimportant and that termination is by disproportionation. Termination by coupling is accounted for by including a factor between 1.0 and 2.0 which depends on the fraction of termination steps occurring in this manner.

Polymerizations involving heterogeneous catalysts can be treated in much the same manner. It is generally thought that the termination steps always occur at the catalyst site so that termination by coupling need not be considered. However, at least one branching mechanism can be postulated which would complicate the kinetic scheme.

Neglecting this complication for the present we can postulate several termination mechanisms and derive the corresponding expressions for the degree of polymerization.

The following mechanisms have been proposed by Natta (40) and Eirich and Mark(17):

a) Disproportionation:

$$\mathrm{Me - - CH_2 - CHR - P} \xrightarrow{k_t} \mathrm{Me - - H + CH_2 = CR - P}$$

b) Transfer with Monomer:

$$\mathrm{Me - - CH_2 - CHR - P + CH_2 = CHR} \xrightarrow{k_{tM}} \mathrm{Me - - CH_2 - CH_2R}$$
$$\mathrm{+ CH_2 = CR - P}$$

c) Transfer with other substances:

$$\mathrm{Me - - CH_2 - CHR - P + SR} \xrightarrow{k_{ts}} \mathrm{Me - - R + S - CH_2 - CHR - P}$$

An example of this last type is transfer with the aluminum alkyl found by Natta.

If we now assume first order rate expressions for each of these mechanisms and consider the case of the polymerization rate which is first order in monomer concentration and independent of the alkyl, we can obtain an expression for the degree of polymerization:

$$\frac{1}{\bar{X}_n} = \frac{k_t + k_{tM} C_M + k_{ts} C_s}{k_p C_M} \qquad (36)$$

The form of the rate expression can be determined independently and by appropriate variation of the reactant concentrations the termination constants of Equation (36) can be determined.

This, however, is a simplified view of the process. It is possible, of course, that the transfer operations occur by reaction of the transfer agent in solution with the growing polymer chain. Also, variations in the form of the rate equation can be easily accounted for, in which case Equation (36) would be adequate. If, however, the transfer agent is adsorbed on the polymerization site before it reacts to terminate the growing chain, then one would have to relate the concentration of adsorbed reactant to the bulk concentration. In this case the Langmuir relationship (Equation 13) could be used and Equation (36) would be modified accordingly.

The problem of branching is somewhat more complicated. One possible branching mechanism involves a "dead" polymer chain which has terminated in a manner such that the terminal group contains a double bond. This double bond is then capable of being adsorbed on the active catalyst site and subsequently being incorporated into a growing polymer chain. This type of "long chain" branching would not greatly affect the polymer crystallinity as does the "short chain" branching common in high pressure polyethylene. It would, however, have a marked effect on both the molecular weight and the molecular weight distribution.

It does not seem likely that the rate of such a branching reaction would be related to the bulk polymer concentration according to the usual adsorption-desorption theories, since it is unlikely that equilibrium exists. Rather, such factors as the specific polymerization rate, the nature of the major termination steps, and the average degree of polymerization of the unbranched polymer are likely to affect the rate of such a branching reaction.

In summary then, the average degree of polymerization can be related to the rates of the various termination steps in the usual manner. This relationship may be complicated by the necessity of dealing with the concentrations of adsorbed reactants rather than with bulk concentrations. The presence of branching reactions will also lead to deviations from the predicted molecular weight.

2. Molecular Weight Determination - Of the three most common methods of measuring molecular weight two are of particular importance in kinetic studies. Osmotic pressure is important because it yields a number average molecular weight, which is the proper average to be used in kinetic relationships. Intrinsic viscosity is important because of the relative ease of obtaining accurate measurements which can generally be related to the osmotic pressure molecular weights. The third, light scattering, yields a weight average molecular weight and is therefore of greater importance in property studies.

The osmotic pressure method is based on the theory that, in dilute solution, the activity of the solvent will be decreased by the presence of a solute. This decrease will be proportional to the mole fraction of the solute so that if the weight fraction is known the molecular weight can be calculated. In this method the decrease in activity is balanced by a pressure (π) applied to the solution. Thermodynamic analysis leads to the relationship between activity and this pressure:

$$-\ln a_1 = \pi V_1/RT \tag{37}$$

where a_1 is the activity of the solvent in the polymer solution and

V_1 the molar volume of the pure solvent. For very dilute solutions the activity can be related to the concentration (c) and molecular weight (M):

$$-\ln a_1 \cong cV_1/M \qquad (38)$$

The approximation involved is removed at infinite dilution so that we obtain

$$(\pi/c)_0 = RT/M \qquad (39)$$

Since we are dealing with polymer samples of many different molecular weights, we must refer to average molecular weights. It can be shown that the osmotic pressure method yields a number average molecular weight ($\bar{M}_n$) which can be defined as:

$$\bar{M}_n = \frac{\sum Ni\ Mi}{\sum\ Ni} \qquad (40)$$

This can be seen intuitively since the method measures the number of solute molecules rather than size of the molecules. Equation (39) must therefore be modified to give:

$$(\pi/c)_0 = RT/\bar{M}_n \qquad (41)$$

which is the familiar relationship for dilute polymer solutions.

The intrinsic viscosity $[\eta]$ of a polymer in a given solvent has been empirically related to molecular weight according to the form:

$$[\eta] = K\ \bar{M}_v^{\ a} \qquad (42)$$

where K and a are constants and $\bar{M}_v$ is the viscosity average molecular weight. This relationship receives theoretical support over ranges as large as a factor of a hundred.

The viscosity average molecular weight is found to be much closer to the weight average than to the number average molecular weight for all distributions likely to be encountered in a high polymer. If, however, measurements are made on a series of polymer samples, all of which have the same molecular weight distribution, the form of Equation (42) will still be valid although K will be in error. This is true due to the fact that for a given distribution the three molecular weight averages are linearly related.

If the distribution of the samples varies, then the relationship between $[\eta]$ and $\bar{M}_n$ will no longer conform to this relationship, and if this variation is irregular no consistent relationship between $[\eta]$ and $\bar{M}_n$ will be found.

Thus, the intrinsic viscosity can be used as a measure of the number average molecular weight but variations from the usual relationship can be expected if the molecular weight distribution is not constant.

IV. EXPERIMENTAL TECHNIQUES

A. Materials

1. Monomer and Solvents - The 1-pentene used in this study was supplied by the Philip's Petroleum Co. and was their "Pure Grade" (99 mol percent minimum). Most of this material was put directly into the dry box in one liter bottles and stored there after sparging with purified nitrogen for about five minutes. Some of the 1-pentene was further purified by storing over metallic sodium although this treatment did not appear to affect the rates appreciably.

The solvent used for the majority of the work was Philips "Pure Grade" n-heptane. This material was further purified to remove trace amounts of unsaturated compounds. Although there was some variation in purification method, the following procedure was generally followed.

Three to four liters of heptane were stirred by means of an air stirrer with successive volumes of concentrated sulfuric acid until no color developed in the acid layer after about six hours. This operation generally required about three one liter volumes of acid over a period of four days. Next, the heptane was washed with distilled water until the water was neutral to litmus paper. The heptane was then passed through a column of silica gel into a distilling flask which had been dried and flushed with nitrogen. 10- 20 cc. of one molar triethyl aluminum was then added and the heptane was distilled under nitrogen. Finally, the heptane was put into the dry box in one liter bottles where it was shaken with silica gel which had been freshly activated for several days at 200° C.

Impurities remaining in the monomer and solvent after purification were determined by titration with dilute aluminum triethyl according to the method of Orzechowski (72). This technique, which gives the amount of alkyl required to neutralize the impurities present, consists in adding incrementally a 0.1 molar solution of alkyl in n-heptane to a known quantity of solvent. After each increment a drop of a dilute (0.05M) solution of titanium tetrachloride is added, and the formation of a yellow color indicates the presence of excess alkyl thereby allowing the calculation of the amount of alkyl required to neutralize the impurities present.

In this way it was found that the level of impurities in both the n-heptane and the 1-pentene was less than 0.5 millimoles per liter as aluminum triethyl (if water were the sole impurity this would correspond to about 40 ppm.).

In addition, infrared spectrographs of typical samples of n-heptane and 1-pentene were obtained and these are shown in Figure 32.

2. Catalyst Components - The catalyst employed in this work was solid, anhydrous titanium trichloride in conjunction with aluminum triethyl.

Two grades of titanium trichloride were investigated, both of which were obtained through the Anderson Chemical Co. of Weston, Michigan, a division of Stauffer Chemical Co. The first of these was anhydrous titanium trichloride, practical powder, while the other was anhydrous titanium trichloride, HRA (hydrogen reduced, activated).

Both samples of titanium trichloride were reported to have been produced commercially by the hydrogen reduction of titanium tetrachloride and therefore should be the α or violet crystalline form. The activated titanium trichloride was obtained some time after the "practical" material and it was reported to have been activated through a ball milling process. Some of the properties of the $TiCl_3$ (pract.) are given in table 24.

In order to facilitate the handling of the small quantities of titanium trichloride required for the polymerizations, several suspensions of the solid titanium trichloride in n-heptane were prepared. These were prepared in the dry box by adding 1-5 g. of titanium trichloride to about 150 cc. of n-heptane in 8 oz. bottles fitted with butyl rubber seals. The required quantity of titanium trichloride could then be transferred from these bottles to the polymerization vessels with a hypodermic syringe.

The aluminum triethyl was obtained from the Hercules Powder Co., Wilmington, Delaware as a one molar solution in n-heptane. This material was used without further treatment.

B. Rate Measurements

1. Preparation of Reaction Mixtures

- The polymerizations were carried out in glass flasks kept at constant temperatures in a water or oil bath. All of the components of the reaction mixture were added to this reaction flask inside of a dry box having an atmosphere of purified nitrogen.

The dry box was a standard model (2C304) supplied by the Kewaunee Mfg. Co., Adrian, Michigan. A slight positive pressure was maintained inside the dry box by constantly adding purified nitrogen which escaped through an inert liquid bubbler when the pressure exceeded several inches of water. Airco oil pumped nitrogen was further dried by passing it through three columns (500 mm high X 40 mm dia.) the first two of which were packed with Drierite while the third was packed with calcium hydride. Analysis of this nitrogen stream by the Mass Spectometer showed that it contained less than 0.04 percent oxygen and less than 0.07 percent water. By a similar analysis, a typical sample of the dry box atmosphere was found to contain less than 0.1 percent oxygen and less than 0.2 percent water. The drybox was located in a constant temperature room which was maintained within one degree of 24°C.

The reaction flasks were conical flasks with four vertical indentations in the sides which helped provide efficient mixing. The volume of these flasks was about 150 cc. Prior to each run the flask to be used was filled with chromic acid cleaning solution and allowed to stand for at least one hour after which it was rinsed thoroughly with distilled water and then dried for more than three hours at 200°C. Hypodermic syringes used in the transfer of catalyst components were also washed with water and dried at 200°C. This glassware was put directly into the antichamber of the dry box while still hot and the antichamber was then evacuated by means of a mechanical vacuum pump. After partial pressurization with purified nitrogen the antichamber was re-evacuated and finally filled with nitrogen before the glassware was transferred to the main chamber of the dry box.

Inside of the dry box a teflon coated magnetic stirrer and the reactants were added to the reaction flask which was capped with a rubber serum bottle stopper. The order of addition for all but a few runs was: solvent, pentene, aluminum triethyl, and titanium trichloride. The weight of each reactant was determined by difference to the nearest 0.01 g. after roughly measuring out each component volumetrically. The total volume of the polymerization mixture was generally about 50 cc although volumes to to 125 cc were used.

After the addition of the solvent and monomer, the flask was stoppered and both of the catalyst components were added by means of a hypodermic syringe. Before the addition of the titanium trichloride, up to 50 cc of nitrogen were added to the flask to build up the pressure after which the solution was shaken so as to allow the aluminum triethyl to scavenge any impurities present.

Finally, the titanium trichloride, suspended in n-heptane, was added to the flask. It was found that, in order to obtain reasonably reproducible rates, the catalyst suspension had to be shaken well and the sample withdrawn fairly rapidly.

The flask was then taken out of the dry box, put into a constant temperature bath, and the magnetic stirrer was turned on. The usual time lapse between the addition of the titanium trichloride and putting the flask into the bath was about five minutes.

2. Determination of the Rate of Polymerization - The time of the polymerization was measured with an electric timer starting from the

time the reaction flask was put into the constant temperature bath. The reaction mixture was stirred magnetically with sufficient speed to keep the mixture dispersed. The bath was maintained at constant temperature by means of a mercury regulator together with a relay system and heating coil. While in the bath the flask was encased with a brass cage as a safety precaution.

Periodically during the reaction, samples were withdrawn from the polymerization mixture with a hypodermic syringe equipped with a metal stopcock. The syringe, stopcock, and needle were dried and flushed with nitrogen before each sample, but no nitrogen was added to replace the sample volume so that the chance of introducing impurities was kept to a minimum. The slight change in pressure during the reaction did not appear to affect the polymerization rate. The hypodermic was tared before taking the sample and the weight of the sample was determined by weighing the hypodermic plus the contents immediately after withdrawing the sample. The closed stopcock prevented appreciable evaporation of the sample even at the higher temperatures. The usual sample size was about 2 cc. After weighing, the sample was added to methanol and the time noted. The hypodermic was rinsed with a small amount of n-heptane and this was also added to the methanol. The time required between the withdrawal of the sample and the addition to the methanol was about one minute.

Upon addition of the sample to the methanol the polymer was precipitated while the solvent and catalyst dissolved in the methanol. The solid polymer was then filtered on a medium sintered-glass filter, dried under vacuum to constant weight, and weighed.

The polymerizations were run for durations of from one to four hours, depending upon the expected rate, and usually five samples were taken spaced evenly over the entire time.

The polymer concentration, expressed as grams of polymer per gram of solution, was then plotted as a function of time and the dependence obtained was generally linear. A typical curve is shown in Figure 1. The slope of this plot is the rate expressed in grams of polymer per gram of solution per minute. The curves are found to remain linear in these batch polymerizations mainly because the decrease in monomer concentration is small.

However, in a few polymerizations a decrease in rate is observed toward the end of the run. This decrease is greater than would be explained by a decrease in monomer concentration and has been attributed to the introduction of impurities (water or oxygen) into the reaction mixture while taking one of the samples. This is often supported by the corresponding presence of a white vapor in the flask characteristic of the reaction of these impurities with the aluminum alkyl. In such cases the affected points are disregarded in the calculation of the rate.

The method of determining polymer concentrations by precipitation in methanol was compared with the method of evaporating samples to constant weight without precipitation. No difference in the rate

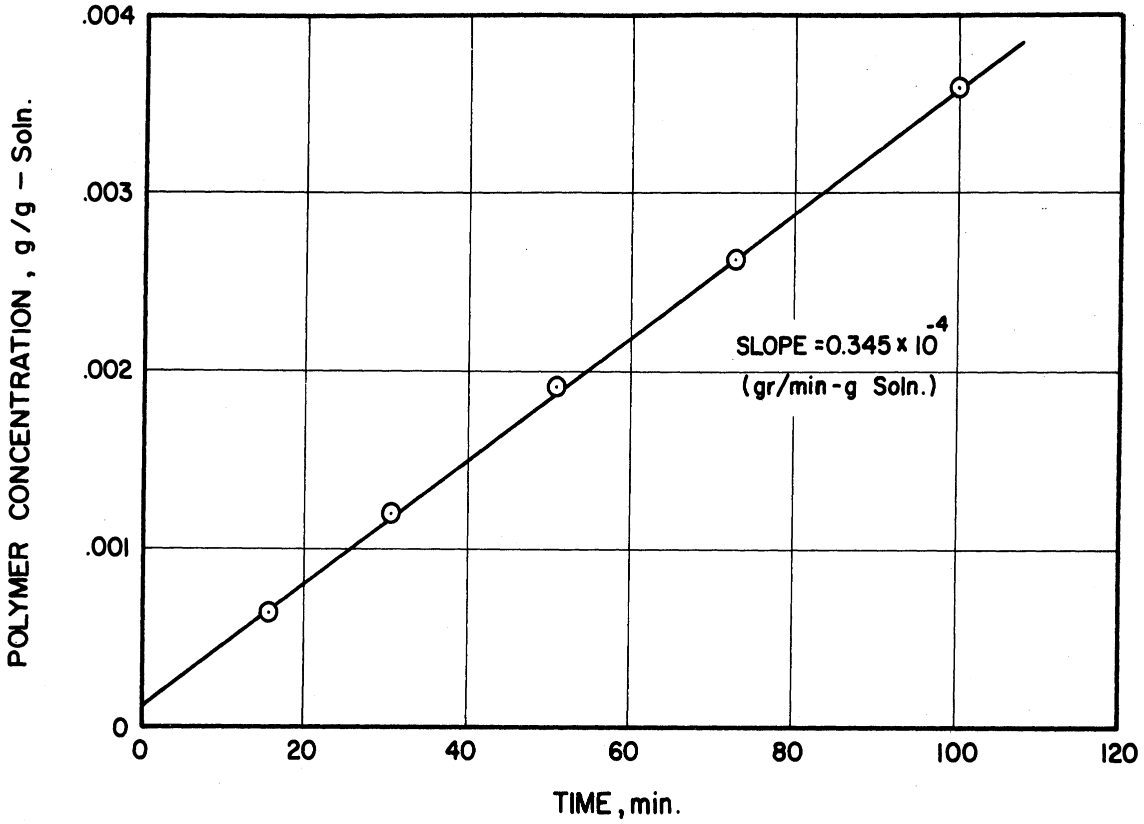


Figure 1. Data for Rate Determination

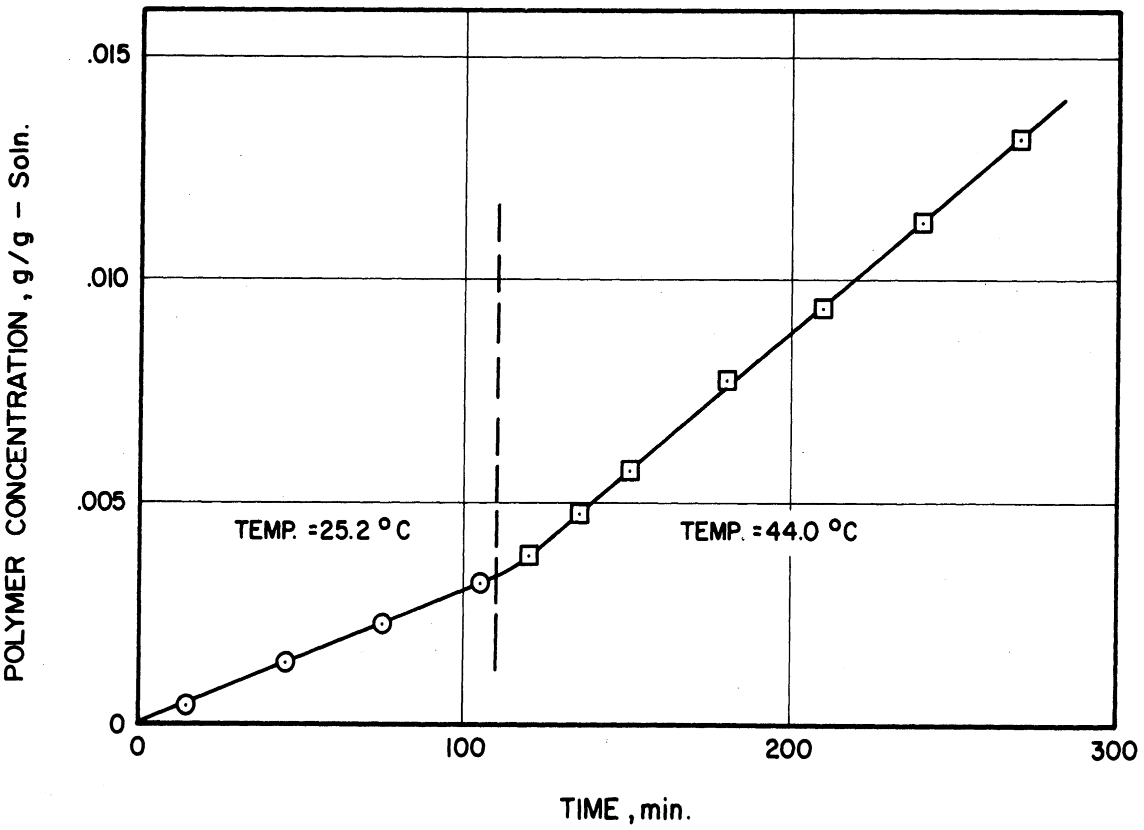


Figure 2. Data for Rate Determination-Effect of Temperature

as determined by the two methods was observed, and since the precipitation method was less time consuming it was employed.

In the determination of the effect of temperature on the rate one further step was employed. The reaction flask was first put in a bath at 25°C and the rate was measured in the usual manner. Then the flask was removed and put in a bath at another temperature and a second rate was obtained. Typical data of this type are shown in Figures 2 and 3. The rapid decrease in rate at the high temperature as shown in Figure 3 seemed to be a fairly reproduceable phenomena rather than due to impurities and its possible significance will be discussed in a later section (page 81).

Information in two other areas had to be obtained experimentally in connection with the rate determinations. In the first case the temperature of the reaction mixture was measured as a function of time so as to determine how rapidly temperature equilibrium was attained. It was found that in the most severe case (from room temperature to 90°C) the temperature of the reaction mixture was within two degrees of that of the bath in 7 minutes, and equilibrium was essentially attained in 15 minutes.

Secondly, since the concentrations of the various components should be expressed in weight per unit volume, the density of the reaction mixture under various conditions had to be measured or calculated. Densities of n-heptane over the entire range of temperatures

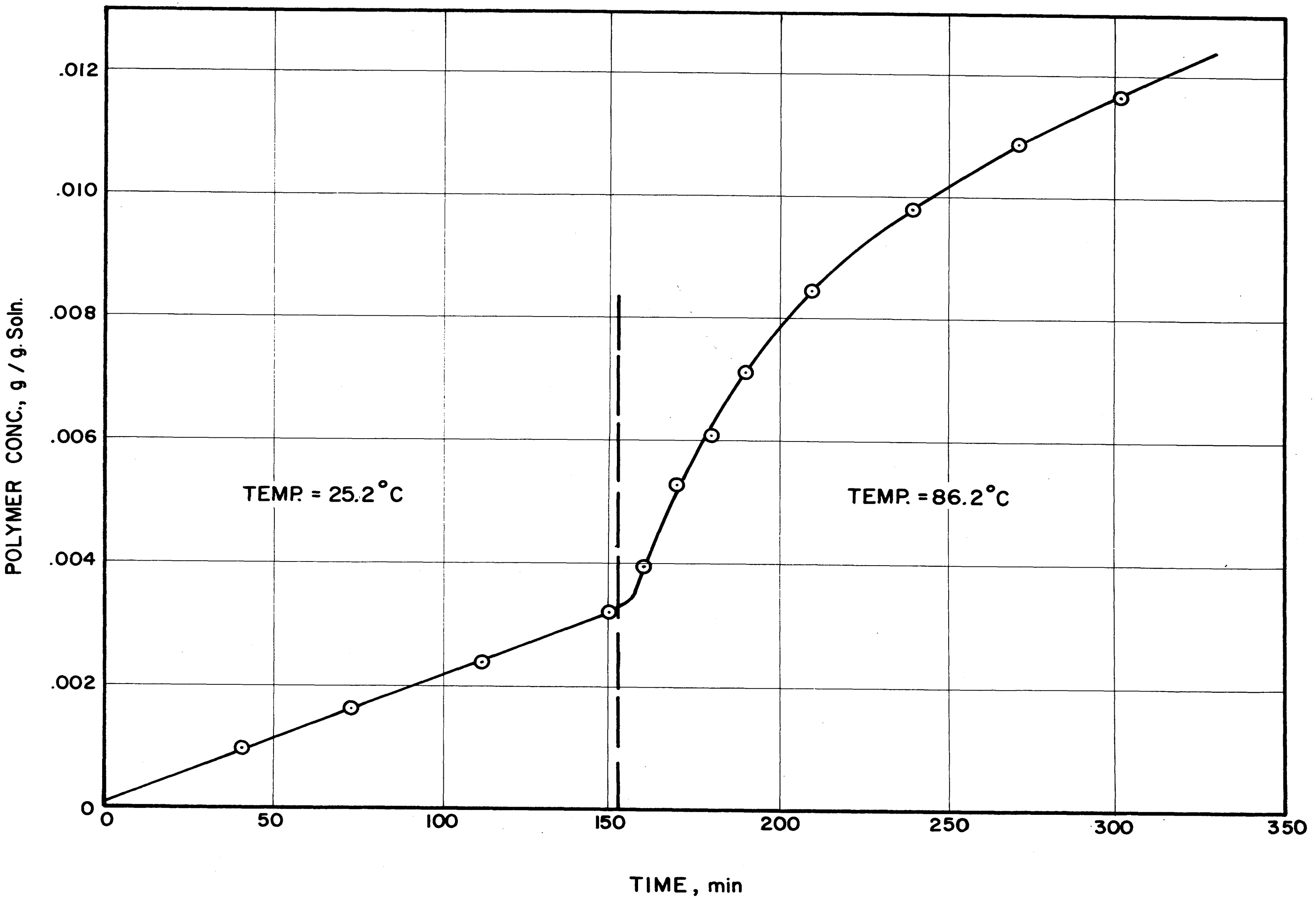


Figure 3. Data for Rate Determination-Effect of Temperature

were available from the literature(78) but since 1-pentene boils below 30°C no data for it was available at the higher temperatures. Densities of a pentene-heptane mixture were determined at several temperatures as well as the densities of the pure heptane which were in excellent agreement with the literature values. These data are plotted in Figure 31 in the appendix. Assuming a density of 0.87 g. per cc. for the polymer and neglecting the contributions due to the catalyst components, the density of the reaction mixture was calculated using the principle of additive volumes. The calculated values were found to agree well with the few experimental values which were obtained.

C. Molecular Weight Determination

1. Treatment of the Polymer - After taking samples for the rate determination about 40 cc. of the reaction mixture remained, and this was added directly to about 100 cc. of dilute hydrochloric acid. More n-heptane was added and the entire mixture was shaken vigorously until the organic layer was clear. The acid layer was removed and the polymer, dissolved in n-heptane, was precipitated in an excess of methyl alcohol. The polymer was then separated and dried under vacuum at room temperature.

The solutions for viscosity were prepared by dissolving a weighed quantity of polymer in toluene and diluting this solution to 50.0 cc. in volumetric flasks. This polymer solution was then filtered through a coarse sintered glass filter.

The concentration was determined from the weight of the polymer added to the known volume of solvent and was checked by evaporation a 10.0 cc. aliquot of the filtered polymer solution to constant weight. If these two concentration values did not agree within 2 percent, a second aliquot was evaporated to dryness and an average value was used.

2. <u>Intrinsic Viscosity</u> - Viscosity measurements were made in a modified Ubbelhode suspended-level viscometer made by Canadian Laboratory Supplies, Ltd., Montreal, Quebec, according to a design developed at the Polymer Corporation, Sarnia, Ontario (10). The capillary was 18.5 cm long and had an inside diameter of 0.0356 cm.

The viscometer was suspended in a water bath at 34.8 ± 0.02°C and flow times were measured to with 0.05 sec. for the solvent and for several concentrations of the polymer solution. The flow time for toluene was about 96 seconds, and the concentrations of the polymer solution was adjusted so as to give flow times of from 1.1 to 2.0 times that of the solvent.

A small kinetic energy correction was applied to the flow times. The relative viscosity (η_r) was obtained for a given polymer concentration from the ratio of the corrected flow time of the solution to that of the pure solvent. The specific viscosity ($\eta_{sp} = \eta_r - 1$) divided by the concentration was then extrapolated graphically to zero concentration to give the intrinsic viscosity ($[\eta]$). Extrapolation of the function $(\ln \eta_r)/c$ to zero concentration also yields the intrinsic viscosity, giving a check on the extrapolation procedure.

These relationships can be expressed in the form proposed by Huggins (27)

$$\eta_{sp}/c = [\eta] + k' [\eta]^2 c \tag{43}$$

and

$$(\ln \eta_r)/c = [\eta] - k'' [\eta]^2 c \tag{44}$$

and it can be shown that $k'' = k' - 1/2$. This, then, provides one further check on the method of extrapolation. k' was found to be in the range from 0.34 to 0.37 for polypentene in toluene.

A typical set of data is shown in Table VI with the corresponding double extrapolation plot shown in Figure 26.

3. Osmotic Pressure - Osmotic pressure measurements of the static head type were made using Johnson-Sands type osmometers. The semipermeable membranes used were "undried regenerated cellulose" having a wet thickness of 0.004 inches. They were supplied by the Sylvania Industrial Corp., Fredericksburg, Virginia.

The membranes were conditioned by gradually displacing the water in the membrane with acetone (in a four step procedure) and then transferring the membrane's directly to toluene.

Solutions of the polymer in toluene, varying in concentration from 0.1 to 1.0 g. per 100 cc., were prepared as described previously (page 48). Three or four concentrations were required for each molecular weight determination.

The osmometer assemblies were placed in a water bath maintained at 34.8 ± .02°C. The difference in liquid level between the osmotic pressure and reference capillaries was obtained with a cathetometer as a function of time. Equilibrium was generally reached after several days and readings were continued for at least six days. Often, after equilibrium had been reached, a decrease in the height was noted which was ascribed to the "leakage" of low molecular weight polymer through the membrane. Thus, the linear portion of the height vs. time plot was extrapolated to zero time. In this way, the osmotic pressure rise, expressed in terms of centimeters of toluene, was obtained for a series of polymer concentrations.

Since polymer solutions are non-ideal at finite concentrations, extrapolation to zero concentration is necessary. The relationship which is found to represent the osmotic pressure behavior at finite concentrations is:

$$\pi/C = (\pi/C)_o + B\,C \tag{45}$$

where π is the osmotic pressure, C the polymer concentration, and B a constant. By plotting (π/C) versus concentration an intercept is obtained which corresponds to the osmotic pressure of the ideal polymer solution. The number average molecular weight $(\bar{M}_n)$ can then be obtained from the relationship:

$$\bar{M}_n = RT/\ (\pi/C)_o \tag{46}$$

where R is the gas constant and T the absolute temperature.

A typical set of data are given in Table VII and plotted in Figures 27 and 28. Sample calculations are also given in Table VII.

D. Crystallinity Measurements

1. Preparation of the Samples - Film samples of the polypentene were used for both the x-ray and density measurements. Polymer which had been treated as described previously (page 48) was dissolved in toluene to give about a 2 percent solution. This solution was then filtered through a coarse sintered glass filter directly onto a mercury surface after which the toluene was allowed to evaporate under partial vacuum at room temperature. The resulting films varied in thickness from 15 to 40 mils.

These films were then exposed to a vacuum of about 10^{-3} mm. Hg. for several weeks during which time they were periodically heated to 50°C and then cooled slowly to room temperature. By this process it was hoped that all of the toluene would be removed and that maximum degree of crystallinity would develop in the polymer films.

