SOME ASPECTS OF THE
POLYMERIZATION OF 4-VINYL PYRIDINE INITIATED
BY BUTYL LITHIUM

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To my wife, Joan
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ABSTRACT

The butyl lithium initiated polymerization of 4-vinyl pyridine in hydrocarbon media proceeds by an anionic addition mechanism. The colorless, soluble reactants rapidly form a granular intensely colored polymer precipitate at temperatures below -30°C. in heptane and toluene diluents. When the reaction is carried out in impurity free systems, the highly colored reaction system remains unchanged for indefinite periods of time. The addition of more monomer to an already polymerized reaction system, produces continued growth of polymer chains. As predicted for anionic polymerization, the measured number average molecular weights of polymers produced by the polymerization reaction are equivalent to the ratio,

\[
\frac{\text{weight of polymer}}{\text{equivalents of initiator}}.
\]

In the past six years there have been many investigations into the kinetics and molecular weight distributions of homogeneous anionic polymerizations. Little work has been done on heterophase anionic polymerizations. The extremely narrow molecular weight distributions that result from many of the homogeneous reactions can be of great value in the production of polymers with well defined properties. The question is, what type of kinetics and molecular weight distributions can be expected from an anionic polymerization in which a precipitate is formed.
A dilatometric technique was employed to follow the rate of polymerization of 4-vinyl pyridine initiated by butyl lithium in toluene media. Initial monomer and initiator concentrations were varied over a four fold range. Rate measurements were made over the range -30°C to +30°C. The polymer produced in these reactions was fractionated by elution chromatography using tert-butyl alcohol and benzene solvent-non-solvent mixtures, and the molecular weight distributions of the polymers were constructed from fractionation data.

The polymerization of 4-vinyl pyridine initiated by butyl lithium in toluene diluent, produces a bimodal molecular weight distribution consisting of two fairly narrow molecular weight ranges. An examination of the rate of reaction indicates a rate mechanism proportional to the monomer concentration, and to the square root of the "effective" initiator concentration. The bimodal molecular weight distribution is the result of the occlusion of a portion of the growing chains in the polymer precipitate. These trapped reaction sites (which amount to 95% and up of the total initiator concentration) are no longer capable of growth due to the absence of available monomer. The remaining "effective" reaction sites grow to high molecular weight and are responsible for the observed kinetics. Thus two distinct molecular weight materials are produced. The activation energy for the propagation step was determined as 12.7 Kcal/mol.
I. INTRODUCTION

A. Significance of Study

The addition polymerization of a vast number of monomers initiated by (or catalyzed by) inorganic and organometallic compounds has been the subject of enormous attention for the past eight years. The various categories of catalysts, alone, is a huge topic. Several of the larger groups of catalysts and initiators, both homogeneous and heterogeneous, have been (1) the transition metal halide-organoaluminum coordinate catalysts, (2) the transition metal oxide catalysts, and (3) alkali metal and alkali metal alkyl and aryl catalysts and initiators. Many related topics of theoretical and commercial interest have been studied. Prominent among these have been the study of kinetic mechanisms, the study of stereoregularity, and the study of molecular weight distributions in high polymers. Much of the work on the transition metal halide catalysts and the metal oxide catalysts have been directed toward kinetic mechanisms and stereospecific polymerizations. Much of the work on the alkali metal and alkali metal organic initiators has been on the study of kinetic mechanisms and molecular weight distributions. Little attention has been given to the relation of molecular weight distribution and polymerization mechanism in heterogeneous complex catalysts systems, mainly because the kinetic mechanisms are too complex for more than empirical treatment. The resulting molecular weight distributions are generally broad. On the other hand, much attention has been given to these subjects in the homogeneous polymerization systems initiated by soluble
organometallic compounds. In many instances, in these systems the mecha-
nisms are so simple that mechanisms and molecular weight distributions
can be rigorously treated mathematically.

Since molecular weight distributions of polymers strongly af-
flect the physical properties and possible applications of the polymeric
product, it is desirable to control a polymerization reaction to produce
the optimum range of molecular weights in a given product. Before a pro-
cess can be controlled, however, one must have a basic understanding of
the mechanism and its controllable features. Unfortunately, most of the
industrially important addition polymerization processes are based on
reaction mechanisms such as free radical chain growth and coordinate
catalysis that involve so many possible competing reactions that fine
control becomes impossible. One of the more promising polymerization
reactions that has been studied recently, however, has been the homoge-
neous anionic polymerization of several vinyl monomers by soluble or-
ganometallic initiators.

These polymerization reactions, under proper conditions, have
yielded almost monodisperse molecular weight distributions at almost any
desired degree of polymerization. This unusual result, unusual at least
with respect to most polymerization reactions, can be attributed to a
polymerization mechanism that has only two steps, initiation and propa-
gation. This mechanism can be represented as

\[
\text{initiation} \quad \text{I} + \text{M} \rightarrow \text{P}_1
\]

\[
\text{propagation} \quad \text{P}_i + \text{M} \rightarrow \text{P}_{i+1}
\]

The resulting set of products \( \{\text{P}_i\} \) can remain reactive almost indefi-
nitely and have been named "living polymers."\(^{(45)}\) It was suggested that
such "living polymers" could be used to synthesize all sorts of block co-polymers by the controlled alternate addition of various monomers to reaction systems consisting of polymeric anions. Seemingly, an endless variety of tailor-made polymers could be produced by such a technique. The capability of building specific properties into tailor-made polymers, and in particular, the ability to control molecular weight averages and distributions to a fine degree can be of significant industrial as well as theoretical potential.

During a preliminary experimental investigation of typical anionic polymerization systems, the reaction of butyl lithium and \( \text{vinyl pyridine} \) was found to produce an intensely colored granular polymeric precipitate in toluene and heptane diluents. It was noted that in spite of the large amount of current literature available on the kinetics and molecular weight distributions of homogeneous anionic polymerizations, no one has reported any work on anionic heterophase reactions. (We distinguish the simple anionic polymerization mechanism from the more complex heterogeneous Ziegler coordinate polymerizations.) Such a heterophase system could be the prototype of many commercial resin processes, since the raw polymer that is produced can be extremely pure (inorganic catalyst residues of 60 to 100 ppm) and in a form ideal for further polymer processing. The question that is posed by the formation of a precipitate, however, is what type of kinetics and molecular weight distribution can be expected. In view of the comparisons one might draw with regard to other heterophase polymerizations as well as with homogeneous anionic polymerizations, the study of the kinetics of this polymerization system seemed worthwhile.
B. Initiation in Anionic Polymerization

Anionic polymerization covers a broad number of polymerization reactions dating back many years. Flory\textsuperscript{(11)} gives a brief description of some of the earlier reactions utilizing metallic sodium with diene monomers and of polymerization of vinyl monomers via alkali metals in liquid ammonia. Indeed, Ziegler\textsuperscript{(55,56)} reports the study of the low molecular weight polymerization reactions of butadiene with butyl lithium as early as 1934. It was not until Szwarz\textsuperscript{(45)} coined the term "living" polymers in 1956 in regard to the polymerization of styrene by sodium napthalene complex that any extensive interest was shown to the subject of anionic polymerization. It is this restricted area of anionic polymerization --- a non-terminating homogeneous polymerization in non-proton donating media --- that we shall refer to hereafter as simply anionic polymerization. Many of the vinyl polymerizations initiated by sodium napthalene complex in ether type solvents and by butyl lithium in both ether and hydrocarbon solvents belong to the category just described. The two initiators, sodium napthalene and butyl lithium, represent two distinctly different forms of anionic initiation. The sodium napthalene complex initiates by electron transfer\textsuperscript{(45)} to monomer to produce a radical-anion that may undergo both ionic polymerization and radical dimerization.

\[ \dot{E} + M \rightarrow \cdot M^\ominus \]
\[ \cdot M^\ominus + M \rightarrow \cdot M - M^\ominus \]
\[ \cdot M - M^\ominus + \cdot M - M^\ominus \rightarrow \overset{\ominus}{M} - M - M - M^\ominus \]
On the other hand, butyl lithium initiates by addition across the double bond of an unsaturated monomer and is incorporated in the growing polymer chain.\(^{(50)}\)

\[
\begin{align*}
B_u Li + i^2C = CH &\xrightarrow{X} B_u - CH_2 - CH^- \xrightarrow{X} \delta^- \quad \downarrow \delta^+
\end{align*}
\]

The lithium-carbon bond in the compound butyl lithium is considered to be covalent. When the lithium becomes attached to a carbon which also has an electrophilic group attached such as the benzene ring in styrene or the nitrile group in acrylonitrile, however, the lithium-carbon bond takes on the form of a stable ionic pair which is capable of addition polymerization. Termination of this active ion pair can take place via transfer of a proton from a suitable proton donor such as an alcohol or by reaction with compounds such as oxygen or carbon dioxide. Therefore, the requirements for this type of anionic polymerization is a system consisting of a monomer with a suitable electron attracting side group attached to the carbon-carbon double bond in a non proton-donating media. The alpha-olefins such as ethylene, propylene etc. which have electro-positive groups attached to the carbon do not polymerize by addition of butyl lithium although butyl lithium will add across the carbon-carbon double bond in these compounds.

One molecule of butyl lithium generates one growing chain.

This seems to be a general mechanism for all organolithium initiations. Glusker\(^{(16)}\) has shown the same results in the polymerization of methyl-methacrylate by 9-flourenyl lithium. On the other hand, the radical-anion product of the electron transfer reaction is subject to radical combination to form dianions - i.e., one growing chain with two growing
The results of the stoichiometry of these reactions is simply that the number average molecular weight of the polymer produced in these systems in the absence of chain transfer can be calculated by the ratio of \( \frac{\text{monomer}}{\frac{1}{2} \text{catalyst}} \) for sodium napthalene initiation\(^{(49)}\) and by the ratio of \( \frac{\text{monomer}}{\text{catalyst}} \) for butyl lithium initiation,\(^{(16,50)}\) at 100 per cent conversion.

C. Some Kinetic Studies in Anionic Polymerization

Numerous kinetic studies have been made on the polymerizations of styrene,\(^{(24,35,50,51,54)}\) on methyl methacrylate,\(^{(15,16,17,23,53)}\) on butadiene,\(^{(6,24,32)}\) and on isoprene\(^{(6,22,26,32,40,41,42,43)}\) by organolithium compounds. The papers most relevant to the current study are those by Welch\(^{(50,51)}\) and Worsfold, Bywater\(^{(54)}\) on the polymerization of styrene, those by Glusker et al.\(^{(15,16,17)}\) on methacrylate, and those of Morton et al.\(^{(32)}\) on isoprene and butadiene.

Welch\(^{(50)}\) studied the polymerization of styrene initiated by butyl lithium in benzene and toluene solutions in the temperature range 20° to 50°C with catalyst concentrations from .002 m/liter to .04 m/liter and monomer concentrations up to 3.7 m/liter. He found that for n-butyl lithium concentrations less than .020M the rate of propagation was proportional to the concentrations of initiator and styrene. For higher concentrations of initiator he found the rate was independent of initiator concentration but proportional to monomer concentration. He found no termination reaction and a rate of initiation about one-fifth the rate of propagation. The method employed for the determination of the "effective" concentration of initiator (which is extremely sensitive to
impurities) was by means of the number average degree of polymerization of the polymeric product through the relation

\[ \bar{M}_n = \frac{\text{monomer} \cdot \text{yield}}{\text{catalyst}} \]

A subsequent study\(^{(51)}\) showed that additions of such Lewis bases as tetrahydrofuran and triethylamine had a marked acceleration effect on the rate of polymerization.

Worsfold and Bywater\(^{(54)}\) studied the initiation and polymerization of styrene in benzene via butyl lithium over the temperature range of 10°C to 30°C with catalyst concentrations from 0.0000675 m/liter to 0.0388 m/liter and with monomer concentrations ranging from 0.00185 m/liter to 0.0276 m/liter. They found an initiation rate that could be expressed as

\[ -\frac{\text{d(butyl lithium)}}{\text{dt}} = k_1 (\text{butyl lithium})^{1/6} (\text{styrene}) \]

and a polymerization rate that could be expressed as

\[ -\frac{\text{d(styrene)}}{\text{dt}} = k_2 (\text{total butyl lithium})^{1/2} (\text{styrene}) \]

They reported an activation energy of 14.3 Kcal/mol for the propagation reaction and rate constants from which a pre-exponential frequency factor of 2.93 x 10^8 could be calculated. The ratio of \(k_2/k_1\) was given as 600/1.

Glusker and coworkers\(^{(15,16,17)}\) have studied the initiation and polymerization of methyl methacrylate using fluorenyl lithium as initiator and tritiated acetic acid as terminator. By this method any
flourenyl lithium not reacted would form radioactive flourene with the tritiated acetic acid. They found only 1.67% of the initiator remaining after 5 seconds of reaction at -60°C. They found that rate data could be correlated by the following initiation and polymerization scheme since plots of \( \ln \frac{M}{M_0} \) vs time were accurately linear to over 90% conversion.

**initiation**

\[
- \frac{d(\text{initiator})}{dt} = k_i(\text{initiator})(\text{monomer})
\]

**propagation**

\[
- \frac{d(\text{monomer})}{dt} = k_p(\text{total initiator})(\text{monomer})
\]

They found that the rate plots when extrapolated to zero time gave a positive intercept equivalent to the consumption of 3 moles of monomer per mole of initiator. Furthermore unlike the organolithium polymerizations of other monomers, they obtained extremely broad molecular weight distributions and showed that less than 10% of the initiator started chains that had molecular weights higher than 2000. This evidence pointed to the equilibrium formation of an intermediate cyclic complex which would react with monomer only on disassociation.

Morton et al. (32) studied the polymerization of isoprene and butadiene in hexane and tetrahydrofuran solvents with butyl lithium initiator. They found a polymerization reaction that had a \( \frac{1}{2} \) order dependence on total butyl lithium concentration and first order dependence on monomer concentration. They showed that the reaction was much more rapid when carried out in ether solvent. Activation energies for
isoprene and butadiene in hexane were given as 22 Kcal/mol and 21.3 Kcal/mole, respectively, whereas the same reactions carried out in tetrahydrofuran gave activation energies of 7 Kcal/mole and 7.2 Kcal/mole. The 1/2 order dependence of the rate on butyl lithium concentration was accounted for by an equilibrium association of the growing polymeric anions in hexane solvent. The further observation that the viscosity of the "living" polymer solution became drastically reduced upon the addition of a small amount of terminating agent, enabled Morton to determine the degree of association independent of the rate measurements.

By using the bulk viscosity (or concentrated solution viscosity) relation

$$\eta = K M^{3.4}$$

These investigators found that the molecular weight of the "living" polymer was twice that of the terminated polymer. They reasoned, therefore, that the length of the growing polymeric anions was double that of the terminated chains via an association of the active chains as diagramed below

R --- C⁶⁻ --- Lᵢ⁺
   \vdots
Lᵢ⁺ --- C⁶⁻ --- R

The addition of ether type solvents reduced the degree of association by complexing with the lithium ions. Thus in pure tetrahydrofuran the growing chains were not associated and were therefore capable of more rapid polymerization.
D. Molecular Weight Distributions in Non-Terminating Polymerizations

The general trend of the group of rate studies just described, suggest the following mechanism for anionic polymerization. (Subject to further refinement to account for equilibrium complex formation)

initiation \[ I + M \rightarrow P_1 \]

propagation \[ P_i + M \rightarrow P_{i+1} \]

\[ P_2 + M \rightarrow P_3 \]

where

- \( I \) is the concentration of initiator
- \( P_i \) is the concentration of active polymer containing \( i \) monomer units
- \( M \) is the concentration of monomer
- \( I_0, M_0, P_{i0} \) is the initial quantity, respectively
- \( k_i \) and \( k_p \) are the rate constants of initiation and propagation.

The differential rate expressions are:

\[ -\frac{dI}{dt} = k_i (I)(M) \]

\[ \frac{dP}{dt} = k_i (I)(M) - k_p (P_i)(M) \]

\[ \frac{dP_i}{dt} = k_2 (P_{i-1})(M) - k_p (P_i)(M) \]

\[ -\frac{dM}{dt} = k_i (I)(M) + k_p \left( \sum_{i=1}^{\infty} P_i \right)(M) \]
Bresler et al. \(^{(6)}\) have solved this series of equations for the set of initial conditions \(\{P_i\} = 0\) at \(t = 0\) by introducing a new variable \(\tau = \int_0^t M(t) dt\) \(\text{d}\tau = M\text{d}t\). The solution for \(P_i(\tau)\) is

\[
P_i = \frac{\lambda_i}{\lambda_i - \lambda_i} \left( \frac{\lambda_i}{\lambda_i - \lambda_i} \right)^i I_0 e^{-\lambda_i \tau} \sum_{m=0}^{\infty} \left( \frac{\lambda_i - \lambda_i}{\lambda_i} \right)^m m! \tag{1}\]

or

\[
P_i = \frac{\lambda_i}{\lambda_i - \lambda_i} \left( \frac{\lambda_i}{\lambda_i - \lambda_i} \right)^i I_0 e^{-\lambda_i \tau} \frac{\gamma \left\{ i \left[ \left( \lambda_i - \lambda_i \right) \tau \right] \right\}}{\Gamma(i)} \tag{2}\]

where \(\gamma\) and \(\Gamma\) are incomplete and complete gamma functions of their respective arguments. The solution for \(I(\tau)\) is

\[
I = I_0 e^{-\lambda_i \tau} \tag{3}\]

Since it can be shown that \(\sum_{i=1}^{\infty} P_i = I_0 - I\) the solution for \(M(\tau)\) is

\[
\delta(t) = \frac{M_0 - M}{M_0} = \frac{\lambda_i I_0 \tau}{M_0} + \left( \frac{\lambda_i - \lambda_i}{\lambda_i} \right) \frac{I_0}{M_0} \left( 1 - e^{-\lambda_i \tau} \right) \tag{4}\]

where \(\delta\) is the fraction of conversion.

