

KINETIC STUDIES OF SOLID-PHASE
POLYCONDENSATION IN TWO POLYAMIDES
AND A POLYESTER

by

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I. INTRODUCTION

The polymer industry is one of today's fastest growing industries. In the past fifteen years, the rate of production increased more than ten times faster than that of metals and the volume exceeded that of non-ferrous metals.

A majority of commercial polymers is prepared by a liquid-phase process which has a history of about forty years. No commercial polymer has been made by the solid-phase process primarily because of low reaction rate. However, such a process has attracted increasing attention during the last ten years. Publications are many, but virtually all of them deal with the solid-phase polymerization of addition polymers by irradiation.

The phenomenon of polycondensation in the solid phase was noted in 1939. A few publications have appeared in the literature, but with little mention of the reaction mechanism. Therefore, a study of the kinetics of solid-phase polycondensation is a contribution to the understanding of reaction mechanisms as well as of the properties of condensation polymers.

The objective of this investigation was to study the kinetics of thermally-induced polycondensation below the melting temperatures of the polymers. Variables considered were polymer particle size, reaction temperature, and reaction time. Materials used were three typical condensation polymers: poly(hexamethylene adipamide), poly(hexamethylene sebacamide), and poly(ethylene terephthalate). The former two are polyamides and the latter is a polyester. Reactions were carried out isothermally at 120, 140, 160, and 180 °C for the polyamides and 160, 180, and 200 °C for the polyester. Durations of the reactions were 5, 10, 15, and 20 hours, measured from the end of the heat-up periods. To account for the changes of polymers occurring during the reaction heat-up periods, separate tests were made to obtain samples at the end of these periods for analyses. Dry nitrogen was used to exclude air in the reactors to minimize oxidation of polymers. The nitrogen also served as a carrier gas for the by-products evolved.

Polymer resins produced in the experiments were analyzed for their intrinsic viscosities from which the number-average molecular weights were computed. Some selected polymers were examined for their thermal behaviors by differential thermal analysis. Significant

increases in the average molecular weight were noted for the three types of polymers investigated. A kinetic model derived based on the diffusion of by-products was proposed to describe the reaction.

II. LITERATURE REVIEW

This section reviews literature related to this investigation. Available literature were searched through Chemical Abstracts, Chemical Titles, Journal of Polymer Science Index, Rheology Abstracts, Dissertation Abstracts, and the Carol M. Newman Library card catalog. Four principal categories are included: polymerization reactions and polymerization processes, polyamides and polyesters, kinetics of condensation polymerization, and polymerizations in the solid phase.

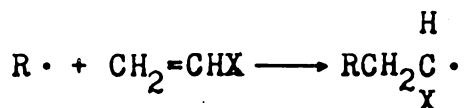
Polymerization Reactions and Polymerization Processes

Polymerization Reactions. Polymerization reactions are the chemical reactions in which polyfunctional molecules combine to form polymers. The mechanism of combination, as noted by Carothers⁽²⁷⁾, may follow either an addition or a condensation process. Hence, a polymerization reaction can in general be classified into addition or condensation polymerization.

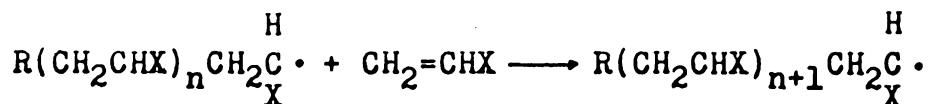
Addition polymerization, or polyaddition, proceeds by recurring interaction of unsaturated monomers⁽¹⁰⁵⁾.

The reaction is a chain process with a chain carrier which is of an ionic or a free radical type⁽²²⁾. Polyaddition, like chain reactions for small molecules, has three important steps, namely, initiation, propagation, and termination⁽¹²⁾. A typical addition polymerization is the reaction of the carbon-carbon bond to give vinyl polymers⁽⁹⁷⁾ as shown below.

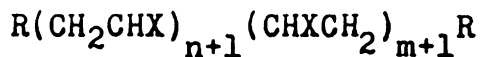
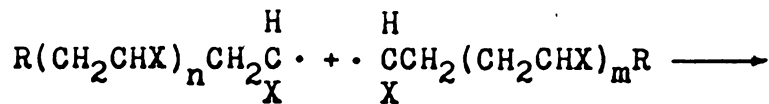
Initiation:



Propagation:



Termination:



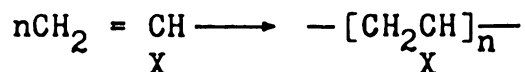
where:

R = radical initiator

X = side group on the C - C chain

m, n = numbers of repeating units.

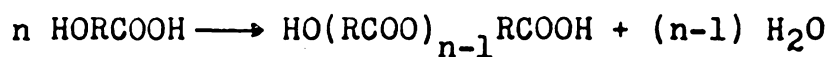
For simplicity, the overall reaction is frequently expressed as



Note that the molecular formula of the repeating unit, or "mer," in the polymer is identical with that of the monomer, differing from it only in the shifting of certain bonds. Addition polymerization occurs rapidly, so that even in the early stage of the reaction materials of high molecular weight are present in the system⁽¹³⁾. Long reaction times result in high yields but have little influence on the polymer molecular weight⁽¹³⁾.

Condensation polymerization, or polycondensation, occurs between monomeric molecules possessing at least two functional groups, usually hydroxyl, amino, or carboxylic. These functional groups may undergo condensation reactions with elimination of by-products, such as water and nitrogen⁽²³⁾. It is not generally recognized, but some condensation polymers are formed without by-products. Therefore, one cannot classify a polymerization reaction as being "addition" simply because there are no by-products^(13,42,70). Condensation polymerization is a stepwise process and, in many respects, resembles the condensation of analogous small

molecules⁽¹⁰⁵⁾. When a difunctional molecule is used, a linear polymer is formed. If, on the other hand, monomeric molecules having more than two functional groups are employed, a branched or a network polymer may be the resulting product⁽⁸⁶⁾. An example for a condensation polymerization is the formation of polyesters from ω -hydroxyacid,



where:

R = aliphatic group

n = stoichiometric coefficient.

During a condensation polymerization the monomer disappears early in the reaction and the molecular weight of the polymer increases steadily throughout the reaction time. Long reaction time is usually necessary in order to obtain products of high molecular weights⁽¹³⁾.

Polymerization Processes. The many differences between addition and condensation polymerization reactions determine to a large extent the type of commercial processes used. Although gas-, liquid-, and solid-phase processes are all possible, in commercial practice the liquid-phase process is most widely used. The

liquid-phase process can be further classified into bulk (or mass), solution, emulsion, and suspension processes.

In the bulk process polymerization is carried out in the absence of a solvent or a diluent. The system may either be homogeneous or heterogeneous. A typical example for a homogeneous bulk process is that of styrene, where the reaction mass consists of polystyrene dissolved in its own monomer. The high-pressure process for the manufacture of polyethylene, on the other hand, belongs to a heterogeneous bulk process. In general, a bulk process is more suitable for the preparation of condensation polymers, since the reactions are mildly exothermic and most of the reactions occur when the viscosity of the mixture is still low enough to allow ready mixing, heat transfer, and elimination of by-products⁽¹⁴⁾. An up-to-date review on the bulk process can be found in the article by Wohl⁽¹³⁰⁾.

In solution process polymerization monomers are dissolved in a suitable solvent. The solvent is a non-polymerizable component. This process is particularly attractive to highly exothermic reactions⁽¹⁴⁾. However, should dry polymers be desired as the final product, removal of the solvent presents a problem.

Black⁽¹⁸⁾ has given an excellent review of the practical aspects of the solution process.

The emulsion process requires the use of an emulsifier. Monomers are dispersed with the aid of a surface-active agent in a non-solvent and polymerized. The dispersed droplets are usually of the order of 10^{-4} centimeter in diameter. The size of droplets has pronounced effects on the physical properties of polymers. Advantages of this process, as indicated by Gellner⁽⁶¹⁾, include the feasibility of obtaining polymers of high molecular weight at a high rate of reaction, excellent heat transfer to permit good temperature control, and suitability for producing very soft and tacky polymers. Contamination with the emulsifier, however, may lead to poor stability of the product⁽¹⁴⁾. All polymers made by this process are addition polymers and must be started by free-radical initiators⁽⁶¹⁾. A unique application of this process is in the manufacture of polymer emulsions, often referred to as "latex."