2. Density Measurements - The densities of these film samples were determined in a density gradient column. The column was set up according to a method described in the literature (1,88). It was about 40 cm. high by 7 cm. in diameter and was maintained at 25.0°C ± 0.1°C by means of constant temperature water bath. The liquids used in the column were water and isopropyl alcohol.

Glass floats, blown from 2 mm O.D. capilliary tubing were calibrated by titrating the IPA with water to find the composition which just balanced the float. The liquid density was then determined with a Westphal balance. Four of these floats were obtained in the desired density range.

The floats settled rapidly when put into the column reaching their respective levels in less than a minute and no change in position was noted after 10 minutes. Furthermore, no change in the position of the floats was noted after 24 hours during which time all of the film densities were obtained. Figure 33 shows the calibration of density as a function of height in the column as determined by the float positions.

The density of the polymer film samples was then determined by dropping pieces of the film into the column and noting the equilibrium height. These pieces were of different shapes but all roughly 4 mm in diameter. The heights, measured by a cathetometer, were taken for the approximate center of gravity for the specimen. For the polymer samples, equilibrium was reached more slowly than for the glass floats. A time of about one hour was required before no further change in position was noted.

3. X-Ray Measurements - X-ray diffraction patterns were obtained using a Phillips x-ray unit with a flat film camera. Nickel filtered Cu K radiation was used. Kodak non-screen medical film was employed and the sample to film distance was 4.4 cm. The films were exposed for 15 minutes while the x-ray unit was operating at 40 kilovolts and 20 milliamps.

The x-ray unit was also equipped with a goniometer which made possible the quantitative determination of the intensity of the diffracted x-rays as a function of the radial angle (2θ). The transmission technique was used and the diffraction pattern was determined for the range in 2θ from 4° to 30°. The x-ray beam was collimated with two 1° slits.

A typical diffraction pattern of this type is shown in Figure 29. Two major corrections must be made if the patterns of two different samples are to be compared quantitatively. The first is for background scattering and this can be obtained by measuring the x-ray intensity over the angular range to be studied, with no sample present. This scattering was found to be essentially constant for the time in which measurements were made. The x-ray pattern for a given sample is corrected by subtracting the intensity of background radiation for a given angle from the observed intensity at that angle. The second correction is for sample thickness. In the case of transmission patterns the intensity of the radiation at any angle should be directly proportional to the thickness of the sample, if absorption by the sample can be neglected. Experiments showed that this assumption was essentially valid, especially since sample thicknesses did not vary greatly.

The corrected intensity at a given angle $(I_{2\theta})_{corr}$ was obtained then according to the relationship:

$$(I_{2\theta})_{corr} = \frac{(I_{2\theta})_{obs.} - (I_{2\theta})_B}{t} \qquad (47)$$

where $(I_{2\theta})_{obs}$ is the observed intensity, $(I_{2\theta})_B$ the intensity of background scattering, and t the sample thickness.

E. Surface Area Measurements

1. <u>Volumetric Adsorption Apparatus</u> - The apparatus used to make the surface area measurements was essentially the same as that described by Craig(9). It consisted of a standard vacuum manifold to

which was connected a system containing a monometer, a calibrated gas burette, connections for the sample tubes, and a reservoir for the nitrogen.

Matheson prepurified nitrogen (99.996 mol percent min.) was used without further treatment. The sample tubes, about 10 cc in volume, had two inlets. One was a capillary tube with which the sample tube was connected to the system. The second was a section of 8 mm tubing through which the $TiCl_3$ was added to the sample tube which was sealed off with a torch immediately after filling.

2. General Procedure - The titanium trichloride was added to the sample tubes inside of the dry box and the entrance tubing sealed off with a torch. (The titanium trichloride weight was obtained by difference from the tube weight before and after filling.) The sample tube was then connected to the system and evacuated obernight or until a pressure of 10^{-4} mm. of mercury or less was obtained.

The total volume of the system was adjusted by means of the gas burette. This volume, up to the stopcock connecting the sample to the system, was known from previous calculation but the void volume in the sample tube was not known. This was calculated, using ideal gas law relationships, by adding nitrogen to the system, noting the pressure and then opening the stopcock to the evacuated sample tube (at room temperature) and noting the decrease in pressure. During a run this void volume in the sample tube consisted in two parts, the volume at room temperature and that at the liquid nitrogen temperature. The room temperature volume was calculated from the dimensions of the capillary tubing.

After determining these volumes the sample tube was immersed in liquid nitrogen and after equilibrium was reached the pressure was recorded along with appropriate temperatures. The temperature of the liquid nitrogen was determined with a vapor pressure thermometer. From these data the volume increment adsorbed could be calculated. The stopcock was then closed, more nitrogen was let into the system, and the pressure noted. The stopcock was reopened and a second equilibrium point was obtained by noting the equilibrium pressure and making the appropriate calculations. In this manner three or four equilibrium points between $p/p_o = 0.05$ and $p/p_o = 0.35$ were obtained.

3. Calculations - The volume of nitrogen adsorbed between any two equilibrium points was calculated from the following equation:

$$V^* = \frac{22,414}{R}\left[\frac{(p_i - p_f)V_1}{T_b} - \frac{(p_f - p_f')\,V_2}{T_r} - \frac{(p_f - p_f')V_3}{T_{N_2}}(1+\alpha)\right] \qquad (48)$$

where

V^* = volume of gas adsorbed between any two equilibrium points at standard temperature and pressure.

R = 62,360 cc. mm. mole $^{-1}$ deg^{-1}

$(p_i - p_f)$ = pressure decrease during adsorption step

$(p_f - p_f')$ = difference between final equilibrium pressure and previous equilibrium pressure.

V_1 = calibrated volume

V_2 = void volume at room temperature

V_3 = void volume at liquid nitrogen temperature

T_b = temperature of gas burette

T_r = room temperature

T_{N_2} = temperature of liquid nitrogen

α = constant related to non-ideality of N_2 gas.

From these equilibrium data the surface area of the titanium trichloride was obtained using the multilayer adsorption theory of Brunauer, Emmett, and Teller (6). In its linear form the B. E. T. equation is:

$$\frac{p/p_o}{V_T\,(1 - p/p_o} = \frac{1}{V_m\,C} + \frac{C-1}{V_m\,C}\left(\frac{p}{p_o}\right) \qquad (49)$$

where

V_T = total volume of nitrogen adsorbed at pressure p

p = pressure

p_o = saturation pressure of the adsorbate

V_m = volume of nitrogen adsorbed at monolayer coverage

C = a constant related to the heat of adsorption

Thus, a plot of $\left(\frac{p/p_o}{V\,(1 - p/p_o)}\right)$ versus (p/p_o) should give a straight line whose slope is $(C-1)/V_m C$ and whose intercept is $1/V_m C$. From these two values the volume of nitrogen adsorbed at monolayer coverage can be calculated, and accepting a value of 16.2 $\mathring{A}^2$ as the cross sectional area of the nitrogen molecule the specific surface area (s) can be calculated according to the relation:

$$s = 16.2 \frac{Vm}{g} \left(\frac{p}{RT} \right) \qquad (50)$$

where T and p refer to standard temperature and pressure and g is the weight of the titanium trichloride.

One set of data together with the calculated data are given in Table IX while Figure 30 shows the data plotted according to the B. E. T. equation.

F. Experimental Errors

1. Rate Measurements - In the determination of the actual rate of polymerization determinant experimental errors arose in (1) the weighing of the sample, (2) the weighing of the polymer sample, and (3) the time measurement. The usual sample weight was about 1.5 g. and this was weighed to the nearest 0.001 g. The polymer weight varied from 0.001 to 0.03 g. and this could be obtained to within 0.0001 g. The times were measured to the nearest tenth of a minute with the usual time interval being about 100 minutes. Since at least 5 points were obtained, the rate being the slope of the line through these points,

a fair estimate of the probable error in the calculated rates could be obtained. This estimate of the possible error ranged from ± 10 percent for the low rates to about ± 1 percent for the higher ones.

These estimates would also include the less determinant errors involved. These would include (1) evaporation of the sample after withdrawal, (2) non-homogeneous sampling, (3) incomplete drying of the polymer, and (4) loss of the polymer in transfer operation. It is felt that errors introduced in these ways were generally neglible since the estimated errors correspond fairly well to the determinant errors.

The monomer concentration measurement should involve errors of less than 1 percent while the weighing of the $TiCl_3$ into the reaction flask should involve errors of less than 3 percent. However, the problem of reproducible sampling of the $TiCl_3$ suspension in n-heptane probably introduced errors of up to 20 percent in the measurement of the actual $TiCl_3$ concentration.

The bath temperature was maintained within ± 0.1°C of the desired temperature and it was felt that heat transfer was quite adequate to maintain the reaction temperature within these limits for most of the work. However, since the heat of polymerization is large it is quite possible that some temperature rise occured during runs with high rates of polymerization. Since this would be a "snowballing" effect this probably explains the occasional high rates obtained at very high monomer concentrations.

In general rates could be reproduced within about 15 percent but occasionally greater deviations were found.

2. Molecular Weight Measurements - The determinant errors involved in measuring the intrinsic viscosity were errors in measuring flow times and errors in measuring the concentration. Errors such as the presence of dust in the capillary or in dilution would normally be noticed in analysis of the data. The concentrations could be measured to within about 2 percent while the other errors appeared to be of negligible significance. Duplicate runs were found to be reproducible within about 5 percent.

The aluminum triethyl concentration was determined by weight, the error in which was less than 2 percent. However no analysis of the concentration of the original $AlEt_3$ solution in n-heptane was obtained so that there is a possible error of perhaps 10 percent in the absolute concentrations. This would not affect the relative concentration or the conclusions drawn from these data. Impurities in the reaction mixture would cause a decrease in the $AlEt_3$ concentration. An estimate of the concentration of such impurities was measured by titration and found to be less than 0.001 moles per liter. This would be appreciable at the lower $AlEt_3$ concentrations (25 percent at the lowest concentration used) but varied too much to allow a correction factor to be applied.

The major errors involved in measuring the osmotic pressure molecular weights cannot be evaluated precisely. These would include leakage of the low molecular weight polymer through the membrane and errors in extrapolating the osmotic rise to zero time. In general, osmotic pressure gives molecular weights within about 20 percent. It is felt that these data are somewhat less accurate than this.

3. Crystallinity Measurements - The relative densities of the polymer films should be quite precise (within 0.1 percent). The major errors involved in this measurement would be the presence of bubbles or foreign material in the film and this generally was quite apparent.

The absolute densities depend on the calibration of the floats for the density gradient column and could be in error by as much as 1 percent.

The absolute crystallinities calculated from the density measurements depend on an estimated density of the pure crystalline polymer and this estimate could be in considerable error. Thus, these crystallinities could be in error by as much as a factor of 2.

No quantitative data were obtained from the x-ray investigation.

4. Surface Area Measurements - The reproducibility of the surface area measurement was quite good (variation of less than 5 percent).

Measurements subject to experimental error would include weighing of the sample (± 1 percent), measurement of the volume of nitrogen adsorbed ($<$ 1 percent), and temperature measurements (small effect). The presence of impurities in the sample and nitrogen would introduce errors which account for the observed variation. These errors, furthermore, would be similar for each of the four runs made so that the error involved may be somewhat greater than the variation which was observed.

V. RESULTS AND DISCUSSION

A. Rate of Polymerization

1. Preliminary Studies - The rate of polymerization investigation was primarily concerned with the effects of temperature, monomer and titanium trichloride concentrations, and specific surface area of the catalyst. A number of other reaction variables were investigated for the purpose of showing either that the reaction rate was independent of the variable or what magnitude of error might be expected from unintentional changes in the variable.

The polymerization rates, in terms of grams of polymer formed per hour per liter of reaction mixture, were obtained according to the methods described previously (page 42).

The effect of stirring rate was obtained by varying the setting on a magnetic stirrer such that the rotation of the stirring bar was varied from zero to the maximum stable rate. The reaction flask was baffled so as to promote mixing. The results, presented in Table XII, show that no appreciable effect was obtained.

The aluminum triethyl concentration (C_A) was varied over a ten fold range and polymerization rates were obtained. Again, no effect was obtained and these results are shown in Table XIII.

Several runs were made under typical conditions except that one of the catalyst components was left out. Thus, a run was made with titanium trichloride and 1-pentene but no aluminum triethyl; and one with aluminum triethyl and 1-pentene but no titanium trichloride; and one with aluminum triethyl, 1-pentene, and the supernatant heptane from a titanium trichloride suspension but no solid titanium trichloride. This last run was to check whether there was a sufficient quantity of titanium tetrachloride (or other soluble material) in the titanium trichloride suspension to affect the polymerization rate. No polymer was obtained from any of these runs after long reaction times.

Variations in method of preparing the reaction mixture were investigated. The usual preparation method (mixing together solvent, monomer, and alkyl and then adding titanium trichloride) was checked with regard to the time between addition of alkyl and titanium trichloride and the temperature at which the catalyst components were mixed. No effect of time between addition of components was noted but about a ten percent decrease in the rate was noted when the catalyst was mixed at 10°C rather than the usual 24°C. Since the temperature at which the catalysts were mixed was held at 24° ± 1.0°C, this variation was not considered important.

As a further check in variations of preparative methods, the order of reactant addition was investigated. If the monomer, solvent, and titanium trichloride are mixed first and then the aluminum alkyl added, an appreciable decrease from the expected rate is observed. If the two catalyst components are mixed and immediately added to the reaction mixture the predicted rate is obtained. If the premixed catalysts are allowed to stand for longer periods of time at room temperature the activity of the catalyst decreases until after about two weeks essentially no polymerization is obtained. Further discussion of these last observations will be presented in a later section (page 87).

Finally, a qualitative study of the effect of impurities was made. It was found that polar impurities such as oxygen and water have no effect on the rate if they are added before the titanium trichloride is added. If they are added after the titanium trichloride, then an appreciable decrease in rate is noted.

These results have been interpreted in light of the theoretical discussion presented previously. The independence of the rate of polymerization on the stirring rate, while not a conclusive proof, supports the theory that diffusion rates are not important in the overall rate process. The independence of the rate on the aluminum alkyl concentration suggests that the alkyl is strongly adsorbed on the titanium trichloride surface or is present in excess. This latter statement is supported by a radio active tracer study made by Natta (42) which showed that with a similar catalyst system the ratio of moles of active sites to the moles of solid titanium trichloride was about 100:1. Appreciable variation in this ratio can be expected for different catalysts but it does indicate that for the apparent Al/Ti ratios used in this study, the ratio of moles of alkyl to moles of active titanium trichloride sites is probably closer to 100:1 than to unity and thus the alkyl would be in large excess.

The fact that no polymerization occurred in the absence of alkyl again supports the adsorption mechanism proposed, and suggests that there should be a range of alkyl concentrations at which the rate is proportional to this concentration. The nature of the alkyl in its role as scavenger for impurities made it impractical to obtain rates at alkyl concentrations much lower than were obtained.

The effect of polar impurities can be explained by the fact that the aluminum triethyl acts as a scavenger, and since it is present in excess, changes in its concentration will not affect the rate. Thus, when polar impurities are introduced before the titanium trichloride is added, they will react with the alkyl. If they are added after the titanium trichloride, then a portion of these impurities will react with active sites on the titanium trichloride. This also serves to explain the lower rates obtained when the titanium trichloride is added to the reaction mixture before the alkyl.

2. Effect of Titanium Trichloride Concentration - The effect of the titanium trichloride concentration on the rate of polymerization was determined by varying the quantity of a single titanium trichloride suspension in the reaction mixture over a six fold range while all other variables were held constant. These results, as shown in Figure 4 (also see Table XIV), indicate a first order dependence of the rate on the titanium trichloride concentration but a non-zero intercept.

This non-zero intercept was attributed to impurities in the reaction mixture which did not react with the aluminum alkyl but which did react with the active catalyst sites.

Knowing the apparent concentration of the titanium trichloride in the suspension which was added to the reaction mixture, one should be able to relate the reaction rate to the actual concentration of solid titanium trichloride in the reaction mixture. It was found, however, that when a second suspension of titanium trichloride in n-heptane was prepared (using the same solid titanium trichloride) the rate results, based on the calculated concentration of solid titanium trichloride in the reaction mixture, did not yield the same rate constant obtained with the first titanium trichloride suspension.

In light of the previous discussion of the effect of impurities, an explanation for this difference was apparent. The n-heptane

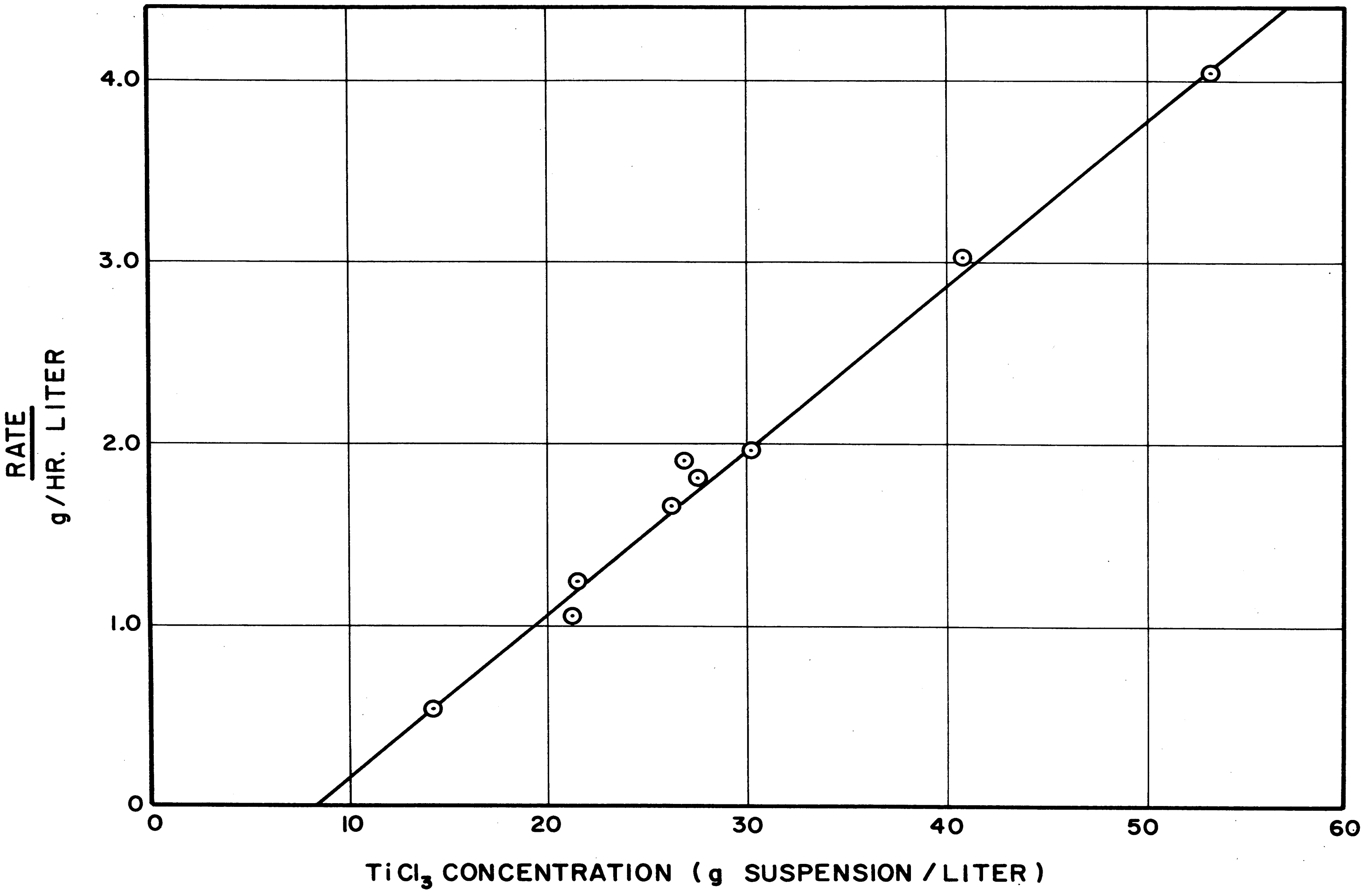


Figure 4. Effect of $TiCl_3$ Concentration on the Polymerization Rate

used in the preparation of the titanium trichloride suspension contained a small quantity of impurites which reacted with the active sites on the surface of the solid titanium trichloride. Thus, if the impurity level in the n-heptane varies or the heptane-titanium trichloride ratio is changed, the extent to which the impurities cause a decrease in active titanium trichloride concentration will change.

In order to obtain a rate constant characteristic of the solid titanium trichloride the relative impurity level in the titanium trichloride suspensions was varied systematically. This was accomplished by preparing a series of titanium suspensions using the same batch of n-heptane and the same solid titanium trichloride but varying the concentration of the titanium trichloride in the suspensions. Rate measurements were then made using varying amounts of each of the titanium trichloride suspensions. If these results are plotted in terms of rate vs. apparent titanium trichloride concentration in the reaction mixture, linear relationships are obtained which have the same non-zero intercept but which vary in slope (or specific rate) according to the concentration of the titanium trichloride in the n-heptane suspension. A typical set of results for three different titanium trichloride suspensions are shown in Figure 5.

We can now use these data to calculate the concentration of impurities in the n-heptane, used for making up the titanium

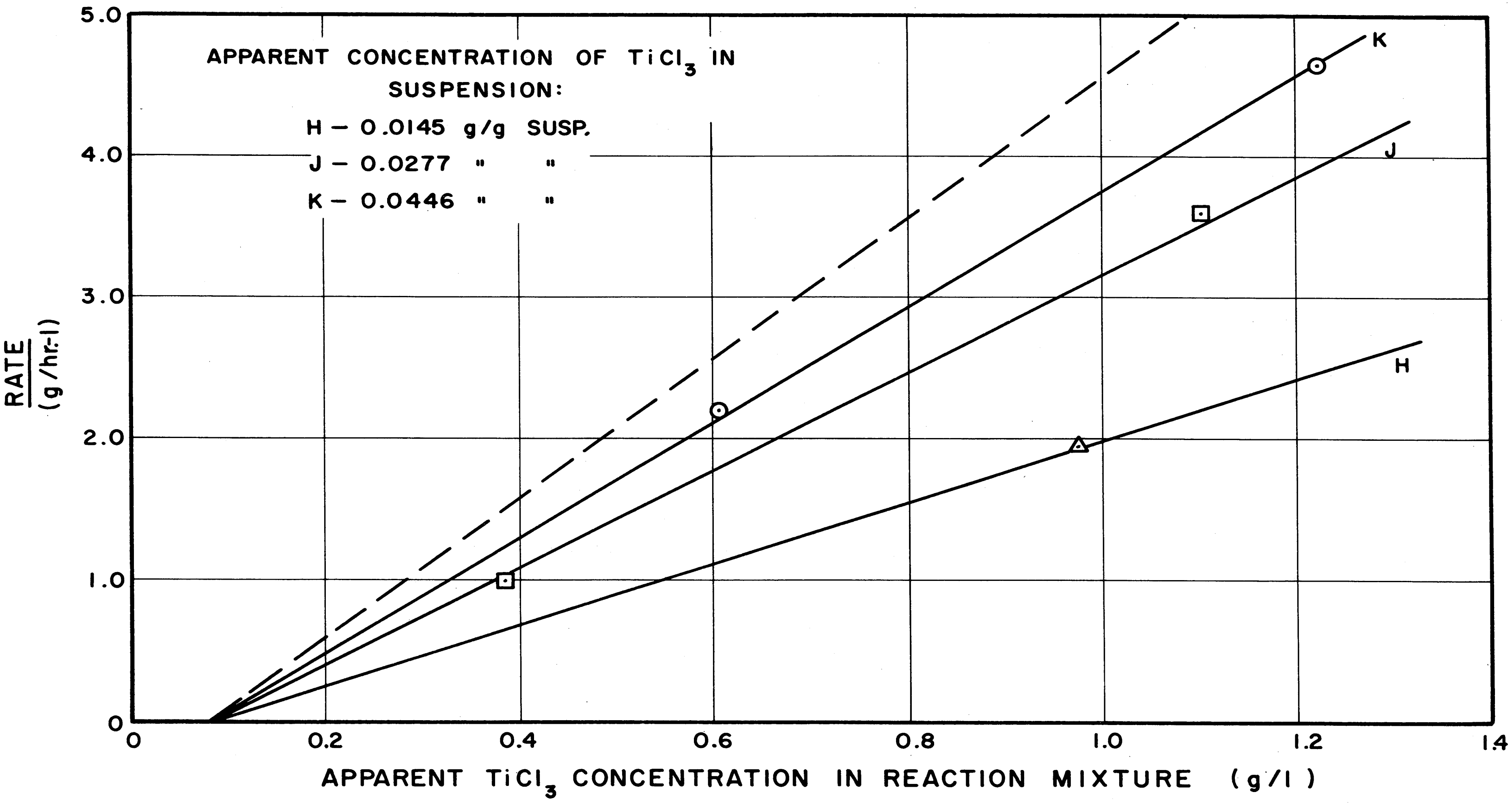


Figure 5. Effect of $TiCl_3$ Concentration on Rate Using Various $TiCl_3$ Suspensions

trichloride suspensions, in terms of grams of solid titanium trichloride deactivated per gram of n-heptane. This quantity can be determined from data for two titanium trichloride suspensions so that the use of more than two suspensions gives a check not only on the value of the impurity concentration but also on the validity of the method.

The concentration of "active" titanium trichloride in each suspension can then be calculated (see Table V). If the data used in Figure 5 are plotted as a function of the titanium trichloride concentrations in the reaction mixture, based on these "active" titanium trichloride concentrations, the dashed line in Figure 5 is obtained.

In addition to the three titanium trichloride suspensions shown in Figure 5 six other suspensions were prepared using a different n-heptane batch and a similar set of data was obtained. Both of these sets of data are shown in Figure 6 and it can be seen that excellent agreement was obtained. Because different batches of solvent and monomer were used in the polymerizations for the two sets of data, slightly different non-zero intercepts were found from the rate vs. titanium trichloride concentration curve. Thus in Figure 6 both sets of data have been corrected to give a zero intercept so that the data can be compared directly.

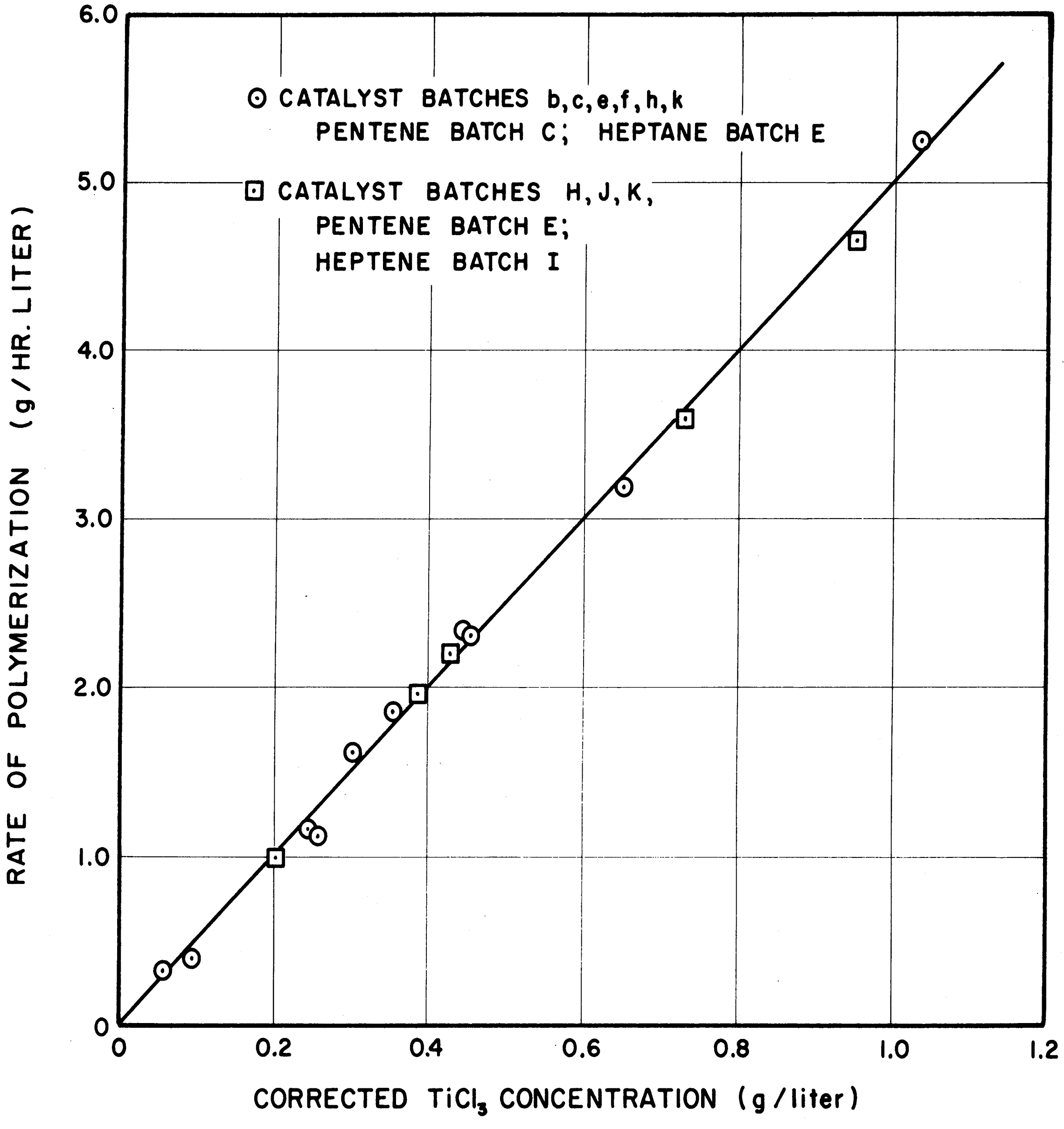


Figure 6. Rate of Polymerization vs. Active $TiCl_3$ Concentration

In this manner a specific rate (g. /hr - g. $TiCl_3$) was obtained at one temperature and monomer concentration, which was believed to be characteristic of the solid titanium trichloride.

On further situation arose which required correction of the calculated data. This was a decrease in the activity of the titanium trichloride suspensions with time. This decrease in activity was noted when, after several days, an attempt to duplicate some of the data discussed above resulted in lower rates than would be predicted. In order to account for this, "calibration runs", that is, runs made under the same conditions as the original set of data, were made periodically and an "activity" was calculated from the ratio of the rate obtained to the predicted rate. This activity is plotted in Figure 7 as a function of time for the two titanium trichloride suspensions used for the bulk of the rate determinations. It can be seen that after an initial drop of ten to fifteen percent this activity appeared to remain constant except for a possible further drop at the end of the time during which rate measurements were made.

Thus, for the purpose of correlating the rate data obtained as a function of monomer concentration, the concentrations of titanium trichloride in the two catalyst suspensions were corrected by constant factors. In light of the experimental errors encountered in this work, these corrections are not of great significance.