For any given degree of conversion, \(\delta\), one can obtain a value of \(\tau\) from (4) from which the concentration of \(P_i\) can be computed for all \(i\).

Since the number average degree of polymerization is defined by

\[
\bar{i} = \frac{M_0 - M}{\sum_{i=1}^{\infty} P_i} \tag{5}\]
then from (4)

\[ \bar{I} = \frac{M_0 \Delta}{I_0 - I} \]

For the special case where \( k_1 = k_p = k \) the results reduce to

\[ \hat{P}_i(t) = \frac{I_0 e^{-k \tau} (k \tau)^i}{i!} \]

\[ \sum_{i=1}^{\infty} \hat{P}_i = I_0 (1 - e^{-k \tau}) = I_0 - I \]

and

\[ \Delta = \frac{k \tau}{M_0} \]

The result in (7) is the well known Poisson distribution with mean \( k_\tau^* \) and standard deviation \( \sqrt{k_\tau} \). Then from (4) and (5)

\[ \bar{I} = \frac{M_0 \Delta}{I_0 (1 - e^{-k \tau})} \]

Furthermore from (8)

\[ \bar{I} = \frac{k \tau}{1 - e^{-k \tau}} \]

Hence, the number distribution has a mean of \( \bar{I} \) and a standard deviation \( \sqrt{\bar{I}} \).

*Actually since \( \bar{I} \) starts from 1 the mean of this distribution is \( k_\tau/1-e^{-k \tau} \).
By exactly the same procedure it is easily shown that if $k_1 \gg k_p$, such that at approximately zero time $P_1(0^+) = I_0$. Then

$$P_i(t) = \frac{I_0 (k_p t)^{i-1}}{(i-1)!} e^{-k_p t}$$

(11)

$$\sum_{i=1}^{\infty} P_i = I_0$$

and

$$M = M_0 e^{-k_p I_0 t}$$

(12)

and

$$\bar{l} = \frac{M_0 \delta}{I_0}$$

(13)

Equations (6), (9), and (13) all substantiate the correlation that the number average molecular weight can be obtained by $\frac{\text{monomer}}{\text{initiator}} \times \text{yield}$, particularly at high conversion.

Equation (6) points out, furthermore, that in the case of a small initiation rate constant, $k_1$, one would compute an error in determining the initiator concentration from the relation

$$I_0 = \frac{\text{monomer} \times \text{degree of conversion}}{\text{number average degree of polymerization}}$$

This error is magnified if that number average degree of polymerization were obtained by viscometric methods which are insensitive to the lower molecular weight chains that would be produced by slow initiation. This probably accounts for the results found by Welch\(^{51}\) at high initiator concentration.
No consideration has been given to the effect of impurities or chain transfer in this development of the molecular weight distributions. The effect of impurities on the molecular weight distributions in reactions that generate monofunctional chains has been shown(9, 37, 46) to broaden the molecular weight distributions from that expected in the previous development. However, even at high concentrations of impurities equivalent to the initiator concentration, the ratio of weight average molecular weight, $M_w$, to number average molecular weight, $M_n$, never exceeded 2.

The effect of chain transfer was considered by Bresler et al.(6) and Litt.(25) The result of chain transfer would also broaden the molecular weight distribution and change the number average molecular weight of the resultant polymer. Based on the study of the distributions of polyisoprene and polybutadiene(6) initiated by butyl lithium, as well as the agreement of number average molecular weights with the correlation, $M_n = \frac{\text{monomer}}{\text{initiator}} \times \text{yield}$ in all of the kinetic studies described, it is reasonable to neglect chain transfer as a factor in the development presented here.

E. 4-Vinyl Pyridine

4-Vinyl pyridine is a colorless liquid with a reported density $d_4^{25}$ of .979(36) a refractive index, $N_D^{25}$, in the range 1.5490 - 1.5500(36) with a temperature coefficient for $N_D$ of -.0005°C⁻¹, and boiling points of 54°C at 5 mm, 56°C at 9 mm, 58°C at 11 mm, 68°C at 18 mm, 73°C at 26 mm.(5, 10, 13) A published correlation of the vapor pressure of vinyl pyridine with temperature is

$$\log_{10} \text{Pressure (mm)} = 9.21 - \frac{2710}{T}$$

(Reference 36)
4-Vinyl pyridine can be prepared by the condensation of formaldehyde with \( \gamma \)-picoline to produce 4-ethanol pyridine. The 4-ethanol pyridine can be dehydrated to form 4-vinyl pyridine whose structural formula is below

\[
\text{CH}_2 = \text{CH} \\
\text{HC} \quad \text{C} \quad \text{CH} \\
\text{HC} \quad \text{N} \quad \text{CH}
\]

Recipes for bulk, bead, and emulsion polymerization of the polymer have been reported by Fitzgerald and Fuoss.\(^{10}\) A detailed study of the kinetics of the free radical polymerization has been made by Onyon.\(^{36}\)

Since the nitrogen atom in the pyridine ring can be quaternized by the addition of a suitable alkyl halide such as n-butyl bromide, some interest has been shown in poly-4-vinyl pyridine and its polyelectrolyte derivatives in fundamental studies on polyelectrolyte solutions. In this category are the studies of the hydrodynamic properties of poly 4-vinyl pyridine and poly-4-vinyl-N-n-butyl pyridinium bromide by Jordan \textit{et al.},\(^{20}\) studies of the osmotic pressure of the polyelectrolyte in ethanol by Strauss and Fuoss,\(^{44}\) studies of the quaternization kinetics of poly 4-vinyl pyridine by Fuoss \textit{et al.},\(^{13}\) and studies of light scattering and viscometric properties of poly vinyl pyridine by Boyes and Strauss\(^{5}\) and Berkowitz \textit{et al.}\(^{3}\) The latter reports a correlation of intrinsic viscosity - molecular weight for ethanol solutions of poly 4-vinyl pyridine

\[
|\eta| = 2.5 \times 10^{-4} \text{ M}^{-1/68}
\]
II. EXPERIMENTAL

The experimental procedures and the equipment associated with them can be separated into three main categories concerned with; (1) preparation of materials, (2) kinetic measurements, and (3) molecular weight distribution analysis. Following the description of the equipment and procedures in these three groups there will be a discussion of the treatment of the data and the errors associated with the data treatment. Errors associated with the measurements will be included with a description of the specific measurements.

A. Preparative Equipment and Procedures

1. High Vacuum Manifold

Due to the sensitivity of anionic polymerization reactions to impurities such as water, oxygen, carbon dioxide, etc., both the reagents and polymerization reaction systems had to be thoroughly dried and degassed. For this purpose a standard all glass high vacuum manifold ($10^{-6}$ mm Hg) was constructed with a number of ground joint and O-ring joint connections for attachment of glassware. All ground glass connections and high vacuum stopcocks were greased with Spectro Vac stopcock grease, Robert W. Austin, Ph.D. Pasadena, California. O-ring joint connections were made with Buna-N or Viton rubber O-rings. The vacuum was maintained by a Cenco-megavac mechanical forepump and 3-stage mercury diffusion pump in series. Pumps were protected by traps cooled with liquid nitrogen or dry ice-alcohol slush. Pressure measurements were made with a McCleod gauge that was precalibrated in readings of mm of Hg. A picture of the high vacuum manifold equipped for polymer freeze drying is shown in Figure 5.
Figure 1. Concentric Tube Fractional Distillation Column.
2. **Fractional Distillation Column**

The fractional distillation column consisted of an all glass, wetted wall, vacuum jacketed column, (see Figure 1). The vapor-liquid contacting region of the column was the 1 mm x 18 inch long annulus between a removable 15 mm O.D. Pyrex tube and the inner surface of the vacuum jacket. Reflux was controllable by means of a rotatable cold finger condenser positioned at the top of the concentric tube section. The cold finger condenser, which had drip tips, could be positioned either with both drip tips condensing distillate back down the column or with one drip tip positioned down the column and the other positioned to split distillate in two. In this latter position the reflux ratio was approximately 3 to 1. Distillations were carried out under partial vacuum conditions under nitrogen. The control of the partial pressure of the system was maintained by adjusting the rate of flow of nitrogen through a highly sensitive needle valve while pumping with a mechanical pump protected by a dry ice-alcohol cold trap. Pressure readings were made on a barometer attached to the system. A thermometer fitted through the cold finger condenser was used to measure temperatures at the distillate outlet.

3. **Solvent Preparation**

Toluene (Baker, reagent grade) and Heptane (Phillips, 99 mol%) were stirred with concentrated sulfuric acid until the solvents would no longer darken fresh acid. The solvents were then washed in turn with dilute sodium hydroxide solution and distilled water and then dried by filtering through dryerite onto dryerite. For final preparation the solvents were dried over phosphorus pentoxide, frozen with liquid nitrogen,
degassed on the high vacuum manifold and distilled in vacuo into a pre-
weighed solvent ampoule filled with a breakseal side arm (breakseal tubes
are pictured in Pyrex catalog LG-2) and containing a fresh sodium mirror.
The contents of the solvent ampoule were then frozen and the Pyrex
vacuum connection to the ampoule closed by gas-oxygen flame under a
vacuum of $10^{-5}$ to $10^{-6}$ mm Hg. The solvent ampoules along with the Pyrex
vacuum connection were then weighed to determine the contents by differ-
ence in weight. Solvent weights were of the order of 60 to 80 gms,
accurate to $\pm 0.03$ gms. The solvents, thus stored over sodium mirrors
under their own vapor pressure, were kept in a freezer at $-20^\circ$C.

4. Monomer Preparation

4-vinyl pyridine (Reilly Coal Tar and Chemical, 95% minimum
purity) was dried over calcium hydride and fractionally distilled under
dry nitrogen (Matheson prepurified grade dried over Dryerite) into a
distribution flask containing calcium hydride similar to one described
by Wenger.\(^{(52)}\) The distribution flask was then transferred to the high
vacuum manifold; the contents were frozen with liquid nitrogen and de-
gassed. The distribution flask had previously been dried by brush heat-
ing while maintaining a flow of nitrogen through the distillation system.
The distribution flask was further dried by brush heating the attached
monomer ampoules during the degassing procedure. After degassing of
the monomer, it was refrozen and the distribution flask was sealed off
with an oxygen-gas flame at a vacuum of $10^{-5}$ to $10^{-6}$ mm Hg. The monomer
was allowed to warm to room temperature and was then distilled from the
vacuum distribution flask into the attached calibrated monomer breakseal
ampoules (usually five). The ampoules were then detached individually by sealing off with an oxygen-gas flame. The numbered ampoules had been previously calibrated by filling them with measured amounts of distilled water from a burette and scribing a mark at the appropriate level in the breakseal tube (volumes were 2 to 8 ± .05 ml). The monomer ampoules were stored in the dark at -20°C and were used within a period of two to three weeks.

The monomer prepared on the fractional distillation column represented approximately the middle third of the initial charge, with a boiling point range of no greater than 1/2°C. At 14 mm pressure the boiling point was 68°C. The refractive index measured, at 25.5°C on an Abbe refractometer, model 33-45-23 was \( N_D = 1.5489 \) with a range between 1.5482 to 1.5492,

5. **Butyl Lithium Preparation**

Butyl chloride (Baker spectro grade) for the preparation of butyl lithium, was dried over phosphorus pentoxide, degassed and distilled on the high vacuum system into weighed break seal ampoules. Amounts of butyl chloride were determined by weight.

Butyl lithium was prepared by the reaction of butyl chloride and excess lithium metal in heptane solvent in an all glass reaction vessel dried and sealed off under high vacuum (10^-6 mm). The reaction vessel consisted of a 300 ml Pyrex flask containing freshly cut lithium metal. The flask had three side arms to which were sealed (1) an ampoule containing 4.45 ± .03 g butyl chloride, (2) an ampoule containing purified heptane, 52.74 ± .03 g, and (3) a receiving flask with an
additional breakseal side arm. The reaction vessel was evacuated on the high vacuum manifold, flame dried, and sealed off with an oxygen-gas flame. The breakseal on the solvent ampoule was broken open by means of a Pyrex covered iron bar and the contents were poured into the vessel containing the lithium. The solvent ampoule was removed by sealing off. The contents were cooled to approximately 10°C and the butyl chloride ampoule was broken open and drained. Solvent was flushed into the ampoule to assure quantitative transfer. The reaction was allowed to proceed in an ice bath for 24 hours and then the contents were filtered through an acid washed and dried fiber glass packing in the third side arm into the receiving vessel. The receiving vessel was sealed off at a constriction.

6. Butyl Lithium Analysis and Dilution

The contents of the receiving flask which were water clear, were transferred to another vacuum distribution flask via breakseal. This vacuum distribution flask had seven volumetrically calibrated ampoules attached. The butyl lithium solution was distributed into the ampoules which were sealed off individually. Three of the samples were broken open in water and titrated with .04346N acid using phenolphthalein as indicator. The concentration of butyl lithium was determined as .470 ± .003. Calculations showed that this value corresponded to an 81.1% yield based on butyl chloride.

One of the remaining .470N butyl lithium solution ampoules was sealed onto another vacuum distribution flask for further dilution with purified heptane. After the usual evacuation and sealing off procedure,
heptane and butyl lithium ampoules were broken open and mixed in the
distribution flask. Seven side arm calibrated ampoules were filled
with the diluted butyl lithium solution and sealed off. Three were
broken open and hydrolyzed with water and titrated as before. The
dilute solution was found to be $0.0271N \pm 0.0003$ in butyl lithium which
compares with a theoretical value of $0.0277N$. The remaining four am-
poules were stored at $-20^\circ C$ for use in kinetic experiments. The balance
of the dilute solution was stored in the vacuum distribution flask for
a repeat of the procedure. No further titrations were performed on
the solution. The one batch of dilute solution was sufficient for the
entire set of kinetic experiments. It continued to remain clear and
colorless.

B. Rate Measurement Equipment and Procedures

1. Dilatometers

Dilatometers for use in the kinetic experiments were constructed
from 50 ml flat bottom Pyrex boiling flasks and 2 mm bore Pyrex capillary
tubing. The tubes had been previously calibrated between scribed marks
according to the method described by Bekkedahl.\(^2\) A typical capillary
volume was $0.0386 \pm 0.0007 \text{ cm}^3/\text{cm length}$. A teflon covered magnetic stir-
ring bar had been placed in the dilatometer bulb prior to the addition
of the capillary stem. The volume of the bulb up to the lower reference
mark on the stem was obtained by filling the dilatometer bulb with toluene
by means of a hypodermic syringe. The toluene was taken from a graduate
cylinder and the volume of the dilatometer bulb was obtained by noting
the initial and final amounts in the graduate cylinder. A typical volume
was 58 ± 5 ml. The dilatometers were then rinsed with acetone, water, aqua regia, and water and dried in an oven at 120°C.

2. Constant Temperature Bath

The temperature bath for dilatometric measurements consisted of a nine inch diameter battery jar 18 inches high filled with water for the runs carried out at 31.4°C and filled with isopropanol for the low temperature runs. The bath was supported on a stand so that a magnetic stirrer could be placed below the bath. Other accessories to the bath included a 500 watt immersion heater, mercury thermal switch, super-sensitive relay, and air stirrer. Temperature control at 31.4°C was ± .01°C. For low temperature runs 2°C to -30°C, a 24 inch long, two inch diameter thin wall pipe, closed at the bottom, was suspended in the alcohol bath. The tube was filled with dry ice to cool the bath and the rate of cooling was controlled by the depth of immersion of the pipe in the bath fluid. Final temperature control was maintained by the immersion heater. To prevent frost formation, the bath was enclosed on the four sides and bottom by a box constructed of plexiglas. The bath fluid was initially cooled by adding dry ice directly to the bath. As a result, cold carbon dioxide filled the plexiglas container and helped prevent frost formation. From time to time isopropanol would be sprayed on the outside glass wall of the bath to remove any light frost. The bath was maintained up to eight hours at -30°C. Temperature variation at -30°C was ± .15°C, at -15°C and 2°C ± .1°C.
Figure 2. Vacuum Mixing Vessel and Reaction Dilatometer Assembly.
3. Mixing Vessel and Reaction Dilatometer Assembly

The reaction dilatometer and mixing vessel assembly is pictured in Figure 2. It consists of a 250 ml Pyrex flask to which an O-ring high vacuum joint has been added. Attached to side arms are ampoules of previously prepared solvent and initiator. One additional side arm tube leads to the dilatometer to which an ampoule of monomer had been sealed.