In the suspension process, monomers are suspended or dispersed in a non-solvent without the aid of a surface-active agent. The dispersed droplets are large in comparison with those present in an emulsion process, usually in the range of 0.01 to 0.5 centimeter in

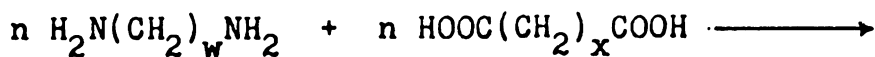
diameter. These liquid droplets of monomer become solid spherical particles at the completion of the reaction. In the dispersed condition, the removal of the excess heat of reaction presents no problem and thus good temperature control is easily attainable. Church⁽³¹⁾ has indicated that the suspension process is the most economical method of polymerization, using water for the most part as the suspension medium. The suspension process has been widely used to manufacture thermoplastic resins, such as low density and high density polyethylene, poly(vinyl chloride), and polytetrafluoroethylene.

Polyamides and Polyesters

Polyamides and polyesters are two major examples of condensation polymers. Such prominent artificial fibers as the nylons and the poly(ethylene terephthalate) are condensation polymers.

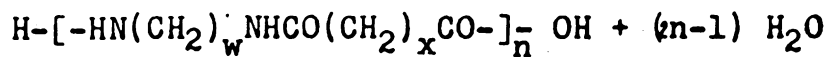
Polyamides. Polyamides are linear polymers normally prepared by the condensation of dicarboxylic acids with diamines, by the auto-condensation of amino carboxylic acids, or by simple addition of their

corresponding lactams⁽⁵⁸⁾. General schemes of the reactions may be expressed as

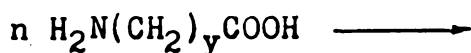


Diamine

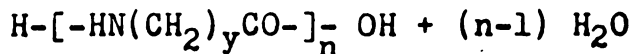
Dicarboxylic Acid



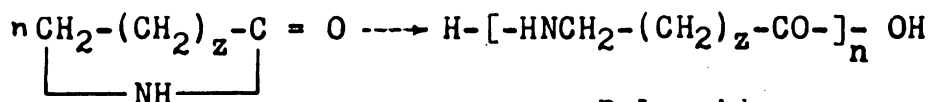
Polyamide



Amino Carboxylic Acid



Polyamide



Polyamide

Lactam

where:

n = stoichiometric coefficient

w, x, y, z = numbers of repeating units.

Poly(hexamethylene adipamide), nylon 66, is made by reacting hexamethylenediamine ($w=6$) with adipic acid ($x=4$); whereas, poly(hexamethylene sebacamide), nylon 6-10, is prepared from reacting hexamethylenediamine

with sebacic acid($x=8$). Autocondensation of 11-amino-undecanoic acid($y=10$) gives nylon 11. Simple addition of caprolactam($z=4$) yields polycaprolactam, generically known as nylon 6⁽⁶⁷⁾.

In order to obtain high molecular weight polyamides the reacting functional groups must be paired accurately so that their rates of disappearance are identical⁽⁸⁶⁾. This is accomplished by first preparing the polyamide salts which are easily separated from the solution by crystallization followed by purification. Polymerization is then carried out on the salts. By-products are removed to unbalance the chemical equilibrium in favor of the polymer formation. When control of the molecular weight is desired, an excess of one reagent over the other may be used, but more frequently a calculated amount of monobasic acid is added as a molecular weight or viscosity stabilizer⁽⁸⁶⁾. As an example⁽¹⁵⁾, in preparing poly-(hexamethylene adipamide) a 1:1 salt of hexamethylenediamine and adipic acid, isolated from methanol, is dissolved in water and added to an autoclave with 0.5-1 mole per cent acetic acid as a viscosity stabilizer. As the temperature is raised, the steam generated purges the air from the vessel. Pressure is kept at 250 pounds per square inch, gage, as the temperature is raised to 270

to 280 °C. Pressure is then reduced, and a vacuum may be applied. The reaction must be carried out in an inert atmosphere. After a total time of three to four hours, nitrogen pressure is used to extrude the nylon as a ribbon through a valve in the bottom of the autoclave. The ribbon is subsequently cut into cubes or chips as the finished product. Many patents (11,24,25,26,37,109) have been issued for the production of polyamides.

Polyamides are widely used both as synthetic fibers and as thermoplastic resins for injection molding and extrusion. They are outstanding for toughness, abrasion resistance, form stability at elevated temperatures, strength, lightness in weight, and chemical resistance (58). Table I summarizes the X-ray crystalline melting points, normal softening range, and the normal range of specific gravity for the three principal types of polyamides.

These three types of polyamide are insoluble in the usual organic solvents, such as alcohol, ketones, or hydrocarbons, but will dissolve in highly polar solvents, such as the phenols, formic acid, and concentrated mineral acids, and in calcium chloride-methanol or lithium chloride-methanol mixtures (58).

Polyamides are crystalline in a sense that they give a well defined X-ray pattern. The maximum crystallinity

TABLE I

Useful Physical Properties of
Three Principal Polyamides

Polymer	X-Ray Crystalline Melting Point °C	Normal Softening Range °C	Specific Gravity
Polycaprolactam	230	196-230	1.12-1.14
Poly(hexamethylene adipamide)	270	250-270	1.12-1.14
Poly(hexamethylene sebacamide)	220	208-220	1.07-1.09

Frey, H. J. and J. R. Knox: Polyamides, "Analytical Chemistry of Polymers," Part I (F. M. Kline, Editor), p. 274. Interscience Publishers, Inc., New York, N. Y., 1963.

that can be attained varies with the nature of the monomers used. If the carbon chain lengths in the monomers are such as to permit alignment between the carbonyl and amide group and thus form hydrogen bonds in the plane of the chains, a fairly high degree of crystallinity can be obtained⁽⁵⁸⁾. Three approaches are normally used to estimate the percentage of crystallinity: X-ray diffraction, density measurements, and infrared spectroscopy. The method by density measurements is, however, the simplest.

The average molecular weights of polyamides are usually determined by end-group measurements. However, correlations between the intrinsic viscosity and the molecular weight are available so that the average molecular weight can be calculated from intrinsic viscosity measurements. Taylor⁽¹¹⁹⁾ established the following relationship based on 25 samples of poly(hexamethylene adipamide).

$$[\eta] = 11 \times 10^{-4} \bar{M}_n^{0.72} \quad (1)$$

or

$$\bar{M}_n = 13,000 [\eta]^{1.39} \quad (2)$$

where:

- $[\eta]$ = intrinsic viscosity, dl/gm, determined
in 90% formic acid and at 25 ± 0.03 °C
- \bar{M}_n = number-average molecular weight.

The range of \bar{M}_n was 5,000 to 25,000. The largest deviation of \bar{M}_n in the above correlation was reported to be 10 per cent.

For poly(hexamethylene sebacamide) Morgan and Kwolek⁽⁹⁵⁾ gave the following correlation,

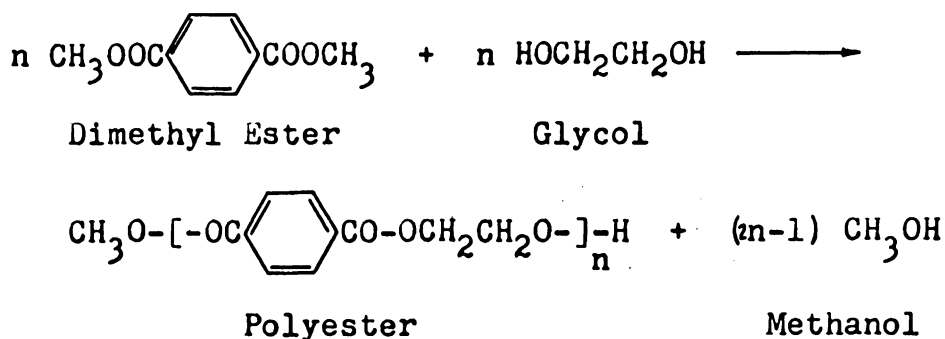
$$[\eta] = 1.35 \times 10^{-4} \bar{M}_n^{0.96} \quad (3)$$

or

$$\bar{M}_n = 10,700 [\eta]^{1.04} \quad (4)$$

The solvent used was m-cresol and the measurements were made at 25 °C. The range of \bar{M}_n was 8,200 to 23,800.