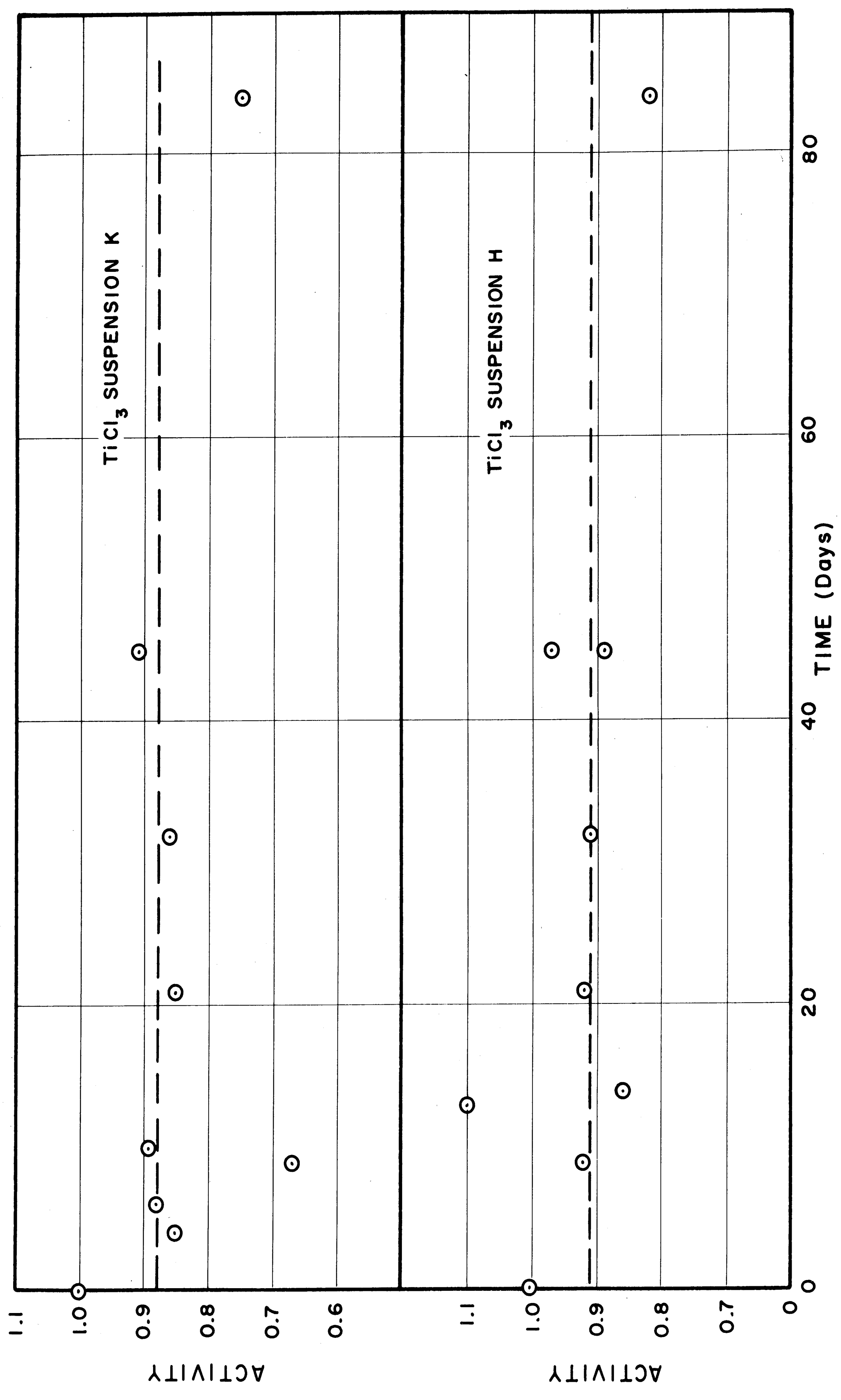


Figure 7. Activity of $TiCl_3$ Suspensions vs. Time

3. Effect of Monomer Concentration - In order to study the effect of monomer concentration, the rate vs. titanium trichloride concentration relationship was determined for a series of monomer concentrations varying from 5 to 95 percent by volume, at two temperatures. These data, shown in Figures 8, 9 and 10 indicate the same first order dependence on the titanium trichloride concentration as was obtained above. No definite trend is obtained in the non-zero intercepts of these curves due to the necessity of using different batches of monomer and solvent for the different monomer concentrations.

The slope of each of these lines, a specific rate of polymerization, was then plotted as a function of monomer concentration as shown in Figure 11. The plots for the two temperatures both appear to be linear although some deviation from linearity might be inferred at the higher monomer concentrations at the lower temperature.

This first order dependence of the rate on the monomer concentration is in accord with the proposed adsorption mechanism for the case in which the monomer is weakly adsorbed on the catalyst site. If the deviation from linearity were to be real, this also would be in accord with the adsorption mechanism for the case of intermediate monomer adsorption; but it is not felt that the data are accurate enough to support, with any force, anything other than a first order dependence on monomer concentration.

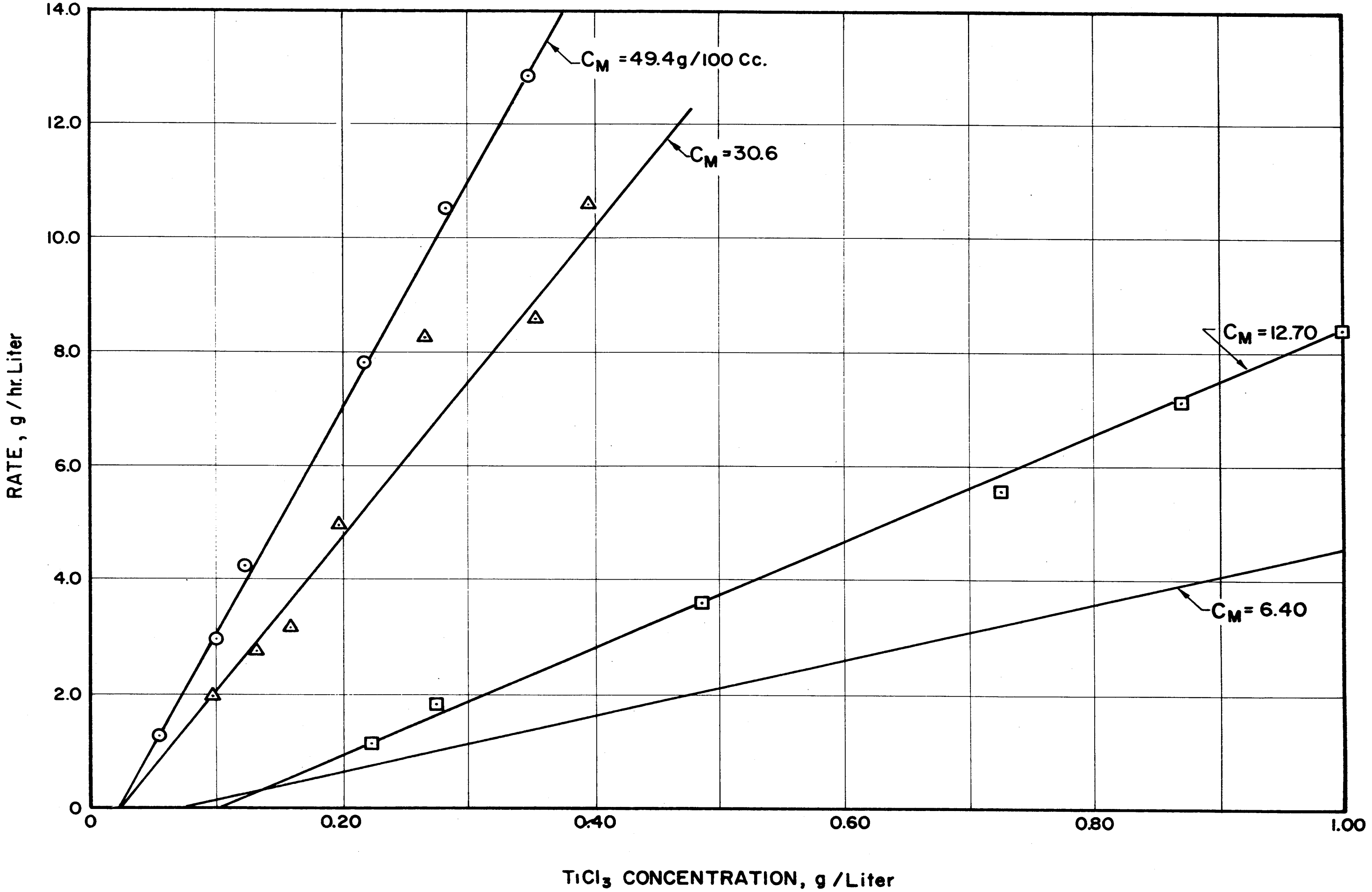


Figure 8. Effect of $TiCl_3$ Concentration on Rate at Various Monomer Concentrations, Temp. 44°C

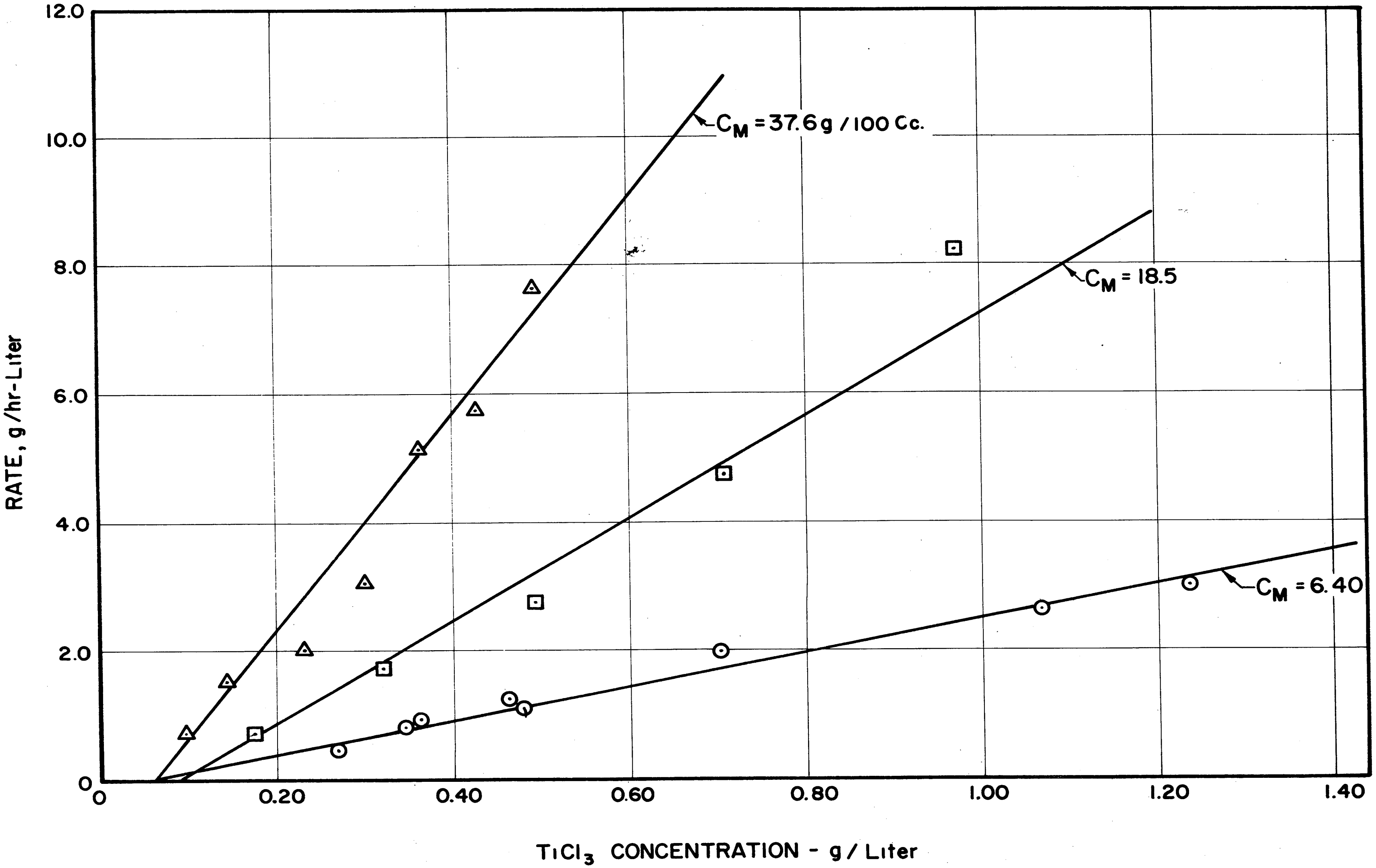


Figure 9. Effect of TiCl$_3$ Concentration on Rate at Various Monomer Concentrations, Temp. - 25.2°C

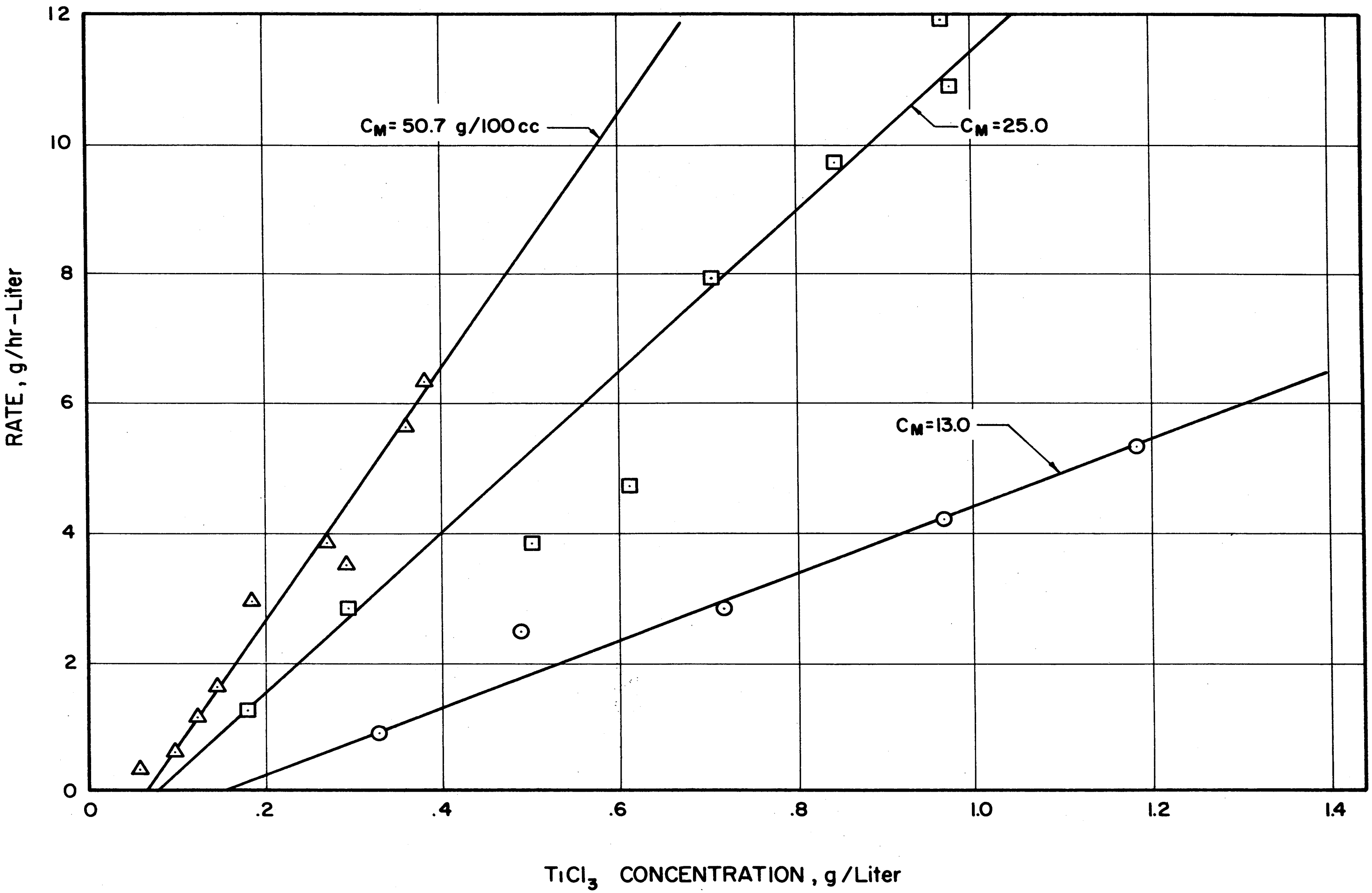


Figure 10. Effect of $TiCl_3$ Concentration on Rate at Various Monomer Concentrations, Temp. 25.2°C

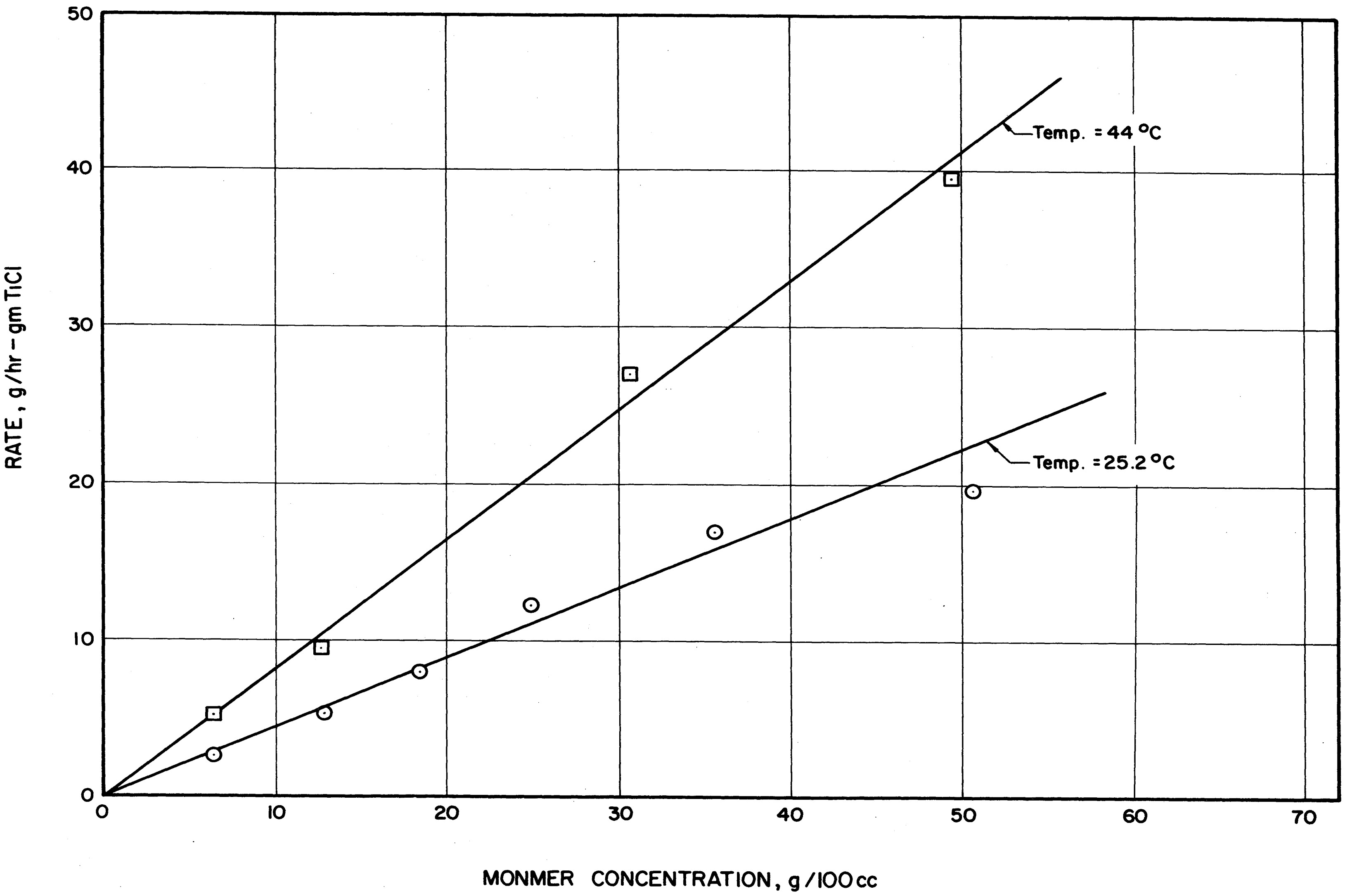


Figure 11. Effect of Monomer Concentration on the Rate of Polymerization

4. Temperature Effects - The effect of temperature on the rate was determined by measuring the polymerization rates at two temperatures for the same reaction mixture as described previously (page 46). The second of these rates was corrected for changes in specific volume (due to the temperature change) and for monomer concentration (due to conversion to polymer). The ratio of these two rates was found to be essentially independent of all reactant concentrations over the range studied, as would be expected on the basis of the rate equation obtained thus far.

A range of temperatures from 0° to 86°C was studied. These data are shown in Figure 12 in the usual Arrhenius form. In this case the logarithm of the ratio of the rate at temperature (T) to the rate at 25.2°C is plotted vs. reciprocal temperature.

Several observations concerning these data should be made. First, in the polymerization in the range of 0°C a noticeable agglomeration of the catalyst occurred. Second, in the polymerization at 86°C a rapid decrease in the rate of polymerization was noted with time, as can be seen from Figure 3. Both of these situations could possibly cause a decrease in the observed rate. The low temperature might lead to diffusion problems while at the higher temperature, where the initial rate should be used, the problem of temperature equilibrium in the reaction flask could become important. The rates at 86.2° were

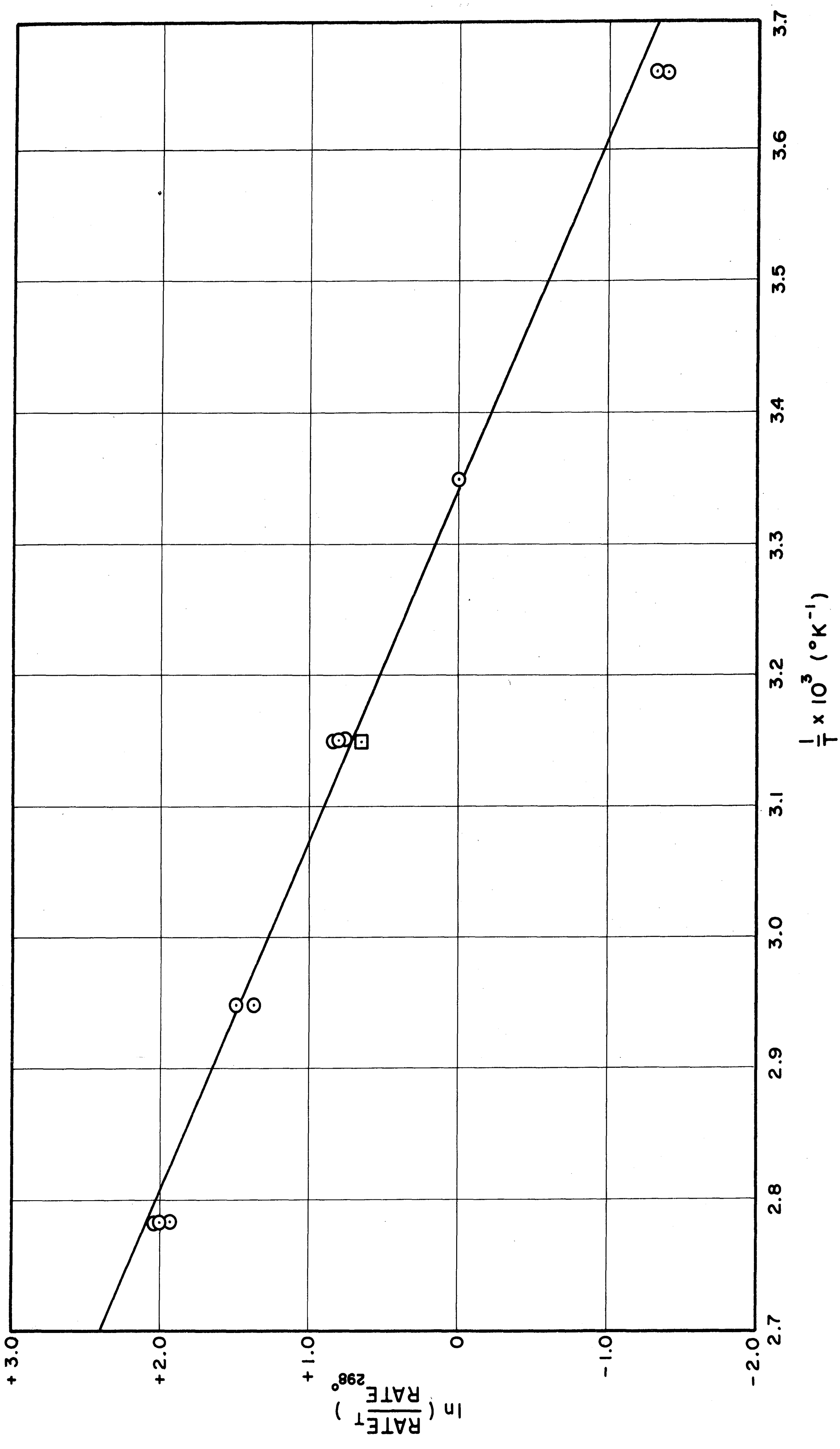


Figure 12. Effect of Temperature on the Rate of Polymerization

obtained by extrapolating the function $\left(\frac{[P] - [P]_0}{t}\right)$ to zero time where $[P]_0$ is the polymer concentration when the reaction flask is put into the high temperature bath. The data at 86.2°C from Figure 3 have been extrapolated in this manner in Figure 13 where it can be seen that the non-linear extrapolation is subject to some error.

Thus, in Figure 12, the Arrhenius relationship has been interpreted as being linear. From the slope of this plot an activation energy of 7.5 kcal per mole is obtained. For this particular system the linear Arrhenius relationship is consistent with the equations derived for the case of more than one type of propagation step because the difference in overall activation energies, as determined from crystallinity measurements, was found to be very small (see page 117).

An analysis of the decrease in rate with time as observed at the higher temperatures lead to some interesting, although approximate results. As a first approximation this decrease in rate can be explained by a decrease in titanium trichloride activity which if first order with respect to the titanium trichloride concentration

$$-\frac{d\,C^*_{Ti}}{dt} = k_d\,C^*_{Ti} \qquad (51)$$

where C^*_{Ti} is the concentration of active titanium trichloride in the reaction mixture and k_d the first order rate constant for deactivation. Integrating this expression we can obtain an expression for C^*_{Ti} which

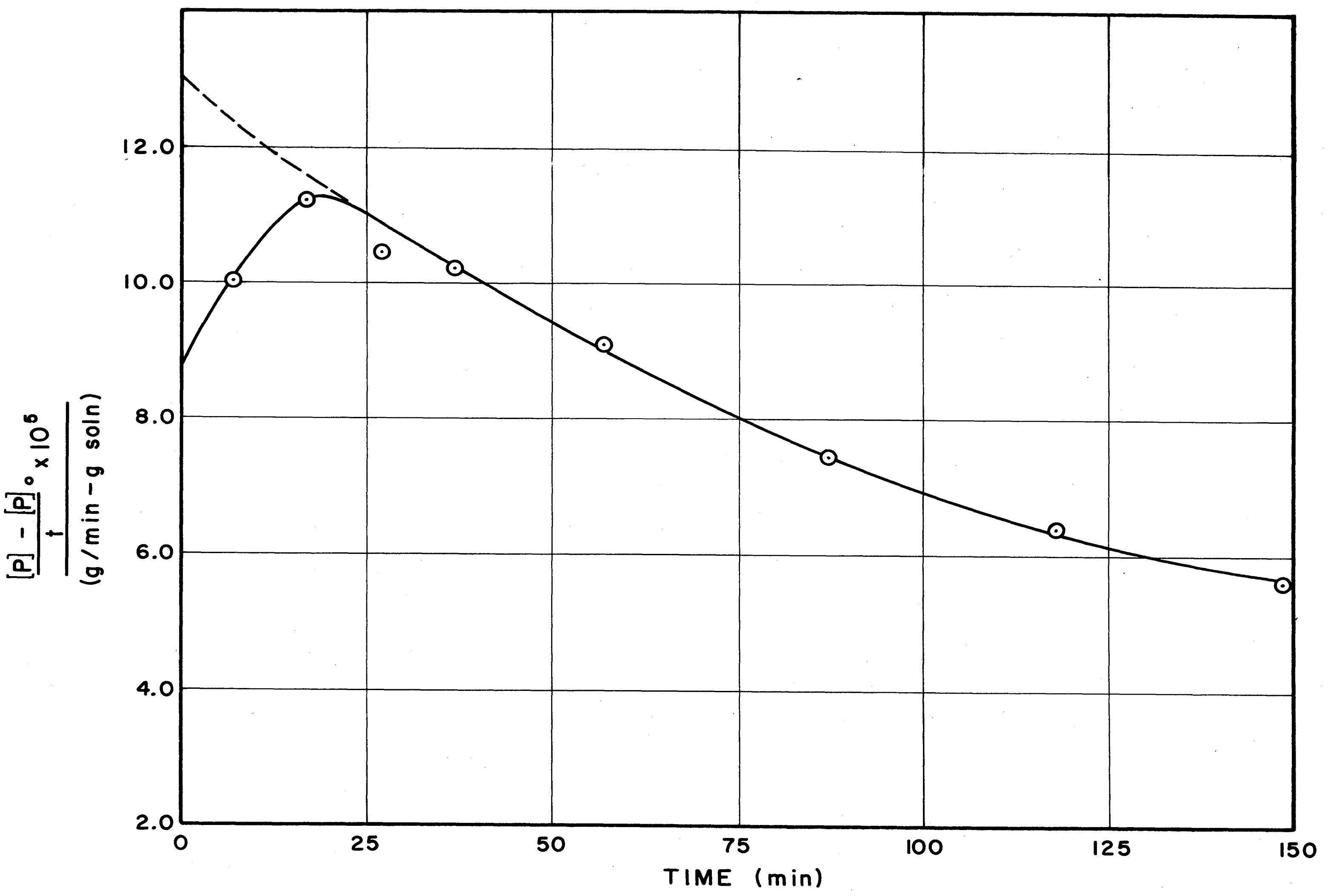


Figure 13. Determination of Initial Rate for Polymerization at 86°C

be used in the rate equation:

$$\frac{d\,[P]}{d\,t} = k_p\, C_M\, (C^*_{Ti})_o\, e^{-k_d\, t} \qquad (52)$$

Thus, a plot of the logarithm of the rate vs. time should yield a straight line whose slope is k_d and whose intercept is the logarithm of the initial rate. Such a plot of the differentiated data from Figure 3 is shown in Figure 14. From this plot it can be seen that, while an approximate fit of the data is obtained, the fit is poorest at low times and therefore this method has not been used to obtain initial rates.

Values of k_d have been obtained in this manner for the four runs made at 86°C and the two runs made at 65°C. These are shown in Table I. At the lower temperatures the effect was too small to detect. However, a rough value of the activation energy for this deactivation can be obtained from these few data and this value is found to be about 20 kcal/mol.