4. Polymerization Experimental Procedure

The mixing vessel and reaction dilatometer assembly, as just described and pictured in Figure 2 was connected to the high vacuum manifold and brush flamed at a vacuum of $10^{-6}$ mm Hg. The assembly system was evacuated for two hours with intermittent heating and then sealed off at restriction C with an oxygen-gas flame. The solvent ampoule was broken open by means of the Pyrex covered breaker bar, and the contents were emptied into the mixing vessel. The solvent ampoule was then removed by sealing off at A. The initiator ampoule was then broken open and the contents were drained into the mixing vessel. The initiator ampoule was refilled with solvent three to four times to assure quantitative transfer, and the resulting solution was mixed thoroughly by flushing back and forth from the dilatometer to the mixing vessel. Finally the dilatometer bulb was filled to a predetermined mark and the dilatometer with attached monomer ampoule was sealed off at D.

The filling level mark on the dilatometer bulb was predetermined as follows. After the volume of the dilatometer had been determined (page 22) the dilatometer was filled to the top of the capillary stem with toluene at the temperature at which the reaction was to be run. Then a volume of liquid was removed from the dilatometer
via hypodermic syringe equal to the volume of monomer
to be added. The remaining contents of the dilatometer
were allowed to reach room temperature and its level
was scribed on the dilatometer bulb.

The detached partially filled dilatometer was chilled in a
dry ice alcohol slush at -78°C for 10 to 15 minutes. The monomer am-
poule was broken open and the monomer was allowed to drain into the
dilatometer bulb which was kept at -78°C. A magnetic stirrer placed
below the dilatometer was used to stir the contents thoroughly for 25
minutes to an hour. At -78°C the entire contents of the dilatometer
were in the bulb section. The upper portion of the dilatometer was
heated to assure that all of the monomer was transferred to the bulb.
The empty monomer ampoule was removed at E so that the dilatometer
could be completely submerged in the constant temperature bath. The
dilatometer was placed in the temperature bath and allowed to warm to
bath temperature. The reaction mixture was colored a dull red and
appeared turbid upon removal from the dry-ice slush. An orange-red
fine particle precipitate formed rapidly during the warm up period.
As the reaction mixture approached bath temperature, liquid would ex-
pand into the capillary stem. Since the density of the precipitate was
greater than that of the solution, little or no polymer would rise in
the capillary. The contents of the reaction dilatometer were mixed
during this period by means of the magnetic stirring bar in the dil-
atometer bulb. Mixing was fair to poor due to the large volume of sol-
ids present in the reaction. After the liquid in the capillary stem
had apparently reached a maximum height, a precision timer was started
and measurements of the height of the liquid in the stem were begun.
Measurements were made with a Gaertner Precision Cathetometer, (Central Scientific Co.) with a measuring accuracy of ± .005 cms.

At the end of the rate measurements, the dilatometer was removed from the constant temperature bath, chilled in a dry-ice alcohol slush and broken open. The contents of the dilatometer were carefully transferred into a beaker containing 100 ml toluene and 1 ml of butyl alcohol (Baker reagent grade). The orange-red precipitate would turn white almost immediately although faint traces of color would remain for one to two hours. The precipitate was washed in successive portions of toluene and then filtered and placed in a tared vacuum flask and placed on the vacuum manifold for drying. The residual solvent and monomer were removed at room temperature. Evaporation of the toluene washings left no residue in those instances where conversion was high, and left an oily liquid (monomer) for runs stopped at low conversion. A check on the effective recovery of the polymer was done by placing 1.672 grams of dried polymer in a 5 volume per cent solution of 4-vinyl pyridine in toluene. After following the procedure used in recovering polymer from a typical reaction, 1.646 gms of polymer were recovered, 98.4% of theoretical.

In one alternate procedure monomer and solvent were premixed in the vacuum mixing and reaction assembly. No trace of polymer was formed. When finally the initiator ampoule was broken open, polymer formed rapidly and plugged the capillary stem of the dilatometer.

5. Specific Volume Measurements

The rate measurements obtained as described in the preceding section were values of the height, h, as a function of time. Since the
Figure 3. The Temperature Dependence of the Specific Volumes of 4-Vinyl Pyridine Monomer and Polymer.
change in height is proportional to the change in volume that occurs, one can obtain useful information from this data alone. In order to obtain absolute rate values, however, one must also have partial specific volumes of monomer and polymer under the conditions of the reaction. Measurements of the specific volumes of monomer, solvent, and polymer were carried out in a calibrated picnometer at temperatures above room temperature, and in a calibrated dilatometer for temperatures below room temperature. The measurements of the specific volume of solvent, monomer, and monomer-solvent mixtures at -29.8°C are shown in Table II. A comparison of these values with those calculated for "ideal" solution mixtures show that the specific volume of the monomer in solution, over the range of interest, is the same as the specific volume of the pure monomer. Measurements of the specific volume of the polymer were performed on polymer samples in toluene suspension. The specific volume measurements of monomer and polymer as a function of temperature are shown in Figure 3. Maximum error in monomer and polymer values is estimated at .5% and 2%, respectively.

C. Polymer Fractionation and Molecular Weight Measurements Equipment and Procedure

1. Fractionating Column

The fractionating column used for the elution fractionation of poly 4-vinyl pyridine is shown in Figure 4. The packed polymer-coated bed was supported on a coarse fritted glass filter in a 35 mm O.D. Pyrex tube surrounded by a constant temperature jacket. Temperature was maintained in the jacket by boiling pentane at total reflux.
Figure 4. Elution Fractionation Column.
A solvent preheater at the top of the packed bed provided suitable holdup of the incoming solvent-nonsolvent mixtures till they could reach operating temperature. Flow through the column was controlled by means of a teflon stopcock at the bottom of the column.

2. **Fractionation Procedure**

1.6 to 1.8 gms of poly 4-vinyl pyridine and .04 gms hydroquinone stabilizer were dissolved in 100 ml of methanol (Merck reagent grade). 400 gms of carefully washed and dried Ottawa sand (graded 30 to 40 mesh) were added to the polymer solution and stirred until no excess liquid was present. The damp sand slurry was then spread in an open Pyrex photo tray and air dried. The sand was turned frequently in order to assure as uniform a deposit of polymer as possible. 200 ml of benzene (Merck reagent grade) and 50 gms of uncoated sand were poured into the empty column. The dried, coated sand was added followed by a small top layer of uncoated sand. The entire packed bed was 20 inches long. The pentane reboiler was heated and allowed to reflux for two hours before beginning the fractionation. The stopcock was set at the bottom to produce a flow of 100 to 120 cm$^3$ per hour through the column (14 to 17 drops per 15 seconds). This setting had to be adjusted from time to time due to changes in the viscosity of the extracted solution. The first fraction (numbered 0) amounted to 185 ml of benzene (liquid holdup was estimated at 15 ml). Each subsequent fraction removed equaled the corresponding volume of solvent-nonsolvent mixture that was placed in the column at the top (usually 90 ml). Solvent (tertiary butyl alcohol-Eastman reagent grade) and nonsolvent (benzene) mixtures were made up by volume starting at 25 per cent tertiary butyl alcohol. Eight
Figure 5. Freeze Drying on High Vacuum Manifold.
fractions were usually taken which accounted for 95% and up of the total polymer. One additional clean up fraction was taken, by allowing pure solvent to sit in the column for 24 hours. This fraction was used to account for the total polymer, but was not used in subsequent molecular weight distribution analysis. (See Data Treatment.) They were placed in the solvent preheater at the top of the column, and poured onto the bed when the preceding slug had just drained below the top of the packed bed. The solutions taken off at the bottom were poured into tared vacuum flasks and frozen. The solvent was sublimed from the frozen polymer-solvent structure on the high vacuum manifold. Figure 5 show the high vacuum system set up for "freeze drying" of three polymer samples. The sublimed solvent was collected on the cold finger condensers using dry ice-alcohol slush as shown in the picture. Earlier attempts to collect the sublimed solvent in U-tube and concentric tube traps resulted in shattered flying glass. The frozen collected solvent would expand when the dry ice-alcohol slush container was removed from the trap and would produce enormous pressures on the inside walls of the U-tube and concentric tube traps. The condensation of the sublimed solvent on the outside of the cold finger condensers eliminated this problem.

3. Molecular Weight Measurements

a. Viscosity Measurements

The molecular weights of the fractionated samples and the gross polymers were obtained by dilute solution viscometry. The Ubbelohde dilution viscometers used for these measurements have been described by
Long. (27) The general techniques and treatment of viscosity data have been conveniently summarized in Allen. For more elaborate theoretical discussions of dilute solution viscosities, one may refer to Flory (11) or Tompa. (47)

An intrinsic viscosity-molecular weight correlation for dilute solutions of poly 4-vinyl pyridine in absolute ethanol has been obtained by Yamin (3) as

\[ |\eta|_e = 2.5 \times 10^{-4} \text{ M}^{.68} \]

Since the available methanol reagent was of much better quality than the available absolute ethanol, and since the flow times of the pure methanol were much more suitable for measurements (118 seconds as opposed to 210 seconds for ethanol), the viscosity measurements were carried out in methanol solution. We can eliminate \( M \) from the following two equations

\[ |\eta|_e = C_e M^{a_e} \]
\[ |\eta|_m = C_m M^{a_m} \]

and obtain the relation

\[ \log |\eta|_m = \frac{a_m}{a_e} \log |\eta|_e + \frac{a_m}{a_e} \left[ \log \frac{C_m}{C_e} - \log C_e \right] \]

By obtaining the intrinsic viscosities, \( |\eta| \), of the same polymer fractions in both methanol and ethanol and plotting \( \log |\eta|_m \) versus \( \log |\eta|_e \) one can obtain the appropriate values for \( a_m \) and \( C_m \) from the slope and intercept. Such a plot is shown in Figure 6 for five samples whose intrinsic viscosity in methanol ranged from .40 to 7.45. The values are
Figure 6. Intrinsic Viscosities Measured in Methanol and Ethanol Solvents.
reported in Table III. The relation

$$|\eta|_m = 2.4 \times 10^{-4} M^{0.69}$$  \hspace{1cm} (14)$$

was obtained by a least-squares evaluation of the slope and intercept. This equation was used to calculate the viscosity average molecular weights of polymer and polymer fractions.

The specific viscosity, $\eta_{sp}$, of a dilute polymer solution is related to flow times of polymer solutions, $t$, and pure solvent, $t_0$, in a capillary viscometer by

$$\eta_{sp} = \frac{t - t_0}{t_0}$$

The values of $\eta_{sp}$ were measured for three different concentrations of polymer in solvent for each polymer sample. A sample data and calculation sheet appears in Table IV. Values of the intrinsic viscosity, $|\eta|$ were obtained by extrapolation of dual linear plots of $\frac{\eta_{sp}}{c}$ versus $c$ and $\ln(\frac{\eta_{sp} + 1}{c})$ versus $c$, according to the following empirical equations to zero concentration.

$$\frac{\eta_{sp}}{c} = |\eta| + k' |\eta|^2 c$$

and

$$\frac{\ln(\eta_{sp} + 1)}{c} = \frac{\ln \eta_{rel}}{c} = |\eta| - k'' |\eta|^2 c$$

The data for sample 2-21 are shown plotted in Figure 7. Values for $k'$ were calculated from the slopes of the upper plot and are reported along with $|\eta|$ for the various samples in Table V.
Figure 7. Specific Viscosity Data, Polymer 2-21.
b. Osmotic Pressure Measurements

The osmotic pressure, \( \pi \), of a polymer solution measures the activity of the solvent in the polymer solution relative to the pure solvent. Thermodynamics yields the relation

\[
\pi \bar{V}_i = RT \ln a_i,
\]

when \( \bar{V}_i \) is the partial molal volume and \( a_i \) is the activity of the solvent in solution. By application of the Flory-Huggins lattice theory,\(^{11,47} \) one can obtain a power series expansion of \( \ln a_i \) in terms of the concentration, \( c_i \), of a particular polymer solute and arrive at the expression

\[
\frac{\pi_i}{c_i} = \frac{RT}{M_i} + A_1 c_i + A_2 c_i^2
\]

where \( M_i \) is the molecular weight of a particular polymer species. Since the number average molecular weight, \( \bar{M}_n \), is defined by

\[
\bar{M}_n = \frac{\sum N_i M_i}{\sum N_i} = \frac{\sum c_i}{\sum \frac{c_i}{M_i}} = \frac{\sum c_i}{\sum \frac{c_i}{M_i}}
\]

where \( N_i \) is the number of chains of molecular weight \( M_i \), and \( c_i \) is the weight of the chains of molecular weight \( M_i \), and since

\[
\pi = \sum \pi_i
\]

one can obtain the number average molecular weight of a polydisperse molecular weight sample by osmotic pressure measurements. In view of the importance of the number average molecular weight and hence the number average degree of polymerization in the development of anionic polymerization theory, its measurement was important.

Osmotic pressure measurements were made on three polymer samples, two polydisperse polymers and one fractionated sample. The
results can be found in Table VI, Appendix IV. A Zimm-Myerson osmometer (J.V. Stabin Co. - model ML) fitted with grade number 450 regenerated cellulose membranes was used for the measurements. The osmometer and techniques of osmometry are well described in Chapter V of "Number Average Molecular Weights" by Bonnar, Dimbat and Stross, Interscience Publishers, 1958.

The results of the measurements on the two polydisperse polymers 1-8 and 2-19 are similar to results obtained by Strauss and Fuosa in their studies of the osmotic pressure of polyelectrolyte solutions. It is conceivable that lithium butoxide and butyl chloride remnants of the initiator could form quaternary compounds with the nitrogen atom in the pyridine ring, and therefore, contribute to the observable osmotic pressure. As a result the osmotic pressure could not be used to determine the number average molecular weights of the polydisperse samples. The osmotic pressure measurements on the fractionated sample exhibited behavior more characteristic of unchanged macromolecule solutions. The number average molecular weight of polymer fraction 2-28-3 was determined and compared with the viscometric average molecular weight of that fraction. The results are

\[
\bar{M}_n = 44,400 \\
\bar{M}_v = 47,000
\]

D. **Data Treatment**

1. **Kinetic Measurements**

The data of the kinetic experiments were in the form of height (centimeters) versus time (seconds). Since the polymerization experiments
were carried out in different dilatometers, each with its own characteristic capillary volume, it was necessary to convert all of the data to some standard scale such as per cent conversion versus time. Since $h_0 - h(t)$ is equal to the fraction of conversion, the value of $h_0$, the height of the solution in the dilatometer extrapolated to zero conversion, and $h_\infty$, the height of the solution in the system at a projected 100% conversion, were the only two values needed. They were obtained from the following data:

1. $\Delta \bar{V}$, the change in specific volume produced by one gram of monomer converting to one gram of polymer, cm$^3$/gm at the temperature of experiment
2. $\Delta V/\Delta h$, the volume characteristic of the dilatometer stem used in the experiment, cm$^3$/cm
3. $h_T$ and $G_T$, the stem height (cms) and weight of polymer (gms) at the termination of the rate measurements
4. $M$, the weight of the monomer (gms) in the experiment.

$\bar{V}$, divided by $\Delta V/\Delta h$ yields $\Delta \bar{h}$, the change in height in the capillary stem due to the formation of one gram of polymer. This value varied from one experiment to another between 3 and 4 cms/gm. From $\Delta \bar{h}$, $h_0$ can be calculated by

$$h_0 = h_T + G_T \times \Delta \bar{h}$$

Furthermore, from $h_0$

$$h_\infty = h_0 - M \times \Delta \bar{h}$$

the values of per cent conversion versus time are reported in Table VIII, Appendix IV.
2. Molecular Weight Distribution
   
a. Cumulative Weight Distributions

   The results of elution fractionation and subsequent viscosity molecular weight determinations were the weights of the individual fractions and their corresponding intrinsic viscosities. Viscosity average molecular weights, $\bar{M}_v$, were calculated from the intrinsic viscosity measurements, and the fractions of any one polymer were arranged in order of increasing molecular weights. The cumulative weight distribution function, $W_1 = f(M_1)$,

   where

   $W_1$ is the cumulative weight fraction of all material whose molecular weight is less than or equal to $M_i$, and

   $M_i$ is the molecular weight of a chain of $i$ monomer units,

   was constructed according to the method of Mark and Raff.(29) Their method is based on the assumption that the molecular weights in any one fraction are distributed symmetrically around the mean and that there is negligible overlap of molecular weight species from one fraction to the next. Accordingly, the value of $W_1$ in the equation can be calculated from the sum of all weight fractions of material with molecular weights less than $M_i$ plus $1/2$ the weight fraction of the material whose molecular weight is $M_i$. These values are reported in Table IX, Appendix IV as Adjusted Cumulative Weight Per Cent.

   The fact that the viscosity molecular weight average, $\bar{M}_v$, is used to represent the mean molecular weight of a given fraction raises the question of whether or not it is legitimate to split a given weight
fraction in two around \( \bar{M}_v \). Since \(|\eta| = CM^a\), \(\bar{M}_v\) is defined as

\[
\bar{M}_v = \left[ \sum c_i M_i^a \right]^{1/a} = \left[ \sum N_i M_i^{(1+a)/a} / \sum N_i M_i \right]^{1/a}
\]

The theory of the frictional properties of polymer solutions predicts that the values of \(a\) lie between 1/2 and 1. Thus the value of \(\bar{M}_v\) lies between \(\bar{M}_n\) and \(\bar{M}_w\), the number average and weight average molecular weights, respectively, and depends on the distribution of the sample. Now for a fraction having a very narrow distribution, say Poisson,

\[
\bar{M}_w = \bar{M}_n = \bar{M}_v
\]

It is therefore correct to consider that 1/2 of the fraction contains molecular weights below \(\bar{M}_v\) and that 1/2 of the fraction contains molecular weights above \(\bar{M}_v\). In the case of the measurements \(\bar{M}_n\) and \(\bar{M}_v\), for fraction 2-28-3, the ratio \(\bar{M}_v/\bar{M}_n = 1.06\). This gives some assurance of moderately narrow distributions. This result was obtained for a moderately low molecular weight fraction and may not hold true for the higher molecular weight fractions. In a study of the elution chromatography fractionation of cis-1,4 polybutadiene,\(^{(19)}\) the authors have indicated that the resolution of higher molecular weight materials becomes increasingly more difficult. Fortunately, it is still possible to show that it is legitimate to split even a polydisperse fraction in two about the viscosity average molecular weight.\(^*\)

The unusual molecular weight distribution results that were obtained required a slight adjustment to the treatment just presented.