Polyesters⁽¹⁶⁾. Poly(ethylene terephthalate) is a major item in the family of commercial polyesters. The production of this polymer is somewhat different from that of polyamides, because the chemical equilibrium is less favorable to polyester formation, and the equivalence of reactants is difficult to maintain, since the salts do not form. Furthermore, the dibasic aromatic acids are very difficult to purify. The situation is met by taking advantage of the rapid ester-interchange reactions. Dimethyl ester of terephthalic acid is usually used in the presence of a catalyst like lithium, or sodium, or their alkoxides⁽¹³²⁾.



Initially, glycol is added in excess and the reaction begins at 150 °C at atmospheric pressure. The methanol by-product is continuously removed in a fractionating column. The batch heats up as the reaction proceeds, driving it to completion at about 230 °C. The product at this step is a mixture of glycol, bishydroxyethyl terephthalate, and polymer of low molecular weight. For the second step, the auto-polymerization of bishydroxyethyl terephthalate, the mix is heated to 280 °C and glycol is removed under vacuum. The polycondensation reaction is continued until the melt viscosity of the product reaches the desired level (2,000 to 5,000 poise)⁽¹³⁰⁾. Patented processes can be found in references 4, 30, 102, and 128.

Poly(ethylene terephthalate) has a high crystalline melting point (265 °C) and glass transition temperature (about 80 °C)⁽¹⁰⁷⁾. Its chemical and solvent resistance is similar to that of polyamide. It also has outstanding work recovery as well as low moisture absorption.

Ringwald⁽¹⁰⁴⁾ presented a good summary of the physical constants of poly(ethylene terephthalate).

The relation between the intrinsic viscosity and the number-average molecular weight has been given by Conix⁽³³⁾.

$$[\eta] = 2.1 \times 10^{-4} \bar{M}_n^{0.82} \quad (5)$$

$$\bar{M}_n = 30,500 [\eta]^{1.22} \quad (6)$$

Viscosity was measured in 50:50 by weight of phenol and tetrachloroethane mixture at 25 °C. Conix computed the number-average molecular weight from end-group determinations.

Kinetics of Condensation Polymerization

Research effort on the kinetics of condensation polymerization has been directed primarily toward the derivations of theoretical molecular size, or weight, distributions. More direct correlation between the rates of reaction, or degree of polymerization, and time appears to have been neglected. Included in this portion of the literature review are: kinetics of simple condensation polymerization, theory of reactivity of large

molecules, and general kinetic treatments of condensation polymerization.

Kinetics of Simple Condensation Polymerization.

Studies on the reaction rates for homologous series were among the earliest investigations in the field of reaction kinetics. The results in Table II show that the velocity constant for the reaction of various members of a given series approaches an asymptotic limit as the chain length increases^(51,70). It is of interest to note that the rate constants for esterification of monobasic acids do not differ greatly from those for the dibasic acids. Furthermore, the differences disappear as the chain length increases. These results suggest that reactivities of the functional groups remain unchanged as the size of the reacting molecule increases.

Flory⁽⁴⁴⁾ investigated the effects of molecular weight and viscosity on the reaction rates of polyesterifications. Diethylene glycol, lauryl alcohol, and decamethylene glycol were separately reacted with adipic acid without catalyst. Also, lauryl alcohol and lauric acid were reacted in the absence of a catalyst. While the molecular weight of the products increased about fourteen-fold, their kinetic data, expressed in terms of the concentration of the functional group, followed a

TABLE II

Velocity Constants^a for Homologous Series

Chain Length n	k ^b x 10 ⁴ at 25 °C	k ^c x 10 ⁴ at 25 °C	k ^d at 50 °C	k ^e x 10 ⁴ at 30 °C
1	22.1		33.7	26.6
2	15.3	6.0	24.7	2.37
3	7.5	8.7	12.2	0.923
4	7.4	8.4	13.3	0.669
5	7.4	7.8	14.5	
6		7.3	12.7	
7			13.3	0.668
8	7.5			0.667
9	7.4			
Higher	7.6 ^f			0.690 ^g

^a Velocity constants are expressed in (gram equivalent/liter)⁻¹second⁻¹.

^b H(CH₂)_nCOOH + C₂H₅OH, catalyzed by HCl.

^c (CH₂)_n(COOH)₂ + C₂H₅OH, catalyzed by HCl.

^d H(CH₂)_nCOOC₂H₅ + KOH.

^e H(CH₂)_nI + NaOCH₂C₆H₅.

^f Average ± 0.2 for n = 11, 13, 15, and 17.

^g Determined for n = 16.

Flory, P. J.: "Principles of Polymer Chemistry," p. 71.
Cornell University Press, Ithaca, N. Y., 1953.

third-order reaction. When diethylene glycol and adipic acid were reacted using p-toluenesulfonic acid as catalyst, the results indicated the reaction being of second order with respect to the concentration of the functional groups. In this case, the viscosity of the reaction mix increased two thousand-fold. The difference in the order of reaction was explained by Goldschmidt and co-workers⁽⁶³⁾. They have shown that esterification reactions are hydrogen ion catalyzed. In the absence of a strong acid catalyst a second molecule of the carboxylic acid undergoing esterification functions as catalyst.

Theory of Reactivity of Large Molecules. Flory⁽⁵²⁾ presented the theory of the reactivity of large molecules on the basis of voluminous experimental evidence. In brief, the theory states that the inherent reactivity of a functional group remains independent of the molecular size, except when the molecule is quite small. He noted that increasing viscosity does not reduce functional group reactivity and cautioned that one should not confuse the reactivity of a functional group with the diffusional rate of molecules as a whole. Although a large molecule travels slowly with time in a viscous medium the terminal functional group moves readily over a considerable region through rearrangements in the configuration of nearby

segments of the chain. The actual collision of a functional group against its immediate neighbors may occur at a frequency comparable to, or at least not much less than, that prevailing in low viscosity liquids. Therefore, the reactivity of a functional group will bear little relationship to the mobility of the molecule as a whole or to the macroscopic viscosity of the reaction medium.

In the study of the viscous flow of large molecules, Kauzmann and Eyring⁽⁷⁵⁾ have indicated that, just as the individual segments of a long chain move about at a rate independent of the total chain length, so small molecules should be able to move about at a constant and rather rapid rate, which is independent of the overall lengths of surrounding chains and hence of the viscosity of the mixture. Even if reacting groups located on two different macromolecules take part in a given reaction, it seems likely that there is sufficient articulation among segments to allow freedom of movement over a considerable region, so that diffusion processes may not even be important in influencing the rates of reactions involving large molecules.

It is possible that the average collision frequency is diminished somewhat as the polymerization progresses.

To this, Flory^(42,44,52) complemented the theory by using Eyring's theory of reaction rates. According to Eyring's theory, the velocity constant, for a bimolecular reaction, is given by

$$k = \frac{KT}{h} \frac{F_{ab}^*}{F_a F_b} \exp\left(-\frac{E_0}{RT}\right) \quad (7)$$

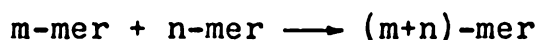
where:

- k = reaction velocity constant
- K = Boltzmann's constant
- T = absolute temperature
- h = Planck's constant
- F_{ab}^* = partition function for the activated complex
- F_a, F_b = partition functions for the reactants A and B, respectively
- E_0 = energy of activated complex at absolute zero
- R = gas constant.

An increase in the complexity of one or both of the reactants modifies F_{ab}^* as well as the product $F_a F_b$. Unless this increase in complexity involves alteration of the molecules in the immediate vicinity of the functional group, F_{ab}^* and $F_a F_b$ will be modified by very nearly identical factors for the added degrees

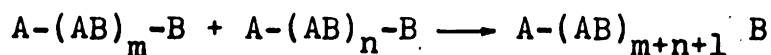
of freedom. Hence the rate of reaction will remain relatively unchanged.

The theory of reactivity of large molecules applies to both addition and condensation polymerizations. The impact of this theory to condensation polymerization has been illustrated in the analysis of reaction, expressed in a general form below⁽⁴²⁾,



in which m and n can assume every possible combination of positive integers. If it were necessary to assign a separate rate constant, $k_{m,n}$, for each of the above reactions, kinetic analysis would be extremely difficult. However, according to the theory, a single rate constant is all that is needed for all steps of the reactions involved.