TABLE I

First order rate constants in the deactivation of $TiCl_3$

Run	Temperature (°C)	k_d (hr^{-1})	Al/Ti (mol ratio)
254	86.2	0.81	2.5
255	86.2	0.54	6.7
256	86.2	0.63	3.3
257	86.2	0.72	2.8
261	65.6	0.16	3.3
262	65.6	0.11	1.2

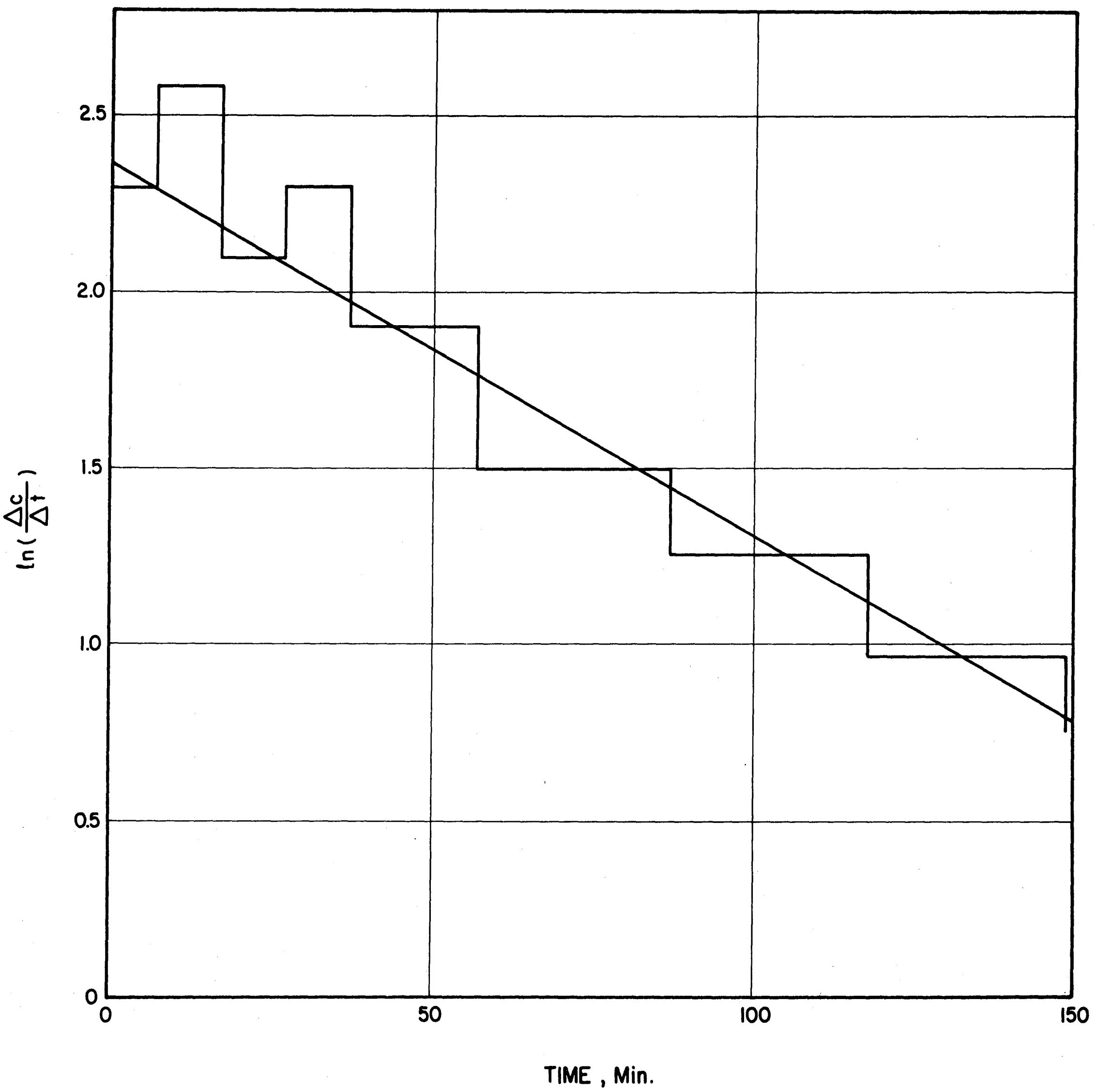


Figure 14. Correlation of Decrease in Polymerization Rate According to First Order Deactivation of $TiCl_3$

One further observation, mentioned previously, which could be related to these data is the decrease in catalytic activity noted when the titanium trichloride and aluminum triethyl were premixed and allowed to stand at room temperature before addition to the reaction mixture. This decrease in activity showed up over a period of days rather than hours and would therefore be of the proper order of magnitude as predicted by the data at higher temperatures. If these phenomena are related it would indicate that this deactivation involved the aluminum triethyl as well as the titanium trichloride. One possible explanation could be that the aluminum triethyl caused the reduction of the titanium trichloride to a lower valence state which was of reduced catalytic activity. In such a case the deactivation rates shown in Table I would be a function of the Al/Ti ratio, but it is not felt that the data are of sufficient accuracy either to support or refute this model.

One other possible explanation for this decrease in activity would be that the $TiCl_3$ particles agglomerate and that this process is faster at the higher temperatures. This has been suggested by Natta (56) for the system $TiCl_3$-$AlEt_3$-propylene, but he found a steady state rate of polymerization after relatively short time intervals which was not observed in this work.

Danusso (15) has reported behavior of a similar nature for the system styrene-$TiCl_4$-$AlEt_3$.

5. Effect of Surface Area - The theory, as developed previously suggests that the rate of polymerization should be proportional to the specific surface area of the $TiCl_3$. In order to study this variable, a second sample of $TiCl_3$ was obtained which was reported to have a higher catalytic activity. This sample was designated as HRA (Hydrogen Reduced, Activated).

A specific rate, characteristic of this sample of $TiCl_3$, was obtained at one temperature and monomer concentration according to the method outlined on page 70. Three $TiCl_3$ suspensions were prepared and the rate data obtained are presented in Table XVI. These data were less precise than those obtained with the first $TiCl_3$ sample because of the smaller quantities of catalyst which were required to obtain a given rate of polymerization. Nevertheless, a rate constant was obtained (believed to be accurate within about 8 percent) which was greater than the first by a factor of 37.

The surface area of these two samples of solid $TiCl_3$ was determined by nitrogen adsorption according to the method described previously. The results of these measurements, shown in Table II, indicate that the ratio of the surface areas of these two samples is only 3.9 to 1.0.

TABLE II

Effect of Surface Area on the Rate of Polymerization

$TiCl_3$ Grade	Sample	Surface Area (m^2/g)	Polymerization Rate[1] ($g/hr.\ g\ TiCl_3$)
Practical	1	0.785	5.0(± 0.2)
	2	0.744	
	avg.	0.77	
HRA	3	2.89	
	4	3.12	185 (± 15)
	avg.	3.0	
Ratio (HRA/Pract)		3.9	37

1. Rate obtained at 44°C and $C_m = 6.40$ g/dl

The data from the surface area determination can also be used to obtain the free energy of adsorption as a function of surface coverage. This relationship should be a measure of the heterogeneity of the surface. It was found that this relationship was almost identical for the two $TiCl_3$ samples and that the surfaces appeared to be quite homogeneous with respect to the adsorption of nitrogen (see Figure 15).

The disparity between the ratio of specific rates and the ratio of the specific surface areas for the two grades of $TiCl_3$ is somewhat surprising. If we accept the proposed mechanism we must conclude that the concentration of active sites per unit of surface area is lower for the $TiCl_3$ (Pract.) by almost a factor of ten.

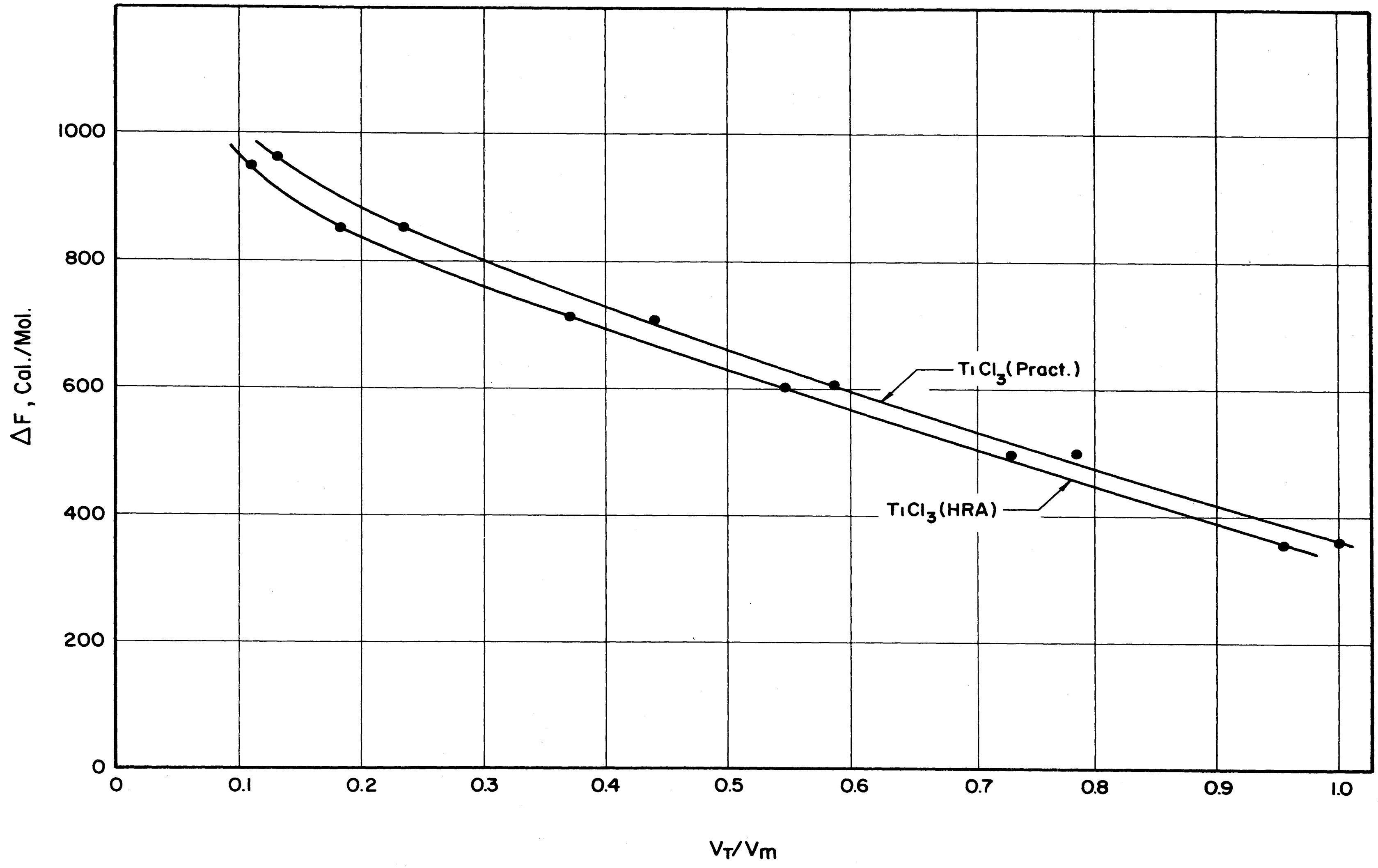


Figure 15. Adsorption Free Energy as a Function of Surface Coverage

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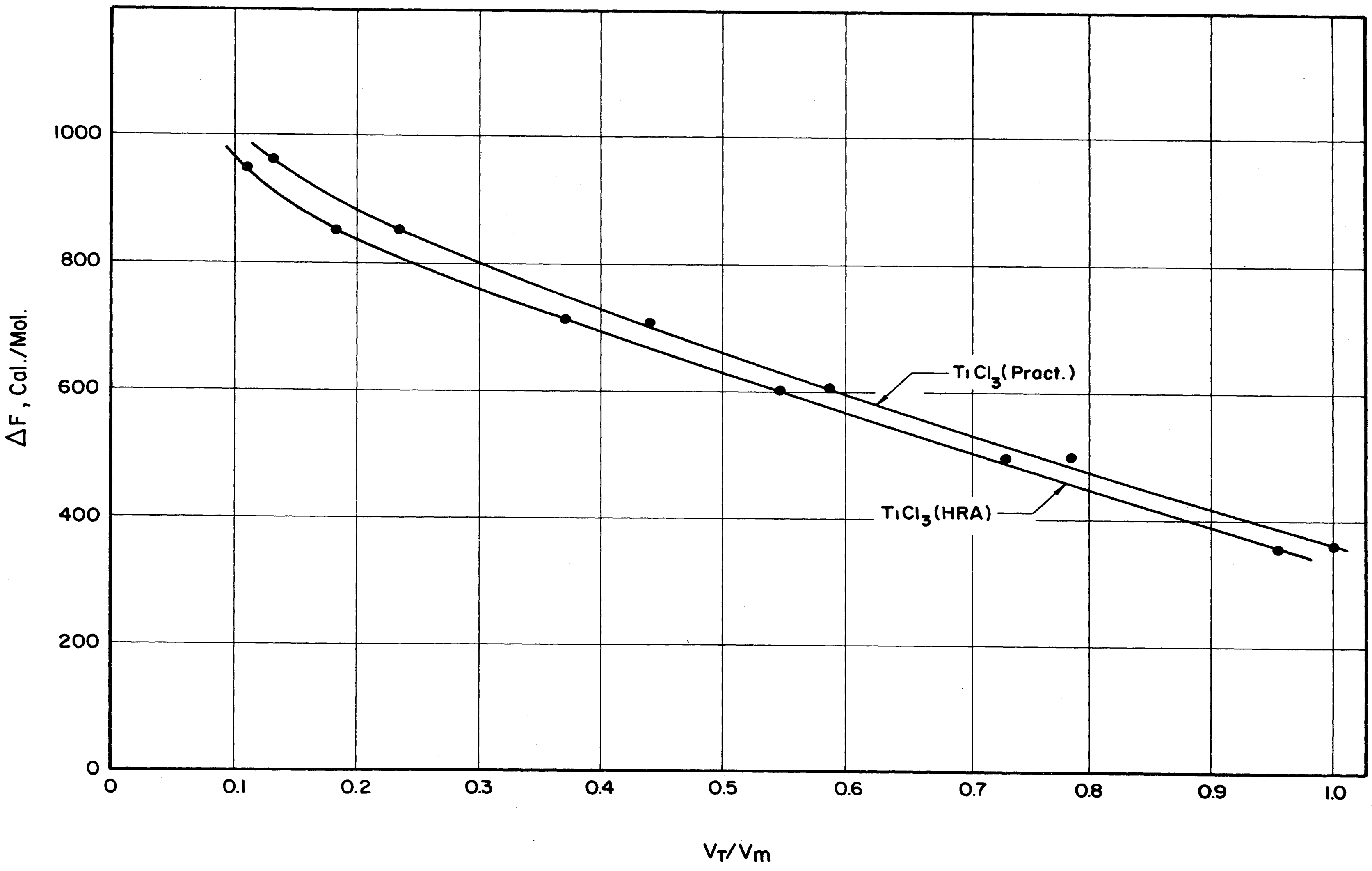


Figure 15. Adsorption Free Energy as a Function of Surface Coverage

In light of the possible differences in the processing of the two grades of $TiCl_3$, it does not seem justifiable to compare them solely on the basis of surface area. Thus both grades were reported to have been produced by the hydrogen reduction of $TiCl_4$, the major difference being that the $TiCl_3$(HRA) was subsequently put through a ball milling process. However, the activated material was obtained some six months after obtaining the 'Practical' grade material, during which time the industrial demand for the product was increasing rapidly so that process improvements were probably being made. Even if no change in the process had occurred it is quite possible that the level of contaminants (oxygen, water vapor, etc.) varied from one batch to the next, thereby changing the catalyst activity.

As mentioned above, Natta (56) has observed a dependence of the rate on particle size such that (a) a steady state rate of polymerization is attained independent of the initial particle size of the $TiCl_3$, (b) the time required to reach this steady state rate is inversely proportionly to the rate, and (c) small particle sizes will give high initial rates which then drop off to the steady state rate. Even though such a mechanism may serve to explain the decrease in rate observed at higher temperatures it should not affect the treatment of the surface area data. Thus, no change in rate with time was observed at the temperatures used to obtain the specific rates given in Table II. It would seem likely, then, that these rates would correspond to the initial rates which Natta found to be dependent on the particle size rather than to the steady state rates.

6. Overall Rate Equation - The results described above can be expressed in terms of an equation for rate of polymerization in terms of the variables studied:

$$\frac{dP}{dt} = A\, e^{-\Delta E/RT}\, C_M\, G^*_{Ti} \qquad (53)$$

where:

$\frac{dP}{dt}$ = Rate of Polymerization (g. polymer/hr)

A = $10^{5.04}$ (dl/hr - g. $TiCl_3$)

ΔE = Overall activation energy = 7,500 (cal/mol)

T = Polymerization Temperature (°K)

C_M = Monomer Concentration (g/dl.)

G^*_{Ti} = Weight of active titanium trichloride (g.)

R = Gas constant = 1.987 (cal./mol. -°K)

The weight of active titanium trichloride will be a function of the weight of titanium trichloride added (G_{Ti}), the quantity of impurities present (G_i), the polymerization temperature and the time of reaction (t):

$$G^*_{Ti} = (G_{Ti} - G_i)\, e^{-k_d t} \qquad (54)$$

where k_d is almost constant except for its temperature dependence.

This temperature dependence can be approximated by the following equation:

$$k_d \cong 10^{11.86} e^{-20,000/RT} \qquad (55)$$

These equations apply to the polymerization of 1-pentene in an inert solvent using a catalyst of titanium trichloride and aluminum triethyl. The titanium trichloride referred to is the "practical powder", although the data for the titanium trichloride (HRA) could be expected to have the same form and activation energy with the pre-exponetial factor A being a factor of 37 greater.

The form of Equation (53) is in agreement with the results obtained by Natta (40) on the system titanium trichloride-aluminum triethyl-propylene, as well as similar results on the system of titanium trichloride-aluminum triethyl-styrene obtained by both Danusso et al., (15) and Burnett and Tait (7). The activation energy obtained is in agreement with that obtained by Burnett and Tait (8 kcal/mol) but somewhat lower than those found by Natta, Danusso et al., for both styrene and propylene (~10 kcal/mol).

B. Degree of Polymerization

1. Preliminary Studies - In the study of the effect of reaction conditions on the degree of polymerization (or molecular weight) intrinsic viscosities were measured as a function of the appropriate variables.

These intrinsic viscosities were then related to the number average degree of polymerization. About fifty runs were made for the specific purpose of obtaining polymer for molecular weight determination. These runs were made with a special titanium trichloride suspension which had been washed thoroughly with n-heptane to remove any soluble material. The method of treating the polymer and obtaining the intrinsic viscosities have been described in a previous section (page 48).

Again, several variables were investigated in order to show that no effect was obtained or to determine what error might be expected from unintentional variations. The concentration of titanium trichloride over a tenfold range, the percent conversion over a tenfold range, and the time of reaction over a twofold range were found to have no effect on the intrinsic viscosity. (see Table XX).

The effect of low titanium tetrachloride concentration was checked because it was found that by washing the titanium trichloride used in the polymerizations, the intrinsic viscosity of the produc was increased appreciably. It was thought that perhaps the soluble titanium tetrachloride was causing this decrease. However, although the titanium tetrachloride did have a small effect, it did not account for the relatively large effect of washing. These data are also shown in Table XX.

These results are all in accord with the theory presented previously (page 32). Natta, however, found a decrease in intrinsic viscosity with increasing titanium trichloride concentration (40). It should be noted that these molecular weight results cannot be compared directly with those of Natta since they have been made on the total polymer while Natta's were obtained mainly for the crystalline fraction obtained by extraction. Also, these polymer samples are all from reactions carried to less than 5 percent conversion so that although no effect of conversion was found here it is quite possible that conversion could be an important factor at a higher level.

2. Relationship Between Intrinsic Viscosity and Number Average Degree of Polymerization - The correlation of intrinsic viscosities with both monomer concentration and aluminum triethyl concentration, while influenced by theoretical considerations, is for the most part empirical. In light of the nature of the data which were obtained the object of this discussion is to show that the data can be explained by the proposed theory rather than offering the data as conclusive proof of the theory.

The intrinsic viscosity data at 22°C are given in Table XXI. One correction has been applied to the intrinsic viscosities from one set of runs (No. 275) and this was to account for a difference of 3°C in the polymerization temperature. The method of correction is included in Table XXI and is based on results of a temperature study which will be presented in a later section (page 107).

The effect of monomer concentration on the intrinsic viscosity ($[\eta]$) is shown in Figure 16 where the aluminum alkyl concentration is a parameter. From theoretical considerations presented earlier one would expect this relationship to be of the form:

$$\frac{1}{\bar{X}_n} = K\left(\frac{1}{[\eta]}\right)^{1/a} = A + \frac{B}{C_M} \qquad (56)$$

where a and K are constants from the relationship between $[\eta]$ and the number average degree of polymerization ($\bar{X}_n$), and A and B are combinations of rate constants. The major assumptions involved in obtaining this relation are: (1) that the transfer reaction involving the monomer is first order with respect to that concentration; (2) that the other termination reactions are independent of the monomer concentration; and (3) that the breadth of the molecular weight distribution of the polymer (as characterized by the ratio $\bar{M}_v/\bar{M}_n$) is independent of reaction conditions.

It was found, however, that the intrinsic viscosity data could not be correlated satisfactorally in this manner. Furthermore, the dependence of the intrinsic viscosity on the monomer concentration did not appear to follow any simple mathematical relationship. Although the form of this dependence seemed to be independent of the $AlEt_3$ concentration. This suggested that the relationship between $[\eta]$ and $\bar{X}_n$ of Equation (56) was not valid.

In order to provide a basis for the correlation of the intrinsic viscosity data, it was assumed that the relationship between $\bar{X}_n$ and the monomer concentration given in Equation (56) was valid. From the data for a single alkyl concentration in Figure 16 a relationship could then be obtained between the measured $[\eta]$ and a "corrected intrinsic viscosity" which would satisfy Equation (56). This "corrected intrinsic viscosity" should be directly proportional to $\bar{X}_n$. This relationship is shown by the solid curve in Figure 17, where the "corrected intrinsic viscosities have been multiplied by a constant factor to give $\bar{X}_n$.

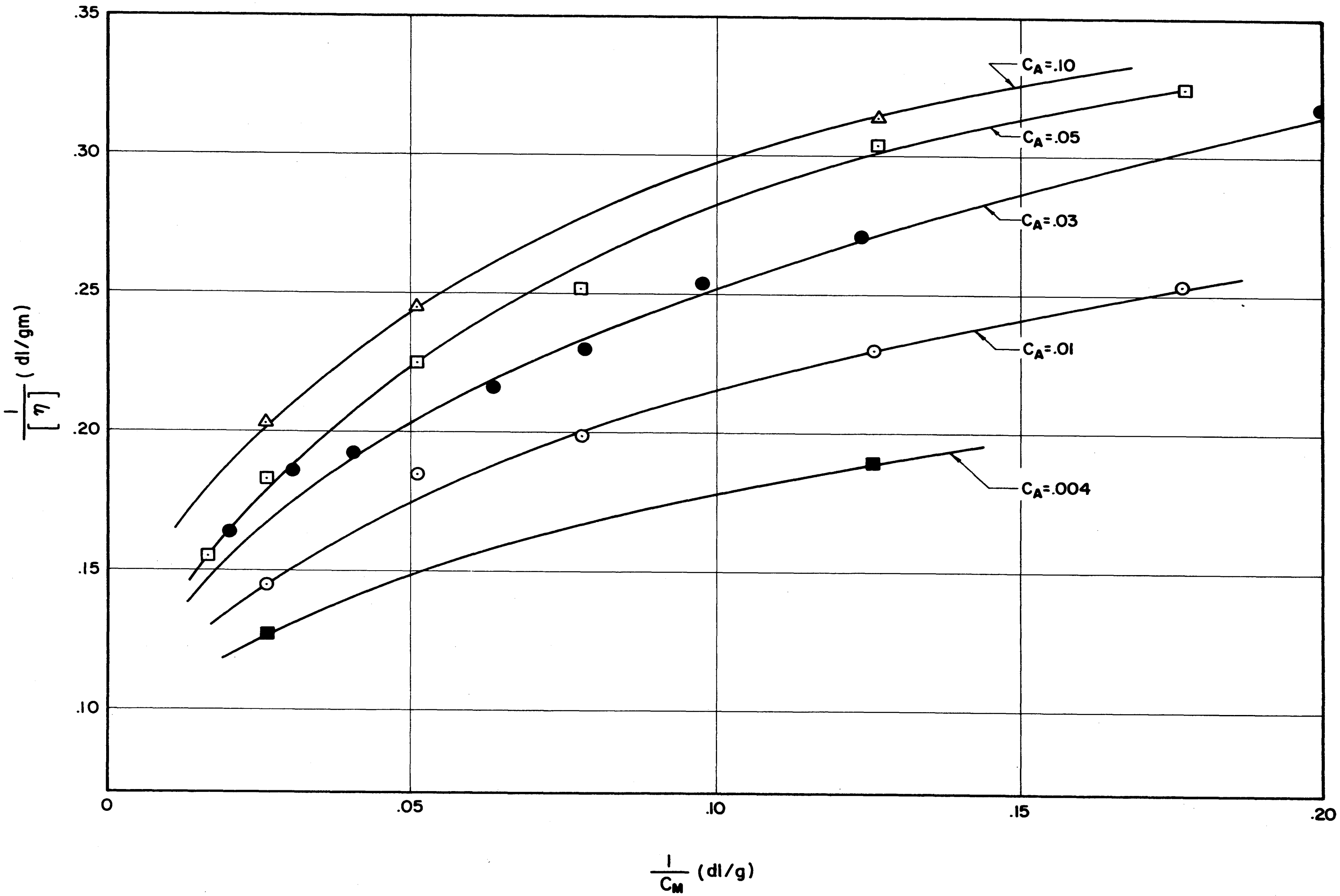


Figure 16. Effect of Monomer Concentration on the Intrinsic Viscosity (Temp = 25°C)

As a check on this relationship, osmotic pressure molecular weights were measured on several of these samples. These measurements are shown in Figure 17 as experimental points and they appear to agree reasonably well with the curve obtained from the corrected intrinsic viscosities.

A more fundamental approach would be either to obtain osmotic pressure molecular weights for each sample or to obtain the $[\eta]$ vs. $\bar{X}_n$ relationship from osmotic pressure measurements. The first method is impractical because of the lack of precision of osmotic pressure measurements. The latter method would also require quite a few measurments in order to obtain a relationship with any reliability. In the method which was used a fairly precise curve was obtained on an empirical basis and a few osmotic pressure measurements were made to give the relationship some theoretical support.

The unusual nature of this relationship requires som rationalization. First of all, at the lower values of $[\eta]$ the curve is linear with a slope of 0.64 which would be reasonable for a series of polymer samples of the same breadth of molecular weight distribution. At the higher values of $[\eta]$ the curve departs radically from linearity indicating a marked increase in the ratio of $\bar{M}_v$ to $\bar{M}_n$, a measure of the breadth of distribution. One explanation for this behavior is that some sort of branching reaction occurs which is favored by either a high degree of

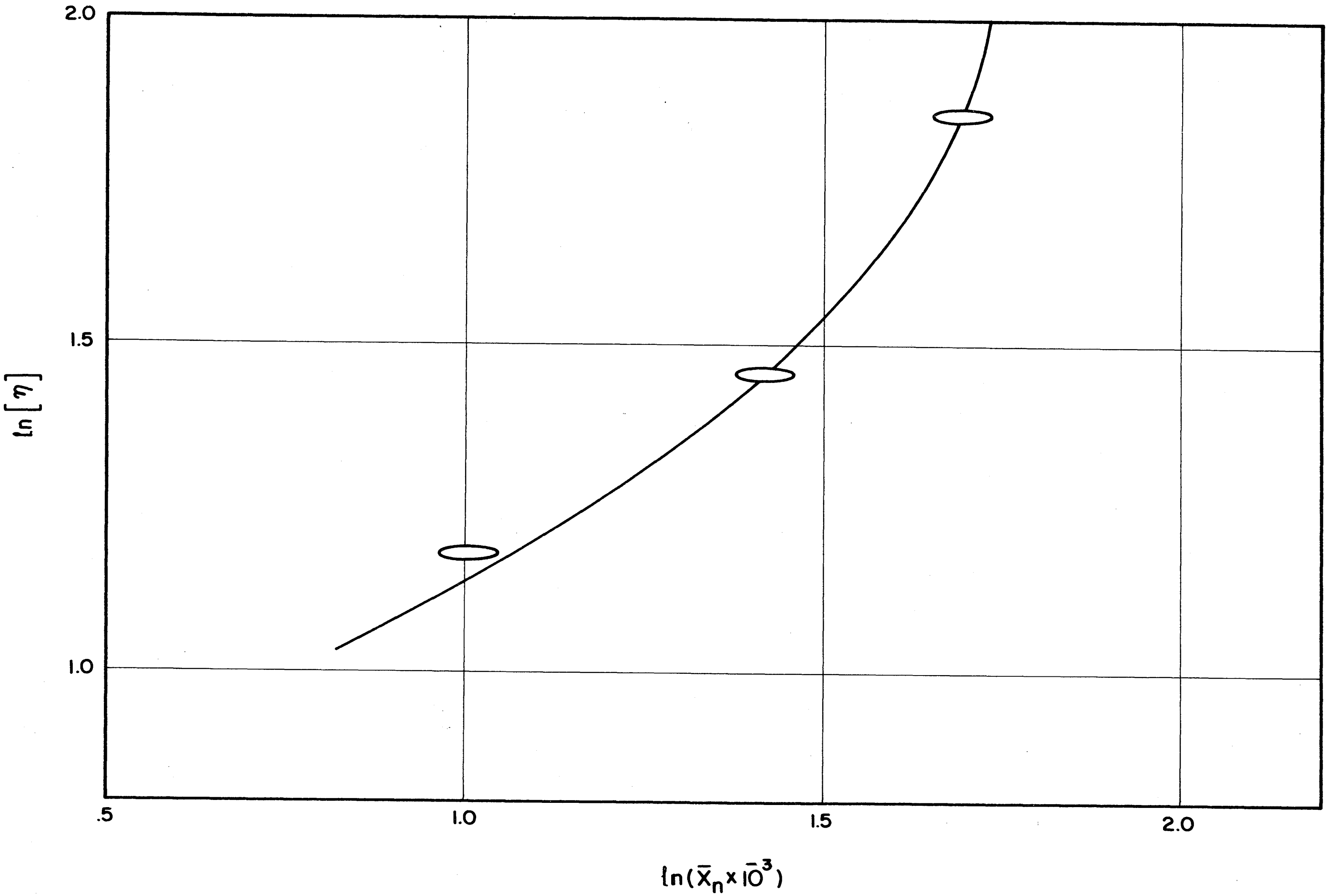


Figure 17. Relationship Between Intrinsic Viscosity and the Number Average Degree of Polymerization

polymerization of the unbranched polymer itself or else by the same conditions which favor a high degree of polymerization. The type of branching mechanism whereby a "dead" polymer molecule containing a terminal double bond forms a branch by polymerization through this double bond could behave in this manner. Thus, if the dead polymer molecule becomes more difficult to desorb as it becomes larger, it would remain in the vicinity of the active catalyst site longer and therefore have a better opportunity to form a branch. Or, in the termination mechanisms proposed by Natta (see page 33) termination by transfer with the aluminum triethyl does not result in a terminal double bond while termination by the monomolecular process or by transfer with the monomer do result in a terminal double bond. This branching process would be favored by a higher fraction of termination processes resulting in a terminal double bond and therefore by high monomer concentrations and low aluminum triethyl concentrations. But these conditions are exactly those which favor high molecular weights so that it appears as if the branching were dependent on the molecular weight of the unbranched polymer.