\(^*\)Appendix II
These results will be discussed in detail later on. For the meantime it is sufficient to point out that two separate batches of molecular weight species appeared in the fractionation of any of the polymers. One had a number average molecular weight around 35,000 the other 1,000,000 or more. The cumulative weight distribution could be easily constructed in the range of molecular weights in either of the two batches by the method of Mark and Raff. It was inconceivable, however, that the molecular weights in the last fraction of the low molecular batch, $\bar{M}_v$ around 150,000, would extend continuously into the range of the next fraction whose molecular weight was 1,000,000. An arbitrary cut off point between the low molecular weight material and high molecular weight material had to be determined. These cut off limits on molecular weight were arbitrarily set approximately 100,000 above the last low molecular weight fraction and 200,000 below the next molecular weight fraction. Some of the sample cumulative distribution curves can be seen in Figures 14 and 15. Fortunately, as arbitrary as this treatment seems, it has little effect on the desired results. An explanation of the treatment of derivatives of the cumulative distribution will explain this point.

b. **Derivatives of the Cumulative Distribution**

The derivation of the theoretical molecular weight distributions in anionic polymerization lead to a number frequency distribution. Therefore, we would like to obtain such a distribution from our cumulative weight distribution data. It can be shown* that the derivatives of the

*Appendix III
cumulative weight distribution function, \( \frac{dW_i}{dM_i} \) give the weight frequency distribution function

\[
\omega_i = \frac{dW_i}{dM_i} = \theta(M_i)
\]

Furthermore, the number frequency distribution can be obtained from the same derivatives by

\[
\beta_i = \frac{1}{M_i} \frac{dW_i}{dM_i} = \Phi(M_i)
\]

It can also be shown* that the area under a plot of the number frequency distribution is the number of chains in a one gram sample of polymer, and that, therefore, the reciprocal of area is the number average molecular weight of the polymer. These are the values we hope to obtain in our analysis of the molecular weight distribution.

The numerical differentiation of data is usually subject to large error. In order to minimize this error, the differentiation of the cumulative weight distribution was accomplished by applying the basic theorem of calculus, The Law of the Mean,

\[
\frac{f(b) - f(a)}{b-a} = f'(x_i) \quad a < x_i < b
\]

to various pairs of points in the column of adjusted cumulative weight per cent in Table IX. The values \( f(b) \) and \( f(a) \) refer to the adjusted cumulative weight per cent at molecular weights \( b \) and \( a \) respectively. In as far as the data are correct, the value of \( f'(x_1) \) is an exact value. The only question that remains is the point, \( x_1 \) on the cumulative weight distribution curve to which this derivative

*Appendix III
applies. The Law of the Mean requires that the value of $x_1$ be located between points $a$ and $b$. In order to assign a specific value to $x_1$ several successive derivatives were examined. For instance if there were four points $a$, $b$, $c$, $d$, then derivatives would be evaluated for the intervals $ab$, $bc$, $cd$, $ac$, and $bd$, in order to assign a specific value for $x_1$ between $b$ and $c$ corresponding to \( \frac{f(c) - f(b)}{(c - b)} \).

The value assigned to $x_1$ would be closer to $b$ or $c$ depending on whether the value of the derivative for the interval $bc$ was close to the corresponding values for $ab$ and $ac$ or $bd$ and $cd$. The method is still subject to large errors as far as the actual values \( \frac{1}{M_1} \frac{dW_i}{dM_1} \) are concerned due to the error in evaluating \( \frac{1}{M_1} \). Fortunately, we only need the values obtained by integration of these values with respect to $M_1$. We are only interested in the value of

\[
\int_0^\infty \left[ \frac{1}{M_i} \frac{dW_i}{dM_i} \right] dM_i
\]

(15)

Suppose that the error in assigning the correct value for $M_1$ for the derivative $\frac{dW_i}{dM_1}$ is $\varepsilon$. Then instead of (15) we will be evaluating

\[
\int_0^\infty \left[ \frac{1}{(M_1 + \varepsilon)} \frac{dW_i}{dM_i} \right] d(M_1 + \varepsilon)
\]

This can be written as

\[
\int_0^\infty \frac{dW_i}{dM_i} \ d \ln \left[ M_i \left( 1 + \frac{\varepsilon}{M_i} \right) \right]
\]

or

\[
\int_0^\infty \left[ \frac{1}{M_i} \frac{dW_i}{dM_i} \right] dM_i + \int_0^\infty \frac{dW_i}{dM_i} \ d \ln \left( 1 + \frac{\varepsilon}{M_i} \right)
\]
By expanding \( \ln(1 + \frac{\epsilon}{M_i}) \) we obtain finally

\[
\int_0^\infty \left[ \frac{1}{M_i} \frac{dW_i}{dM_i} \right] dM_i \quad - \quad \int_0^\infty \left[ \frac{\epsilon}{M_i^2} \frac{dW_i}{dM_i} \right] dM_i \tag{16}
\]

The first integral represents the true value and the second represents the error in evaluating the area under the frequency distribution curve. If the value \( \epsilon \) is a constant, \( C \), times \( M_i \) then the actual value obtained will be \( (1 - C) \) times the true area. If we evaluated every \( M_i \), 10% too high in the construction of the frequency distribution curve, then the total error would be 10%. Since it is possible to have both positive and negative error, \( \pm \epsilon \), in the assignment of values of \( M_i \), some of the error may be canceled out. The derivatives \( \frac{dW_i}{dM_i} \) and \( \frac{1}{M_i} \frac{dW_i}{dM_i} \) are given in Table X, Appendix IV.

Some typical frequency distribution plots can be seen in Figure 16. We can now return to the question of the error introduced in the construction of the cumulative weight distribution by the assignment of arbitrary cut off values on the upper end of the low molecular weight distribution and lower end of the high molecular weight distribution. The raw data show no molecular weight species between 300,000 and 1,000,000. This requires no matter what the true distribution looks like in this region of the molecular weight scale that the values of \( \frac{dW_i}{dM_i} \) be very small if not zero. This region of the molecular scale contributes little to the integral

\[
\int_0^\infty \left[ \frac{1}{M_i} \frac{dW_i}{dM_i} \right] dM_i
\]
Figure 8. Infrared Absorption Spectrum of 4-Vinyl Pyridine.
Figure 9. Infrared Absorption Spectrum of Poly 4-Vinyl Pyridine.
particularly at larger values of $M_i$. Therefore, even though we may be
in error in the arbitrary limits set for the cut off values, we do not
effect the value,

$$\int \left[ \frac{1}{M_i} \frac{dW_i}{dM_i} \right] dM_i$$

that is our primary interest.

E. Miscellaneous Experimental Measurements

1. Infrared Absorption Spectra

Some infrared absorption spectra were made of the monomer and
of films of the polymer. The absorption patterns were produced either
on a Perkin Elmer Model 21 Linear Wave Number Infrared Spectrometer or
on a Baird Model B Linear Wave Length Infrared Spectrometer using a so-
dium chloride prism. Solutions of 4-vinyl pyridine monomer, consisting
of 2 grams monomer in 50 ml carbon disulfide solution were run against
a reference cell containing carbon disulfide. The polymer was dissolved
in methanol and films were cast on mercury and air dried. Some of the
films were placed under high vacuum for 24 hours to remove the residual
solvent. No difference could be seen in the absorption patterns between
these films and those that were simply air dried. The absorption pat-
terns appear in Figures 8 and 9.

2. Particle Size and Shape

At one point in the study, particle size distribution became
of interest. In order to determine size distribution, photographs were
taken of magnified random samples of the polymer. For magnification
Figure 10. Transmitted Light Photographs of Polyvinyl Pyridine Particles, 255x, 660x.
Figure 11. Transmitted Light Photographs of Polyvinyl Pyridine Particles, 1500x, 16000x.
up to 850X the photographs were made on a Leitz Aristophot camera and optical microscope. The polymer samples were placed on glass slides in a drop of toluene and smeared across the glass. For magnification from 1500X to 16,000X the photographs were taken on a RCA Model EML Electron Microscope. The particles had to be mounted on nickel screens. This was accomplished by dusting particles onto the screens from a camel hair brush. The photographs of these particles therefore will not represent a random sample of particle sizes. The photographs appear in Figures 10 and 11.
III. DISCUSSION OF RESULTS

A. Introduction

The results of the kinetic and molecular weight distribution experiments of the butyl lithium intitiated polymerization of 4-vinyl pyridine will be discussed in terms of the restricted theory of homogeneous anionic polymerizations described previously. The following topics will be covered. First, we shall consider the experimental evidence that suggests an anionic mechanism for the polymerization of 4-vinyl pyridine initiated by butyl lithium. Next, we will discuss the results of the kinetic experiments in terms of (a) the dependence of the rate of polymerization on monomer concentration and (b) the dependence of the rate on initiator concentration. Several alternate models and the experimental evidence will be considered to explain the apparent effect of initiator concentration on the observable polymerization rates. Then we shall describe the results of the molecular weight distribution analysis and, in addition, the model most suited to describe the results of the polymerization experiments. The validity of this model will be discussed in terms of (1) the experimental error involved in the measurements and (2) possible competing reactions that are ignored by the model. We will complete the discussion of results with a brief description of assorted miscellaneous items.

B. Anionic Polymerization Mechanism

A summary of the reaction conditions and results of all significant experiments is presented in Table I. In order to discuss the results
| Exp. | Temp. °C | \( \text{I}_0 \times 10^3 \) | C | Conversion at Initial Measurement | Polymer Grams | Yield % | \( \frac{\text{n}}{\text{g}} \) | \( M_w \times 10^{-3} \) | \( k_2 \times \text{Yield} \times 10^{-3} \) | \( M_w \times 10^{-3} \) | \( k_2 \lambda_1 \times 10^5 \) | \( \sqrt{F}_0 \times 10^3 \) | \( k_2 \) |
|------|----------|-----------------|---|--------------------------------|-----------------|--------|--------------|----------------|-------------------------------|--------------|------------------|----------------|-------------|---------|
| 2-15 | 31.4     | 1.35            | 632 | 23.5                          | 2.53           | 65.4   | 3.68         | 1170            | 113            |                   |               |                 |               |             |
| 2-17 | 31.4     | 1.11            | 621 | 40.5                          | 3.56           | 98.4   | 3.12         | 915             | 54.5           | 50.6           | 9.34          | 0.798         | 2.82        | 331        |
| 2-18 | 31.4     | 1.13            | 1.30 | 55.2                          | 6.63           | 73.5   | 4.34         | 1500            | 103            | 108.5          | 15.68         | 5.16        | 7.19        | 217        |
| 2-19 | 31.4     | 1.12            | 0.32 | 41.3                          | 1.81           | 93.3   | 1.84         | 427             | 26.6           | 7.66           |               |              |             |            |
| 2-20a | 31.4   | 1.94            | 1.94 | 2.98                          | 835            |         |             |                 |                 |               |                 |              |             |
| 2-21 | 31.4     | 1.10            | 0.635 | 53.9                          | 3.60           | 92.9   | 2.79         | 783             | 56.6           | 7.71           |               |              |             |
| 2-22b | 31.4 | 1.10 {1.09}    | 0.621 | 48.0d                         | 3.76           | 96.0   | 3.66         | 1160            | 58.3           |               |               |              |             |
| 2-23 | 31.4     | 1.23            | 0.622 | 82.1                          | 3.67           | 94.4   | 1.36         | 276             | 27.7           | 6.82           |               |              |             |
| 2-24 | 31.4     | 1.13            | 1.19 | 48.4                          | 6.28           | 80.5   | 3.02         | 878             | 68.5           | 97.5           | 9.58          | 2.49        | 4.99        | 0.192       |
| 2-25a | 78     | 1.05            | 0.630 | .0675 | 1.77 | .27           | 86 | 1.10        |                 |                 |               |               |              |             |
| 2-26 | 31.4     | 1.12            | 0.635 | 3.95                          | 3.62           | 92.8   | 3.16         | 940             | 55            | 6.49           |               |              |             |
| 2-27 | 31.4     | 1.04            | 1.21 | 4.62                          | 59.2           | 2.96   | 811           | 72.8            | 81.3           |               |               |              |             |
| 2-28b | 31.4 | 1.09 {1.293} | 48.9 | 2.83                          | 75.7           | 3.21   | 959           | 42.7            | 43.3           | .67            | (.281)       | (1.95)      | (.0334)    |
| 2-29 | 2.0     | .977            | 1.16 | 16.6                          | 3.37           | 45.5   | 2.58         | 675             | 56.7           | 71.0           | 1.48          | 1.95        | 4.46        | .0332       |
| 2-30 | -15.3   | 1.00            | 1.17 | 24.4e                         | 2.96           | 41.4   | 1.76         | 400             | 49.4           | 53.0           | .549          | 2.23        | 4.73        | .0116       |

a. Reverse Addition  
b. Two Stage Monomer Addition  
c. Initiation Reaction  
d. Estimated  
e. Reaction Run At -30°C For Half Hour  
f. Two weeks at room temperature
of these experiments in terms of the theory of anionic polymerization, it is first necessary, of course, to show that it is appropriate to describe the butyl lithium initiated polymerization of 4-vinyl pyridine by an anionic mechanism. Such a mechanism has the following characteristics:

1. the presence of growing polymeric anions that are not capable of self-termination,
2. the production of anionic ends by a suitable initiator resulting in a constant concentration of active ends at the end of the initiation period,
3. an equality between the number of initiation molecules consumed and the number of anionic ends produced.

In addition, the reaction system may produce intense colors which disappear on termination. Furthermore, the number of polymer chains produced may be equivalent to the number of initiator molecules (in the absence of chain transfer).

The butyl lithium initiated polymerization of 4-vinyl pyridine in hydrocarbon solvents does exhibit these characteristics. First of all, the polymerization of otherwise colorless reactants and products produces an intermediate highly intense, orange-red polymer under impurity free conditions which remains visibly unchanged for long periods. Samples were kept in vacuo for periods up to two months. Secondly, the results of Experiments 2-17, 2-19, 2-22, and 2-28, as shown in Table I, indicate clearly the characteristics of an anionic polymerization. Experiments 2-22 and 2-28 were carried out under approximately the same conditions.
of total reactant concentrations as those of Experiments 2-17 except that half of the monomer was added initially, and the remainder, two to three days later. Thus the conditions for the first part of Experiments 2-22 and 2-28 were approximately the same as those of Experiment 2-19 in which a 93.3% yield of polymer was obtained in a period of less than two hours. Yet both systems of the double-addition experiments were reactive to the second addition of monomer after the two to three day interim delay. Furthermore the number of chains per unit volume (calculated from the formula \[
\text{chains per liter} = \frac{105 \times M_0 \times \text{percent yield}}{100 \times M_n}
\] ) agrees within experimental error with the initial concentration of initiator in the Experiments 2-17 and 2-28.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>(I_0 \ \text{mols/liter} )</th>
<th>(\text{chains/liter} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-17</td>
<td>(1.11 \times 10^{-3} )</td>
<td>(1.19 \times 10^{-3} )</td>
</tr>
<tr>
<td>2-28</td>
<td>(1.09 \times 10^{-3} )</td>
<td>(1.07 \times 10^{-3} )</td>
</tr>
</tbody>
</table>

These results imply, first, that all of the initiator was consumed in the formation of polymeric anions from the monomer available (Experiment 2-17), and second, that the polymerization which follows the addition of more monomer to a system of polymeric anions does not take place via generation of new chains (Experiment 2-28), but by addition to existing active chains. Hence, one can conclude that the butyl lithium initiator generates one active chain end for each initiator molecule and, furthermore, no chain transfer mechanism exists in this polymerization. Thus, the number average molecular weight may be calculated for this polymerization
by
\[ \dot{M}_n = \frac{\text{polymer yield (grams)}}{\text{total initiator (equivalents)}} \]
or
\[ \dot{M}_n = \frac{M_0}{I_0} \times \text{yield} \]

It should also be noted, however, that the results, just shown, do not preclude a partial termination of the active chain ends by any of several mechanisms. The previous results would still be obtained. Evidence of such "termination" of active chain ends can be found in the molecular weight distributions of the polymer product. This subject will be postponed until the results of the fractionation experiments are discussed.

C. Kinetic Experiments

1. First Order Monomer Concentration Dependence

The results of the dilatometric kinetic experiments are presented in tabular form in Table VIII in Appendix IV as per cent conversion versus time. Theory suggests the relationship

\[ \ln \frac{M}{M_0} = -k_p I_o t \]

for the special case of rapid initiation. This relation can be written in terms of conversion as

\[ \ln(1 - \text{fraction of conversion}) = -k_p I_o t \]

Hence, to satisfy theory, plots of \( \ln(1 - \text{fraction of conversion}) \) versus time should yield straight lines with slope, \(-kI_o\). For convenience,
the data was plotted as $\log (100 - \text{per cent conversion})$ versus time and indeed yielded straight line plots for all values of $M_o$. As a typical example the data of Experiment 2-26 is shown in Figure 12.