General Kinetic Treatments of Condensation Polymerization^(23,53,78). Consider a condensation reaction proceeding in a manner shown below:



where:

(AB) = structural unit of polymer containing end groups A and B

m, n = number of structural units.

Define A_0 and B_0 to be the initial concentrations of the functional groups A and B, respectively. Let "a" and "b" be the fractions of A and B groups consumed at time, t. If the rate of disappearance of A is of second-order with respect to the concentrations of A and B, then

$$-\frac{d(1-a)A_0}{dt} = k(1-a)(1-b)A_0B_0 \quad (8)$$

If $A_0 = B_0$ and $a = b = p$, equation 8 simplifies to

$$-\frac{d(1-p)}{dt} = k(1-p)^2 A_0 \quad (9)$$

Integrating equation 9, from an initial condition of $p = 0$ at $t = 0$, gives

$$\frac{1}{(1-p)} = kA_0t + 1 \quad (10)$$

Equation 10 is an expression for a second-order reaction. Polyesterification of diethylene glycol and adipic acid catalyzed by p-toluenesulfonic acid was shown by Flory⁽⁴⁴⁾ to be a second-order reaction. Polyamidation was reported to be a second-order reaction also⁽⁴⁵⁾.

For uncatalyzed polyesterification, a second molecule of the carboxylic acid functions as catalyst⁽⁶³⁾. The rate equation in this case is

$$-\frac{d(1-a)A_0}{dt} = k'(1-a)^2(1-b)A_0^2 B_0 \quad (11)$$

in which A is assumed to represent the concentration of the carboxyl end group and k' the rate constant for the catalyzed reaction. Following the same argument used in obtaining equation 10, equation 11 becomes

$$\frac{1}{(1-p)^2} = 2k'A_0^2 t + 1 . \quad (12)$$

This is an expression for a third-order reaction.

Reactions belonging to this category are: a series of polyesterifications studied by Flory⁽⁴⁴⁾, polymerization of ω -hydroxyundecanoic acid at 200 °C by Baker, Fuller, and Heiss⁽⁶⁾, and reaction of ethylene glycol with succinic acid by Flory⁽⁴³⁾.

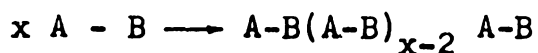
The quantity, $1/(1-p)$, is equivalent to the number-average degree of polymerization \bar{x}_n , which relates to the number-average molecular weight \bar{M}_n , as follows,

$$\bar{M}_n = M_0 \bar{x}_n = M_0/(1-p) \quad (13)$$

where M_0 is the mean molecular weight of a structural unit. Thus, for a second-order reaction a plot of \bar{M}_n against time yields a straight line; whereas, for a third-order reaction, a plot of \bar{M}_n^2 versus time gives a straight line relationship.

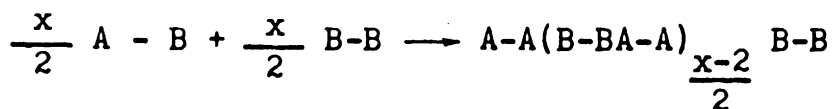
Flory's "most probable molecular size distribution" of linear condensation polymers⁽⁴⁶⁾ is the most significant theoretical treatment of the kinetics of condensation polymerization. Two types of linear condensation reactions were considered:

Type I:

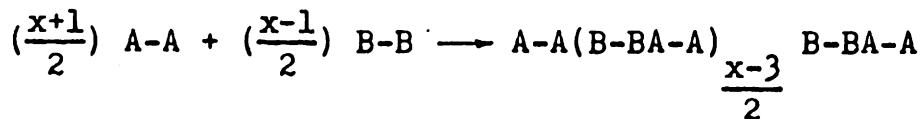


Type II:

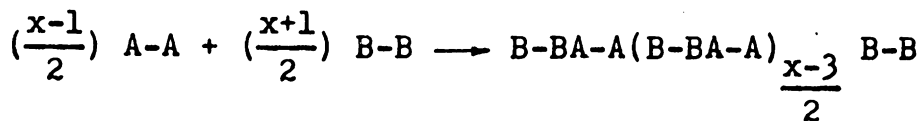
(a) If x is an even integer



(b) If x is odd, either



or



where A and B represent functional groups and AB, or BA, the product of their reaction with one another.

In the derivations above, it is assumed that the probability of any given functional group having reacted is independent of chain length. This agrees with the theory of reactivity of large molecules. For polymers formed from a Type I reaction, the distribution function for the total number of x-mers is

$$N_x = N_0(1-p)^2 p^{x-1} \quad (14)$$

and that for the weight fraction of x-mers is

$$w_x = x(1-p)^2 p^{x-1} \quad (15)$$

where, in the above two equations:

- x = number of repeating units
- N_x = number of x-mer molecules
- N_0 = total number of units
- p = probability of a given functional group to react
- w_x = weight fraction of x-mer molecules.

For Type II reactions, the distribution functions are complex; however, when average values are considered, equations 14 and 15 may be used without great error, provided that they are rewritten with p' in place of p , where $p' = pr^{1/2}$ with r being the ratio of all A to all B groups (46, 54, 70).

From the most probable distribution, the average molecular weight can be calculated. Three different kinds of average molecular weights are commonly used. They are defined as:

$$\text{Number-average molecular weight, } \bar{M}_n = \frac{\sum_1^{\infty} M_x N_x}{\sum_1^{\infty} N_x} \quad (16)$$

$$\text{Weight-average molecular weight, } \bar{M}_w = \frac{\sum_1^{\infty} M_x^2 N_x}{\sum_1^{\infty} M_x N_x} \quad (17)$$

$$\text{Z-average molecular weight, } \bar{M}_z = \frac{\sum_1^{\infty} M_x^3 N_x}{\sum_1^{\infty} M_x^2 N_x} \quad (18)$$

where \bar{M}_x is the molecular weight of an x-mer molecule.

For a polymer of uniform molecular weight distribution,

$$\bar{M}_n = \bar{M}_w = \bar{M}_z.$$

Flory⁽⁴⁶⁾ evaluated these three average molecular weights by using equation 14 for the expression of N_x and obtained the following:

$$\bar{M}_n = \frac{M_0}{1-p} \quad (19)$$

$$\bar{M}_w = \frac{M_0(1+p)}{1-p} \quad (20)$$

$$\bar{M}_z = \frac{M_0(1+4p+p^2)}{1-p^2} \quad (21)$$

where M_0 is the molecular weight of a structural unit.

When the extent of reaction is high ($p = 1$), the ratio, $(\bar{M}_n : \bar{M}_w : \bar{M}_z)$, becomes approximately $(1 : 2 : 3)$. Frequently this ratio is used as a measure of the spread of the molecular weight distribution of a polymer.

Other theoretical studies by Flory consist of the random reorganization of molecular weight distribution in linear condensation polymers⁽⁵⁶⁾, and the molecular size distribution in three dimensional polymers^(47,48,49).

A group of scientists led by Korshak^(19,20) has disputed the validity of the distribution function, equation 14, by Flory. They contend that the effects of hydrolysis and interchange are neglected in the derivation. However, the functions proposed by

Korshak et al. are too complicated to apply, when compared to Flory's functions which have been verified experimentally⁽⁷⁰⁾.

According to Stockmayer^(106,114,115), the kinetic process for a system composed of N f-functional units may be described by the following set of differential equations.

$$\frac{1}{k} \frac{dm_n}{dt} = \frac{1}{2} \sum_{s=1}^{s=n-1} (fs-2s+2)(fn-fs+2n-2s+2) m_s m_{n-s} - (fn-2n+2) m_n \sum_{s=1}^{\infty} (fs-2s+2)m_s \quad (22)$$

where:

- m_n = number of n-mer molecules
- k = rate constant
- t = time
- s = dummy variable.

In this equation, the first sum represents the formation of n-mers by reactions between pairs of smaller molecules, and the second term represents their destruction through reaction with other molecules. All possible steps have the same bimolecular rate constant k. Intramolecular

reactions are assumed to be negligible. The solution of this equation is

$$m_n = \frac{fN(1-p)^2}{p} \frac{(fn-n)!}{n! (fn-2n+2)!} [p(1-p)^{f-2}]^n \quad (23)$$

where:

$$\frac{dp}{dt} = fNk(1-p)^2 \quad (24)$$

or

$$p = \frac{fnkt}{1+fnkt} \quad (25)$$

and p has the same meaning as before.