3. Effect of Monomer and Aluminum Alkyl Concentration - The effect of monomer concentration on the intrinsic viscosity has been shown in Figure 16. If the number average degree of polymerization for each of these samples is obtained using the relationship described above, the resulting

relationship between $(1/\bar{X}_n)$ and $(1/C_M)$ is linear as can be seen from Figure 18. This, of course, is to be expected since these data were used to calculate the $\bar{X}_n$ vs. $[\eta]$ relationship on the basis that this relationship should be linear. Nevertheless, it can be seen that this method does a reasonable job of correlating the data.

The form of the dependence of $\bar{X}_n$ on the aluminum alkyl concentration (C_A) can be found by plotting the slopes of the curves in Figure 18 vs. C_A. This is shown in Figure 19 where two calculated curves have been drawn in. The solid line represents a correlation on the basis of the Langmuir adsorption isotherm:

$$R_{tA} = k_{tA}\left(\frac{K_A\, C_A}{1 + K_A C_A}\right) \tag{57}$$

where R_{tA} is the rate of termination by transfer with alkyl, k_{tA} the rate constant, and K_A the reciprocal of the equilibrium dissociation constant.

The dashed line represents a correlation based on the relationship reported by Natta:

$$R_{ta} = k'_{tA}\, C_A^{1/2}$$

This method of correlation is also a particular case of the Freundlich adsorption isotherm.

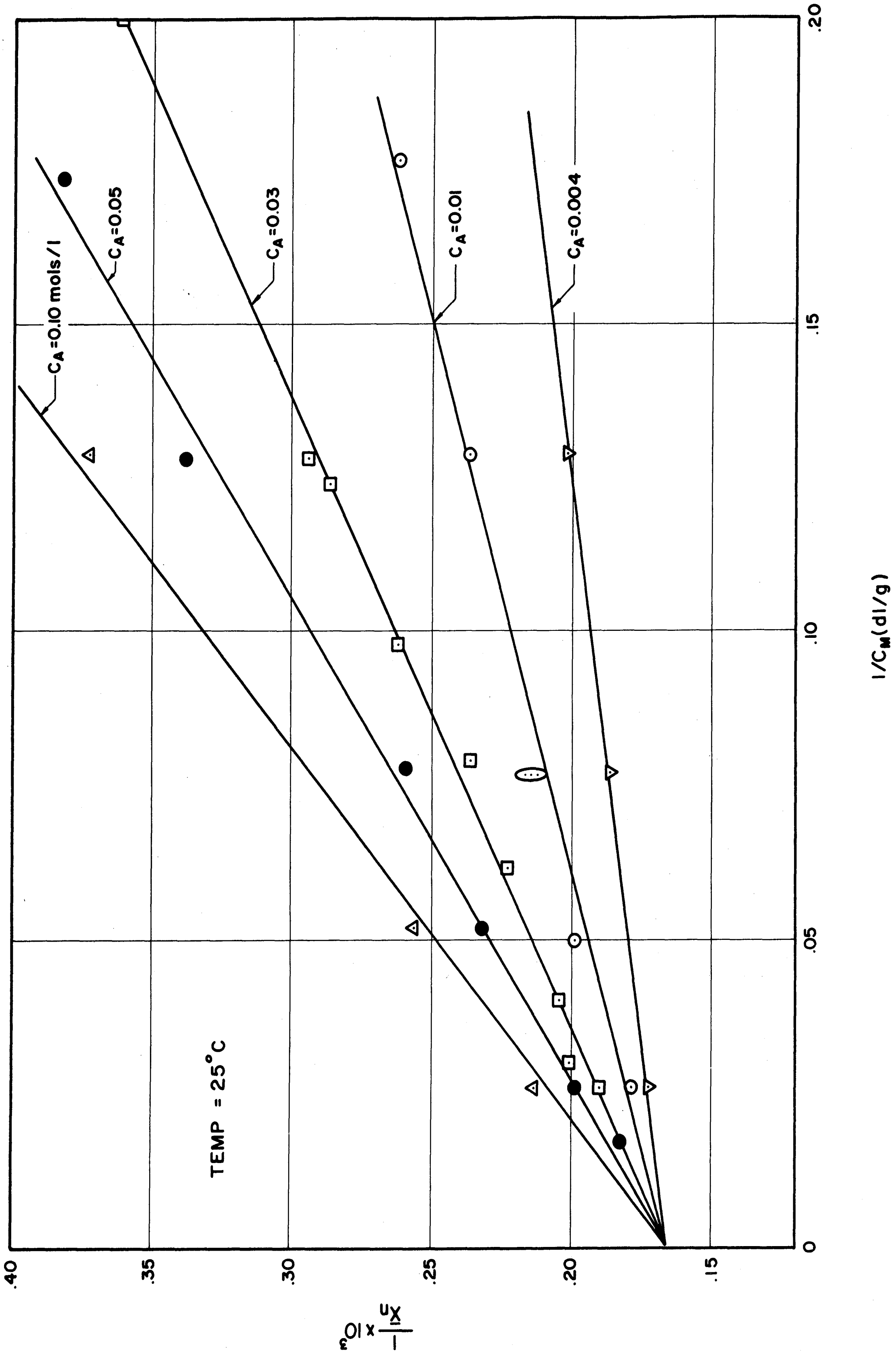


Figure 18. Effect of Monomer Concentration on the Degree of Polymerization

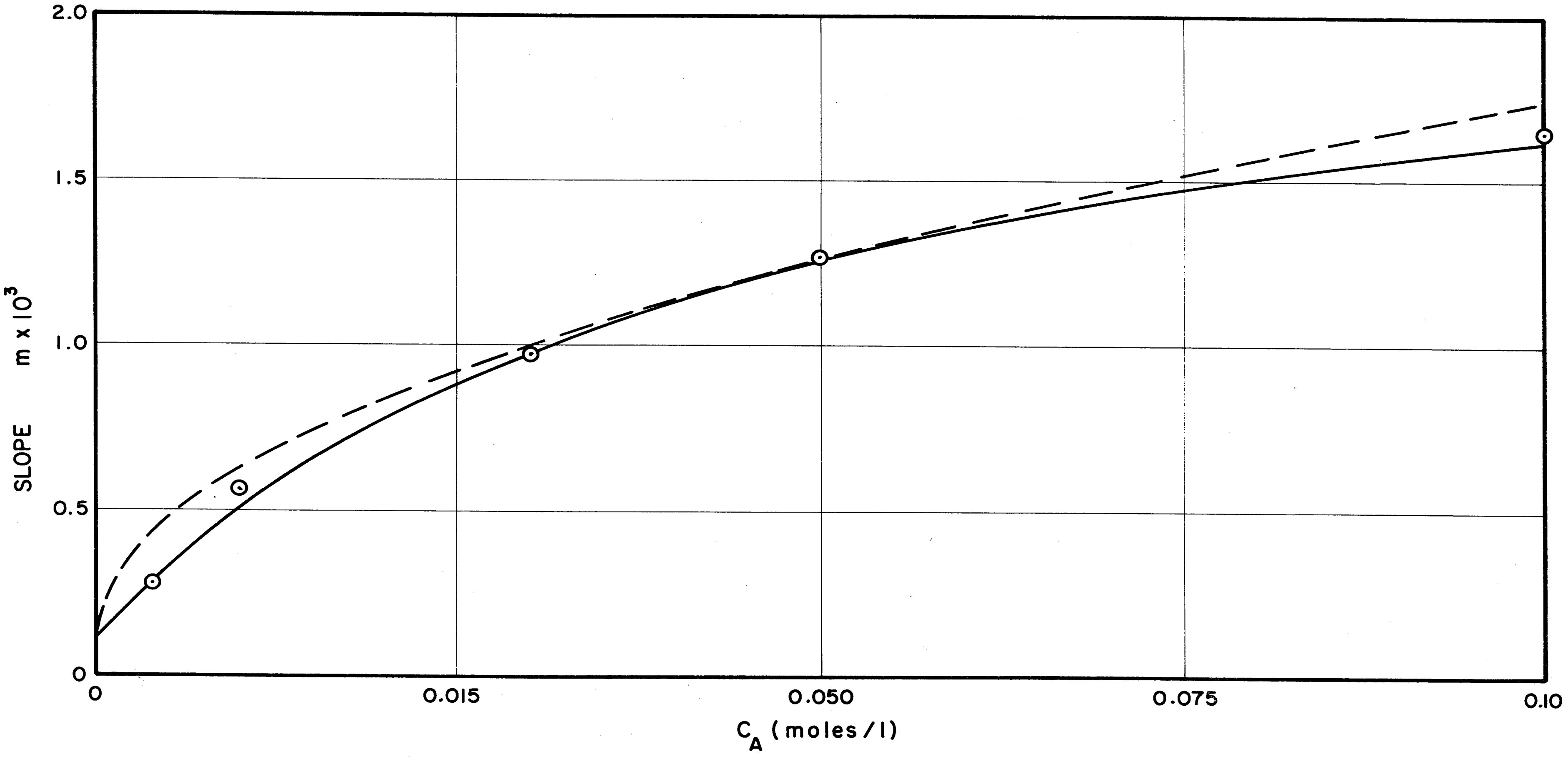


Figure 19. Effect of $AlEt_3$ Concentration on the Slope of the $(1/C_M$ vs. $1/\bar{X}_n)$ Curves in Figure 18.

If the appropriate constants are calculated from these curves the general relationship between $\bar{X}_n$ and C_A can be calculated. Figure 20 shows the data for the effect of C_A on $\bar{X}_n$ for three different monomer concentrations and the corresponding calculated curves for the two methods of correlation.

From these data the following equations, expressing the dependence of $\bar{X}_n$ on reaction conditions, can be deduced:

$$\frac{1}{\bar{X}_n} = \frac{k_t + k_{tM}\,C_M + k_{tA}\left(\dfrac{K_A\,C_A}{1 + K_A\,C_A}\right)}{k_p\,C_M} \qquad (59)$$

or:

$$\frac{1}{\bar{X}_n} = \frac{k_t + k_{tM}\,C_M + k'_{tA}\,C_A^{1/2}}{k_p\,C_M} \qquad (60)$$

where k_p is the rate constant for propagation and k_t is the rate constant for monomolecular termination but would also include any termination process dependent on some substance whose concentration remained essentially constant.

From Figures 18 and 20 the constants of these equations can be determined. First, the intercept of the curves in the $1/\bar{X}_n$ vs. $1/C_M$ plot is k_{tM}/k_p. The slope of these curves will be:

$$m = \frac{k_t}{k_p} + \frac{k_{tA}}{k_p} \cdot f\,(C_A) \qquad (61)$$

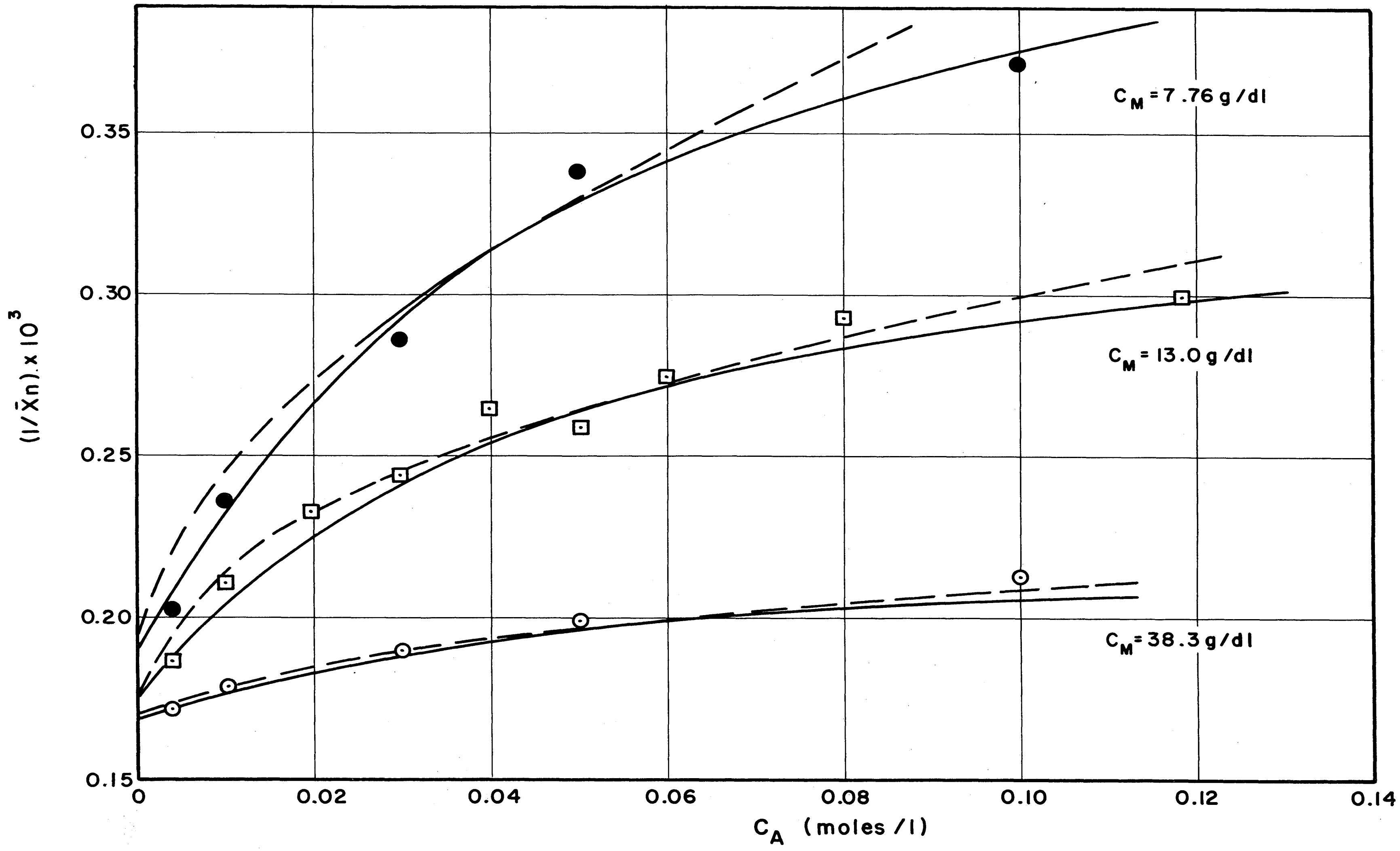


Figure 20. Effect of $AlEt_3$ Concentration on the Degree of Polymerization (Temp=25°C)

where $f(C_A)$ will be one of the two functions described previously. Plotting these slopes vs. C_A as in Figure 19, the intercept will yield k_t/k_p. By plotting the slopes vs. $(C_A^{1/2})$, k'_{tA} can be obtained from the slope. If $1/(m - \frac{k_t}{k_p})$ is plotted vs. $1/C_A$ the slope and intercept of this curve will yield both k_{tA} and K_A of Equation (59).

The values of these constants will be presented in the next section together with similar constants obtained for a different temperature of polymerization.

Equation (60) is the form of the relationship reported by Natta on the titanium-trichloride-aluminum triethyl-propylene system with two exceptions. First, he obtained this relationship with the intrinsic viscosities of the crystalline fractions of his polymer. Second, he found a dependence of the intrinsic viscosity on the titanium trichloride concentration.

It is felt that the Langmuir adsorption model, as expressed in Equation (59), has a better theoretical basis than does Equation (60), either from the standpoint of Freundlich adsorption or from the standpoint of equilibrium between the aluminum alkyl and dissociation products. Furthermore, although the data are not sufficiently accurate to decide between the two models, they do seem to fit the Langmuir model somewhat better, especially at high alkyl concentrations.

Thus, accepting the relationship between $[\eta]$ and $\bar{X}_n$ proposed in the preceding section, the molecular weight data can be satisfactorily correlated on a basis of the following termination reactions: (1) spontaneous or monomolecular dissociation of the growing polymer chain from the catalyst site (k_t); (2) termination by transfer with an adsorbed monomer unit (k_{tM}); and (3) termination by transfer with an adsorbed aluminum alkyl molecule (k_{tA}).

4. Temperature Effects - In order to get some idea of the effect of temperature on the molecular weight a series of runs were made at 53°C. Combining these results with those at 22°C approximate activation energies can be calculated for the various rate constants.

These data are shown in Figures 21 and 22 where $(1/\bar{X}_n)$ is shown as a function of C_A for constant C_M and as a function of $(1/C_M)$ at constant C_A. The curves in Figure 21 are again calculated curves based on the two termination models.

The termination constants can be determined as described previously except that a trial and error process, involving the assumption of a value for k_t, is necessary in order to obtain k_t, k_{tA} and K_A. The resulting constants together with those obtained at the lower temperature are presented in Table III. From these values approximate activation energies can be calculated and these are also given in Table III.

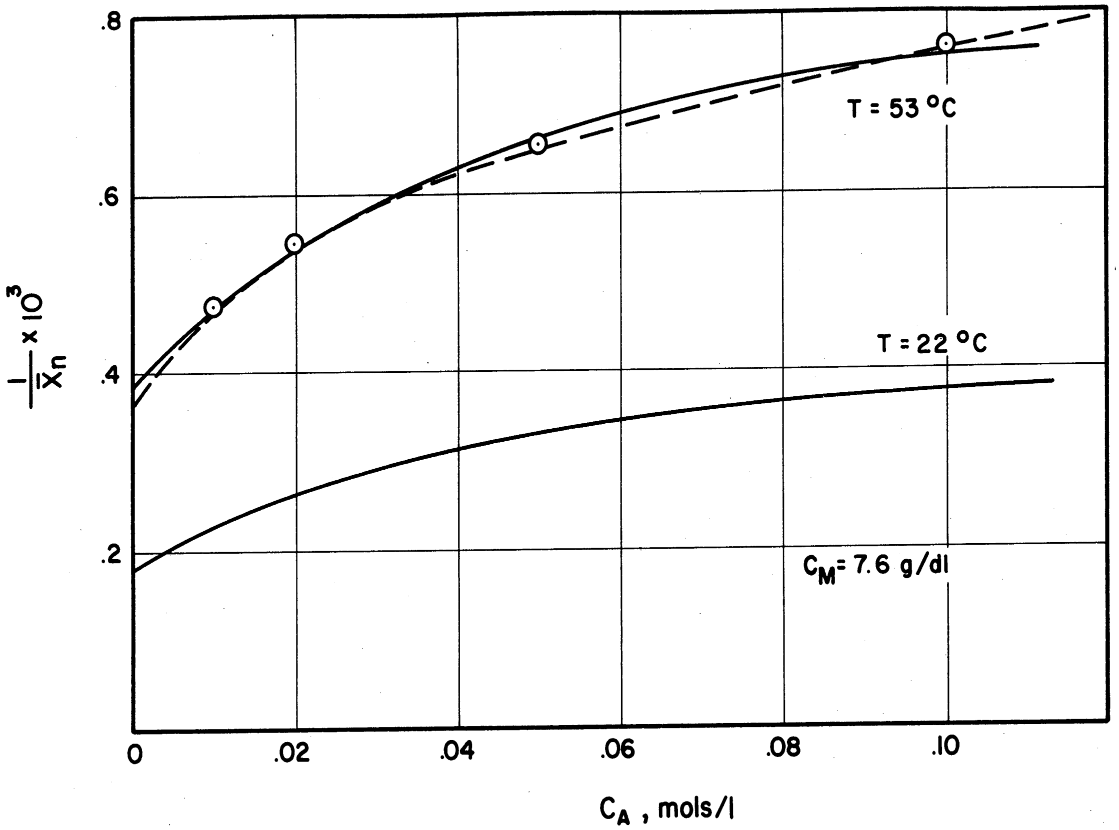


Figure 21. Effect of $AlEt_3$ Concentration on the Degree of Polymerization at 53°C

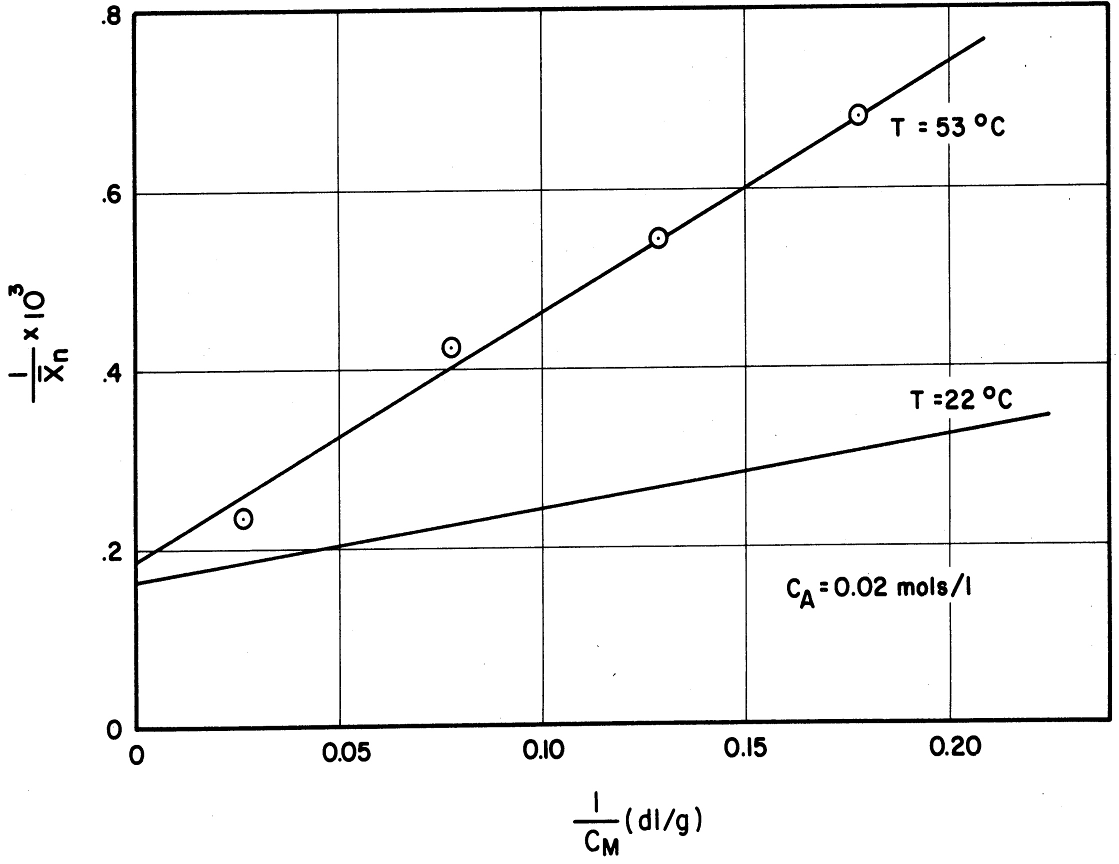


Figure 22. Effect of Monomer Concentration on the Degree of Polymerization at 53°C

TABLE III

Rate Constants and their Activation Energies

Constant	Units	Value 53°C	 22°C	Overall Energy of Activation,etc. (kcal)
Progapation				
k_p	$dl.hr^{-1}g^{-1}$	.363	1.220	7.4
Monomolecular Termination				
k_t	hr^{-1}	$0.363X10^{-3}$	$2.04X10^{-3}$	25
Transfer with Monomer				
k_{tM}	$dl.\ hr^{-1}g^{-1}$	$0.0602X10^{-3}$	$0.222X10^{-3}$	8.1
Transfer with Alkyl (Langmuir)				
k'_{tA}	hr^{-1}	$0.806X10^{-3}$	$5.04X10^{-3}$	11.4
K_A	$l.mol.^{-1}$	22.1	20.9	-0.34
Transfer with Alkyl (Natta)				
k''_{tA}	$l^{1/2}hr^{-1}mol^{-1/2}$	$2.03X10^{-3}$	$12.07\ X\ 10^{-3}$	11.1

The only other mention of effect of temperature on molecular weight for these heterogeneous polymerizations is Natta's statement that little effect was found and that therefore the activation energies of the principle termination steps were about that of the propagation reaction (40)

The activation energies presented here can give some additional information regarding the nature of the termination processes even though they are only approximate values. Both the activation energy for propagation and that for termination by transfer with monomer involve the dissociation energy for monomer adsorption as well as the activation energy of chemical reaction. If the monomer adsorption site is the same for the termination and propagation steps (as the suggested mechanism proposes) then the two dissociation energies would be identical. Thus, the difference in overall activation energies (in this case about 1 kcal/mol) would be the difference in the chemical activation energies. The small difference which was found could indicate that the transition states for the two processes are similar.

The relatively high activation energy found for the monomolecular termination process involves only the chemical activation energy and thus appears to be of the proper order of magnitude.

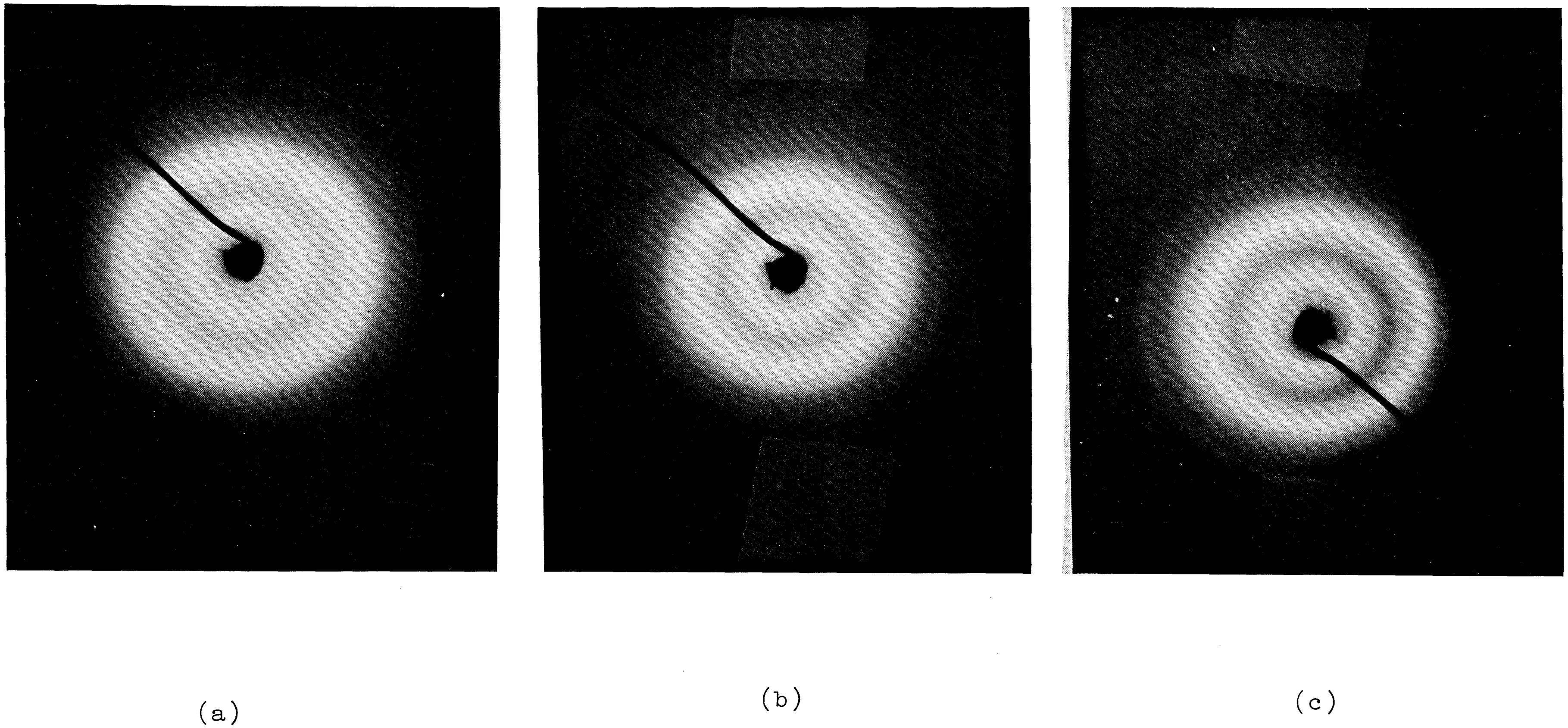
These data do not appear to provide a basis for choosing between the mechanisms proposed for alkyl transfer. Thus, on the basis of Langmuir adsorption, the low dissociation energy would indicate very weak physical adsorption. Since the polymerization rate was found to be independent of the alkyl concentration it was concluded that the alkyl was strongly adsorbed in forming the active catalyst sites. We must conclude then, that the adsorption involving the alkyl in termination reactions is completely different from that involved in forming the active catalyst sites. The chemical activation energy associated with this termination process ($\sim$11 kcal/mol) could be expected for a process involving an exchange of alkyl groups through some ionic mechanism. This would also apply however, to a termination process involving the alkyl in solution as has been suggested by Natta.

C. Degree of Stereospecificity

1. Estimation of the Degree of Crystallinity - An attempt was made, using x-ray measurements, to obtain an absolute percent crystallinity for the poly (1-pentene) samples. Qualitatively it can be seen from x-ray photographs that the polymer produced with the titanium trichloride-aluminum triethyl system is at least partially crystalline. Figure 23 shows pictures of (a) the amorphous polymer, (b) very slightly crystalline polymer (titanium tetrachloride-aluminum triethyl polymerized) and (c) fairly crystalline polymer (titanium trichloride-aluminum triethyl polymerized).

If the scattering intensities are calculated as a function of 2θ, according to the method described on page 54, the curves shown in Figure 24 are obtained. From these curves, as well as from the pictures themselves, it can be seen that the major crystalline peaks occur at approximately the same values of 2θ as the peaks of the amorphous halo. Thus, it becomes impossible to obtain with any accuracy the curve due to amorphous scattering for the partially crystalline material, and the curve is needed for calculating the percent crystallinity.

This problem would be less serious for a highly crystalline polymer. However, attempts to obtain a more crystalline material by means of solvent extraction were also unsuccessful. Extraction with both ethyl acetate and ether effected some separation but the insoluble material did not show any appreciable increase in crystallinity, which would indicate that the fractionation took place largely on a molecular weight basis.