An examination of this plot indicates two nonlinear portions, one at the early set of measurements and one at high conversion. The first nonlinear portion results from experimental procedure. In many cases the chilled dilatometer had not reached temperature equilibrium with the constant temperature bath after the initial warmup period of seven to ten minutes. The normal shrinkage in capillary height due to polymerization was offset to some extent by expansion due to temperature rise in the dilatometer prior to equilibrium. This is clearly seen in several sets of experimental data in which the initial measurements indicate an increase in the capillary height (a decrease in conversion). Therefore, this nonlinear portion of the figure has no significance as far as the interpretation of the kinetics is concerned.

The second nonlinear portion of the plot of $\log (100 - \text{per cent conversion})$ versus time, which constitutes a decrease in rate from the expected over-all first order reaction, is attributed to a decrease in the number of available effective active ends. This slowing down of the rate of reaction usually takes place above 85 per cent conversion. Such a result can be produced by several mechanisms. First, the small amount of monomer remaining after high conversion may not be distributed homogeneously throughout the reaction dilatometer because of the presence of the swollen polymer precipitate. Secondly, it is possible that as the polymerization proceeds, active chain ends become occluded inside the
Figure 13. Comparison of Kinetic Experimental Data Runs 2-17, 2-18, and 2-19.
polymer matrix and become inactive in the sense that monomer can no
longer reach these active sites. Finally, active ends can be deactivated
by such side reaction as branching on the nitrogen atom in the pyridine
ring or termination with impurities. Further data, to be discussed,
suggests one of the first two mechanisms rather than the latter. Other
investigators\(^{15, 24}\) report a similar decrease in the expected over-all
first order rate of polymerization in similar systems at high conversion
(over 90 per cent), even in homogeneous systems.

The values of the slopes of plots of \(\ln(1 - \text{fraction of con-
version})\) versus time were calculated for the linear portion of the plot
from the formula

\[
\frac{d\ln M}{dt} = \ln \left( \frac{1 - \text{fraction of conversion at } t / 1 - \text{fraction of conversion at } t_2'}{t - t_2'} \right)
\]

where \(t_2'\) is the time at the end of the initial unsteady temperature
period. The value of the slope was calculated for as many data points as
existed for the linear portion of each plot and averaged. The average
values of each kinetic run are reported in Column 11 of Table I.

2. **Initiator Concentration Dependence**

Since \(\frac{d\ln M}{dt} = -k_p I_o\), one should expect the value, \(\frac{d\ln M}{dt}\) to
remain constant in all experiments utilizing the same initiator concen-
tration. Logarithmic plots of three kinetic runs, 2-17, 2-18, and 2-19 are
shown in Figure 13. The figure indicates an apparent deviation from the
theory presented. There are several alternate explanations of this
abnormal behavior and we shall consider these in turn. Unfortunately,
none of the alternate explanations can be supported by the kinetic data, and we will have to turn to the results of the molecular weight distribution analysis before we can obtain the correct explanation.

a. **Initiation Rate**

Recall that the values of slopes of the first order logarithmic plots represent the product of the polymerization rate constant and the concentration of active ends, $k_1 \Sigma P_i$. Recall, furthermore, that, the concentration of active ends, $\Sigma P_i$, is equal to $I_0 - I$

and that

$$\frac{-dI}{dt} = k_1(I)(M)$$

Since the product, $k_p \Sigma P_i$, is a constant with respect to time for any given run over the measured range of the experiment, we can eliminate both the possibility of an initiation reaction or an impurity termination reaction taking place concurrently with the polymerization reaction during the rate measurement period. Furthermore, since all of the initiator can be accounted for by the number of chains in the polymer product, we can conclude that the initiation step is at least rapid enough to be completed before the kinetic measurements had begun. Thus $\frac{-dI}{dt} = 0$ and $I = 0$ during the rate measurement period. Therefore it is reasonable on this basis to expect that the product of the rate constant, $k_p$ and the concentration of active chain ends, $k_p \Sigma P_i$ is $k_p x I_0$. 
b. **Impurities**

Another explanation of the variation of the value of the slope at measured constant initiator concentration might be the presence of impurities which consume varying degrees of the initiator or active ends prior to the rate measurements. The source of such impurities can be any or all of the reactants, solvent, monomer, or initiator, or the walls of the mixing and reaction vessel. An examination of preparative procedures, however, points out that the main source of impurities should be the monomer alone. The batches of monomer used in Experiments 2-17, 2-18, and 2-19 were identical in the respect that they were dried, distilled, and degassed in one monomer ampoule distributor and all used within a period of three days. The chronological order of experiments is represented by the experiment number, yet the highest observable overall rate occurred in Experiment 2-18, followed next by Experiment 2-17. Therefore, aging effects can be neglected as a source of error over this short range period. Furthermore, in direct contrast to what would be expected of the presence of impurities in monomer, the observable rates increased with increasing monomer-to-initiator ratio. We can safely conclude, therefore, that the variation in expected rates cannot be explained by the presence of impurities in so far as any group of similar experiments are concerned.

c. **Monomer Initiator Complex Formation**

The observation that the rates increased with increasing monomer-to-initiator ratio could suggest the possibility of some type of equilibrium complex formation to form active centers with monomer.
Although this type of a mechanism cannot be completely discounted, it seems unlikely on the following basis. First of all most types of equilibrium complex formation mechanisms would involve other than pseudo first order kinetic schemes with respect to monomer. Secondly, although the monomer concentrations in the three experiments under discussion were approximately in the ratio 1:2:4, two of the observable rates were quite close together while the third was practically double the other two. Such effects might only be explained by a rather complicated mechanism, which can hardly be justified on the basis of current literature on anionic polymerization mechanisms.

d. Surface Area Effects

Finally, it is possible to suggest a diffusion controlled polymerization scheme in which the observable rate of polymerization is a function of the amount of polymer precipitate in the reaction system. This type of mechanism would require that the locus of polymerization be on or in the polymer matrix. Qualitative observations indicate that such is the case since negligible polymer was ever formed in the supernatant liquid solution of monomer and solvent in the capillary stem of the dilatometer. Recent work\(^{(30)}\) on the free radical kinetics of precipitation polymerization of vinyl chloride indicated a rate acceleration proportional to the amount of polymer in early stages of polymerization and to the amount of polymer to the 2/3 power at later stages. Such observations indicate a reaction locus in the interior of the polymer particles at early formation of the polymer precipitate and on the surface of the polymer aggregates at later stages.
One should recall that the rate of polymerization in free radical systems,

$$\frac{-dM}{dt} = k_p(R)(M)$$

depends on the "steady state" concentration of radicals in the reaction. The radicals are subject to constant generation and termination during the reaction.

$$\frac{dR}{dt} = k_iI - k_tR$$

The "steady state" assumption is that the initiation rate becomes equaled by the termination rate at some steady state value of \( \dot{R} = \frac{k_iI}{k_t} \). The mechanism proposed for the free radical polymerization rate behavior that is observed in the heterophase polymerization of vinyl chloride is that radicals are generated on the surface that is formed. These surface radicals cannot terminate as rapidly, and therefore the "steady state" concentration of radicals increases. As more surface area is formed, more radicals can be generated on the surface and the rate accelerates.

The anionic polymerization mechanism that we are discussing on the other hand, does not include constant generation and termination of active sites. Therefore, we would not expect the number of active sites to depend on surface area. Examination of the data in Columns 4 and 11 of Table I clearly show that the observable rates scatter both up and down with respect to the amount of polymer present in the reaction. In
Figure 14. Cumulative Weight Distribution Polymer 2-27.
Figure 15. Cumulative Weight Distribution Polymer 2-28.
spite of the fact that the reaction takes place at the active chain ends which most probably are all located on or in the polymer precipitate, there is no correlation between the amount of polymer present at the time of rate measurements and the observed rates.

D. Molecular Weight Distributions

An explanation for the apparent deviation of the observable rates from that expected by theory can be found in evidence supplied by molecular weight distribution analysis. The results of fractionation and molecular weight determination experiments will be found in Table IX, Appendix IV. As an example, the cumulative weight distribution functions for polymers 2-27 and 2-28 are plotted in Figures 14 and 15. For an explanation of the methods employed in determining this function and the related derivative functions refer to the experimental section on data treatment, page 41.

1. Distribution Analysis and Polymerization Mechanism

Examination of the raw fractionation data conclusively points out the existence of two distinct batches of polymer in any given polymer sample, one in a comparatively low molecular weight range of 10,000 to 300,000 and the second, covering a spread of 300,000 in the range from one to four million depending on the experiment. No polymer fraction was ever obtained with a molecular weight between 300,000 and 900,000. This clearly bimodal distribution suggests the following model. Polymer particle formation at some early critical chain length of the growing polymeric anion traps out varying amounts of the active ends so that these occluded chain
ends can no longer grow except with whatever monomer is also trapped out in the polymer particle. Furthermore, the diffusion of monomer into the particles or particle agglomerates is negligibly slow and, therefore, only those reactive chain ends at the surface of the precipitate are available for further growth. Since the rate measurements were made only after large solids formation, it is reasonable to expect that the rates observed were due only to the participation of these "surface" anions. Therefore, if it is possible to calculate the number of chain ends capable of continued growth in each polymerization, it should be possible to make a correlation between the over-all observable rates.

In other words, we would like to know the fraction, \( f \), of the original \( I_0 \) chains that contribute to the observable rates.

It is possible to obtain values of the number of chains which correspond to any molecular weight range by suitable treatment of the number frequency distribution. It can be shown* that the reciprocal of the area under the entire curve of the frequency distribution is equal to the number average molecular weight of the polymer sample. Furthermore, the area under a portion of the number frequency distribution curve is representative of the total number of chains in a one gram fraction whose limits of molecular weight correspond to the low and high values of the abscissa of the portion of the curve in question.

The frequency distributions of polymer samples 2-17, 2-18, and 2-24 are presented for comparison in Figure 16. The values given for areas 1 and 2 correspond to the areas under the low molecular weight and high molecular weight distribution curves, respectively, as determined

* Appendix III
Figure 16. Comparison of Number Frequency Molecular Weight Distributions of Polymers 2-17, 2-18, and 2-24.
by plenimeter measurements of enlarged plots of each individual distribution. If one now calculates the number of chains represented by the low molecular weight fractions from the values given for area 1, one finds that the percentage of chains in the low end of the distribution represents 95 per cent and up of the total chains in any one experiment. In other words, if the model is correct, less than 5 per cent of the initiator is responsible for the observed kinetics. This is not a surprising conclusion and might be guessed in advance by examining the viscometric molecular weight, $\bar{M}_V$, of unfractionated polymer as shown in Column 8 of Table I. It was presupposed at the start of this study, that the reaction system corresponded to a non-terminating anionic polymerization based solely on the highly reactive, intensely colored polymer that was produced. On the basis of a typical anionic polymerization, one should expect number average molecular weights which are equal to the weight of polymer divided by total initiator; and which have, hopefully, a narrow molecular weight distribution about this average. These number average molecular weights which we can refer to as $\bar{M}_n$-theoretical are tabulated in Column 9 of Table I. A quick comparison of the two molecular weight averages indicates that the smallest ratio $\bar{M}_V/\bar{M}_n$-theoretical is eight to one and ranges as high as twenty-three to one. These large ratios are indicative of broad molecular weight distributions, which could only be produced by a process in which a small percentage of the chains could grow to extremely large molecular weights.

The number average molecular weight of each fractionated polymer was calculated from the values of the areas under the frequency distribution
curve of each polymer. These values are reported as $\bar{M}_n$-measured in Column 10 of Table I. Considering the amount of error involved in the fractionation of high polymer and the subsequent construction of cumulative and frequency distribution functions, the agreement between theoretical and measured values is excellent!

2. Rate Dependence on Available Sites

Having obtained the values for the percentage of chains included in the low molecular weight portions of the fractionated samples, we can now calculate the concentration of the effective active ends, $f\text{I}_0$, and the value of $k_p$ corresponding to the appropriate slope, $k_p \cdot f\text{I}_0$. The values, $f\text{I}_0$, are reported in Column 12 of Table I. Unfortunately, the values of $k_p$ at 31.4°C, calculated in this manner, do not agree. We must turn to the results of other investigators (26, 32, 54) of butyl lithium initiated polymerizations to find a suggestion for some other possible correlation.

It is well known that soluble organolithium compounds exist in solution in associated forms in equilibrium with unassociated organolithium compounds as represented by the equilibrium equation

$$(\text{RLi})_n \rightleftharpoons n(\text{RLi})$$

or

$$(\text{RLi})_n \rightleftharpoons (\text{RLi})_{n-1} + \text{RLi}$$

In kinetic studies of the polymerization of styrene (54), butadiene (32), and isoprene (26, 32), investigators have reported polymerization rates
which are dependent on the 1/2 order of the total organolithium concentration. These authors suggest that the growing polymeric chains are associated as dimeric chains in equilibrium with single chains and that only the single chains add monomer. In formula notation we have

\[ 2B_u(M_n)^- L_i^+ \xrightarrow{K_e} [B_u(M_n)^- L_i^+]_2 \]

\[ B_u(M_n)^- L_i^+ + M \xrightarrow{K_p} B_u(M_{n+1})^- L_i^+ \]

\[ \frac{dM}{dt} = K_p [B_u(M_n)^- L_i^+] [M] \]

\[ B_u(M_n)^- L_i^+ = \frac{\sqrt{[B_u(M_n)^- L_i^+]_2}}{K_e} \]

Thus for large \( K_e \)

\[ \frac{dM}{dt} = K_p \left( \frac{I_o}{K_e} \right)^{\frac{1}{2}} [M] \]  \hspace{1cm} (17)

Furthermore, Morton(32,33) has shown by measurements of the bulk viscosity of growing polymeric anion solutions, that polystyryl lithium, poly-isopropenyl lithium, and poly-butadienyl lithium exist as dimers in hydrocarbon solution. Qualitative observations which will be mentioned under miscellaneous results support this associated chain concept for the polyvinyl pyridinyl lithium system.

In view of the correlations obtained in these similar systems, a rate constant, \( k_2 \), was calculated from the slopes of the plots of kinetic data and the corresponding concentration values of the available
reactive chain ends by the equation

$$k_2 = -\frac{d\ln n^M}{dT} \frac{1}{\sqrt{P}} \text{ (18)}$$

In comparing Equations (17) and (18) one sees that $k_2 = \frac{k_p}{\sqrt{k_e}}$ and that the units of $k_2$ are liters$^{1/2}$ mols$^{-1/2}$ sec$^{-1}$. These values are reported in Column 14 of Table I.

E. Validity of Model

1. Sources of Error

The values of $k_2$ reported for Experiments 2-17, 2-18, 2-24, and 2-28, which were all conducted at $31.4^\circ$C, do little to support the validity of the preceding development. It is necessary, therefore, to examine the sources of error involved both in the evaluation of fractionation data and in the assumptions which underly the physical model of the polymerization system.

The two main sources of error are:

1. The evaluation of the molecular weight distribution to obtain the quantity $n$.

2. The assumption that all of the chain ends that are represented by the high molecular weight chains contribute to the observable kinetics, and that there are no additional competing reactions.

2. Computational Errors

The cumulative errors produced as a result of 1., the fractionation experiments, 2., the subsequent determination of a suitable
cumulative weight distribution, 3., the differentiation of the cumulative
distribution data, and 4., the graphical integration of the function
\[ \frac{1}{M_i} \frac{dW_i}{dM_i} \] can best be appraised by comparing the theoretical number
average molecular weights with those obtained by the preceding four steps.
(Columns 9, and 10, of Table I.) Now the evaluation of the quantity, \( f \),
depends on the relative areas under the two portions of the frequency
distribution plot. The number average molecular weight, however, depends
primarily on the area under the first portion of the frequency distribu-
tion curve, due to the strong dependence of number average molecular
weight on the amount of low molecular weight chains present in a sample.
A comparison of \( \bar{M}_n \) - measured and \( \bar{M}_n \) - theoretical in Experiments 2-17,
2-18, and 2-24 suggests that errors might have been committed resulting
in an over-estimate of the area for distribution 2-17 and underestimation
of the area for distributions 2-18 and 2-24. (Recall that \( \bar{M}_n \) is
inversely proportional to the area.) Since the values for \( f \) are based
on the ratio of the area under the high molecular weight peak to the total
area, this results in an underestimation of this value in 2-17 and an
overestimation in 2-18 and 2-24. The resulting effect on the value
obtained for \( k_2 \) is that the value obtained in Experiment 2-17 would be
too high, and the values obtained in 2-18 and 2-24 would be too low,
Therefore, at least qualitatively, we can justify the spread in the values
obtained for these three experiments.