In the same paper⁽¹¹⁵⁾ Stockmayer also gave the expressions for number-, and weight-average degrees of polymerization.

$$\bar{x}_n = \frac{2}{2-pf} \quad (26)$$

$$\bar{x}_w = \frac{1+p}{1-(f-1)p} \quad (27)$$

Substituting the expression for p (equation 25) into equations 26 and 27 yields

$$\bar{x}_n = \frac{2 + 2fnkt}{2 + (2f-f^2)Nkt} \quad (28)$$

and

$$\bar{x}_w = \frac{1 + 2fNkt}{1 + (2f-f^2)Nkt} \quad (29)$$

Since

$$\bar{x}_n = \frac{\bar{M}_n}{M_0} \quad \text{and} \quad \bar{x}_w = \frac{\bar{M}_w}{M_0},$$

Bechtold⁽⁹⁾ suggested that by fitting the experimental values of \bar{M}_n or \bar{M}_w at various intervals in the reaction, the values of k and f could be determined. When non-integral values of f provide the best fit, he concluded that unequal reactivity of the functional group or cyclization was the cause. Emmert⁽³⁹⁾, on the other hand, linearized equations 28 and 29 to give

$$\frac{1}{\bar{x}_n-1} = \frac{2}{f^2 Nkt} + \frac{2f-f^2}{f^2} \quad (30)$$

and

$$\frac{1}{\bar{x}_w-1} = \frac{1}{f^2 Nkt} + \frac{2f-f^2}{f^2} \quad (31)$$

Thus, plotting $1/(\bar{x}_n-1)$ or $1/(\bar{x}_w-1)$ against $1/t$ should yield a straight line and the values of k and f can be uniquely evaluated, provided that the reaction is bimolecular in nature. If the value of f is not an

integer, Emmert stated that a non-second order reaction was involved or competing reactions were present.

Various methods have been proposed for solving a set of differential equations such as equation 22. Two major approaches are to use moment generating functions or Z-transforms.

Liu and Amundson⁽⁸²⁾ employed the moment-generating-function technique to calculate the molecular weight distribution of linear polymers obtained from isothermal processes. A brief discussion was also given for non-isothermal processes. A similar approach was also used by Hermans⁽⁶⁹⁾ who considered the chain length distribution resulting from the random reaction of chain ends with all monomer units, e.g., transesterification, transamidation. Tadmor⁽¹¹⁷⁾, using the same technique, derived the distributions of linear polymers when reactions were carried out in a batch and a continuous stirred tank reactor. For the continuous stirred tank case, both the segregated and homogeneous types were investigated.

Theoretical derivations of molecular weight distributions by the method of Z-transform include the work by Abraham⁽¹⁾ and Kilkson⁽⁷⁶⁾. Both authors considered the effect of reaction path on product

distributions. In addition, Kilkson took the residence time distribution of the reaction mix into account.

In contrast to the two methods mentioned above, Sippel and Heim^(110,111) adopted Tung's distribution⁽¹²²⁾ to analyze condensation polymerizations. Formation of poly(hexamethylene adipamide) was discussed.

Polymerization in the Solid Phase

Studies of solid-phase reactions, as pointed out by Morawetz⁽⁹³⁾, have concentrated almost exclusively on the behavior of inorganic reagents, so that an extensive review by Cohen⁽³²⁾ does not even mention organic solids. However, in the past ten years reactions of organic solids have drawn some attention and several review articles^(84,93,94,99,101) have been written.

Addition Polymerization. Research in the field of solid-phase polymerization has emphasized addition polymerizations induced by irradiation or other means.

Mesrobian and co-workers⁽⁸⁹⁾ published a paper on the gamma-ray polymerization of acrylamide in the solid state. Irradiation was made with cobalt⁶⁰ at 5, 35, and 55 °C. Reaction data indicated that the order of reaction was between zero and 1/2 order. Solid-phase

irradiation polymerizations, by cobalt⁶⁰ at 25 °C, of acrylamide, N,N'-methylenebisacrylamide, N-tert-butylacrylamide were studied by Adler, Ballantine, and Baysal⁽³⁾. They assumed that the polymerization occurred at the interface between an amorphous polymer region and a crystalline monomer region and the rate was controlled in part by the local build-up and release of internal stress. Tsuda⁽¹²¹⁾ concluded from the study on solid-phase polymerizations of formaldehyde and acrylonitrile by gamma-ray irradiation that ions or highly excited molecules trapped in the solid state initiated the reaction by warming the irradiated monomers. Other studies involving the use of gamma-ray include the work by Morawetz and Rubin⁽⁹²⁾ for alkaliacrylates and methacrylates. Miura, Hirai, and Kawamatsu dealt with the copolymerization reactions of chloromethyl and fluoromethyl compounds of ethyloxetane⁽⁹⁰⁾.

Hsia Chen, and Graber^(64,71) investigated the effects of morphological factors on the polymerization of tributylvinylphosphonium bromide irradiated with X-rays. They found the morphological factors that exerted an influence on solid-state polymerization were the spatial arrangement of active groups of monomers in the crystal lattice. The rate of reaction, however, was

independent of the size of crystal and the stable form polymerized at equal rates in all crystallographic directions.

Lawton, Grubb, and Balwit⁽⁷⁹⁾ studied the addition polymerization of hexamethylenecyclotrisiloxane monomer exposed to high-energy electrons.

A patent concerning the manufacture of polyacrylonitrile using monomer powder in the presence of a catalyst was issued to Fikentscher and Herrle⁽⁴¹⁾.

Bamford, Jenkins, and Ward⁽⁷⁾ investigated the photopolymerization (ultraviolet) of crystalline methacrylic acid in the solid and near-solid states. They found that the reaction was better explained by phase boundary considerations than by propagation through crystal lattice.

In spite of the extensive experimental data obtained in recent years on solid-state polyaddition, mathematical analysis of the process is limited to the work by Berlin, Barkalov, Gol'danskii, and Enikolopyan⁽¹⁰⁾. They derived the kinetic equations based on the premise that the rate of chain propagation is determined not only by the reactivity of the monomer, but also to a large extent by the mutual spatial orientation of the monomer units. Additionally, the expansion of a crystalline monomer

takes place in only one of the crystallographic directions from the point of origin of the chain up to a defect in the crystal lattice. Three extreme cases were examined; namely, rapid initiation and slow chain propagation, slow initiation and rapid chain propagation, and the extension of the polymer chain not accompanied by the fracture of the latter.

Condensation Polymerization. The phenomenon of solid-phase polycondensation was noted quite early. Pacsu⁽¹⁰⁰⁾ and Frenkel⁽⁵⁷⁾ in 1939 indicated the feasibility of polyamidation in the solid state. In the same year, a patent⁽³⁸⁾ was granted to E. I. du Pont de Nemours and Company on a process for making strongly condensed superpolyamides from heating polyamides of lower molecular weight at a temperature sufficient for polymerization but below the melting point of the polyamide. This process is sometimes referred to as "post-polycondensation," in which the starting material is polymer of low molecular weight rather than monomers. Within the same category the patent granted to Farbenfabriken Bayer A.-G.⁽⁴⁰⁾ was for heating granular polyamide with a relative viscosity of 2.80 to 2.89 at 195 °C in a stream of hot nitrogen for 72 to 75 hours to obtain polymer of relative viscosity, 5.72 to 6.55. Monroe⁽⁹¹⁾ patented a continuous process

employing polyamides having molecular weight greater than 1,000 but less than 15,000 and a particle diameter of up to about 10 millimeters in a fluidized system which is maintained by a stream of oxygen-free gas. The temperature of the gas should be at least about 40 °C below the melting point of the polymer.