(a) (b) (c)

Figure 23. X-Ray Photographs of Poly (1-Pentene) Samples
(a) Amorphous; (b) Slightly Crystalline; (c) 30 percent Crystalline

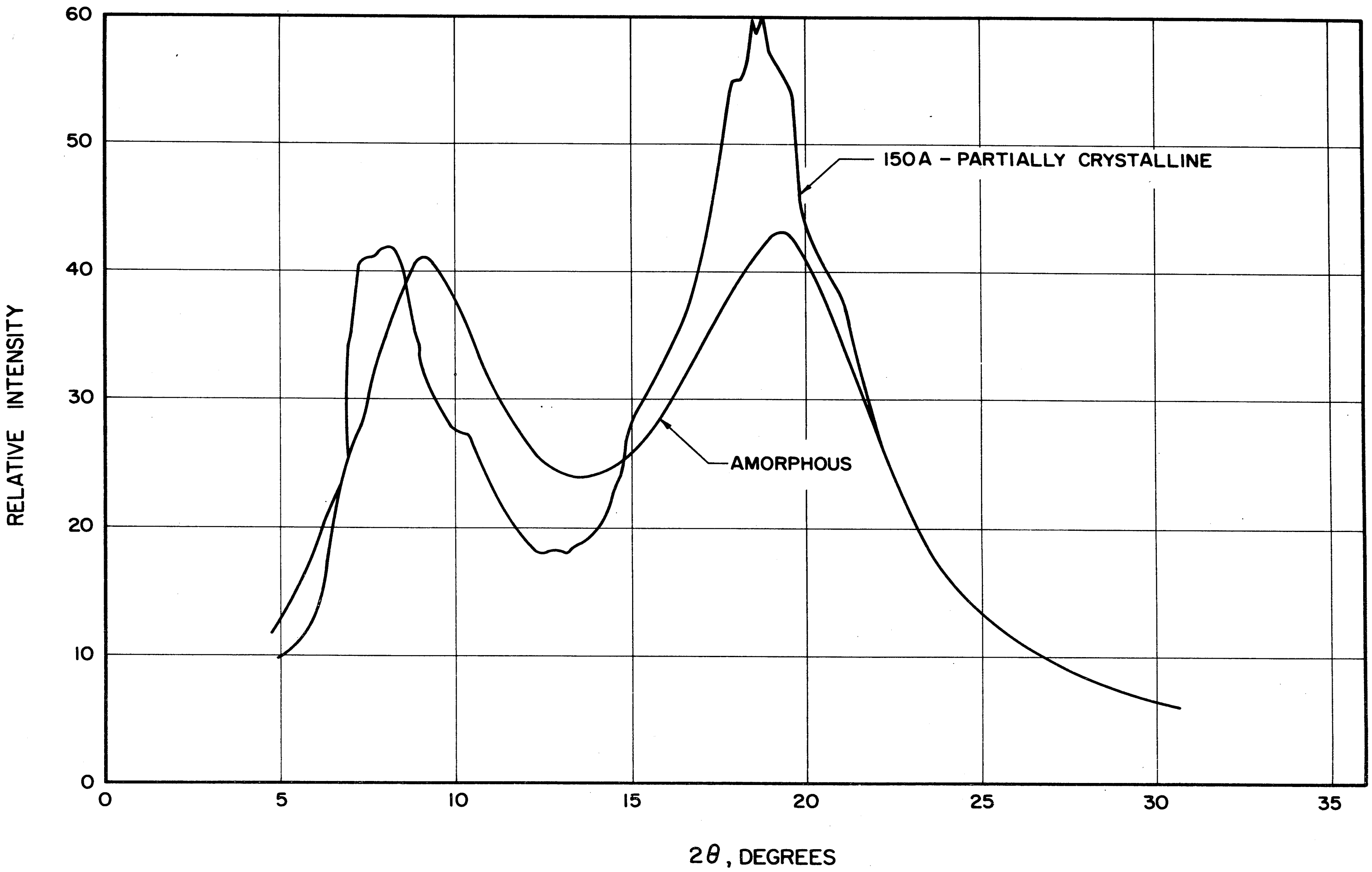


Figure 24. Corrected Intensities from Geiger Counter Trace of X-Ray Scattering of Poly (1-Pentene) Samples

One other method is available for estimating the percent crystallinity from the data obtained in this work and that is from the density measurements. Since the density of the amorphous material could be found experimentally it remains to estimate the density of the completely crystalline material. From the data presented by Natta, (37) and shown in Table IV, a reasonable estimate would seem possible.

TABLE IV

Some Properites of Crystalline and Amorphous Poly (α olefins)

Polymer	Density (gms/cc)	Identity Period along the fiber axis	No. of monomers units in Identity Period
Polypropylene			
Isotactic	0.92	6.50	3
Atactic	0.85	----	-
Polybutene-1			
Isotactic I	0.91	6.45	3
Atactic	0.87	----	-
Polypentene-1	0.87	6.60	-

The crystal structure determination for isotactic polyproylene has been sufficiently complete to allow the calculation of the theoretical density of the pure crystalline material and this value has been reported to be 0.936 (5). Thus it would seem that the density values reported by Natta correspond to mainly crystalline (isotactic) or mainly amorphous (atactic) rather than to the completely crystalline and completely amorphous polymers required for calculation.

Nevertheless, the similarity of the identity period repeat distances supports Natta's claim that these α olefins crystalize in a helical configuration with three monomer units per identity period. It would be expected then that the densities of the purely crystalline material for a series of poly (α olefins) would vary regularly, decreasing slightly as the length of the R group of the olefin ($CH_2 = CHR$) increases. This is supported by the similarity of the experimental densities found for isotactic polypropylene and poly (1-butene).

Using the value of 0.936 for the density of totally crystalline polypropylene one could, on this basis, estimate a value for the density of totally crystalline poly (1-pentene) to be about 0.90 - 0.92. Experimentally it was found that the density of amorphous poly (1-pentene) was 0.857 and that a density of 0.871 was typical of the polymer obtained from polymerization with a titanium trichloride-aluminum triethyl catalyst. From Equation (34) a percent crystallinity for this partially crystalline polymer can be calculated to be about 25 to 30 percent.

2. Effect of Reaction Temperature on Crystallinity - In light of the theoretical considerations concerning the effect of reaction variables on the degree of stereospecificity, and therefore on crystallinity, it was felt that the reaction temperature was the only variable likely to

cause an appreciable effect. Density measurements were made on twelve polymer films as described on page 53 and these results are shown in Table XXIII. Although appreciable differences in density were found in polymers made from different catalyst systems, the effect of reaction temperature on polymer density was found to be slight.

This could be due to one of two factors. First, the difference in density between the totally amorphous and totally crystalline materials was small ($\sim$0.5 g./cc), and second, the variation in polymer crystallinity over the 100°C range of temperatures appeared to be less than ten percent.

The use of the density gradient column made it possible to measure the relative densities with high precision so that errors in these values most likely would be due to variations in the nature of the polymer films. Thus, very small amounts of catalyst residue in the film would cause an appreciable increase in the measured density, although it is felt that the method used in treating the polymer was sufficient to remove essentially all of the catalyst. One further cause for variations in these densities might be a molecular weight effect. In general, the variation in density with molecular weight is negligible at high molecular weights (84), but in light of the suggested relationship between branching and the molecular weight of the polymer sample, some effect is possible. Thus, if a high intrinsic viscosity corresponded to the presence of several branches in the polymer molecule a slight decrease in density might be anticipated.

These considerations tend to raise some doubt as to whether the small observed increase in density with reaction temperature is real. At any rate the differences are much too small to allow a meaningful test of the various theoretical models proposed in an earlier section.

Recognizing these limitations we can use these data to obtain an approximate value for δE, the difference in overall activation energies for the two types of propagation reaction. Since the differences in crystallinity are small it does not make any difference which model is used. In this case the model proposing two types of reaction site has been utilized, so that the two types of propagation reaction refer to the processes at the two types of site, one producing atactic polymer and the other producing isotactic polymer.

From the discussion on page 30 and from Equation (34) it was found that a plot of $\ln(\frac{D}{1-D})$ vs. $(1/T)$ should be linear (where D is the crystalline fraction). Such a plot is shown in Figure 25. The small differences in density magnify the scatter of the data such that the only reasonable conclusion would be that the difference in overall activation energies is less than 1 kcal/mol.

The only other reports concerning the effect of reaction temperature on crystallinity appear to be conflicting. Natta claims that

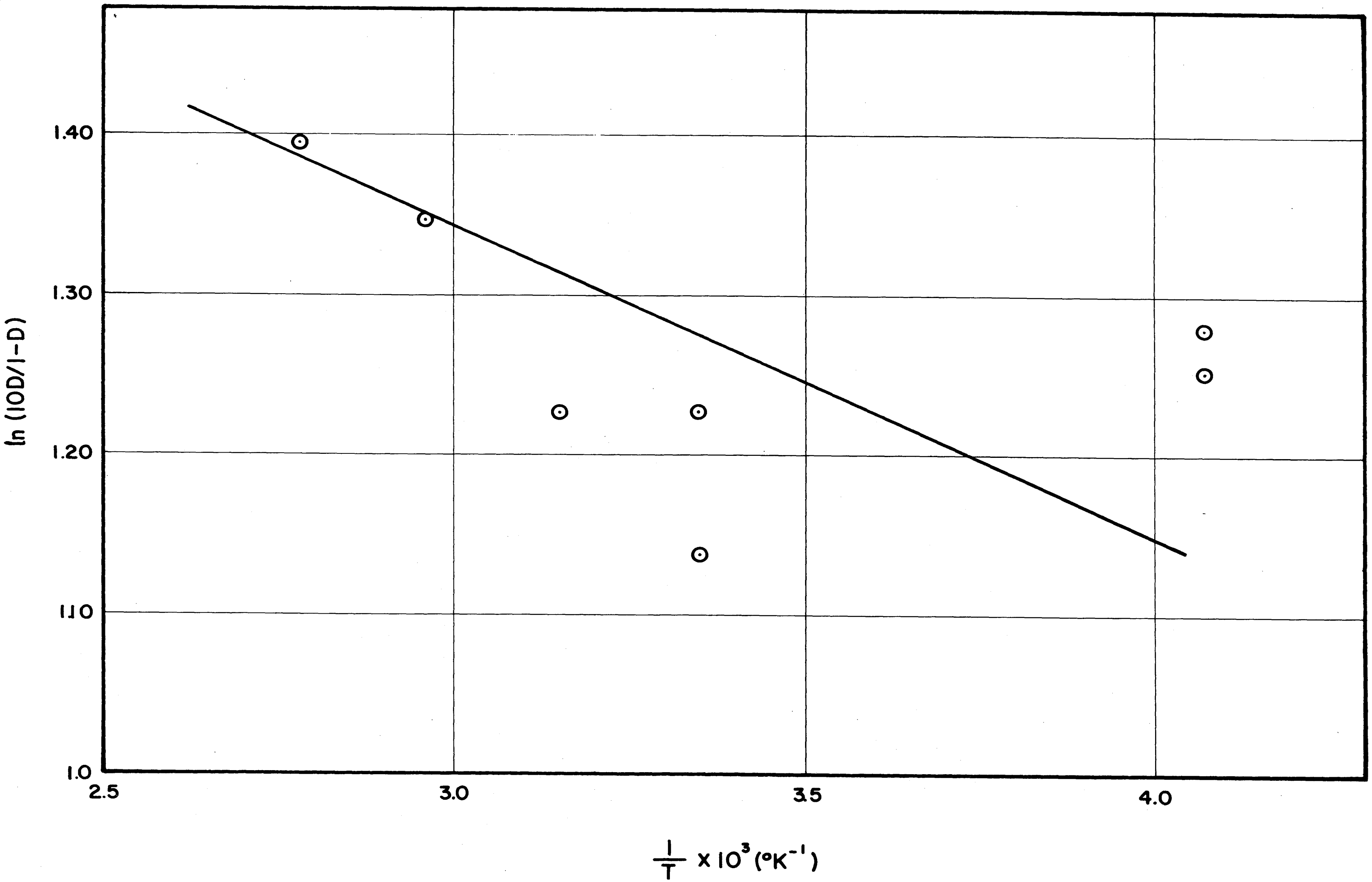


Figure 25. Effect of Temperature on Polymer Crystallinity

increasing the reaction temperature causes a decrease in crystallinity (40) while Bailey and Lundberg give data showing the opposite effect (5). Aside from the fact that both were dealing with the titanium trichloride-aluminum triethyl-propylene system no experimental details were given.

The only variable which was found to have an appreciable effect on the polymer crystallinity was the nature of the catalyst. The titanium trichloride (pract.) together with aluminum triethyl produced polymer with the highest crystallinity. The titanium trichloride (HRA)-aluminum triethyl system produced polymer with a slightly lower crystallinity, while polymer from a titanium tetrachloride-aluminum triethyl system showed very little crystallinity.

In conclusion then, polymerization temperature was found to have little effect on crystallinity whereas the nature of the catalyst had a pronounced effect. These observations are certainly compatible with the theory presented previously but unfortunately do little to support any given theory.

VI. CONCLUSIONS

The results of this study of the polymerization of 1-pentene using a catalyst of titanium trichloride together with triethyl aluminum can be summarized in terms of the following conclusions:

1. Over the range of conditions which were studied the rate of polymerization is first order with respect to the monomer and titanium trichloride concentrations and independent of the triethyl aluminum concentration. However, no polymerization will occur in the absence of the triethyl aluminum.
2. In the range from 0° to 85°C. the temperature dependence of the initial rate of polymerization is of the Arrhenius form with an activation energy of 7.5 kcal/mol.
3. At the higher temperatures investigated the rate of polymerization decreases with time. This change in rate can be correlated satisfactorily by assuming that the titanium trichloride is deactivated by a process which is first order with respect to the titanium trichloride concentration.
4. These observations offer strong evidence in support of a mechanism whereby the aluminum alkyl is strongly adsorbed (or chemically bound) on the titanium trichloride surface forming a catalyst site at which weakly adsorbed monomer is added to the growing polymer chain.

5. Using two different grades of titanium trichloride obtained at different times it is found that the specific rate of polymerization is not directly proportional to the specific surface area of the titanium trichloride.

6. The intrinsic viscosity of the polymer decreases with increasing triethyl aluminum concentration, increases with increasing monomer concentration, and is independent of the titanium trichloride concentration. The relationship between reciprocal intrinsic viscosity and reciprocal monomer concentration is not linear as would be expected.

7. The intrinsic viscosity data dan be correlated satisfactorily by assuming an empirical relationship between the intrinsic viscosity and the number average degree of polymerization such that the ratio of viscosity to number average molecular weight increases with increasing molecular weight. Using this relationship the reciprocal degree of polymerization is directly proportional to the reciprocal monomer concentration and can be related to the concentration of the aluminum alkyl by assuming either an adsorption mechanism or a relationship dependent on the one half power of the aluminum alkyl concentration.

8. These observations would support a termination mechanism involving: (a) spontaneous monomolecular termination of the

growing polymer chain; (b) termination by transfer with adsorbed aluminum alkyl; and (c) termination by transfer with adsorbed aluminum alkyl.

9. The intrinsic viscosity of the polymer is found to decrease with increasing temperature. Approximate activation energies for various termination reactions are found to be: (a) 25 kcal/mol for monomolecular termination; (b) 8 kcal/mol for transfer with monomer; and (c) 11 kcal/mol for transfer with aluminum alkyl.

10. Little change in the density of the polymer is found with changes in the reaction variables of temperature, monomer concentration, and catalyst concentrations. The polymer density is affected appreciably by the nature of the catalyst employed.

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APPENDIX A

SAMPLE DATA AND CALCULATIONS

TABLE V

Calculation of "Active" $TiCl_3$ Concentration

It is assumed that the n-heptane used to prepare the $TiCl_3$ suspension contains G_i/G_s grams of impurity (expressed as grams of solid $TiCl_3$ deactivated) per gram of heptane. $TiCl_3$ suspensions H, J, and K were prepared using the same batch of heptane and the same solid $TiCl_3$ and their "apparent" concentrations (grams $TiCl_3$ added per total gram suspension) were as follows:

Suspension	Apparent Concentration (g./g. susp.)
H	0.0145
J	0.0277
K	0.0446

Several runs were then made using these catalyst suspensions under identical conditions of temperature and monomer concentration but varying the $TiCl_3$ concentration in the reaction mixture:

Run No.	Catalyst Suspension	g. Suspension per liter of reaction mixture	g. $TiCl_3$ per liter of reaction mixture	Rate (g./hr.l.)
141	J	13.9	0.383	0.99
142	K	13.6	0.608	2.18
143	K	27.4	1.224	4.64
144	H	66.8	0.970	1.95
145	J	40.0	1.103	3.60

TABLE V (cont.)

These data are plotted in Figure 5. Straight lines are drawn through these data for each catalyst suspension. Since we assume the non-zero intercept for this type of plot can be attributed to impurities in the reaction mixture which are not scavenged by the $AlEt_3$ and since the reaction conditions and solvent and monomer batches are identical for all of these runs, the intercepts should be identical. The slope of each of these lines gives us a specific rate based on the "apparent" $TiCl_3$ concentrations:

Suspension	Specific Rate (R) g./hr.-g. $TiCl_3$	g. $TiCl_3$ per g. Heptane in Suspension (C)
H	2.15	0.0147
J	3.43	0.0285
K	4.08	0.0467

We now have sufficient data to calculate the active $TiCl_3$ concentration in each suspension. We can express the assumptions we have made in form of equations. First, G_i grams of $TiCl_3$ are deactivated per grams of heptane:

$$G^*_{Ti} = G_{Ti} - G_i \tag{62}$$

where G^*_{Ti} is the weight of active $TiCl_3$ in the suspension and G_{Ti} the weight of $TiCl_3$ added.

$$G_i = K\ G_s \tag{63}$$

where K is a constant and G_s the weight of heptane in the suspension.

TABLE V (cont)

From the data we obtain $R = r/G_{Ti}$ and $C = G_{Ti}/G_s$ for each $TiCl_3$ suspension where r is a rate in grams per hr. We have assumed that the specific rate based on the active $TiCl_3$ ($R^* = r/G^*_{Ti}$) is independent of the catalyst suspension used:

$$\left(\frac{r}{G^*_{Ti}}\right)_H = \left(\frac{r}{G^*_{Ti}}\right)_J = \left(\frac{r}{G^*_{Ti}}\right)_K \qquad (64)$$

Using any of these three equations we can calculate K, the concentration of impurities in the heptane:

$$\left(\frac{r}{G_{Ti} - K\,G_s}\right)_H = \left(\frac{r}{G_{Ti} - K\,G_s}\right)_J \qquad (65)$$

$$K = \frac{R_H - R_J}{\dfrac{R_H}{C_J} - \dfrac{R_J}{C_H}} \qquad (66)$$

Thus we obtain three values for K which sould be similar:

Data Used	K (g. $TiCl_3$ deactivated per 100 g. Heptane)
H - J	0.81
H - K	0.83
J - K	0.93

It will be noted that the value of K used in calculation of the data was somewhat lower (0.73, see Table XIII). This value was obtained

TABLE V (cont.)

by trial and error using the individual runs rather than the method outlined above. The difference between these values will have little significance in the calculations of specific rates.

TABLE VI

INTRINSIC VISCOSITY

Sample Data and Calculations

Data			Calculated Data		
Rel. Conc.	Flow Time (sec.)	$t - \frac{20}{t}$	η_r	η_{sp}/C_r	$\ell n\ \eta_r/C_r$
Solvent	96.25	96.05			
1.00	166.75	166.63	1.7348	0.7348	0.551
0.50	128.28	128.12	1.3339	0.6678	0.577
0.25	111.50	111.42	1..600	0.6400	0.593

Calculations:

1. Kinetic Energy Correction:

$$t_c = t - \frac{20}{t}$$

2. Relative Viscosity

$$\eta_r = (t_c)_{soln.} / (t_c)\ \text{solvent}$$

3. Specific Viscosity

$$\eta_{sp} = \eta_r - 1$$

4. Intrinsic Viscosity:
   Solv. Conc. - 0.167 g/dl.
   From plot (see Figure 26)
   Intercept-0.605

$$[\eta] = 0.605/0.167 = 3.62\ \text{dl/g}$$

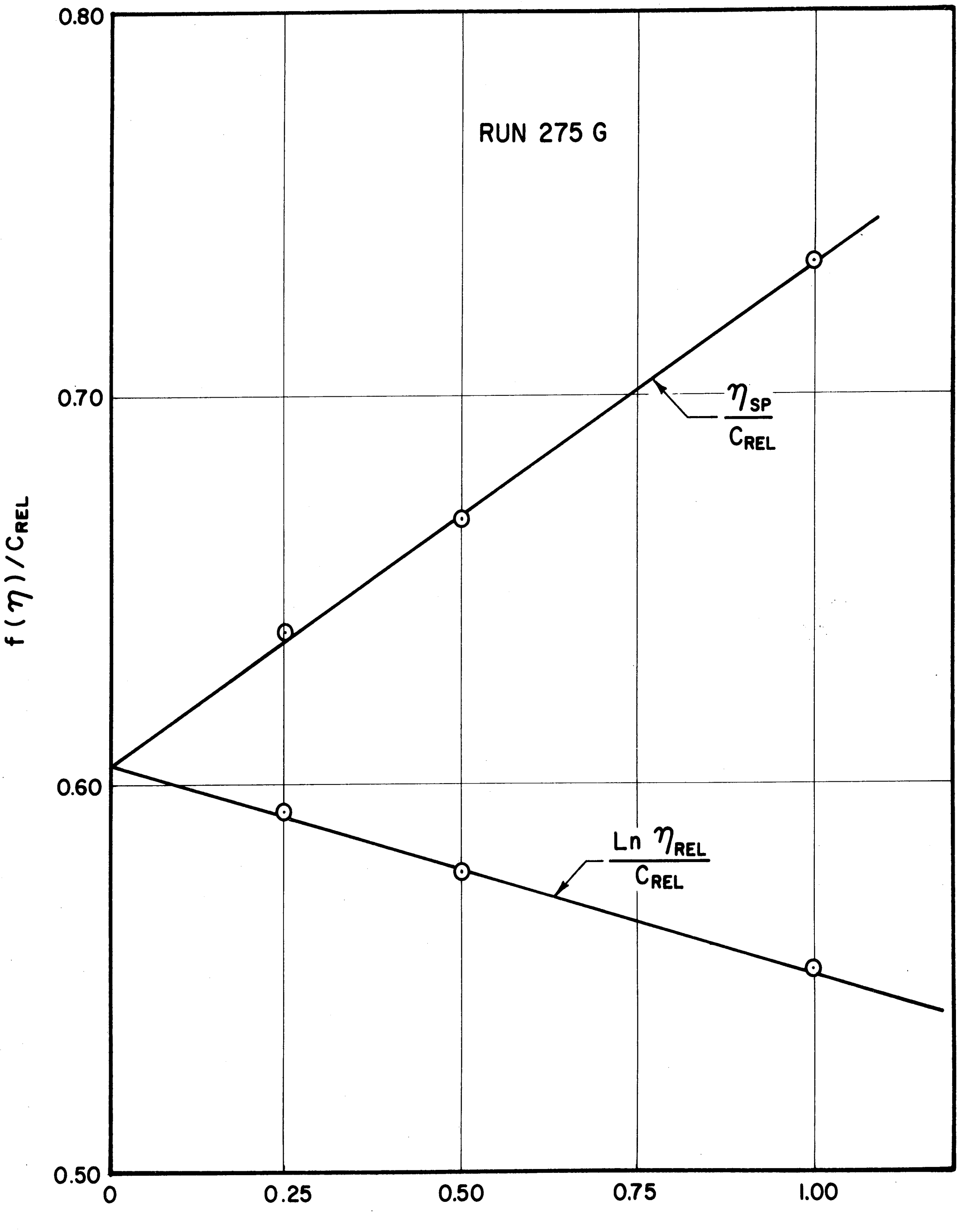

Figure 26. Intrinsic Viscosity Double Extrapolation plot

TABLE VII

OSMOTIC PRESSURE

Sample Calculation and Data

Calculations:

From plot of osmotic pressure (expressed in cm. toluene) as a function of time, obtain equilibrium osmotic pressure for several concentrations. From Figure 27 for runs 306-A:

Cell	Conc.	h (cm. tol.)	h/c (cm-dl/g)
1	1.01	2.18	2.16
2	0.673	1.10	1.63
3	0.673	1.12	1.66
4	0.336	0.42	1.25

From plot of (h/c) vs. C (Figure 28) obtain $(h/c)_0 = 0.80$

Osmotic Pressure: $\pi = \frac{\rho}{(76.0)(13.6)} h$ (atm.)

$$(\pi/c)_0 = RT/\bar{M}_n$$

$$\rho = 0.854 \text{ g./cc}; \; T = 308°K$$

$$R = 0.8206 \text{ dl-atm.-}°K^{-1} - \text{mol}^{-1}$$

$$\bar{M}_n = \frac{3.06 \times 10^5}{(h/c)_0} = 3.83 \times 10^5$$

TABLE VII (cont.)

Sample	([η])	$(h/c)_o$	$\bar{M}_n$	$\bar{X}_n$
306A	6.36	0.80	3.83×10^5	5.47×10^3
306B	4.27	1.06	2.89×10^5	4.12×10^3
306C	3.26	1.60	1.91×10^5	2.73×10^3

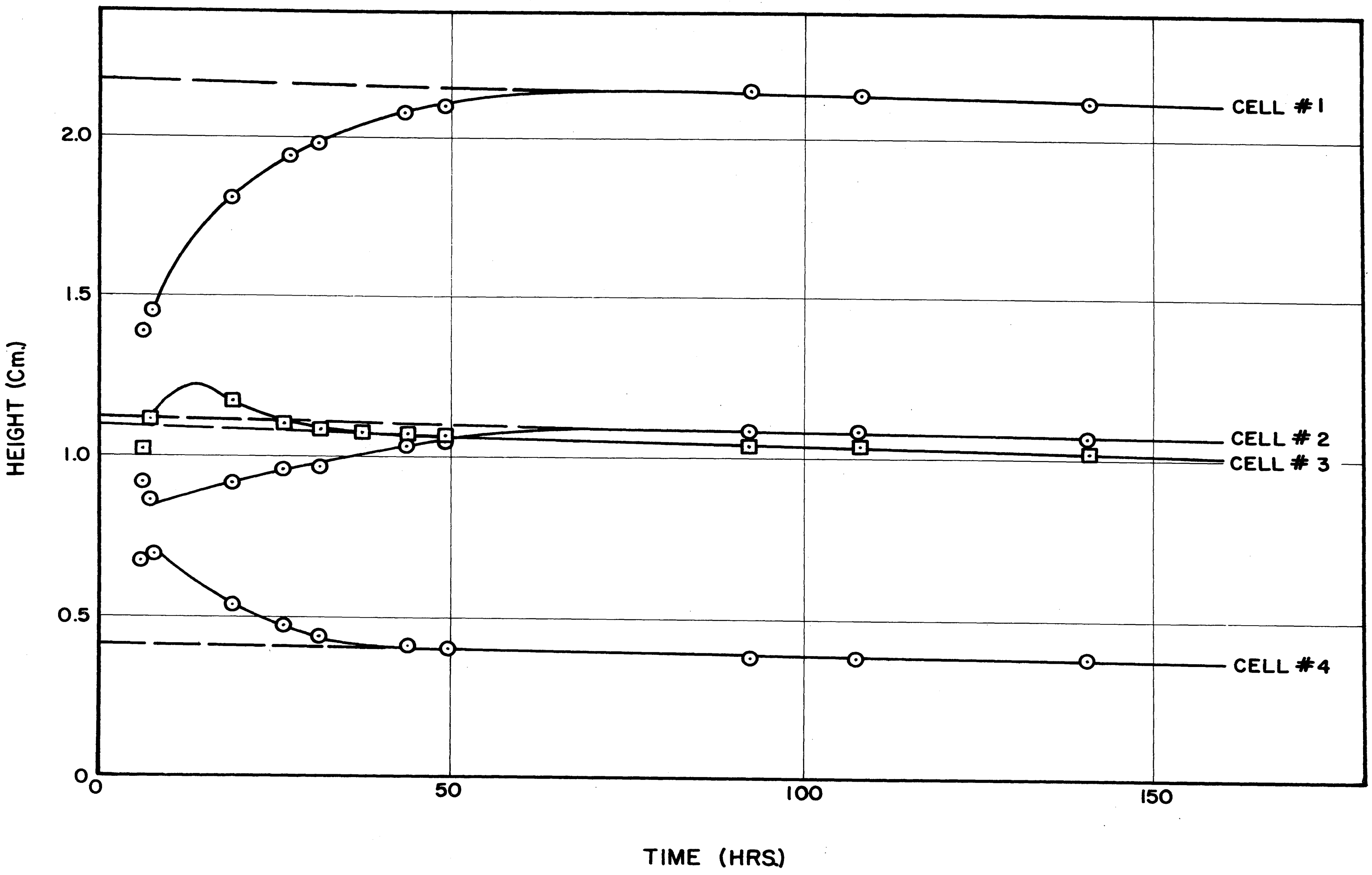

Figure 27. Osmotic Pressure Data; Height vs. Time

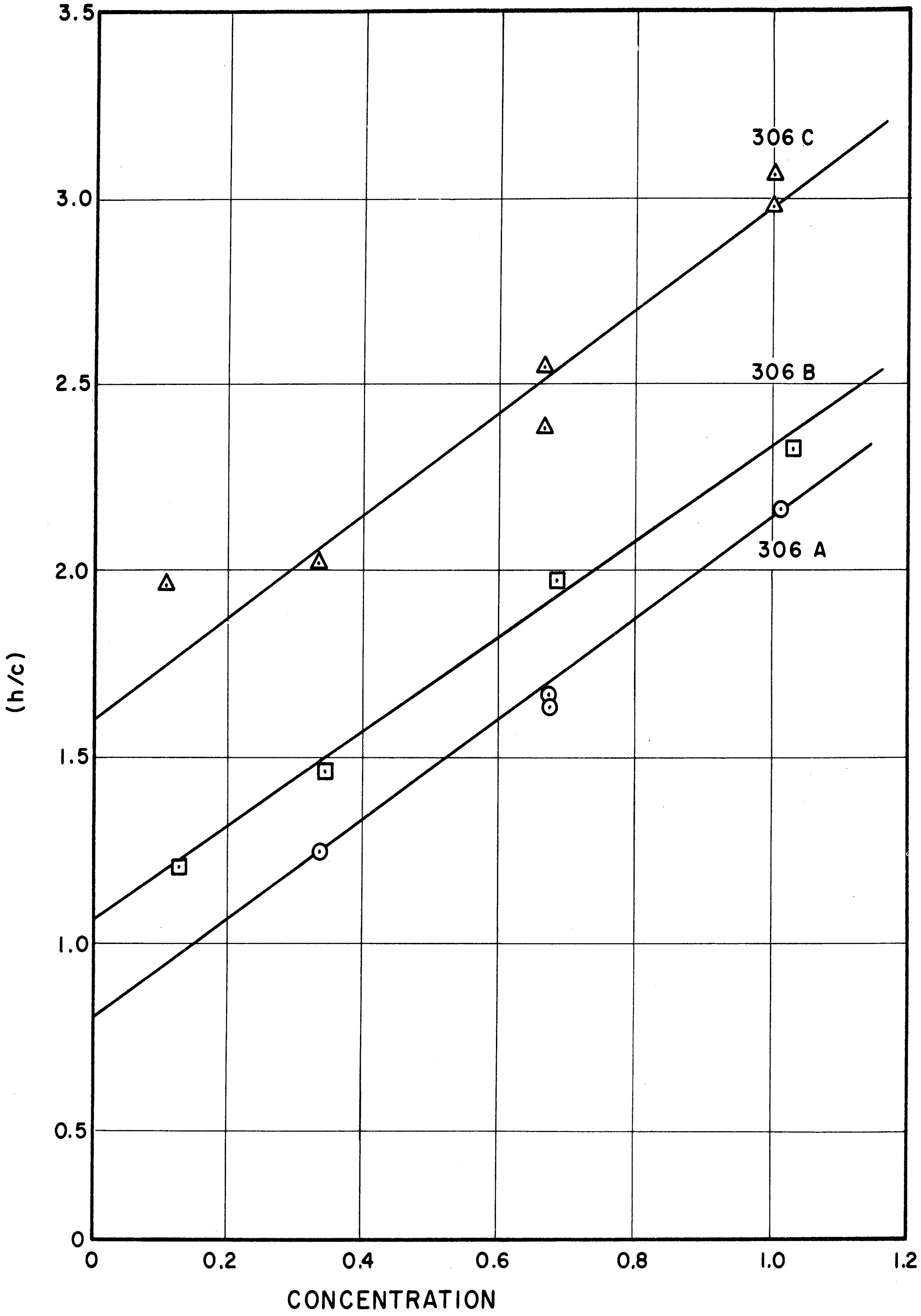

Figure 28. Osmotic Pressure Data; Extrapolation to Zero Concentration

TABLE VIII

Calculated Intensities from Geiger Counter Trace of X-Ray Scattering - Sample 150A