On the other hand the extremely low value reported in Experiment
2-28 cannot be accounted for by the preceding argument. The low value of
\( k_2 \) in this instance can be accounted for by the fact that all of the chain
Figure 17. Polymerization Kinetic Experimental Data Run 2-19.
ends represented by the high end of the distribution no longer contribute
to the observable kinetics. Experiment 2-28 was carried out by addition
of a second amount of monomer to a reaction system that had been allowed
to polymerize for three days. The kinetics of the first stage of this
reaction system could be considered to behave in a fashion similar to
that of Experiment 2-19 which is shown in Figure 17 as a plot of log
(100 - percent conversion) versus time. This plot shows the typical
deviation from first order kinetics at high conversion, which we can
argue is due to continuing occlusion of more and more of the active chain
ends in the polymer matrix. Therefore, it can be concluded, that at the
time the rate measurements were performed on the second monomer addition
in Experiment 2-28, more chain ends had been inactivated than those which
were accounted for in the low molecular weight fractions of polymer 2-28.
Further proof of this argument is that the value of the product \( k_2 \times \sqrt{I_0} \)
obtained from the slope at the tail end of the kinetic data for 2-19
\( (k_2 \times \sqrt{I_0} = - \frac{d\ln M}{dt}) \) equals \( .815 \times 10^{-4} \). The value compares quite well
with the value obtained for the logarithmic linear portion of 2-28 which
is \( .67 \times 10^{-4} \).

This last portion of the discussion raises the very basic question
of whether or not it is correct to assume that the number of active ends
represented in the high molecular portion of the polymer actually is
responsible for the observed kinetics. It is possible that only a portion
of the chains represented by the high molecular weight species are responsi-
ble for the observed kinetics. On the other hand, it is also possible
that some of the low molecular weight chains are entering into competing
reactions which are contributing to the over-all observed rates. Further
examination of the molecular weight distributions can lead us to reject
these possibilities in so far as they effect the kinetic measurements, but
before we can examine them, we must know what type of theoretical distribu-
tion the model would produce.

3. Theoretical Molecular Weight Distribution

Based on the general set of equations presented earlier

\[
\left\{ \begin{array}{c}
P_i + M \\ \rightarrow \\
P_{i+1}
\end{array} \right. 
\]

we obtained the theoretical molecular weight distribution for the case
of rapid initiation - i.e., \( P(0^+) = I_o \)

\[
P_i(T) = \frac{I_o \left( \frac{\lambda_p T}{i-1} \right)^{i-1}}{(i-1)!} e^{-\lambda_p T}
\]

A slight modification is required to adapt this scheme to include equilib-
rium between the growing chains. Let us restrict the notation, \( P_i \), to
signify the reactive disassociated chains. Then the association of chains
is represented by

\[
P_i + P_j \quad \xrightleftharpoons{} \quad [P_i P_j]
\] (19)

at time \( 0^+ \)

\[
P_i + P_i \quad \xrightleftharpoons{} \quad [P_i P_i]
\]

\[
K_e = \frac{[P_i P_i]}{(P_i)^2}
\]
For equilibrium far to the right, large $K_e$,

$$[P_i P_j] \approx I_0, \quad P_i(0^+) = \sqrt{\frac{I_0}{K_e}}$$

Then we may still write

$$P_i + M \rightarrow P_2$$
$$P_2 + M \rightarrow P_3$$
$$P_i + M \rightarrow P_{i+1}$$

The corresponding rate expression for $i$-th species is

$$\frac{dP_i}{dt} = k_p (P_{i-1})(M) - k_p (P_i)(M)$$

the solution for the initial condition

$$P_i(0) = \sqrt{\frac{I_0}{K_e}}, \quad P_{i+1}(0) = 0, \quad (i \neq 0)$$

is

$$P_i(t) = \sqrt{\frac{I_0}{K_e}} \frac{(k_p T)^{i-1}}{(i-1)!} e^{-k_p T}$$

(20)

where

$$T = \int_0^t M dt$$

The total number of active ends remains constant with time since

$$\sum_{i=1}^{\infty} P_i = \sqrt{\frac{I_0}{K_e}}$$
The distribution in (20) represents the distribution of disassociated chains present in the reacting system. For the distribution of the total chains, we require the concentration of the i-th species present both in the complexed form, \((P_i P_j)\), and disassociated form \(P_i\). The distribution of the total chains of length 1 is therefore

\[ Q_i = \sum_{j=1}^{\infty} \left[ P_i P_j \right] + P_i \]  

(21)

The second term on the right is negligible in the case of large \(K_e\).

Since

\[ \left[ P_i P_j \right] = K_e (P_i)(P_j) \]

\[ Q_i = \sum_{j=1}^{\infty} K_e (P_i)(P_j) \]

\[ Q_i = \sum_{j=1}^{\infty} K_e \sqrt{\frac{I_0}{K_e}} e^{-k_T} \frac{(k_T)^{i-1}}{(i-1)!} \sqrt{I_0} \frac{e^{-k_T} (k_T)^{j-1}}{(j-1)!} \]

\[ Q_i = I_0 e^{-k_T} \frac{(k_T)^{i-1}}{(i-1)!} \]  

(22)

Thus the distribution of chain lengths remains Poisson in spite of the equilibrium complex formation.

We shall now consider a similar mathematical treatment in trying to predict with the model that is proposed the results of an actual
experiment. The polymerization kinetic experiments consisted of an initial unsteady temperature period followed by a constant temperature period during which rate measurements were obtained. The unsteady temperature period could in turn be split into two parts; first, the "homogeneous" polymerization period during which all the chains were growing, and second, the heterophase polymerization period in which only a fraction, $f$, of the initial chains continued growth. The time periods are represented schematically in the following diagram:

\[ \text{Absolute Time} \]

\[ t_1' \quad t_2' \quad \text{Rate Measurement Time, } t \]

<table>
<thead>
<tr>
<th>Homogeneous System</th>
<th>Heterophase System</th>
<th>Heterophase System</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rising Temperature</td>
<td>Constant Temperature</td>
<td></td>
</tr>
</tbody>
</table>

The rate expression

\[ \frac{dP_{\bar{e}}}{dt} = k_p (P_i) \langle M \rangle - k_p (P_i) |M| \]

remains the same for the reaction. In the initial two periods however, $k_p$ is not a constant, since as a function of temperature, it varies with time along with the monomer concentration. We make the substitution

\[ \bar{\tau}' = \int_0^{t'} k_p(x) M(x) dx \]
and can immediately write the solution

$$P_i(t') = \sqrt{\frac{I_0}{K_e}} \frac{(\gamma')^{i-1}}{(i-1)!} e^{-\gamma'}$$

The distribution for the total chains is

$$Q_i(t') = I_0 \frac{(\gamma')^{i-1}}{(i-1)!} e^{-\gamma'}$$

At the end of the first time period, $t_1'$, we propose, according to the model, that a fraction, $1-f$, of the total chains, $\Sigma Q_i$, becomes "unavailable", and that the remaining $fI_0$ chains are capable of polymerization. Therefore, a portion of the total chains will have the final fixed distribution

$$(1-f)I_0 \frac{(\gamma')^{i-1}}{(i-1)!} e^{-\gamma'}$$

where $\tau_1'$ is the fixed dimensionless time period for the homogeneous portion of the reaction

$$\tau_1' = \int_0^{t_1'} \lambda_0(x) M(x) dx$$

Let us denote the remaining available associated chain ends by

$$\sum_{i=1}^{\infty} R_i$$

Then

$$\sum_{i=1}^{\infty} R_i = f \sum Q_i = fI_0$$
and if we denote the remaining disassociated active chain ends by
\[ \sum_{i=1}^{\infty} A_i \]
Then
\[ \sum_{i=1}^{\infty} A_i = \sqrt{\frac{fI_0}{K_e}} \]

If we follow the distribution of this portion of the chains from zero absolute time through the first and second time periods we will obtain the distribution at the end of time \( t_1 + t_2 \)

\[ R_i = fI_0 \frac{(\hat{\tau}_2')^{i-1}}{(i-1)!} e^{-\hat{\tau}_2'} \quad (22) \]

and

\[ A_i = \sqrt{\frac{fI_0}{K_e}} \frac{(\hat{\tau}_2')^{i-1}}{(i-1)!} e^{-\hat{\tau}_2'} \quad (23) \]

where
\[ \hat{\tau}_2' = \int_0^{t_2'} k_p(x) M(x) dx + \int_{t_1}^{t_2'} k_p(y) M(y) dy \]

Furthermore the distributions in (22) and (23) represent the initial condition for the steady temperature rate measurement period.

During the constant temperature period we have the rate expression
\[ \frac{dA_i}{dt} = k_p (A_{i-1})(M) - k_p (A_i)(M) \]
Making the substitution $\tau = \int_0^\tau \dot{\mathbf{M}} \, dt$ we solve* the equation above with the initial condition

$$A_i(0) = \sqrt{\frac{f_{I_0}}{K_e}} \frac{(\tau_2')^{i-1}}{(i-1)!} e^{-\tau_2'}$$

The solution is

$$A_i(\tau) = \sqrt{\frac{f_{I_0}}{K_e}} e^{-\tau_2'} e^{-\frac{k_p}{\tau}} \frac{(\frac{k_p}{\tau})^{i-1}}{(i-1)!} \left[ 1 + \frac{\tau_2'}{k_p \tau} \right]^{i-1} \tag{24}$$

It is easily shown* that

$$\sum_i A_i(\tau) = \sqrt{\frac{f_{I_0}}{K_e}}$$

Furthermore

$$R_i = \sum_{j=1}^\infty K_e [A_i A_j]$$

$$= f_{I_0} e^{-\tau_2'} e^{-\frac{k_p}{\tau}} \frac{(\frac{k_p}{\tau})^{i-1}}{(i-1)!} \left[ 1 + \frac{\tau_2'}{k_p \tau} \right]^{i-1}$$

We now define $\alpha_i$ as the mol fraction of the $i$-th specie by

$$\alpha_i = \frac{A_i}{\sum_i A_i} = \frac{R_i}{\sum_i R_i}$$

* Appendix I
\[ \alpha_i = e^{-\beta_i} e^{-\lambda_p \tilde{T}} \frac{(\lambda_p \tilde{T})^{i-1}}{(i-1)!} \left[ 1 + \frac{1}{\lambda_p \tilde{T}} \right]^{i-1} \]  

(25)

Then the number average degree of polymerization, \( \bar{i} \), as well as the mean of the long chain polymer species is

\[ \bar{i} = \sum_{i=1}^{\infty} i \alpha_i \]

The result* is

\[ \bar{i} = \lambda_p \tilde{T} \left[ 1 + \frac{1}{\lambda_p \tilde{T}} \right] \]  

(26)

Solution of (26) for \( \lambda_p \) yields

\[ \lambda_p \tilde{T} = \bar{i} - \tilde{T}' \]  

(27)

The monomer concentration during the constant temperature period can be calculated from the differential equation

\[ -\frac{dM}{dt} = \lambda_p (M) (\sum \bar{A}_i) \]

\[ = \lambda_p (M) \sqrt{\frac{FT_0}{K_c}} \]

The solution is

\[ M = M_{t_0} e^{-\lambda_p \sqrt{\frac{FT_0}{K_c}} t} \]  

(28)

* Appendix I
Since
\[
\tau = \int_0^t M dt
\]

\[
\tau = \frac{M_{e,3}}{\frac{E}{K_e} \sqrt{\frac{F I_0}{K_e}}} \left[ 1 - e^{-\frac{k_p \sqrt{F I_0}}{K_e} t} \right] 
\]

(29)

If we plot Equation (28) as \( \ln \frac{M}{M_{c,0}} \) versus time we obtain a straight line
with slope, \( \frac{k_p}{\sqrt{K_e}} \sqrt{F I_0} \) or \( k_2 \sqrt{F I_0} \).

The preceding derivation provides the following interesting result. The value of \( \tau \) in Equation (27) can be computed by Equation
(29) with the help of the observed rate data, \( k_2 \sqrt{F I_0} \), during the con-
stant temperature period. Furthermore, the values of \( \bar{I} \) and \( \tau_2' \)
correspond to the means of the high molecular weight species and some
intermediate molecular weight species, respectively, and at least in
principle can be obtained from the molecular weight distributions. There-
fore, we could calculate the absolute value of \( k_p \) from Equation (27)
and in addition \( K_e \), since

\[
K_e = \left( \frac{\frac{E}{K_e}}{\frac{E}{K_c}} \right)^2
\]

Unfortunately, in practice, it is impossible to determine the intermediate
value \( \tau_2' \) for this system. This determination would require a dupli-
cation of the experimental conditions of any completed run up to the rate
measurement period with termination of the reaction at this point. The
formation of random amounts of trapped chain ends from experiment to
experiment, makes this impossible in the present heterophase system. The application of this idea, however, should be very simple in those homogeneous polymerization systems already investigated, i.e., the butyl lithium initiated polymerization of butadiene, isoprene, and styrene.

4. Error Due to Possible Competing Reaction

We can return to a final consideration of the validity of the proposed model. The preceding molecular weight distribution derivation for the low and high molecular weight species points out that in spite of equilibrium complex formation and partial inactivation of active ends the theoretical frequency distributions for both polymer fractions should be Poisson. By utilizing the fact that the mean and variance of the Poisson distribution are equal, and by using a normal approximation to the Poisson distribution, we can determine the theoretical range of molecular weight that each of the two frequency curves should cover. The number average molecular weight of the low molecular weight material is almost uniformly 32,000, \( \bar{M} = 300 \). See Table VII. The number average molecular weights of the long chain fractions are between 1,000,000 and 3,000,000 \( \bar{M} = 10,000 \) to \( \bar{M} = 30,000 \). Since 99.7 per cent of the chain lengths should be included in the range of \( -3\bar{M} \) to \( +3\bar{M} \) for the normal distribution approximation, we can compute that the range of molecular weights should ideally be 10,000 molecular weight units for low weight species and 60,000 to 180,000 molecular weight units for the high end species. In no case does the range of the low molecular weight material fit the theoretical range. On the other hand, we find fair to good
Figure 18. Comparison of Number Frequency Molecular Weight Distributions of Low Molecular Weight Fractions of Polymers 2-27, 2-28, and 3-14.
agreement with the expected values for the distributions of high molecular weight material in Experiments 2-17, 2-24, 2-27, 2-29, and 2-30. (Experiments 3-14 and 2-28 should not be expected to fit this correlation because of different experimental conditions.) On the basis of this correlation, as well as the constant slope of the rate data, \( \frac{d \ln M}{dt} \), we can conclude that the chains ends represented by the high molecular weight species all contribute to the observable rate.

The lack of a correlation with theory in regard to the range of the low molecular weight distribution does indicate the continued slow growth of a portion of the low molecular weight material after precipitation. A comparison of the low molecular weight distributions from Experiments 2-27, 2-28, and 3-14, Figure 18, suggests that this growth contributes little to the observable rates. Experiment 2-27 was terminated at approximately the end of the unsteady temperature period (12 minutes) - that is prior to rate measurement period. Yet the frequency distribution for the low molecular weight material in this experiment is as broad as that in Experiments 2-28 and 3-14 which were allowed to react for periods of three days to two weeks! It is reasonable to suggest that the spread of the low molecular weight distribution is due to the finite (as opposed to instantaneous) time required to trap out active chain ends, as well as continued growth of the trapped chain ends with occluded monomer. In either case, the fractionation data just compared indicates that these chain ends do not contribute to the observable rate. One can conclude, therefore, that the proposed model is valid.
Figure 19. Arrhenius Plot of Rate Constant $k_2$. 
F. Miscellaneous Results

1. Activation Energy

The activation energy and frequency factor were calculated from the slope and intercept of an Arrhenius plot (Figure 19) of \( \ln k_2 \) vs \( \frac{1}{T} \). The activation energy over the temperature range -30 to +30 was 12.7 Kcal/mol and the frequency factor was \( 3.65 \times 10^8 \). These values compare favorably with the values reported by Worsfold and Bywater\(^{(54)}\) for the polymerization of styrene in hydrocarbon solvents, \( 14.3 \) Kcal/mol and \( 2.93 \times 10^8 \). Values of the activation energy for the polymerization of isoprene and butadiene are reported by Morton\(^{(32)}\) and coworkers as \( 22 \) Kcal/mol and \( 21.3 \) Kcal/mol, respectively, in hydrocarbon solvents, and \( 7 \) Kcal/mol, and \( 7.2 \) Kcal/mol, respectively, in tetrahydrofuran. The large difference in activation energy for the same polymerization in two different solvents can be explained by the contribution of the activation energy of the equilibrium constant, \( K_e \), to the observable rate constant \( k_2 \). Since

\[
k_2 = \frac{k_p}{\sqrt{K_e}}
\]

\[
E_{a2} = E_{ap} - \frac{1}{2} E_{ae}
\]

Equilibrium association is small or non-existent in ether solvents and, therefore, \( E_{a2} = E_{ap} \). The intermediate value of 12.7 Kcal/mol supports the idea of chain association in the polymerization of 4-vinyl pyridine in hydrocarbon media.
2. Polymeric Anion Association

Further evidence for polymer anion association was found in an early qualitative experiment. In a block copolymerization carried out by the addition of 4-vinyl pyridine to polystyryl anions in toluene solution, a highly colored, completely transparent, viscous solution was formed. The viscosity of the solution became so great, that it could not be poured. When a small amount (1 cc) of butyl alcohol was added as a terminating agent, the solution became a non-viscous water colored solution. The extreme change in viscosity of the growing polymeric anions solution to that of terminated polymer solution was used by Morton(32) to calculate the degree of association of polymeric anions in the polymerizations of isoprene, butadiene, and styrene. Since the homopolymer of 4-vinyl pyridine is insoluble in hydrocarbon media, similar experiments could not be performed.