Research on post-polycondensation has been very limited. Matsuda and co-workers^(87,88) studied the changes of nylon 6 and nylon 66 with heat at temperatures ranging from 200 to 351 °C in a atmosphere of air and of nitrogen. The increase in molecular weight of nylon 6 was analyzed kinetically. The rate equation used is of second-order as indicated below:

$$-\frac{d(N/N_0)}{dt} = \lambda \left[\left(\frac{N}{N_0}\right) - \left(\frac{N}{N_0}\right)_\infty \right]^2 \quad (32)$$

or, after integration,

$$\left[\left(\frac{N}{N_0}\right) - \left(\frac{N}{N_0}\right)_\infty \right]^{-1} = \lambda t + \left[1 - \left(\frac{N}{N_0}\right)_\infty \right]^{-1} \quad (33)$$

where:

$\left(\frac{N}{N_0}\right)$ = ratio of number-average molecular weight at time, t, to that at time zero

$\left(\frac{N}{N_0}\right)_\infty$ = a constant determined by fitting a straight line to the plot of equation 32

λ = rate constant, minute⁻¹

t = time, minutes.

The activation energy was computed to be 12.7 kilocalories per mole for the reaction investigated. This value is larger than the activation energy (8.7 kilocalories per mole) for the condensation of lactam. The difference, as explained by Matsuda and co-workers, is caused by the reduction of the activity of amine end groups due to acetic acid introduced as a viscosity stabilizer during the preparation of the polyamide.

Harding and MacNulty⁽⁶⁶⁾ investigated the embrittlement of nylon 66 between 70 and 250 °C. While the surface of the samples showed a decrease in molecular weight as a result of oxidation, the bulk of the polymer continued to polymerize as indicated by the increase in molecular weight. The increase was slight, e.g., a change from 15,000 to 19,000 after 28 days at 100 °C. They plotted the molecular weight against time, extrapolating to zero time and measuring the gradient to obtain the reaction rate for the pseudo-unimolecular reactions, and reported an activation energy of 19.6 kilocalories per mole. These authors have suggested that the increase of molecular weight observed in the bulk of material is probably a result of the continuation of the normal polymerization reaction, since the continued solubility

of the products indicates an absence of crosslinking reactions.

Achhammer et al.⁽²⁾ proposed that the formation of water during the pyrolysis of nylon in vacuo resulted from crosslinking reactions.

A more specific study on the thermally induced solid-state polymerization in nylon 66 was conducted by Lee⁽⁸⁰⁾. Nylon 66 chips (average diameter 0.073 inch) of initial number average molecular weight about 10,000, were heated at 90, 105, 120, and 135 °C. Nitrogen was used to purge the reactor prior to heating and served as a carrier of the by-product during the reaction. The flow of nitrogen was adjusted to 1.5, 4.5, and 7.64 standard cubic feet per hour (70 °F, 1 atmosphere). The results indicated that the effect of temperature was more pronounced than that of nitrogen flow rates. Kinetic treatment of the data followed the power-law model frequently used in describing reactions occurring in inorganic solids. The rate equation used by Lee is

$$\frac{d\bar{M}_n}{dt} = kt^n \quad (34)$$

or

$$\bar{M}_n - \bar{M}_{no} = \frac{k}{n+1} t^{n+1} \quad (35)$$

where:

- \bar{M}_n = number-average molecular weight at time t
- \bar{M}_{no} = number-average molecular weight of the raw material
- k = rate constant, (hour)⁻⁽ⁿ⁺¹⁾
- n = constant
- t = time, hour.

The constant, n, was determined to be -0.49, and the rate constant was expressed in the Arrhenius form,

$$k = 1.53 \times 10^{10} \exp \left[-12,960/(RT) \right], \quad \text{hour}^{-0.51} \quad (36)$$

in which R is the gas constant and T the absolute temperature.

Solid-state polyamidation beginning with monomers or polymer salts has been reported. Volokhina and co-workers^(126,127) investigated the kinetics of polyamidation of three adipatic ω -amino acids: amino-*enanthoic*, *aminopelargonic*, and *anomoundecanoic*, and of the hexamethylene diamine salts of *adipic*, *thiodivaleric*, and *terephthalic* acids. The technique used is the

two-calorimeter method where the quantity of the compensating current as a function of time yields the quantitative kinetic characteristics of the reaction. Failure in obtaining results for the reaction of hexamethylenediamine salt and adipic acid was attributed to the volatilization of hexamethylenediamine. The heat of reaction of amino acid polycondensation in the solid phase was found to depend greatly on the temperature and varied from 2 to 3 kilocalories per mole per 2 °C. The reactions were said to be autocatalytic, and endothermic with heat of reaction varying from 14 to 18 kilocalories per mole. A series of catalysts was examined, the most effective one being boric acid.

Volokhina and Kudryavtsev⁽¹²⁵⁾ have a patent for a solid-state polyamidation using polyamid-forming monomers in the presence of a catalyst. One per cent by weight concentrations of MgO, Na₂CO₃, or H₃BO₃ in the monomer are used as catalysts.

Polycondensation of ϵ -caprolactam with 0.1 per cent by weight of H₃PO₄ as catalyst has been described in a German patent⁽¹²⁴⁾. The conditions specified to raise specific viscosity from 1.4 to 9.2 are: temperature, 190 °C; pressure, 5 millimeters of mercury; and reaction time, 32 hours.

So far, studies of solid-phase polycondensation have been entirely for polyamides. No research work has been reported for polyesters. There are, however, two patents^(8,102) in which the processes claimed employ polyester prepolymers fluidized with a hot inert gas to yield higher molecular weight products. Reaction temperatures were described to be 20 to 60 °C below the melting point of the polymer.

III. EXPERIMENTAL

This section describes the plan of experimentation, the materials and apparatus used, and the methods of procedure followed in the investigation.

Plan of Experimentation

The approach used in this investigation was as follows.

Design and Construction of Experimental Apparatus.

A batch, fixed-bed reactor was designed by the author. The reactor was small in size so that a short heat-up time could be realized. However, it was large enough to contain samples of sufficient quantities for analyses. A wire screen supported by a punched plate was used to retain a polymer sample of one average particle size. A screen basket which was positioned above the wire screen with spacers was used to hold another sample of the same polymer having a different average particle size. Ample space was provided above the samples for dispersing the incoming nitrogen. The nitrogen was introduced through a copper coil which functioned as a gas preheater. Four reactors were constructed in the Chemical Engineering

Department shop. Details of the design are shown in Figure 1.

In addition to the reactors fabricated, a system consisting of a nitrogen supply and a constant temperature bath, together with necessary control devices, was constructed. Figure 2 is a schematic diagram of the system.

Selection of Polymers. Although numerous types of polyamides and polyesters are commercially available, poly(hexamethylene adipamide), poly(hexamethylene sebacamide), and poly(ethylene terephthalate) were selected for this investigation. The former two are polyamides and the latter is a polyester. These polymers are typical linear condensation polymers. Their physical and chemical properties have been studied extensively and reported in the literature. Except for poly(hexamethylene adipamide), no research work on solid-phase polycondensation was conducted for the other two polymers.

Selection of Analytical Techniques. To follow the extent of reaction, the number-average molecular weights of polymers were calculated from polymer intrinsic viscosities. Generally, the number-average molecular weights are obtained from end-group analysis. However,