θ	Intensity	Background Intensity		Corrected Intensity
Degrees	I	I_o	$I-I_o$	I_c
5	34	26	8.0	10.0
6	30	20	10.0	12.5
7	37	10.5	26.5	33.1
8	42	8.5	33.5	41.8
9	34	7.0	27	33.8
10	28	6.0	22	27.5
11	25	6.0	19	23.7
12	21	6.0	15	18.8
13	20.5	6.0	14.5	18.1
14	21	5.5	15.5	19.4
15	27	5.0	22	27.5
16	31	4.5	26.5	33.1
17	36	4.5	31.5	39.4
18	48	4.0	44.0	55
19	50	4.0	46.0	57.5
20	39.5	4.0	35.5	44.4
21	31	4.0	30.5	38.1
22	27	4.0	23.0	28.7

Sample thickness - 16 mils

Intensity corrected to thickness of 20 mils:

$$I_c = \frac{20}{16}(I-I_o)$$

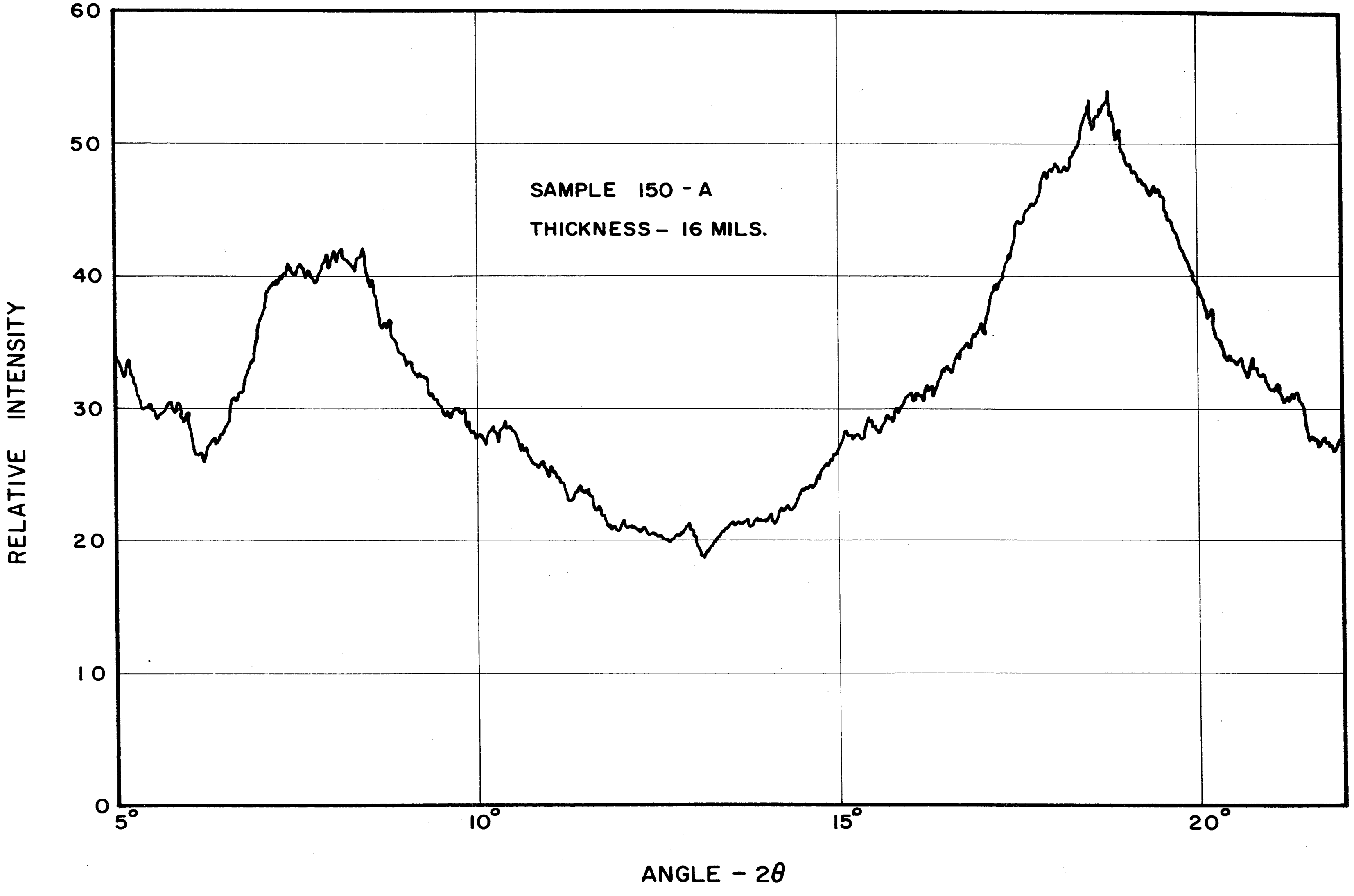

Figure 29. Relative Intensity of X-Ray Scattering as a Function of Angle

TABLE IX

Sample Data and Calculations for Determination of Surface Area

Data and Calculated Data: $TiCl_3$ (HRA) - Sample 1

	Dead Space Determination	Surface Area			
Bulbs	1 + 2 + x	1+2+x	1-3+x	1-3+x	1-3+x
V_1 (cc)	41.7	41.7	62.1	62.1	62.1
h_1 (cm)	4.00	4.00	3.95	3.65	3.85
h_2 (cm)	60.10	60.10	59.70	60.60	49.80
P_i (cm)	56.10	56.10	55.75	56.95	45.95
$(P_i)_c$ (cm)	56.00	56.00	56.65	56.85	45.85
h_3 (cm)	4.05	3.95	3.90	3.80	3.95
h_4 (cm)	47.70	4.45	6.60	15.80	24.30
P_f (cm)	43.65	0.50	3.70	12.00	20.35
$(P_f)_c$ (cm)	43.55	0.40	3.60	11.90	20.25
Bulb Temp (°C)		24.8	26.2	26.7	26.8
Room Temp (°C)		24.6	26.0	26.2	26.6
Liq. N_2 Temp (°K)		77.6	77.6	77.6	77.6
$P_i - P_f$ (cm)		55.60	52.05	44.95	25.60
$P_f - P_f'$ (cm)		0.40	3.20	8.30	8.35
P/P_o		0.005	0.047	0.157	0.266
$1 + \alpha$		1.000	1.002	1.008	1.014
V^* (cc)		2.79	3.715	2.96	1.475
V_T (cc)		2.79	6.505	9.465	10.94
$1-P/P_o$			0.953	0.843	0.734
$(P/P_o)/V_T(1-P/P_o)$ (cc^{-1})			.00758	.01993	.03315

TABLE IX (cont.)

Calculations

1. Dead Space Volume - ($V_2 + V_3 = V_D$)

$$V_1(P_i)_c = (V_1 + V_D)\ (P_f)_c$$

$$V_D = \frac{(41.7)\ (56.00-43.55)}{43.55} = 11.95 \text{ cc}$$

V_2 (the volume at R.T.) is calculated from capillary dimensions.

$$V_2 = 2.65 \text{ cc}$$

$$V_3 = 9.3 \text{ cc}$$

2. Adsorbed Volume (V*)

$$V^* = \frac{22,415}{R} \left(\frac{(P_i - P_f)}{T_B} V_1 - \frac{(P_f - P_f\ \ V_2}{T_R} - \frac{(P_f - P_f')V_3(1+\alpha)}{T_{N2}} \right)$$

e.g.-

$$V^* = \frac{22,415}{62,360} \left(\frac{(52.05)(62.1)}{299.3} - \frac{3.20)(2.65)}{299.1} - \frac{(3.20)(9.3)(1.002)}{77.6} \right)$$

$$V^* = 3.715 \text{ cc}$$

3. Volume adsorbed at monolayer coverage (Vm)

From plot of $(P/P_o)/V_T(1-P/P_o)$ vs. (P/P_o) - (See Figure 30)

Slope = .0021

Intercept = 0.116

$$Vm = \frac{1}{S + I} = \frac{1}{0.116 + .0021} = 8.47 \text{ cc}$$

TABLE IX (cont.)

4. Calculations of Specific Surface Area (A_{sp})

$$\text{Molecules adsorbed} - \frac{V_m(6.023 \times 10^{23})}{22{,}414}$$

Cross sectional area of N_2 molecule - 16.2 $A^{\circ 2}$

Wt. of $TiCl_3$ sample (G_{ti}) - 12.75 g.

$$s = \frac{V_m}{G_{ti}} \frac{(6.023 \times 10^{23})}{(\ 22{,}414\ )} (16.2 \times 10^{-20}\ ) = 4.35 \frac{V_m}{G_{ti}} (m^2/g.)$$

$$s = 4.35 \frac{8.47}{12.75} = 2.89\ (m^2/g.)$$

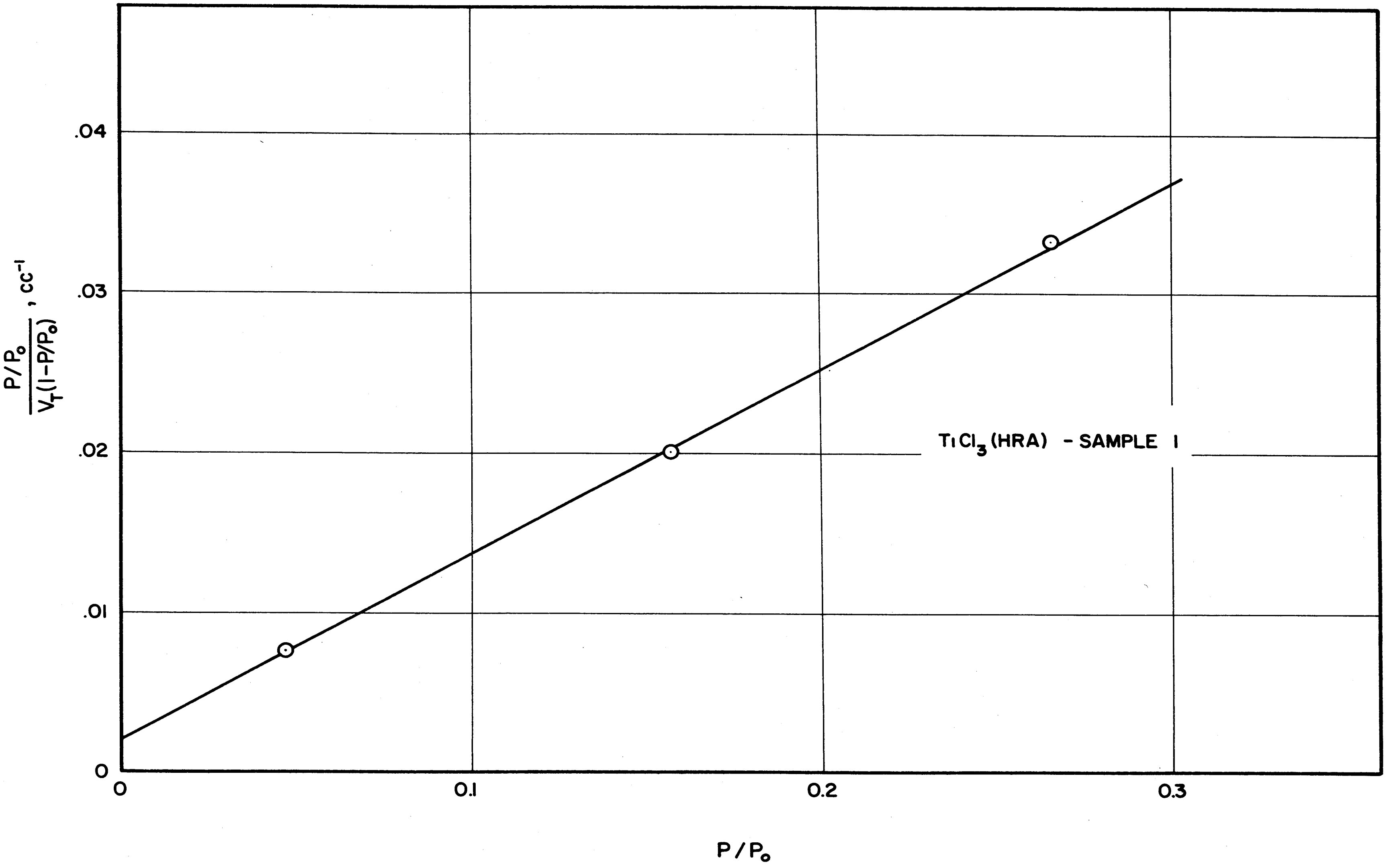

Figure 30. Surface Area Determination - Linear Form of the B. E. T. Plot

TABLE X

Calculation of Free Energy of Adsorption

Calculated Data

P/P_o	V_T	V_T/V_m	$\ln(P_o/P)$	ΔF
	cc			cal/mol
.002	0.95	0.110	6.21	960
.004	1.54	0.182	5.52	851
.010	3.16	0.373	4.61	711
.020	4.63	0.547	3.91	603
.040	6.22	0.735	3.22	496
.100	8.11	0.958	2.30	355

$\Delta F = -RT \ln (P/P_o)$

$T = 77.6° K$

V_T = obtained as a function of (P/P_o) from Figure 30.

APPENDIX B

TABLES OF CALCULATED DATA

TABLE XI

Summary of Rate of Polymerization Data

The following table includes all of the runs made for the determination of the rate of polymerization except those initial runs which were made using $TiCl_3$ suspensions of unknown "active" concentrations. Most of the runs before run 141 were of this nature. There were two reasons for this: first, it was not realized at that time that the deactivation of the $TiCl_3$ due to the heptane could be accounted for; and second, impurities introduced into the catalyst suspensions when taking samples caused sporadic decreases in activity which could not be accounted for. The $TiCl_3$ concentrations of the runs before No. 104 are not "active" $TiCl_3$ concentrations and therefore cannot be compared directly.

Notes are made at the end of this table to explain either unusual conditions or variables, or runs which were not included in the correlated data.

A complete tabulation of all runs made for the purpose of obtaining intrinsic viscosity data is given in Tables XX, XXI and XXII and it was not felt that this material should be duplicated.

TABLE XI (cont.)

EXPERIMENTAL RATE DATA

Run No.	Monomer Conc. (g/dl)	$TiCl_3$ Conc. (g/l)	$AlEt_3$ Conc. (Mol/l)	Temp. (°C)	$TiCl_3$ Susp.	Heptane and Pentene Batch	Rate (g/min.-g) $x10^4$
41	12.8	0.43	0.04	44.0	D	A/A	0.46
42	12.9	0.50	0.04	44.0	D	A/A	0.51
43	12.6	0.35	0.04	44.0	D	A/A	0.27
46	12.7	0.35	0.04	44.0	D	A/A	0.32
47	12.7	0.67	0.04	44.0	D	A/A	0.78
48	12.6	0.43	0.04	44.0	D	A/A	0.44
49	12.6	0.45	0.04	44.0	D	A/A	0.39
50	12.7	0.45	0.04	44.0	D	A/A	0.48
51	12.4	0.44	0.04	44.0	D	B/A	0.51
57	12.7	0.45	0.04	44.0	D	B/B	0.40
58	12.8	0.23	0.04	44.0	D	A/B	0.14
60	12.7	0.88	0.04	44.0	D	A/B	1.04
61	12.5	0.45	0.04	44.0	D	B/B	0.36
62	12.5	0.45	0.04	44.0	D	B/B	0.37
63	12.7	0.45	0.04	44.0	D	B/B	0.36
66	12.6	0.44	0.04	44.0	D	B/B	0.37
67	12.7	0.45	0.04	44.0	D	B/B	0.35
104	6.39	0.078	0.02	44.0	c	C/E	0.08
106	6.37	0.113	0.02	44.0	e	C/E	0.10
107	6.25	0.470	0.02	44.0	f	C/E	0.58
108	6.37	0.268	0.02	44.0	h	C/E	0.28
109	6.27	0.275	0.04	44.0	h	C/E	0.28
110	6.31	0.481	0.02	44.0	h	C/E	0.57
111	6.40	0.673	0.02	44.0	b	C/E	0.83
112	6.41	0.324	0.02	44.0	b	C/E	0.41
113	6.47	0.379	0.02	44.0	c	C/E	0.48
114	6.36	1.056	0.02	44.0	k	C/E	1.32
141	6.40	0.283	0.02	44.0	J	E/I	0.25
142	6.43	0.509	0.02	44.0	K	E/I	0.55
143	6.54	1.033	0.02	44.0	K	E/I	1.20
144	6.47	0.469	0.02	44.0	H	E/I	0.50
145	6.60	0.814	0.02	44.0	J	E/I	0.94
146	12.78	0.816	0.02	44.0	J	E/J	1.42
147	12.63	0.244	0.02	44.0	J	E/J	0.29

TABLE XI (cont.)

Run No.	Monomer Conc. (g/dl)	$TiCl_3$ Conc. (g/l)	$AlEt_3$ Conc. (Mol/l)	Temp. (°C)	$TiCl_3$ Susp.	Heptane and Pentene Batch	Rate (g/min.-g) $\times 10^4$
148	12.72	1.004	0.02	44.0	K	E/J	2.16
149	6.48	0.433	0.02	44.0	J	E/I	0.36
150b	12.78	0.960	0.02	44.0	J	E/J	2.92
151	6.43	0.685	0.02	44.0	J	E/I	0.67
152	12.74	0.496	0.02	44.0	K	E/J	0.92
153	12.74	0.423	0.02	44.0	J	E/J	0.50
154	12.76	0.887	0.02	44.0	K	E/J	1.82
155	12.88	0.287	0.02	44.0	H	E/J	0.47
156	6.36	0.783	0.02	44.0	K	E/I	0.83
157	6.33	0.824	0.02	44.0	J	E/I	0.58
158	6.50	0.291	0.02	44.0	H	E/I	0.23
159b	49.2	0.567	0.02	44.0	J	F/L	6.10
160	49.5	0.258	0.02	44.0	J	F/L	2.08
161	6.38	0.529	0.02	44.0	J	E/I	0.49
162	49.2	0.143	0.02	44.0	J	F/L	1.13
163b	49.5	0.271	0.02	44.0	H	F/L	3.49
164	49.4	0.101	0.02	44.0	H	F/L	0.78
165b	49.7	0.428	0.02	44.0	J	F/L	4.90
166	49.4	0.390	0.02	44.0	H	F/L	3.40
167	6.30	0.300	0.02	44.0	H	E/I	0.305
168b	49.5	0.520	0.02	44.0	J	F/L	5.32
169	49.6	0.316	0.03	44.0	H	F/L	2.80
170	6.50	0.293	0.03	44.0	H	E/I	0.21
171	49.5	0.060	0.03	44.0	H	F/L	0.34
172b	30.5	0.282	0.02	44.0	J	G/L	1.60
173	30.4	0.145	0.02	44.0	H	G/L	0.71
174	30.6	0.297	0.02	44.0	H	G/L	2.14
175	30.5	0.417	0.03	44.0	J	G/L	2.22
176	30.7	0.111	0.03	44.0	J	G/L	0.52
177	30.7	0.231	0.03	44.0	J	G/L	1.30
178b	30.7	0.548	0.04	44.0	J	G/L	3.40
179	30.5	0.175	0.03	44.0	H	G/L	0.82
180	30.8	0.440	0.03	44.0	H	G/L	2.78
181	6.48	0.768	0.03	44.0	K	E/I	0.63
182	6.56	0.296	0.03	44.0	H	E/I	0.24
183	6.44	0.562	0.02	44.0	J	E/I	0.50
184c	13.10	1.121	0.02	25.2	J	E/J	0.56
185	13.08	0.394	0.02	25.2	H	E/J	0.22
186	13.06	2.060	0.02	25.2	K	E/J	1.22

TABLE XI (cont.)

Run No.	Monomer Conc. (g/dl)	$TiCl_3$ Conc. (g/l)	$AlEt_3$ Conc. (Mol/l	Temp. (°C)	$TiCl_3$ Susp.	Hept. and Pentene Batch	Rate (g/min-g) x 10^4
187	13.04	0.547	0.02	25.2	J	E/J	0.30
188	13.02	1.681	0.02	25.2	K	E/J	1.00
189	13.02	0.881	0.02	25.2	K	E/J	0.61
190	13.05	0.831	0.02	25.2	J	E/J	0.59
191	50.8	0.298	0.02	25.2	H	G/L	1.00
192	50.6	0.104	0.02	25.2	H	G/L	0.16
193	13.02	1.274	0.02	25.2	K	E/J	0.59
194	6.54	1.030	0.02	44.0	K	E/I	1.82
195	6.41	0.289	0.02	44.0	H	E/I	0.23
196	6.42	0.674	0.02	44.0	J	E/I	0.63
197d	6.53	0.367	0.02	44.0	K	E/K	0.25
198	6.48	0.365	0.02	44.0	K	E/K	0.31
199	6.46	0.366	0.02	44.0	K	E/K	0.28
200	6.46	0.533	0.04	44.0	K	E/K	0.41
201	6.46	0.518	0.04	44.0	K	E/K	0.34
202	6.45	0.534	0.06	44.0	K	E/K	0.43
203	6.36	0.766	0.06	44.0	K	E/K	0.52
204	6.44	0.229	0.01	44.0	K	E/K	0.14
205	6.48	0.806	0.02	44.0	K	E/K	0.79
206	6.42	0.794	0.01	44.0	K	E/K	0.60
207	6.48	0.503	0.08	44.0	K	E/K	0.31
208	6.47	0.762	0.01	44.0	K	E/K	0.50
209	6.54	0.765	0.004	44.0	K	E/K	0.50
210	6.47	0.520	0.05	44.0	K	E/K	0.31
211	6.45	0.772	0.03	44.0	K	E/K	0.50
212	50.7	0.445	0.02	25.2	J	G/L	1.64
213	50.8	0.204	0.02	25.2	H	G/L	0.77
214	50.8	0.428	0.02	25.2	J	G/L	1.46
215	50.7	0.351	0.02	25.2	H	G/L	0.88
216	50.7	0.062	0.01	25.2	H	G/L	0.077
217	50.7	0.143	0.03	25.2	J	G/L	0.30
218	37.7	0.579	0.02	25.2	J	G/L	1.96
219	37.5	0.155	0.02	25.2	H	G/L	0.39
220	37.6	0.432	0.02	25.2	J	G/L	1.32
221	37.7	0.502	0.02	25.2	J	G/L	1.47
222	37.6	0.105	0.02	25.2	H	G/L	0.186
223	37.8	0.248	0.02	25.2	H	G/L	0.52

TABLE XI (cont.)

Run No.	Monomer Conc. (g/dl)	$TiCl_3$ Conc. (g/l)	$AlEt_3$ Conc. (Mol/l)	Temp. (°C)	$TiCl_3$ Susp.	Hept. and Pentene Batch	Rate (g/min-g) x 10^4
224	37.3	0.352	0.02	25.2	J	G/L	0.75
225	50.8	0.160	0.02	25.2	H	G/L	0.42
226	50.6	0.343	0.02	25.2	J	G/L	0.90
227	12.72	0.560	0.02	44.0	J	E/J	0.98
228	12.76	0.292	0.02	44.0	H	E/J	0.39
229	12.45	0.389	0.02	44.0	H	E/J	0.70
230e	5.93	0.094	0.02	87.5	H	H/M	0.075
231	5.99	0.226	0.02	87.5	H	H/M	0.35
232	5.91	0.181	0.04	87.5	H	H/M	0.20
233	6.01	0.262	0.02	87.5	J	H/M	0.26
234	6.08	0.308	0.02	87.5	H	H/M	0.51
235	6.05	0.400	0.01	87.5	J	H/M	0.62
236	11.58	0.27	0.02	87.5	J	H/M	----
237	24.9	1.139	0.02	25.2	J	H/M	3.00
238	25.9	0.318	0.02	25.2	H	H/M	0.74
239	25.0	0.832	0.02	25.2	J	H/M	2.00
240	25.1	0.992	0.02	25.2	J	H/M	2.46
241	24.9	0.196	0.02	25.2	H	H/M	0.31
242	24.9	0.584	0.02	25.2	J	H/M	0.96
243b	18.6	1.132	0.02	25.2	J	H/M	2.15
244	18.7	0.193	0.02	25.2	H	H/M	0.18
245	25.0	0.716	0.02	25.2	J	H/M	1.19
246	18.4	0.835	0.02	25.2	J	H/M	1.17
247	18.3	0.357	0.02	25.2	H	H/M	0.43
248	18.5	0.578	0.02	25.2	J	H/M	0.69
249	18.3	1.148	0.02	25.2	J	H/M	2.00
250	24.9	1.147	0.02	25.2	J	H/M	2.74
251	12.00	0.577	0.02	25.2	J	H/N	0.565
251	11.48		0.02	44.2	J	H/N	1.17
253	6.28	0.554	0.04	25.2	J	H/N	0.30
253	5.93		0.04	44.2	J	H/N	0.63
254	6.48	0.570	0.01	25.2	J	H/N	0.27
254	5.68		0.01	86.2	J	H/N	1.55
255	6.50	0.430	0.02	25.2	J	H/N	0.23
255	5.75		0.02	86.2	J	H/N	1.28
256	6.42	0.413	0.01	25.2	J	H/N	0.205
256	5.65		0.01	86.2	J	H/N	1.32

TABLE XI (cont.)

Run No.	Monomer Conc. (g/dl)	$TiCl_3$ Conc. (g/l)	$AlEt_3$ Conc. (Mol/l)	Temp. (°C)	$TiCl_3$ Susp.	Hept. and Pentene Batch	Rate (g/min-g) x 10^4
257	5.33	-	0.005	25.2	K	H/N	0.167
257	4.71		0.005	25.2	K	H/N	1.00
258	12.22	0.842	0.01	25.2	J	H/N	0.65
258	12.17		0.01	0.5	J	H/N	0.160
259	12.91	0.575	0.02	25.2	K'	H/O	0.58
260	13.04	0.605	0.02	25.2	K'	H/O	0.62
261	6.23	0.431	0.01	25.2	J	H/O	0.214
261	5.72		0.01	65.6	J	H/O	0.885
262	3.19	0.563	0.004	25.2	J	H/O	0.174
262	2.86		0.004	65.6	J	H/O	0.61
263f	12.45	0.340	0.01	65.6	J	C/O	
264	50.3		0.02	25.2	K'	C/O	0.266
264	49.1		0.02	44.2	K'	C/O	0.606
266	12.77	1.115	0.02	25.2	J	C/O	1.70
266	12.62		0.02	1.0	J	C/O	0.48
267	6.66	1.453	0.02	25.2	J	C/O	0.765
268	6.64	0.845	0.02	25.2	J	C/O	0.505
269	6.57	1.117	0.02	25.2	J	C/O	0.450
270	13.16	1.393	0.02	25.2	J	C/O	1.33
271	13.25	0.391	0.02	25.2	J	C/O	0.226
272	13.16	1.138	0.02	25.2	J	C/O	1.02
273	6.56	1.258	0.02	25.2	J	C/O	0.66
274	6.60	0.296	0.02	25.2	J	C/O	0.115
276	12.42	0.889	0.02	44.0	J	E/J	1.30
277g	12.62	0.281	0.02	44.0	H	E/J	0.283
278	6.34	0.400	0.02	44.0	L	C/P	4.03
279	5.27	0.379	0.02	44.0	M	C/P	3.0
280	6.38	0.291	0.02	44.0	L	C/P	4.6
281	6.33	0.202	0.02	44.0	L	C/P	5.06
282	6.04	0.104	0.02	44.0	M	C/P	1.12
283	6.28	0.185	0.02	44.0	N	C/P	6.12
284	6.24	0.072	0.02	44.0	M	C/P	3.38
285	6.20	0.052	0.02	44.0	M	C/P	0.565
286	6.37	0.103	0.02	44.0	L	C/P	1.90
287	6.35	0.204	0.02	44.0	M	C/P	2.12
288	12.72	0.297	0.02	44.0	H	E/J	0.28
291	12.65	0.557	0.02	44.0	J	E/J	0.482

TABLE XI (cont.)

Run No.	Monomer Conc. (g/dl)	$TiCl_3$ Conc. (g/l)	$AlEt_3$ Conc. (Mol/l)	Temp. (°C)	$TiCl_3$ Susp.	Hept. and Pentene Batch	Rate (g/min-g) x 10^4
290	6.34	0.0415	0.02	44.0	N	C/P	0.515
292	6.32	0.1392	0.02	44.0	L	C/P	3.12
293a[h]	12.8		0.02	25.2	K'	C/Q	0.25
293b	12.8		0.02	25.2	K'	C/Q	0.26
294a	12.8		0.02	25.2	K'	C/Q	0.29
294b	12.8		0.02	25.2	K'	C/Q	0.275
305a	12.9	0.290	0.05	44.0	H	H/S	0.253
305b	12.9	0.291	0.09	44.0	H	H/S	0.276

Notes:

a. The $TiCl_3$ concentration reported for runs before run No. 104 are not corrected for deactivation by the heptane used in the $TiCl_3$ suspension. Runs 104 and following have been so corrected.

b. Rate unexplainably high-data not used in correlation of rates.

c. Runs 184 to 190 were not used in correlation of rates. Runs at this temperature and monomer concentration were repeated later and these data were felt to be more accurate although the difference between the specific rates obtained from the two sets of data is not great.

d. Runs 197 to 211 were used to study techniques in handling the $TiCl_3$ suspension.

e. Runs 230 to 236 were originally to be used for determination of activation energy. Later methods for obtaining this were felt to be considerably more accurate.

TABLE XI (cont.)

f. Run 263 used only to obtain polymer for density determination.

g. Runs 278 to 287 made with suspensions of $TiCl_3$ (HRA).

h. In runs 293 and 294 rates were obtained at 25°C; the reaction mixture was put into deep freeze at -30°C for 24 hours, after which the rate was again measured at 25°C. The b runs are after storage at -30°C.