3. Polymer Chain Linkage

Possible side reactions of butyl lithium or the polymeric anion with the nitrogen-carbon double bond in the ring of 4-vinyl pyridine creates the possibility of (1) ring linkages in the backbone chain of the polymer or (2) chain branching. The presence of the ring in the backbone chain can be detected by the presence of unsaturated vinyl carbon-carbon groups in the polymer. The characteristic infrared absorption band of the vinyl group in vinyl pyridines is reported(14) around 990 cm\(^{-1}\). Infrared absorption patterns for 4-vinyl pyridine monomer and polymer are shown in Figures 8 and 9. The absorption band at 923 cm\(^{-1}\) for the monomer agrees with the literature. You may note the complete absence of this
band in the polymer absorption pattern. If such linkages exist in the polymer chain, they would have to be too few to be observed.

Chain branching, however, can not be as easily dismissed. The value of $k'$ in the Huggins empirical viscosity-concentration equation sometimes can be of value in qualitatively determining branching in polymers.$^{(6, 27)}$ Values of $k'$ for the various polymers and polymer fractions are reported in Table V. There are no apparent trends. Furthermore, available literature$^{(20)}$ on similar values for polymer produced by free radical polymerization are few in number and more widely scattered.

Ziegler and Zeiser$^{(57)}$ studied the reaction of butyl lithium with pyridine. From equimolar quantities of 1.58 m butyl lithium solution and undiluted pyridine they obtained a quantitative yield of $\alpha$-n-butyl pyridine after 3 hours at 90-100°C. Considering that the concentration of butyl lithium in the current experiment was less than $2 \times 10^{-5}$ M at temperatures from -80°C to 30°C, we can neglect any side reactions of butyl lithium with the nitrogen-carbon bond of the 4-vinyl pyridine. There still remains, however, the possibility of some chain branching via the reaction of the polymeric anion in this fashion during the course of the reaction.

4. Particle Size Determination

At an early stage in the study of the polymerization of 4-vinyl pyridine a model of the following nature was considered. The polymer precipitating particles were considered to be spheres into which monomer could diffuse and react throughout the sphere. The boundary value problem for this model was solved for one fixed size particle. In order to apply
this model to the polymerization system, a particle size distribution was needed. Photographs of random samples were taken at various magnifications. Some examples are shown in Figures 10 and 11. It was quickly noted that the small "spherical" particles were, indeed, not solid spheres but either agglomerates of even smaller particles or a spongy porous matrix. Therefore, this approach to the problem was abandoned. The particle sizes, however, can be obtained from the photographs and appear to be in the range from .2 to 5 microns.
IV. SUMMARY AND CONCLUSIONS

The polymerization of 4-vinyl pyridine initiated by butyl lithium belongs to the category of anionic polymerizations dubbed "living polymers". The precipitation of the growing polymeric anions from solution, however, produces what at first seems to be deviations from the expected behavior of anionic polymerizations. These anomalous results can be rationalized with the aid of the molecular weight distributions of the polymer products. The bimodal molecular weight distributions of the polymers are the result of a physical entrapment of a portion of the growing polymeric anions in the polymer precipitate. Thus entrapped, these still reactive sites no longer add monomer due to the slow or negligible diffusion of monomer from the solution into the polymer matrix. Only the small portion of reactive chains (less than 5 per cent) on or near the surface of the polymer precipitate take part in the polymerization reaction after the granular precipitate has been formed. Since the rate studies were made after the precipitate had been formed, the observed rates were a function only of the surface available reactive sites. The rate is proportional to the monomer concentration and proportional to the square root of the effective initiator concentration. The dilatometric kinetic experiments definitely establish the dependence of the rate on monomer concentration. Unfortunately, the accuracy of determining the effective initiator concentration via polymer fractionation is not sufficient alone to definitely establish the 1/2 order dependence on initiator concentration. Further evidence in the form of qualitative observations confirm this 1/2 order relation. 

-95-
half order initiator concentration dependence suggests an equilibrium complex formation of growing polymeric anions. In similar anionic polymerization studies (26, 32, 54) the rate was found to be proportional to the square root of the initiator concentration. One of these studies (32) included an additional determination of the equilibrium complex formation through the unusually high viscosity exhibited by the "living" polymeric anions in solution. The results of this determination showed that the growing polymeric anions were complexed in solution in pairs. A toluene solution of "living" block copolymer produced by adding 4-vinyl pyridine to polystyrene anions, exhibited the characteristic unusually high viscosity of complexed polymeric anions.

On this additional basis, rate constants were computed from the values of the rates obtained from the dilatometric kinetic experiments, and the square root of the effective initiator concentration. A calculation of the temperature dependence of the rate constants according to the Arrhenius correlation produced an activation energy of 12.7 Kcal/mol.
REFERENCES


48. Treloar, F.W., Polymer, 1, (1960), 513.


APPENDIX I

THE SOLUTION OF CONSECUTIVE FIRST ORDER DIFFERENTIAL EQUATIONS FOR THE INITIAL CONDITION OF A POISSON DISTRIBUTION

Given \[ \frac{dA_i}{dt} = \lambda p A_{i-1} M - \lambda p A_i M \]

with initial condition \[ A_i(0) = \sqrt{\frac{F T_o}{K_e}} \frac{\left(c_1\right)^{i-1}}{(i-1)!} e^{-\tau'_2} \]

Then \[ \frac{dA_i}{dt} = -\lambda p A_i M \]

Define \[ d\tau = M dt \]

\[ \frac{dA_i}{d\tau} = -\lambda p A_i \]

The solution is \[ A_i = [A_i]_0 e^{-\lambda p \tau} \]

\[ \frac{dA_2}{d\tau} = \lambda p A_1 - \lambda p A_2 \]

The solution is \[ A_2 = [A_2]_0 \lambda p \tau e^{-\lambda p \tau} + [A_2]_0 e^{-\lambda p \tau} \]

\[ \frac{dA_3}{d\tau} = \lambda p A_2 - \lambda p A_3 \]

The solution is \[ A_3 = [A_3]_0 \frac{(\lambda p \tau)^2}{2!} e^{-\lambda p \tau} + [A_2]_0 \lambda p \tau e^{-\lambda p \tau} + [A_3]_0 e^{-\lambda p \tau} \]

By induction \[ A_i = e^{-\lambda p \tau} \sum_{j=1}^{i} \frac{\left(\lambda p \tau\right)^{i-j}}{(i-j)!} [A_{j-1}]_0 \]

\[ A_i = e^{-\lambda p \tau} \sum_{j=1}^{i} \frac{\left(\lambda p \tau\right)^{i-j}}{(i-j)!} \sqrt{\frac{F T_o}{K_e}} \frac{\left(c_{2j}'\right)^{j-1}}{(j-1)!} e^{-\tau'_2} \]

Shift index \( j/j+1 \)

\[ A_i = \sqrt{\frac{F T_o}{K_e}} e^{-\tau'_2} e^{-\lambda p \tau} \sum_{j=0}^{i} \frac{\left(\lambda p \tau\right)^{i-j-1}}{(i-j-1)!} \frac{\tau'_2}{j!} \]

-101-
\[ A_i = \sqrt{\frac{f T_0}{k_e}} e^{-\tau_2'} e^{-\frac{1}{\beta_\nu \tau}} \left(i_{-1} \frac{(1-\iota)j}{\iota j!} \left(\frac{T_2'}{\beta_\nu \tau}\right)^j \right) \]

\[ A_i = \sqrt{\frac{f T_0}{k_e}} e^{-\tau_2'} e^{-\frac{1}{\beta_\nu \tau}} \left(\frac{U_{\nu \tau}}{\iota (\iota - 1)!} \right) \iota \sum_{j=0}^{\infty} \frac{(-1)^j (1-\iota)_j}{j!} \left(\frac{T_2'}{\beta_\nu \tau}\right)^j \]

\[ A_i = \sqrt{\frac{f T_0}{k_e}} e^{-\tau_2'} e^{-\frac{1}{\beta_\nu \tau}} \left(\frac{U_{\nu \tau}}{\iota (\iota - 1)!} \right) \iota \int_0^\infty \left[i_{-1} \frac{(1-\iota)}{\beta_\nu \tau} \right] \]

For notation see Rainville\(^{(38)}\).

\[ A_i = \sqrt{\frac{f T_0}{k_e}} e^{-\tau_2'} e^{-\frac{1}{\beta_\nu \tau}} \left(\frac{(k_\nu \tau)}{\iota (\iota - 1)!} \right) \left(1 + \frac{T_2'}{\beta_\nu \tau}\right)^{\iota - 1} \]

\[ \sum_{i=1}^{\infty} A_i = \sqrt{\frac{f T_0}{k_e}} e^{-\tau_2'} e^{-\frac{1}{\beta_\nu \tau}} \sum_{i=1}^{\infty} \frac{(k_\nu \tau)^{\iota - 1}}{\iota (\iota - 1)!} \left(1 + \frac{T_2'}{\beta_\nu \tau}\right)^{\iota - 1} \]

\[ = \sqrt{\frac{f T_0}{k_e}} e^{-\tau_2'} e^{-\frac{1}{\beta_\nu \tau}} \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} \frac{\tau_2^{\iota - 1}}{\iota !} \left(\frac{T_2'}{\beta_\nu \tau}\right)^j \]

\[ = \sqrt{\frac{f T_0}{k_e}} e^{-\tau_2'} e^{-\frac{1}{\beta_\nu \tau}} \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} \frac{(k_\nu \tau)^{\iota - 1}}{\iota !} \left(\frac{T_2'}{\beta_\nu \tau}\right)^j \]

\[ = \sqrt{\frac{f T_0}{k_e}} e^{-\tau_2'} e^{-\frac{1}{\beta_\nu \tau}} \sum_{i=0}^{\infty} \frac{(k_\nu \tau)^{\iota - 1}}{\iota !} \sum_{j=0}^{\infty} \left(\frac{T_2'}{\beta_\nu \tau}\right)^j \]

\[ = \sqrt{\frac{f T_0}{k_e}} e^{-\tau_2'} e^{-\frac{1}{\beta_\nu \tau}} \sum_{i=0}^{\infty} \frac{(k_\nu \tau)^{\iota - 1}}{\iota !} \sum_{j=0}^{\infty} \left(\frac{T_2'}{\beta_\nu \tau}\right)^j \]

\[ \sum_{i=1}^{\infty} A_i = \sqrt{\frac{f T_0}{k_e}} e^{-\tau_2'} e^{-\frac{1}{\beta_\nu \tau}} \sum_{i=1}^{\infty} \left(\frac{(k_\nu \tau)^{\iota - 1}}{\iota (\iota - 1)!} \right) \left(1 + \frac{T_2'}{\beta_\nu \tau}\right)^{\iota - 1} \]

\[ \alpha_i = \frac{A_i}{\sum A_i} = e^{-\frac{1}{\beta_\nu \tau}} e^{-\tau_2'} \left(\frac{(k_\nu \tau)^{\iota - 1}}{\iota (\iota - 1)!}\right) \left(1 + \frac{T_2'}{\beta_\nu \tau}\right)^{\iota - 1} \]
\[ \bar{L} = \sum_{i=1}^{\infty} i \alpha_i \]

\[ = e^{-b_p \bar{\tau}} e^{-\frac{\tau_2'}{b_p \bar{\tau}}} \left[ \sum_{i=1}^{\infty} \frac{(b_p \bar{\tau})^{i-1}}{(i-1)!} \left( 1 + \frac{\tau_2'}{b_p \bar{\tau}} \right)^{i-1} \right] \]

\[ = e^{-b_p \bar{\tau}} e^{-\frac{\tau_2'}{b_p \bar{\tau}}} \left[ \sum_{i=1}^{\infty} \frac{(i-1)(b_p \bar{\tau})^{i-1}}{(i-1)!} \left( 1 + \frac{\tau_2'}{b_p \bar{\tau}} \right)^{i-1} + \sum_{i=1}^{\infty} \frac{(b_p \bar{\tau})^{i-1}}{(i-1)!} \left( 1 + \frac{\tau_2'}{b_p \bar{\tau}} \right)^{i-1} \right] \]

\[ = e^{-b_p \bar{\tau}} e^{-\frac{\tau_2'}{b_p \bar{\tau}}} \left[ 1 + \frac{\tau_2'}{b_p \bar{\tau}} \right] \sum_{i=2}^{\infty} \frac{(b_p \bar{\tau})^{i-2}}{(i-2)!} \left( 1 + \frac{\tau_2'}{b_p \bar{\tau}} \right)^{i-2} \]

\[ + e^{-b_p \bar{\tau}} e^{-\frac{\tau_2'}{b_p \bar{\tau}}} \sum_{i=1}^{\infty} \frac{(b_p \bar{\tau})^{i-1}}{(i-1)!} \left( 1 + \frac{\tau_2'}{b_p \bar{\tau}} \right)^{i-1} \]

Shift index on the first sum \( i/i+2 \).

Shift index on the second sum \( i/i+1 \).

As shown
\[ \sum_{i=0}^{\infty} \frac{(b_p \bar{\tau})^i}{i!} \left( 1 + \frac{\tau_2'}{b_p \bar{\tau}} \right)^i = e^{b_p \bar{\tau}} e^{\frac{\tau_2'}{b_p \bar{\tau}}} \]

\[ \bar{L} = b_2 \bar{\tau} \left( 1 + \frac{\tau_2'}{b_2 \bar{\tau}} \right) + 1 \]
APPENDIX II

THE CUMULATIVE WEIGHT FRACTION OF A POLYDISPERSE
SAMPLE AS A FUNCTION OF MOLECULAR WEIGHT

We would like to show that the sum of the weight fractions
(cumulative weight fraction) of all molecular weight species less than
or equal to the intrinsic viscosity molecular weight average is approx-
imately one half, even in polydisperse molecular weight samples. To
accomplish this, we will examine a typical broad molecular weight dis-
tribution function and derive the cumulative weight fraction as a func-
tion of molecular weight (or its equivalent, $x$, the degree of poly-
merization). If we represent the molecular weight distribution function
by $w_y$, then the result we would like to obtain is

$$\mathcal{W}(x) = \sum_{y=1}^{y=x} w_y$$

where $W(x)$ is the cumulative weight fraction as a function of the
degree of polymerization, $x$.

A typical broad molecular weight distribution is the "most
probable distribution" given by Flory\(^{11}\) as

$$w_y = y^2 (1-p)^2 p^{y-1}$$

where $w_y$ is the weight fraction of polymer whose length is $y$ and
$p$ is a parameter whose value is usually between 0.9 and 1.0. The func-
tion we wish to obtain is

$$\mathcal{W}(x) = \sum_{y=1}^{y=x} y^2 (1-p)^2 p^{y-1}$$

\hspace{1cm} \text{(II-1)}
Associated with this weight distribution is the number distribution given by

$$N_y = p^{y-1} (1 - p)^2$$

Then the number average degree of polymerization, $\bar{X}_n$, is

$$\bar{X}_n = \frac{\sum_{x=1}^{\infty} xN_x}{\sum_{x=1}^{\infty} N_x} = \frac{1}{1-p}$$

Therefore,

$$p = \frac{1}{1-\bar{X}_n}$$

If we replace the sum in (II-1) by an integral and substitute in the values of $p$ in terms of the number average degree of polymerization we obtain

$$W(\bar{X}) = \int_{\frac{1}{\bar{X}_n}}^{\frac{\bar{X}}{\bar{X}_n}} \left( 1 - \frac{1}{\bar{X}_n} \right)^{y-1} dy$$

It is more convenient to replace the upper limit of the integral by a multiple, $m$, of the number average molecular weight, $\bar{X}_n$. $x = m\bar{X}_n$.

The solution of this integral for moderate $\bar{X}_n$ $(\bar{X}_n > 50)$ is

$$W(m\bar{X}_n) = 1 - \frac{2}{e^{m\bar{X}_n}}$$

We can now determine the cumulative weight fraction of this distribution up to the viscosity average molecular weight if we know the relation between the viscosity average degree of polymerization and the number average degree of polymerization.
For this distribution Flory\(^{(11)}\) has given the relation,

\[
\bar{M}_n : \bar{M}_v : \bar{M}_w \::\: \bar{X}_n : \bar{X}_v : \bar{X}_w \::\: (l + \alpha) \Gamma(l + \alpha)^{\frac{1}{\alpha}} \cdot 2
\]

where \(\alpha\) is the exponent of the empirical Mark-Houwink equation,

\[
|\eta| = C M^\alpha
\]

For polyvinyl pyridine in methanol \(\alpha = .69\); then \(\bar{X}_v : \bar{X}_n = 1.885\) and

\[
W(1.855 \bar{X}_n) = 1 - \frac{2}{e^{1.855}} = .588
\]
APPENDIX III

RELATION OF WEIGHT FREQUENCY AND NUMBER FREQUENCY MOLECULAR WEIGHT DISTRIBUTIONS TO THE DERIVATIVES OF THE CUMULATIVE WEIGHT DISTRIBUTION

Let

\[ G = \text{total weight of sample} \]

\[ g(n)dn = \text{weight of sample whose chain length is between } n \text{ and } n + dn \]

Then

\[ G = \int_0^\infty g(n)dn \]

\[ G(n) = \int_0^n g(n)dn = \text{weight of material whose chain length } \leq n \]

Let

\[ W(n) = \frac{G(n)}{G} = \text{weight fraction of material whose chain length } \leq n \]

\( W(n) \) is the cumulative weight distribution.

\[ w(n)dn = \frac{g(n)dn}{G} \]

\[ W(n) = \int_0^n w(n)dn \]

\[ \frac{dG(n)}{dn} = g(n) \]

\[ \frac{dW(n)}{dn} = \frac{dG(n)}{Gdn} = \frac{g(n)}{G} = w(n) \]

\( w(n) \) is the weight frequency distribution.
Let
\[ P = \text{total number of chains in sample} \]
\[ p(n) dn = \text{number of chains in sample having a length between } n \text{ and } n + dn \]

Then
\[ P = \int_{0}^{\infty} p(n) dn \]
\[ F(n) = \int_{0}^{n} p(n) dn \]

Let
\[ F(n) = \frac{P(n)}{P} = \text{fraction of chains in sample with length } \leq n \]
\[ f(n) dn = \frac{p(n) dn}{P} = \text{fraction of chains in the sample with length between } n \text{ and } n + dn \]

\( f(n) \) is the number frequency distribution.