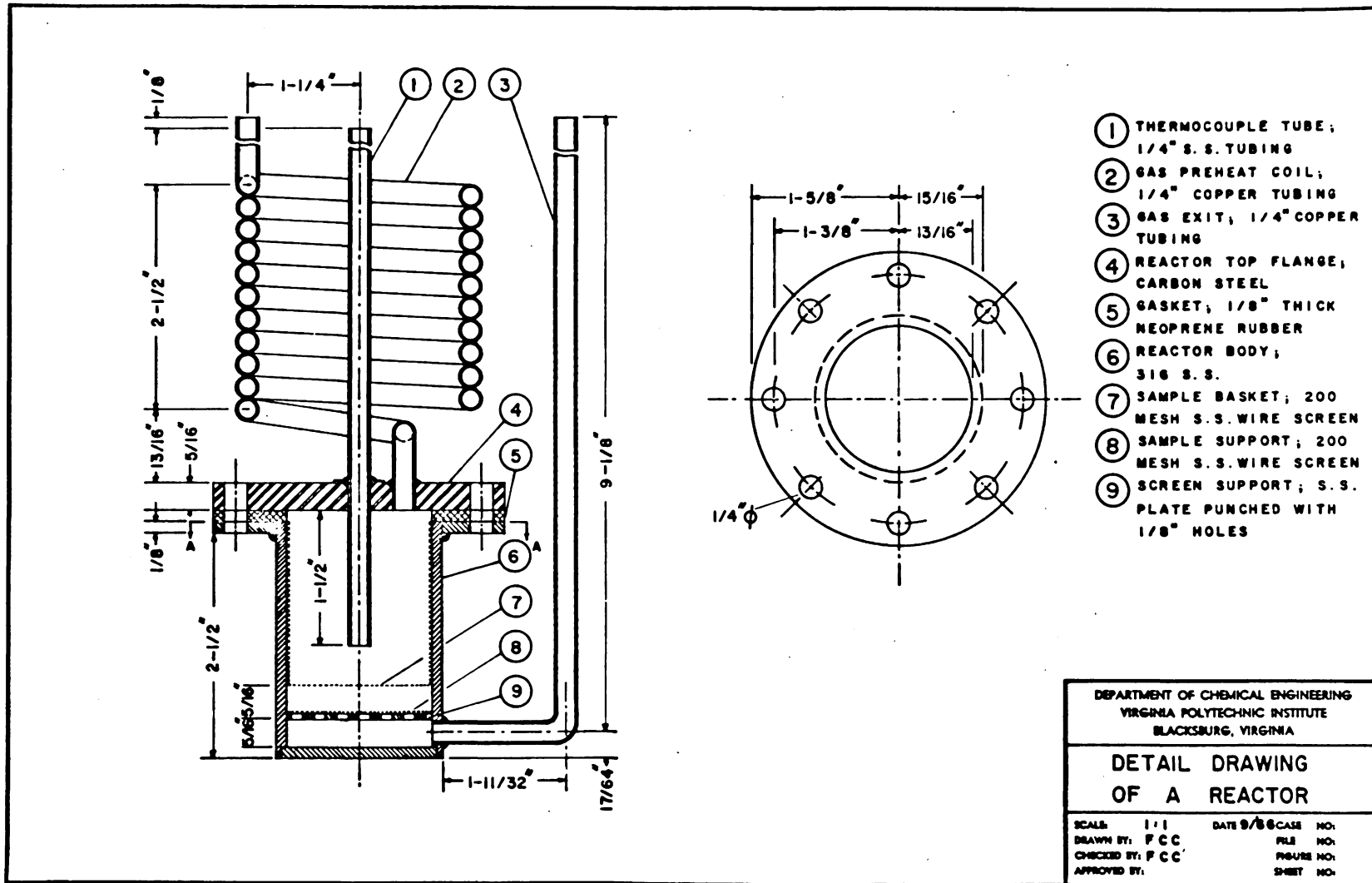
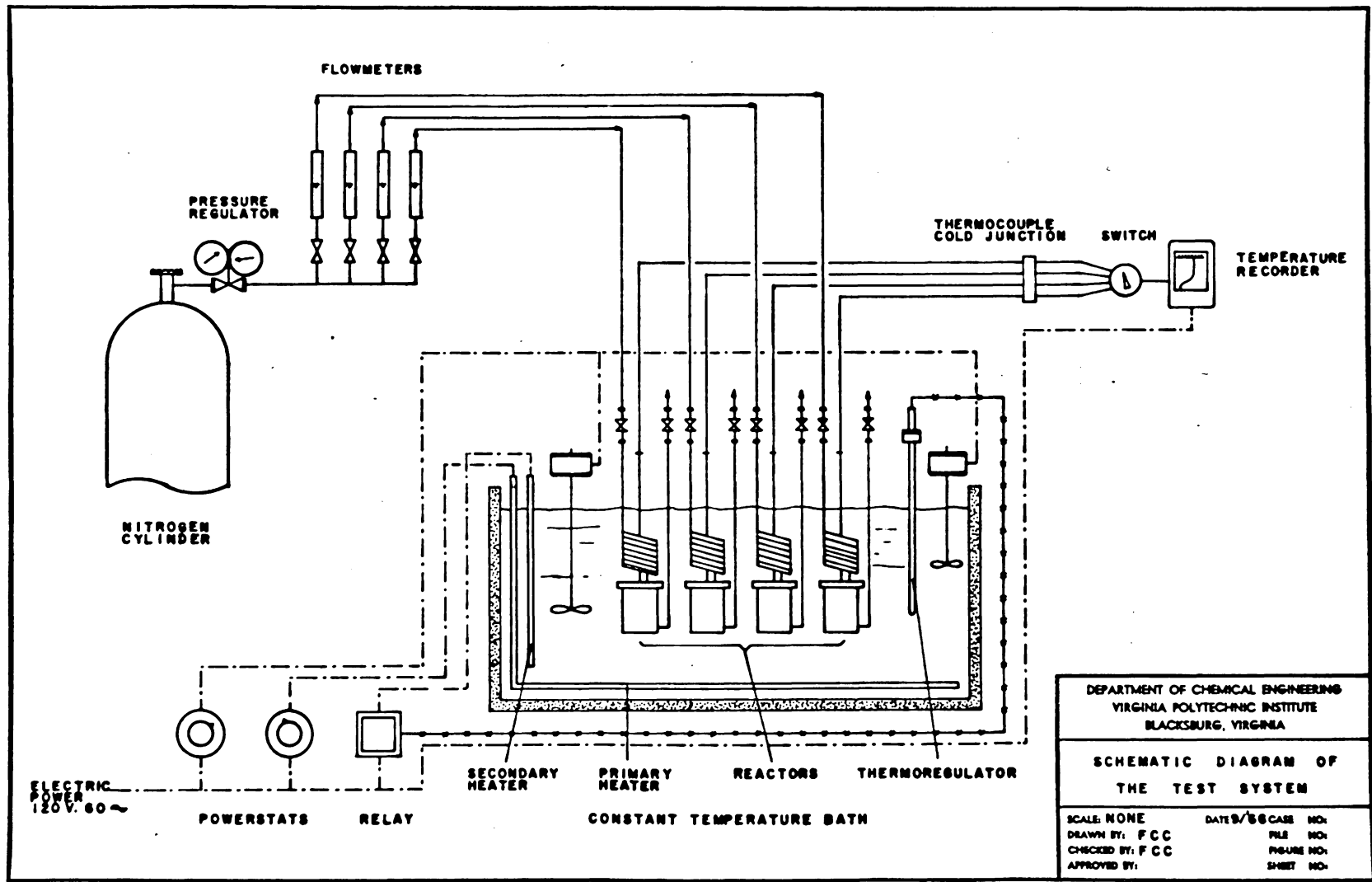


FIGURE 1. DETAIL DRAWING OF A REACTOR



DEPARTMENT OF CHEMICAL ENGINEERING VIRGINIA POLYTECHNIC INSTITUTE BLACKSBURG, VIRGINIA	
SCHEMATIC DIAGRAM OF THE TEST SYSTEM	
SCALE: NONE	DATE: 9/66 CASE NO:
DRAWN BY: FCC	FILE NO:
CHECKED BY: FCC	FIGURE NO:
APPROVED BY:	SHEET NO:

FIGURE 2. SCHEMATIC DIAGRAM OF THE TEST SYSTEM

when empirical correlations between the intrinsic viscosity and the average molecular weight determined by some absolute method are available, the approach by viscometry is often preferred because of its simplicity.

Other analytical techniques used in this investigation were density measurements with a density gradient column and determinations of melting points by differential thermal analysis.

Establishment of Reaction Conditions. In a study⁽⁸⁰⁾ on the solid-phase polymerization of nylon 66, it was concluded that the reaction temperature had more pronounced effects than the rate of flow of the carrier gas. Thus, in this investigation, a fixed flow rate of the carrier gas was adopted.

The range of reaction temperatures was selected based on the results of preliminary tests. If a polymer showed about a 5 per cent increase in molecular weight at an arbitrarily chosen temperature after 20 hours, this temperature was set to be the lowest test temperature for that polymer. Subsequent tests would be made at incremental temperature increases of 20 °C. The maximum temperature was set at 200 °C (limitation of the oil bath), or lower if polymers were found to degrade.

The duration of the reaction was set at 5, 10, 15, and 20 hours.

Techniques for Analysis of Kinetic Data. It was planned that the significance of independent variables would be examined by appropriate statistical methods.

Kinetic data were analyzed first using the models generally accepted to describe linear polycondensation reactions. Should these models fail, the equation used successfully by Lee⁽⁸⁰⁾ would be attempted. If this equation was shown to be inadequate, a new approach would be proposed.

Materials

The following materials were used in this investigation.

Acetone. Technical grade. Manufactured by Shell Chemical Company and repacked by Roanoke Chemical Company, Salem, Virginia. Used in rinsing glassware.