TABLE XII

Effect of Stirring Rate on Rate of Polymerization

C_M = 12.6 g/dl; C_A = 0.04 moles/l
C_{Ti} = 0.45 g/l; Temperature = 44.0°C.

Run No.	Relative Stirring rate	Rate (g./hr-g. $TiCl_3$)
66	0	0.399
62	1	0.373
61	2	0.366
63	2	0.359
57	3	0.368
67	4	0.356

TABLE XIII

Effect of Aluminum Triethyl Concentration on the rate of Polymerization

C_M = 12.9 g./dl; C_{Ti} = 0.29 g./l.
Temperature = 44.0°C.

Run No.	C_A (moles/l)	Rate (g./hr-g $TiCl_3$)
298	.01	0.275
297	.02	0.24
302	.02	0.23
305A	.05	0.26
299	.08	0.33
305B	.09	0.275
300	.12	0.28

TABLE XIV

Effect of Titanium trichloride Concentration on the Rate of Polymerization

Temp. = 44.0° C.; C_A = 0.04 moles/liter

C_M = 12.6 g/dl

Run No.	$TiCl_3$ Concentration g. $TiCl_3$ soln./liter	Rate g/min. - liter
58	14.35	0.54
43	21.3	1.06
46	21.5	1.25
41	26.3	1.66
51	26.9	1.91
50	27.7	1.81
42	30.3	1.96
47	41.0	3.03
60	53.4	4.04

TABLE XV

RATE DATA - Runs used for calculation of active $TiCl_3$ Concentrations.

A. Catalyst batches b, c, e, f, g, h, k

Basis - 0.694 g. $TiCl_3$ deactivated per 100 g. Heptane
C_M = 6.40 g./100 cc.; C_A = 0.02 moles/liter;
Temp. = 44.0°C.
Pentene batch - C; Heptane batch - E

Run No.	Cat. Batch	Calculated C_{Ti} (g./liter)	Corrected C_{Ti}	Corrected Rate (g./hr-liter)
104	c	.078	.058	0.32
106	e	.114	.094	0.40
107	f	.470	.450	2.34
108	h	.268	.248	1.15
109	h	.275	.255	1.13
110	h	.481	.461	2.28
111	b	.673	.653	3.18
112	b	.324	.304	1.02
113	c	.379	.359	1.87
114	k	1.056	1.036	5.24

B. Catalyst batches H, J, K.

Basis - 0.74 g. $TiCl_3$ deactivated per 100 g. Heptane
C = 6.40 g./100 cc.; C = 0.02 moles/liter;
Temp. = 44.0°C.
Pentene batch = E; Heptane batch = I.

Run No.	Cat. Batch	Calculated C_{Ti}	Corrected C_{Ti}	Corrected Rate
141	J	.283	.203	0.99
142	K	.509	.429	2.18
143	K	1.033	.953	4.64
144	H	.469	.389	1.95
145	J	.814	.734	3.60

C_{Ti} corrected for impurities in reaction mixture- Correction for Pentene batch C and Heptane batch E = .02 g. $TiCl_3$/liter.
Correction for Pentene batch E and Heptane batch I = .08 g. $TiCl_3$/liter.

TABLE XVI

Rate Data for $TiCl_3$ (HRA) - Determination of Rate Characteristic of Solid $TiCl_3$

C_M = 6.40 g./dl; Temp. = 44.0°C

C_A = 0.02 moles/l.

Run No.	$TiCl_3$ Batch	Rate (g./hr-1)	Apparent $TiCl_3$ Conc. (g./l.)	Active $TiCl_3$ Conc. (g./l.)
290	N	2.05	.0415	.0328
285	M	2.30	.0525	.0136
282	M	4.69	.104	.0269
286	L	7.54	.103	.0636
287	M	8.44	.204	.0529
292	L	12.50	.139	.0860
284	N	13.7	.072	.0570
279	M	14.4	.379	.0982
281	L	20.2	.202	.1248
283	N	24.6	.185	.1462

Data on $TiCl_3$ Batches:

Batch	Apparent $TiCl_3$ Conc (g./g. soln)	Active $TiCl_3$ Conc. (g./g. soln)
L	.0144	.0089
M	.00742	.00192
N	.0262	.0207

Basis for calculating active concentrations-

.0055 g. $TiCl_3$ deactivated per g. n-Heptane

TABLE XVII

Rate Data; Effect of $TiCl_3$ Concentration at Various Monomer Concentrations

A. At 25.2°C

Run No.	C_M g/dl	C_{Ti} g./l	$TiCl_3$ Batch	Rate (g./hr-l)
274	6.60	0.252	J	0.45
256	6.42	0.351	J	0.83
261	6.23	0.366	J	0.89
255	6.50	0.365	J	0.92
254	6.48	0.484	J	1.08
253	6.28	0.462	J	1.24
268	6.64	0.718	J	1.96
273	6.56	1.068	J	2.61
267	6.66	1.236	J	2.98
271	13.25	0.332	J	0.89
251	12.00	0.491	J	2.46
258	12.22	0.716	J	2.78
272	13.16	0.968	J	4.17
270	13.16	1.185	J	5.29
244	18.7	0.174	H	0.71
247	18.3	0.322	H	1.76
248	18.5	0.491	J	2.77
246	18.4	0.710	J	4.74
249	18.3	0.976	J	8.22
241	24.9	0.176	H	1.23
238	25.9	0.286	H	2.82
242	24.9	0.496	J	3.81
245	25.0	0.610	J	4.71
239	25.0	0.707	J	7.91
240	25.1	0.843	J	9.70
237	24.9	0.967	J	11.91
250	24.9	0.975	J	10.88

TABLE XVII (cont.)

Run No.	C_M g/dl	C_{Ti} g/l	$TiCl_3$ Batch	Rate (g/hr-l)
222	37.6	0.095	H	0.73
219	37.5	0.140	H	1.52
223	37.8	0.233	H	2.02
224	37.3	0.299	J	3.06
220	37.6	0.367	J	5.16
221	37.7	0.427	J	5.73
218	37.7	0.492	J	7.64
216	50.7	0.056	H	0.30
192	50.6	0.093	H	0.62
217	50.7	0.122	J	1.16
225	50.8	0.144	H	1.62
213	50.8	0.184	H	2.97
226	50.6	0.292	J	3.47
214	50.8	0.364	J	5.64
212	50.7	0.378	J	6.33
B. At 44.0°C				
147	12.63	0.208	J	1.14
155	12.88	0.275	H	1.82
152	12.74	0.486	K	3.58
146	12.78	0.693	J	5.53
154	12.76	0.870	K	7.11
148	12.72	0.984	K	8.44
176	30.7	0.094	J	1.99
173	30.4	0.131	H	2.75
179	30.5	0.158	H	3.16
177	30.7	0.196	J	4.99
174	30.6	0.267	H	8.25
175	30.5	0.355	J	8.57
180	30.8	0.396	H	10.62

TABLE XVII (cont.)

Run No.	C_M g/dl	C_{Ti} g/l	$TiCl_3$ Batch	Rate (g/hr-l)
171	49.5	0.054	H	1.30
164	49.4	0.091	H	2.94
162	49.2	0.121	J	4.28
160	49.5	0.219	J	7.82
169	49.6	0.284	H	10.51
166	49.4	0.351	H	12.82

Notes:

1. C_A varied between 0.01 and 0.03 mols/l.
2. Pentene and Heptane batches were the same for each group of runs at a particular temperature and monomer concentration, but were different for the different groups.
3. The rates reported in this table have been corrected for the slight variations in monomer concentration within each group.
4. The $TiCl_3$ concentrations reported in this table have been corrected for decreases in $TiCl_3$ "activity". This activity was considered constant throughout this work for the various $TiCl_3$ batches and had the following values: (H - 0.90; j - 0.85; K - 0.98).

TABLE XVIII

Effect of Monomer Conc. on the Polymerization Rate

at 25.2° C. and 44.0° C.

C_M g./100 cc	Rate g./hr-g. $TiCl_3$	Temp. °C
6.4	2.65	25.2°C
13.0	5.20	25.2°C
18.5	8.0	25.2°C
25.0	12.4	25.2°C
37.6	16.9	25.2°C
50.7	19.6	25.2°C
6.4	5.0	44.0°C
12.7	9.4	44.0°C
30.6	26.9	44.0°C
49.4	39.5	44.0°C

TABLE XIX

Rate Data - Effect of Temperature

Run No.	C_A	Rate at 25.2°C x 10^4	Avg. C_M at 25.2°C	Second Temp.	Rate at T x 10^4	Avg C_M	$\left(\frac{\text{Rate}_T}{\text{Rate}_{25}}\right)_{corr}^{(1)}$
	(mol./l)	$\left(\frac{g}{\text{min-g}}\right)$	(g./dl)	(°C)	$\left(\frac{g}{\text{min-g}}\right)$	(g./dl)	
258	.01	0.65	12.22	0.5	0.160	12.17	0.247
266	.02	1.70	12.77	0.5	0.480	12.62	0.285
251	.02	0.565	12.00	44.2	1.17	11.48	2.16
253	.04	0.30	6.28	44.2	0.63	5.93	2.22
264	.02	0.266	50.3	44.2	0.606	49.1	2.32
From other rate data				44.2			2.01
261	.02	0.214	6.23	65.6	0.885	5.72	4.50
262	.01	0.174	3.19	65.6	0.61	2.86	3.91
254	.01	0.27	6.48	86.2	1.80(2)	5.68	7.72
255	.02	0.23	6.50	86.2	1.39(2)	5.75	6.82
256	.02	0.205	6.42	86.2	1.27(2)	5.65	7.02
257	.01	0.167	5.33	86.2	1.11(2)	4.71	7.50

Notes:

(1) Ratio of rates corrected for change in monomer concentration according to first order dependence.

(2) Rates at 86.2°C dropped off rapidly with time. Rate reported here is initial rate obtained by extrapolation to zero time the function [P]/t *vs.* t. (see Figure 13.)

TABLE XX

Intrinsic Viscosity Data - Preliminary Studies

Temp = 21°C; C_A = 0.03 moles/l; C_M = 19.4 g./dl

Run No.	$TiCl_3$ Conc. g/l	$TiCl_4$ Conc. millimoles per liter	Reaction Time hrs.	Percent Conversion	[η] dl/g.
295A	0.10		5.0	0.26	4.47
B	0.20		5.0	0.70	4.57
C	0.50		2.5	0.96	4.39
D	1.00		2.5	2.54	4.53
E	0.20	0.1	5.0	1.73	4.72
F	0.20	0.2	5.0	1.34	4.60
G	0.20	0.4	5.0	1.93	4.30
H	0	1.0	5.0	0.81	2.03

TABLE XXI

Intrinsic Viscosity Data at 22°C

Run No.	C_A (moles/l.)	C_M (g./dl)	[η] dl/g.	$x_n \times 10^{-3}$	$x_n \times 10^{-3}$ (Corrected)*
296A	.004	38.3	7.80	5.82	
275A	.004	13.0	5.82	5.22	5.38
303A	.004	7.76	5.30	4.94	
296B	.01	38.6	6.93	5.62	
295J	.01	19.8	5.43	5.02	
296F	.01	13.0	5.06	4.78	
275B	.01	13.0	4.73	4.57	4.77
296L	.01	12.9	4.78	4.60	
296M	.01	12.9	4.98	4.73	
296G	.01	7.78	4.37	4.24	
296H	.01	5.66	3.95	3.82	
275C	.02	12.9	4.23	4.11	4.31
275D	.02	13.0	4.22	4.10	4.29
289A	.03	60.8	6.27	5.40	
289B	.03	50.6	6.08	5.33	
296C	.03	38.3	5.97	5.27	
289C	.03	33.2	5.38	4.98	
289D	.03	24.9	5.22	4.90	
289E	.03	15.75	4.64	4.48	
289F	.03	12.7	4.36	4.24	
275E	.03	12.9	4.02	3.87	4.10
289G	.03	10.2	3.96	3.82	
289H	.03	8.07	3.69	3.50	
289J	.03	5.00	3.15	2.77	
275F	.04	12.9	3.73	3.53	3.77
303H	.05	59.5	6.42	5.46	
296D	.05	38.3	5.47	5.03	
303G	.05	19.4	4.47	4.33	
303F	.05	12.85	3.99	3.86	
303C	.05	7.79	3.29	2.96	

TABLE XXI (cont.)

Run No.	C_A (moles/l.)	C_M (g./dl)	$[\eta]$ dl/g	$x_n \times 10^{-3}$	$x_n \times 10^{-3}$ (Corrected)*
303E	.05	5.69	3.04	2.62	
275G	.06	13.0	3.63	3.38	3.64
275H	.08	13.0	3.44	3.16	3.41
296E	.10	38.1	4.92	4.70	
303J	.10	19.35	4.03	3.90	
303D	.10	7.77	3.09	2.69	
275I	.118	13.0	3.38	3.08	3.33
275J	.196	12.8	3.09	2.69	2.94

*Run 275 corrected for difference in polymerization temperature (25°C instead of 22°C) so that the data could be compared directly:

$$\left(\frac{1}{\bar{X}_n}\right)_{22} = 0.85\left(\frac{1}{X_n}\right)_{25} + .024$$

TABLE XXII

Intrinsic Viscosity Data at 53°C

Run No.	C_M	C_A	$[\eta]$	$\bar{X}_n \times 10^{-3}$
	g/dl	moles/l.	dl/g	
304-A	37.5	.020	4.37	4.25
B	12.75	.020	2.87	2.37
C	7.78	.020	2.45	1.84
D	5.63	.020	2.10	1.48
E	7.58	.010	2.65	2.10
F	7.55	.050	2.14	1.53
G	7.61	.100	1.93	1.32

TABLE XXIII

Effect of Reaction Conditions on Density

Sample	Polymerization Temp. °C.	C_M g./dl	C_A moles.l	[η]	Catalyst	$h_{avg.}$ (cm.)	Density	Comments
93-B	-27	25.0	.02	8.1	$TiCl_3$ (Pract.)	40.0	.871	
58A	-27	25.0	.02	8.1	$TiCl_3$ (Pract.)	40.1	.871	
150-B	25.2	45	.02	5	$TiCl_3$ (Pract.)	40.3	.871	
150-D	25.2	20	.02	4.2	$TiCl_3$ (Pract.)	41.0	.870	
93-C	44.0	50.0	.02	4.5	$TiCl_3$ (Pract.)	40.2	.871	
P-263	65	13.0	.01	2.5	$TiCl_3$ (Pract.)	39.5	.872	
150-A	86	13.0	.02	2	$TiCl_3$ (Pract.)	39.1	.873	
150-C	44				$TiCl_3$ (Pract.)	37.4	.875	Extracted with ether
III-55	44				$TiCl_3$ (Pract.)	37.9	.875	Extracted with ether
93-D	25			2.2	$TiCl_4$	50.0	0.860	
93-D-1	25			2.2	$TiCl_4$	53.3	0.857	Heated and Quenched
P-280	44.0	6.4	.02		$TiCl_3$ (HRA)	42.2	.868	

APPENDIX C

MISCELLANEOUS TABLES AND FIGURES

TABLE XXIV

Properties of Titanium Trichloride (Pract. Powder)

Physical	
Appearance	Dark purple powder
Particle Size	0.1 to 10 microns (predominately 2 microns)
Bulk Density	20-25 lbs. per cu. ft.
Heat Stability	Disproportionates above 450°C at atmospheric pressure. Sublimes unchanged at 830°C in the presence of 10 atm. of $TiCl_4$.

Chemical Specifications	
Ti, wt. percent range	30.8 to 31.7
Cl, percent range	67.5 to 69.0
Fe, percent max.	0.02
Ni, percent max.	0.02
Cr, percent max.	0.02
Insolubles (in 10 percent H_2SO_4)	0.10
Cl/Ti ratio, range	2.9 to 3.0
$TiCl_4$, percent max.	4

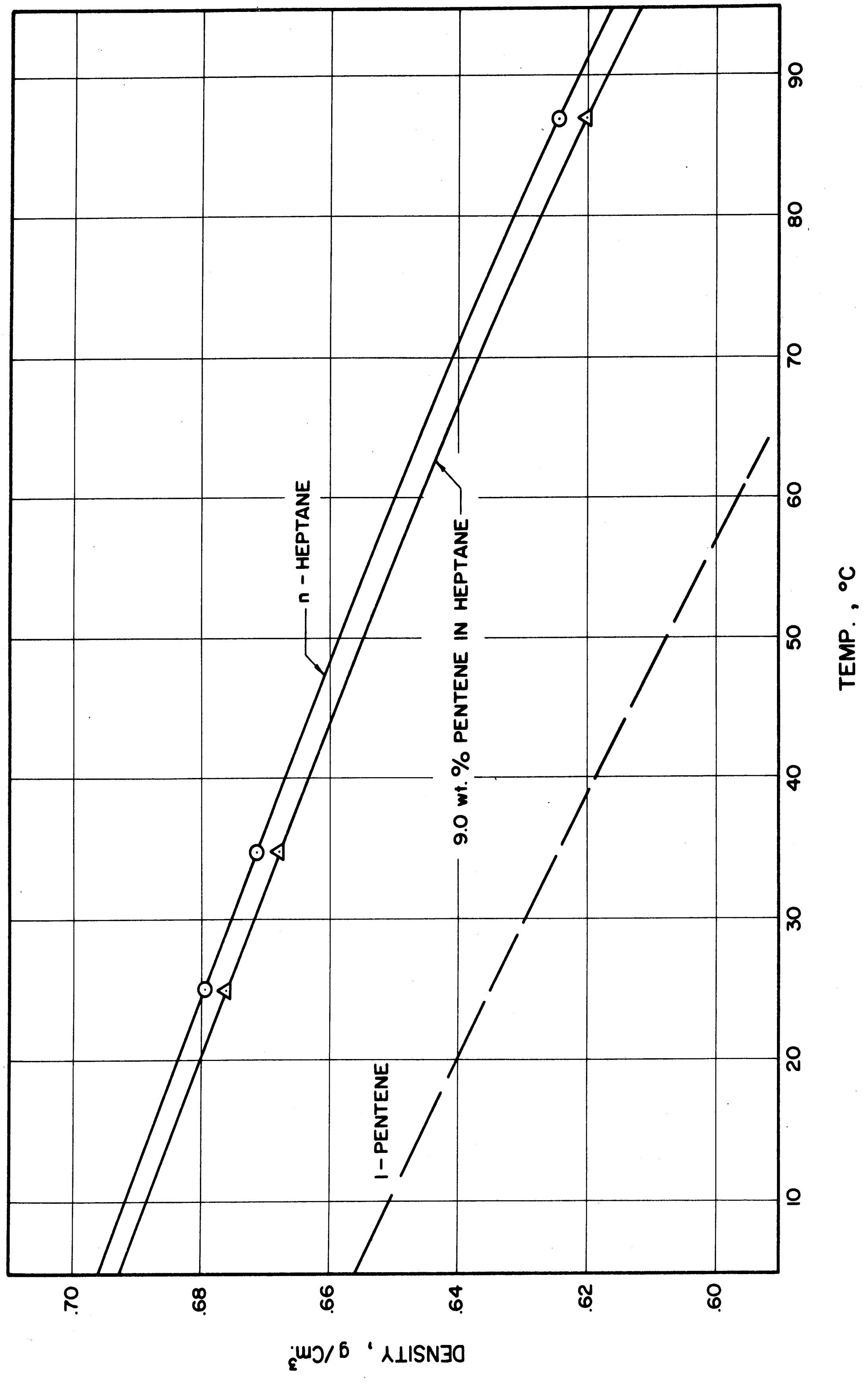

Figure 31. Densities of 1-Pentene and n-Heptane

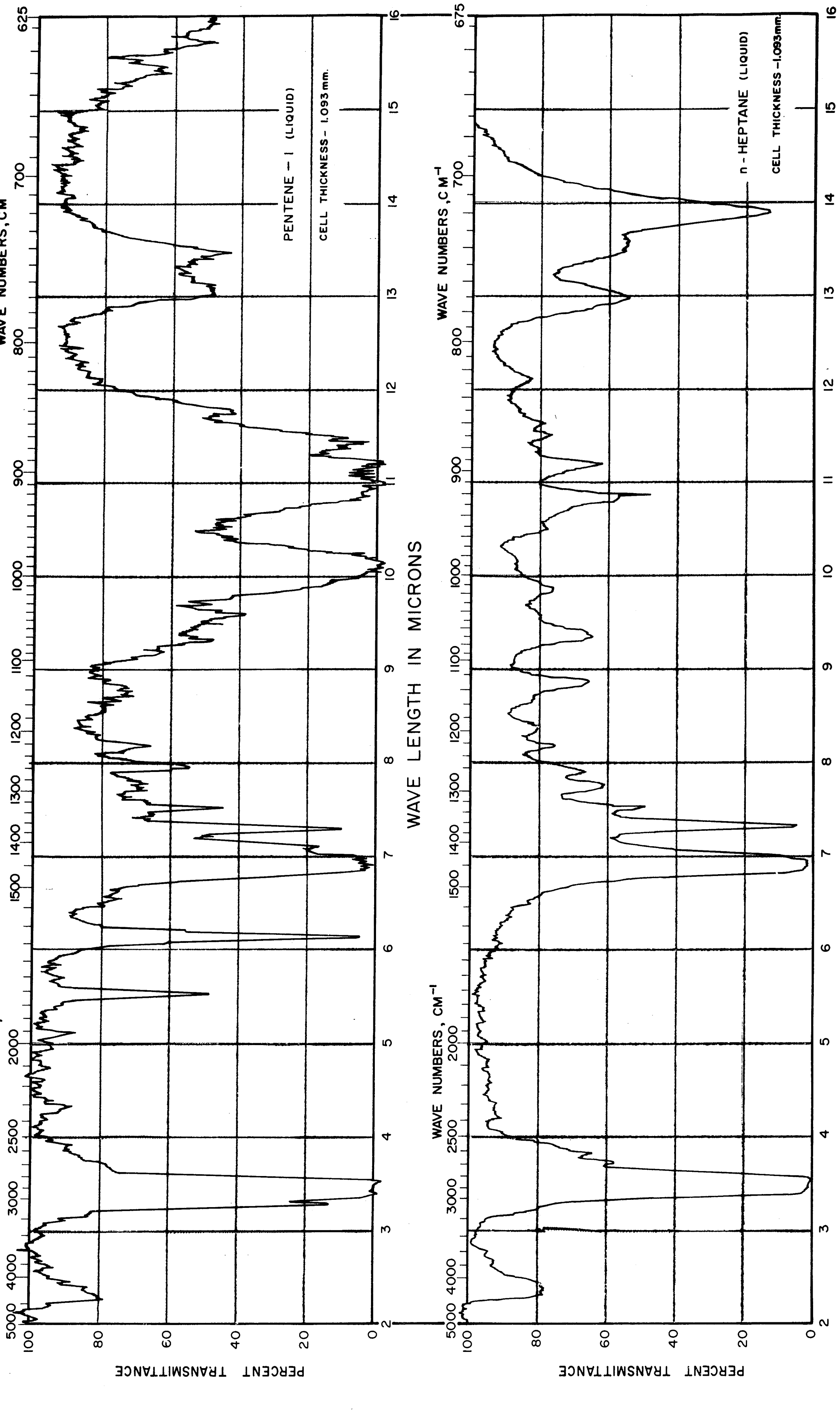

Figure 32. Infra-red Spectra of 1-Pentene and n-Heptane

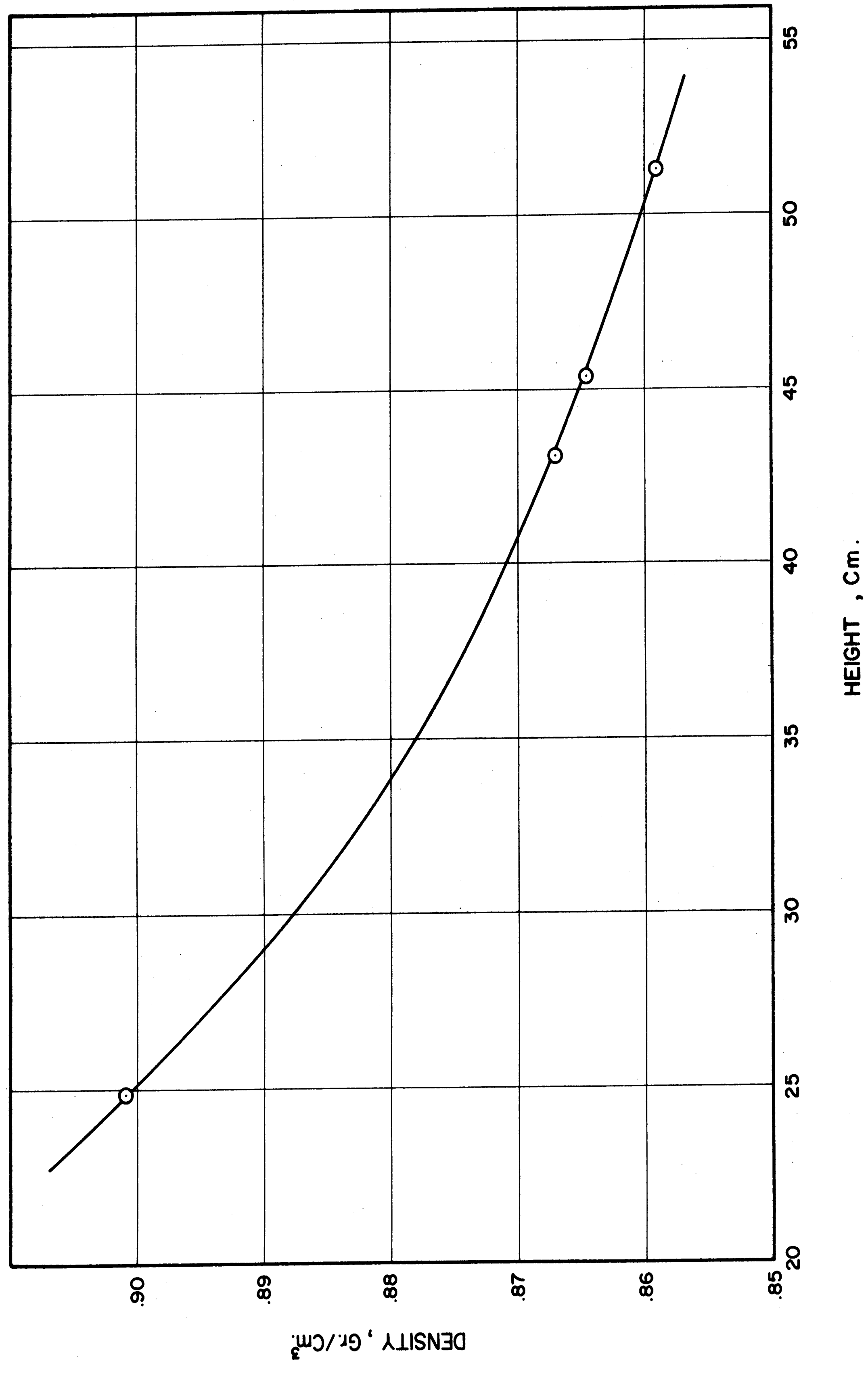

Figure 33. Calibration Curve for Density Gradient Column

NOMENCLATURE

a	Exponent in the empirical relationship between intrinsic viscosity and molecular weight.
a_1	Activity of the solvent.
A_P, A_t, etc.	Frequency factors in the Arrhenius equation as applied to the rates of propagation, termination, etc.
b	Ratio of propagation rates producing isotactic and atactic polymer.
B	Coefficient in the virial expansion of osmotic pressure as a power series in the concentration.
c	Polymer concentration in solution property relationships (g./cc or g./dl.).
c_s	Concentration of sites on $TiCl_3$ surface available for alkyl adsorption (sites/ sq. cm.).
c^*_s	Concentration of active sites for polymerization on $TiCl_3$ surface (sites/sq. cm.).
C_A, C_M, etc.	Concentrations of $AlEt_3$, monomer, etc. in reaction mixture (g./l. or moles/l.).
C^*_{Ti}	Concentration of active $TiCl_3$ in reaction mixture (g./l.).
D	Degree of crystallinity.
D_M, D_A,	Dissociation energies of monomer and $AlEt_3$ on the $TiCl_3$ surface. (cal/mol).
E_P, E_t, etc.	Activation energy for propagation, termination, etc. (cal/mol).
ΔE	Overall activation energy (cal/mol).

δE	Difference in overall activation energies for polymerization at two types of site or for two types of propagation reaction (cal/mol).
f	Fraction of catalyst sites.
ΔF	Change in Gibbs free energy (cal/mol).
G_{Ti}, G_i	Weight of $TiCl_3$ and impurities deactivating $TiCl_3$ (g.).
h	Height (cm).
$I_{2\theta}$	Intensity of X-ray scattering at angle 2θ.
I, [I]	Initiator, concentration of initiator (Sect. III-A-1).
$I\cdot[I\cdot]$	Primary free radical and its concentration (Sect. III-A-1).
k', k"	Constants in the relationship between solution viscosity and concentration.
k_1, k_{-1}	Rate constants for adsorption and desorption from a solid surface.
k_p, k_d, k_t, k_{tc}, k_{td}, k_{ts}, k_{ta}	Reaction rate constants in polymerization reactions for propagation, decomposition of initiator, monomolecular termination, termination by coupling, termination by disproportionation, termination by transfer with S, and termination by transfer with $AlEt_3$.
k_d	Rate constant for deactivation of $TiCl_3$.
K	Constant in the intrinsic viscosity-molecular weight relationship.
K_A, K_M	Equilibrium constants for adsorption of $AlEt_3$ and monomer on the $TiCl_3$ surface.
m	Slope of reciprocal monomer concentration <u>vs.</u> reciprocal degree of polymerization curves.

M	Molecular Weight.
$\bar{M}_n$, $\bar{M}_V$	Number and viscosity average molecular weights.
M, $[M]$	Monomer unit and its concentration (Sect. III-A-1).
$M^{\cdot}_x$	Chain radical containing x units (Sect. III-A-1).
Me	Catalyst site.
n	Number of units.
n_0	Minimum sequence length.
N	Number of polymer molecules.
p	Degree of stereospecificity.
p	Pressure.
P	Polymer unit or weight of polymer (g.).
$[P]$	Polymer concentration.
r_a, r_d	Rate of adsorption and desorption.
R	Gas constant.
R	Alkyl unit.
R_p, R_t, etc.	Rate of propagation, termination, etc. (g./hr-g $TiCl_3$).
s	Specific surface area of the $TiCl_3$ (sq. m./g.).
SH	Transfer agent.
$S^{\cdot}$	Free radical from transfer agent.
T	Absolute temperature (°K).
t	Time.

t	Thickness of polymer film (mils).
$\bar{v}$	Specific volume (cc/g.).
V_1	Molar volume of solvent.
V^*, V_T	Volume and total volume of gas adsorbed in surface area determination (cc).
V_m	Volume of gas adsorbed (cc).
$\bar{X}_n$	Number average degree of polymerization.
η_r	Relative viscosity.
η_{sp}	Specific viscosity ($\eta_{sp} = \eta_r - 1$).
$[\eta]$	Intrinsic viscosity (dl/g.).
θ	Fraction of sites covered.
π	Osmotic pressure (atm.).
ρ	Density (g./cc).