Now
\[ g(n) dn = p(n) dn \ n M_0 \]

where
\[ M_0 = \text{molecular weight of a unit in the chain} \]
\[ w(n) dn = \frac{g(n) dn}{G} = \frac{p(n) dn \ n M_0}{G} \]

\( \bar{M}_n \) is defined by
\[ \bar{M}_n = \frac{G}{P} \]
\[ G = \bar{M}_n P \]
\[ w(n) dn = \frac{p(n) dn \ n M_0}{\bar{M}_n P} = \frac{f(n) dn \ n M_0}{\bar{M}_n} \]
We can plot $W(n)$ vs $n$. The derivatives of this plot, 
\[
\frac{dW(n)}{dn} = w(n).
\]
Define $M_n = nM_0$. By dividing by $M_n$ we obtain the values
\[
\frac{1}{M_n} \frac{dW(n)}{dn} = \frac{w(n)}{nM_0}
\]
but
\[
f(n)dn = \frac{w(n)}{nM_0} \frac{1}{M_n} dn
\]
Therefore
\[
f(n)dn = (\text{values}) dn \frac{1}{M_n}
\]
\[
1 = \int_{0}^{\infty} f(n)dn = \frac{1}{M_n} \int_{0}^{\infty} (\text{values}) dn
\]
The integral on the right is the area under a plot of
\[
\frac{1}{M_n} \frac{dW(n)}{dn}
\]
vs $n$
Therefore
\[
1 = \frac{1}{M_n} \cdot \text{Area}
\]
or
\[
\frac{1}{M_n} = \frac{1}{\text{Area}}
\]
Furthermore
\[
P(n) = \int_{0}^{n} p(n)dn = \int_{0}^{n} P f(n)dn
\]
\[
= \frac{C}{M_n} \int_{0}^{\infty} f(n)dn
\]
but
\[
\int_{0}^{n} f(n)dn = \frac{1}{M_n} \int_{0}^{\infty} (\text{values})dn
\]
The integral, \( \int_0^n (\text{values}) \, dn \), is the area under a plot of \( \frac{1}{M_n} \frac{dW(n)}{dn} \) vs \( n \) from 0 to \( n \). Therefore

\[
P(n) = G \cdot \text{area} \int_0^n \frac{dW(n)}{dn}
\]

If instead of plotting

\[
\frac{1}{M_n} \frac{dW(n)}{dn} \quad \text{vs} \quad n
\]

we plot

\[
\frac{1}{M_n} \frac{dW(n)}{dM_n} \quad \text{vs} \quad M_n
\]

Then

\[
\frac{dW(n)}{dM_n} = \frac{w(n)}{M_o}
\]

\[
f(n)dn = \frac{w(n)dn}{n \cdot M_o} \cdot \frac{1}{M_n}
\]

\[
f(n)dn = \left[ \frac{dW(n)/dM_n}{n \cdot M_o} \right] M_o \cdot dn \cdot \frac{1}{M_n}
\]

Therefore

\[
1 = \int_0^\infty f(n)dn = \int_0^\infty \frac{1}{M_n} \left( \frac{dW(n)}{dM_n} \right) dM_n \cdot \frac{1}{M_n} = \text{Area} \cdot \frac{1}{M_n}
\]

and

\[
\frac{1}{M_n} = \frac{1}{\text{area}}
\]
APPENDIX IV

TABLES OF DATA AND CALCULATIONS
### TABLE II

**SPECIFIC VOLUMES OF TOULUENE-4-VINYL PYRIDINE SOLUTIONS AT -29.8°C**

<table>
<thead>
<tr>
<th>Weight Per Cent 4-Vinyl Pyridine</th>
<th>Measured Specific Volume</th>
<th>Ideal Solution Specific Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>1.096</td>
<td>1.096</td>
</tr>
<tr>
<td>2.74</td>
<td>1.092</td>
<td>1.093</td>
</tr>
<tr>
<td>14.8</td>
<td>1.078</td>
<td>1.078</td>
</tr>
<tr>
<td>100.0</td>
<td>.974</td>
<td>.974</td>
</tr>
</tbody>
</table>

### TABLE III

**INTRINSIC VISCOSITIES OF POLYMER SAMPLES IN METHANOL AND ETHANOL SOLUTIONS**

| Sample | Methanol | Ethanol | log|η| |
|--------|----------|---------|----|---|
|        | [η]      | log|η| |
| 2-17-3 | 4.00     | .396    | -.398 | .408 |
| 2-28-5 | 7.45     | 7.18    | .872  | .856 |
| 1-5    | 2.77     | 2.69    | .442  | .130 |
| 2-7    | 3.84     | 3.65    | .584  | .562 |
| 3-13   | 1.78     | 1.64    | .250  | .215 |

### TABLE IV

**SAMPLE VISCOSITY DATA AND CALCULATIONS**

(Polymer 2-21, Temperature 25.1°C.)

Solution A- .0834 g. polymer in 25 ml. methanol  
Solution B- 20 ml. solution A + 10 ml. methanol  
Solution C- 30 ml. solution B + 20 ml. methanol

<table>
<thead>
<tr>
<th>Solution</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer (g)</td>
<td>.0667</td>
<td>.0667</td>
<td>.0667</td>
</tr>
<tr>
<td>Solvent (ml)</td>
<td>20</td>
<td>30</td>
<td>50</td>
</tr>
<tr>
<td>Conc (g/100ml)</td>
<td>.3336</td>
<td>.2224</td>
<td>.1334</td>
</tr>
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<tr>
<td>T (avg)</td>
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<td>118.0</td>
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<tr>
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<td>90.4</td>
<td>49.9</td>
</tr>
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<td>39.4</td>
<td>26.2</td>
<td>15.7</td>
</tr>
<tr>
<td>T&lt;sub&gt;0&lt;/sub&gt;/T&lt;sub&gt;0&lt;/sub&gt;</td>
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<td>3.170</td>
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<td>.24699</td>
<td>.15320</td>
</tr>
<tr>
<td>ln T/T&lt;sub&gt;0&lt;/sub&gt;</td>
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<td>.56882</td>
<td>.35282</td>
</tr>
<tr>
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<td>c</td>
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</tbody>
</table>

\[ n = 4.5 \times 10^5 \]
| Polymer | $|\eta| \quad |\eta|^2 \quad \text{Slope} \quad \kappa'$ | Polymer | $|\eta| \quad |\eta|^2 \quad \text{Slope} \quad \kappa'$ |
|--------|------------------|------------------|------------------|
| 2-17-4 | 0.947            | 0.897            | 0.319            | 356               | 1-5               | 2.77             | 7.67             | 3.08            | .402 |
| 2-17-5 | 6.15             | 37.82            | 15.88            | 420               | 2-7               | 3.84             | 14.75            | 5.94            | .403 |
| 2-17-6 | 6.30             | 39.69            | 15.15            | 382               | 1-8               | 3.23             | 10.43            | 3.98            | .382 |
| 2-17-7 | 6.20             | 38.44            | 15.92            | 414               | 2-9               | 2.87             | 8.24             | 3.13            | .330 |
| 2-18-4 | 4.65             | 21.6             | 0.985            | 456               | 2-12              | 2.95             | 8.70             | 3.25            | .374 |
| 2-18-5 | 3.74             | 13.99            | 5.22             | 373               | 3-13              | 1.78             | 3.17             | .995            | .311 |
| 2-18-6 | 4.80             | 23.04            | 9.67             | 420               | 2-14              | 5.20             | 27.04            | 10.63           | .395 |
| 2-18-7 | 4.07             | 15.56            | 6.45             | 339               | 2-15              | 3.68             | 13.54            | 5.04            | .372 |
| 2-24-3 | 0.473            | 0.224            | 0.0788           | 352               | 2-17              | 3.115            | 9.70             | 3.42            | .353 |
| 2-24-5 | 4.26             | 18.15            | 8.03             | 442               | 2-18              | 4.34             | 13.84            | 8.02            | .426 |
| 2-24-6 | 4.58             | 20.98            | 8.35             | 415               | 2-19              | 1.837            | 3.37             | 1.11            | .329 |
| 2-24-7 | 4.40             | 19.36            | 7.45             | 335               | 2-21              | 2.79             | 7.78             | 2.91            | .374 |
| 2-27-3 | 0.50             | 0.250            | 0.116            | 464               | 2-22              | 3.66             | 13.40            | 5.74            | .428 |
| 2-27-4 | 0.81             | 0.737            | 0.274            | 372               | 2-23              | 1.357            | 1.84             | 6.33            | .344 |
| 2-27-5 | 4.34             | 18.84            | 6.78             | 360               | 2-24              | 3.02             | 9.12             | 3.34            | .366 |
| 2-27-7 | 4.34             | 18.84            | 7.22             | 383               | 2-26              | 2.86             | 8.18             | 2.53            | .309 |
| 2-28-4 | 1.37             | 1.88             | 0.580            | 309               | 2-27              | 3.21             | 10.30            | 3.02            | .371 |
| 2-28-5 | 7.45             | 55.50            | 26.9             | 435               | 2-28              | 2.52             | 6.35             | 1.76            | .277 |
| 2-28-7 | 7.15             | 51.12            | 24.5             | 479               | 2-29              | 1.76             | 3.10             | .469            | .151 |
| 2-29-4 | 4.48             | 20.07            | 7.18             | 338               | 2-30              | 4.50             | 20.25            | 7.27             | .359 |
| 2-29-6 | 4.50             | 20.25            | 7.27             | 359               | 2-30              | 4.70             | 22.09            | 8.85             | .400 |
| 2-30-5 | 3.53             | 12.46            | 4.40             | 353               | 2-30              | 3.50             | 12.25            | 4.37             | .356 |
| 2-30-6 | 3.50             | 12.25            | 4.37             | 356               | 2-30              | 3.23             | 10.76            | 2.40             | .223 |
### TABLE VI

**OSMOTIC PRESSURE MEASUREMENTS**

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<th>Concentration (g/100gms)</th>
<th>Osmotic head (cms)</th>
<th>π/c</th>
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### TABLE VII

**NUMBER AVERAGE MOLECULAR WEIGHTS OF LOW MOLECULAR MATERIAL**

<table>
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<tr>
<th>Sample</th>
<th>Area x 10⁵</th>
<th>Adjusted Cumulative Weight %</th>
<th>( \bar{M}_n )</th>
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<td>14700</td>
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<td>35700</td>
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<tr>
<td>2-27</td>
<td>1.20</td>
<td>41.1</td>
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</tr>
<tr>
<td>2-28</td>
<td>2.30</td>
<td>69.2</td>
<td>30000</td>
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<tr>
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<td>1.84</td>
<td>60.7</td>
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### TABLE VIII

**RESULTS OF DILATOMETRIC KINETIC EXPERIMENTS**

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<thead>
<tr>
<th>Exp. No.</th>
<th>3-14</th>
<th>3-15</th>
<th>3-16</th>
<th>3-17</th>
<th>3-18</th>
<th>3-19</th>
<th>3-20</th>
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</thead>
<tbody>
<tr>
<td>Time (Sec)</td>
<td>5.3</td>
<td>5.4</td>
<td>6.1</td>
<td>6.3</td>
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<td>6.8</td>
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<tr>
<td>Time (Sec)</td>
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<td>1315</td>
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<td>76.8</td>
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<td>1356</td>
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<td>(33.8)</td>
<td>(58.4)</td>
<td>(56.2)</td>
<td>(53.9)</td>
<td>(337)</td>
<td>(376)</td>
<td>(513)</td>
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<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>2-21</th>
<th>2-22</th>
<th>2-23</th>
<th>2-24</th>
<th>2-25</th>
<th>2-26</th>
<th>2-27</th>
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<td>89.5</td>
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<td>77.8</td>
<td>82.8</td>
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<td>77.6</td>
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<td>1725</td>
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**Note:** The table continues with similar data for Exp. No. 2-28, 2-29, and 2-30 with corresponding per cent and time values.
### TABLE IX
MOLECULAR WEIGHT DISTRIBUTION DATA

<table>
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<tr>
<th>Fraction No.</th>
<th>Wt.</th>
<th>Wt. %</th>
<th>Cumulative Wt. %</th>
<th>Adjusted Cum. Wt. %</th>
<th>$M_w \cdot 10^{-3}$</th>
<th>Fraction No.</th>
<th>Wt.</th>
<th>Wt. %</th>
<th>Cumulative Wt. %</th>
<th>Adjusted Cum. Wt. %</th>
<th>$M_w \cdot 10^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
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<td>4.4</td>
<td>4.4</td>
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<td>5.6</td>
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<td>.026</td>
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**Polymer Sample 2-18**

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<th>Cumulative Wt. %</th>
<th>Adjusted Cum. Wt. %</th>
<th>$M_w \cdot 10^{-3}$</th>
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</thead>
<tbody>
<tr>
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<td>.9</td>
<td>.5</td>
<td>(15)</td>
</tr>
<tr>
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<td>.052</td>
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<td>4.0</td>
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<tr>
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<tr>
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**Polymer Sample 2-24**

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<th>Cumulative Wt. %</th>
<th>Adjusted Cum. Wt. %</th>
<th>$M_w \cdot 10^{-3}$</th>
</tr>
</thead>
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<td>.9</td>
<td>.5</td>
<td>(15)</td>
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<tr>
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<td>4.0</td>
<td>2.5</td>
<td>30</td>
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<tr>
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<td>23.4</td>
<td>13.7</td>
<td>59</td>
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<td>48.0</td>
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*a estimated*
### Polymer Sample 2-27

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<th>Cumulative Wt. %</th>
<th>Adjusted Cum. Wt. %</th>
<th>$M_x \cdot 10^{-3}$</th>
<th>Fraction No.</th>
<th>Wt.</th>
<th>Wt. %</th>
<th>Cumulative Wt. %</th>
<th>Adjusted Cum. Wt. %</th>
<th>$M_x \cdot 10^{-3}$</th>
</tr>
</thead>
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<td>1.0</td>
<td>1.0</td>
<td>.5</td>
<td>9</td>
<td>.105</td>
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<td>6.4</td>
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*estimated

### Polymer Sample 2-28

### Polymer Sample 2-29

### Polymer Sample 2-30
# Table X

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APPENDIX V

NOMENCLATURE

$a, a_e, a_m$ constant, subscript $e$ and $m$ refer to ethanol and methanol, respectively

$A_i$ molar concentration of the $i$-th species, mol/liter

$c_i$ weight concentration of the $i$-th species, g/mol

$C, C_e, C_m$ constant, subscript $e$ and $m$ refer to ethanol and methanol, respectively

$E_a$ activation energy

$f$ fractional number

$f(n)$ frequency number, function of $(n)$

$h, h_o, h_t, h_\infty$ height, centimeters, subscripts $o$, $t$, and $\infty$ refer to the height at zero time, $t$ time, and infinite time

$I, I_o$ initiator concentration m/liter, subscript $o$ refers to initial value

$k_1, k_2, k_p$ rate constants

$K_e$ equilibrium constant

$M, M_o$ monomer concentration, subscript $o$ refers to initial value

$M_i$ molecular weight of a polymer chain containing $i$ units

$\overline{M}, \overline{M}_v, \overline{M}_w$ average molecular weights, subscript $n$, $v$, and $w$ refer to number, viscosity and weight averages

$N_i$ number or mole fraction of species $i$

$P_i, P_{i0}$ molar concentration of polymer containing $i$ units, subscript $o$ refers to initial value

$Q_i$ molar concentration of polymer containing $i$ units
\( R_i \) molar concentration of polymer containing \( i \) units
\( t \) time
\( T \) temperature

\( V, \bar{V} \) volume, specific volume

\( W_i \) cumulative weight fraction including all species less than or equal to \( i \)

\( w_i \) weight fraction of the \( i \)-th specie

\( x \) degree of polymerization

\( \bar{X}_n, \bar{X}_v, \bar{X}_w \) average degree of polymerization, subscripts \( n, v, w \) refer to number, viscosity and weight averages

\( \gamma \) incomplete gamma function

\( \Gamma \) gamma function

\( \Delta \) difference

\( \epsilon \) error

\( \eta_{sp} \) specific viscosity

\( |\eta|, |\eta_e|, |\eta_m| \) intrinsic viscosity, subscripts \( e \) and \( m \) refer to ethanol and methanol

\( \pi \) osmotic pressure

\( \tau, \tau_1, \tau_2 \) "dimensionless" time, equal to \( \int_0^t g(t) dt \)