Acid, Chromic. Technical, 99-99.5 per cent, Fisher Laboratory Chemical, catalog no. A-98. Obtained from the Chemical Engineering Department stockroom. Used in the preparation of cleaning solution.

Acid, Formic. Purified, 90 per cent, Fisher Laboratory Chemical, catalog no. A-119. Purchased

from Fisher Scientific Company, Fair Lawn, New Jersey. Used as solvent for poly(hexamethylene adipamide) resin.

Acid, Sulfuric. Purity 95.0-90.0 per cent, Fisher Reagent Chemical, catalog no. A-300-C. Obtained from Fisher Scientific Company, Silver Spring, Maryland. Used in the preparation of cleaning solution.

Carbon Tetrachloride. Technical, Fisher Laboratory Chemical, catalog no. C-185. Obtained from Fisher Scientific Company, Silver Spring, Maryland. Used in making a density gradient column.

Cresol, Meta. Purified, 95-98 per cent, Fisher Laboratory Chemical, catalog no. C-537. Purchased from Fisher Scientific Company, Silver Spring, Maryland. Used as a solvent for poly(hexamethylene sebacamide) resin.

Fiberglas. Mat. Obtained from the Chemical Engineering Department shop. Used for insulating the oil bath.

Nitrogen, Dry. O. P. Purchased from Industrial Gas Supply, Princeton, West Virginia. Used for purging the reactors and as a carrier gas for by-products evolved from the polymer resins during the reaction.

Oil, Paraffin. N. F., white, light, domestic, viscosity 125/135, Fisher Laboratory Chemical, catalog no. O-119. Purchased from Fisher Scientific Company,

Silver Spring, Maryland. Used in the constant temperature bath.

Paper, Recorder. Range 0-100, no. 600186. Manufactured by Recording Chart Division, Graphic Controls Corporation, 189 Van Rensselaer Street, Buffalo, New York. Used in recording the reactor temperature.

Phenol. Analytical reagent, loose crystals containing 0.05 per cent non-volatile matter. Obtained from Mallinckrodt Chemical Works, New York, New York. Used in preparing solvent for poly(ethylene terephthalate).

Pipe, Stainless Steel. Grade 316, 1-1/2 inch nominal size. Obtained from Celanese Fibers Company, Narrows, Virginia. Used in fabrication of reactors.

Plate, Punched. Stainless steel plate with 1/8-inch holes. Obtained from the Chemical Engineering Department shop. Used in making supports for samples.

Resin, Poly(hexamethylene adipamide). Delustered nylon 66 flakes. Manufactured by E. I. du Pont de Nemours and Company, Martinsville, Virginia. Used as a raw material in this investigation.

Resin, Poly(hexamethylene sebacamide). Nylon 610 chips. Manufactured by E. I. du Pont de Nemours and Company, Parkersburg, West Virginia. Used as a raw material in this investigation.

Resin, Poly(ethylene terephthalate). Dacron powders containing 0.3 per cent of titanium dioxide as delustering agent. Manufactured by E. I. du Pont de Nemours and Company, Kinston, North Carolina. Used as a raw material for this investigation.

Resin, Epoxy. Epoxi-Patch resin and hardener. Manufactured by Hysol Corporation, Olean, New York. Used as a sealing compound for thermocouples.

Screen, Stainless. Mesh, 200 x 200. Obtained from the polymer processing laboratory of the Chemical Engineering Department. Used in making sample containers.

Tetrachloroethane, Symmetric. Technical grade, Fisher Laboratory Chemical, catalog no. A-30. Obtained from Fisher Scientific Company, Silver Spring, Maryland. Used in preparing solvent for poly(ethylene terephthalate).

Tubing, Copper. Outside diameter, 3/8 inch. Obtained from the Chemical Engineering Department shop. Used in the construction of a nitrogen supply system.

Tubing, Copper. Outside diameter, 1/4 inch. Obtained from the Chemical Engineering Department shop. Used in making the gas pre-heat coils and the gas exits on the reactors.

Tubing, Plastic. Imperial Poly-flo tubing P-1/4. Obtained from the Chemical Engineering Department stockroom. Used in the nitrogen supply system.

Tubing, Stainless. Outside diameter, 1/4-inch. Obtained from the Chemical Engineering Department shop. Used for housing thermocouple wires.

Wire, Constantan. Number 30, B. & S. gage. Manufactured by Leeds and Northrup Company, Philadelphia, Pennsylvania. Used in making thermocouples.

Wire, Iron. Number 30, B. & S. gage. Manufactured by Leeds and Northrup Company, Philadelphia, Pennsylvania. Used in making thermocouples.

Xylene. Fisher certified reagent, A. C. S. catalog no. X-5. Obtained from Fisher Scientific Company, Silver Spring, Maryland. Used in preparing the density gradient column.

Apparatus

The apparatus used in this investigation are described in the following paragraphs.

Balance, Student Analytical. Manufactured by Volland and Sons, Inc., New Rochelle, New York. Used to weigh polymer samples.

Balance, Triple Beam. Ohaus model 1750 S, 610-gm beam capacity. Distributed by Fisher Scientific Company, Silver Spring, Maryland. Used to weigh polymer samples.

Bath, Constant Temperature. Model M-1, serial no. M1251, range 75-210 °F. Manufactured by Cannon Instrument Company, State College and Boalsburg, Pennsylvania. Used in determinations of the intrinsic viscosities of polymers.

Desiccator. Scheibler, plain, 200-mm inside diameter. Obtained from the Chemical Engineering Department stockroom. Used for storing polymer samples.

Differential Thermal Analyzer. Manufactured by Robert L. Stone Company, Austin, Texas. Furnace catalog no. F-1DF, platform assembly model no. J-2, serial no. 167. Available in the Metals and Ceramic Engineering Department. Used to examine the thermal characteristics of polymers.

Flask. Erlenmeyer form, pyrex brand glass, graduated, 125-ml capacity. Obtained from Fisher Scientific Company, Silver Spring, Maryland. Used for storing polymer solutions.

Flask. Erlenmeyer form, pyrex brand glass, 50-ml capacity. Obtained from Fisher Scientific Company, Silver Spring, Maryland. Used for storing filtered polymer solutions.

Float. Density, 1.0000, 1.1000, 1.2000, and 1.3000 gm/cu cm at 23 °C. Purchased from Scientific Glass Apparatus Company, Inc., 735 Broad Street, Bloomfield, New Jersey. Used to calibrate the density gradient column.

Flowmeter. Fisher Flowmeter Kit, catalog no. 11-164-3, code no. 01-N-150A. Float 11-164-14, 5/32 in., stainless steel. Borrowed from the Metals and Ceramic Engineering Department. Used to calibrate nitrogen flowmeters.

Flowmeter. Tube no. 603, series no. R-2-15-B. Manufactured by the Matheson Company, Inc., East Rutherford, New Jersey. Used to indicate and regulate the flow of nitrogen.

Funnel. Büchner, pyrex brand glass, fritted, medium grade porosity, 60-ml capacity, 40-mm inside diameter. Purchased from Fisher Scientific Company, Silver Spring, Maryland. Used to filter solvents and polymer solutions.

Funnel. Chemical, shaft stem, blown glass, student grade, 7 cm diameter, 6.5 cm stem length. Obtained from the Chemical Engineering Department stockroom. Used for filling burets with solvents.

Heater. Immersion, 1000-watt. Obtained from the Chemical Engineering Department stockroom. Used as the primary heater in the oil bath.

Heater. Immersion, 500-watt. Obtained from the Chemical Engineering Department stockroom. Used as the secondary heater in the oil bath.

Oven. Drying, equipped with two 250-watt infrared lamps. Manufactured by Arthur H. Thomas Company, Philadelphia, Pennsylvania. Used to dry glassware.

Pipet. Volumetric or transfer, pyrex brand glass, 10-ml capacity. Obtained from the Chemical Engineering Department stockroom. Used to measure the volume of polymer solutions and to transfer polymer solutions into viscometers.

Potentiometer. Serial no. 55218. Manufactured by Rubicon Company, Philadelphia, Pennsylvania. Used in calibrations of thermocouples and the Leeds and Northrup Speedomax H recorder.

Powerstat. Variable transformer, 8 amp load. Manufactured by the Superior Electric Company, Bristol, Connecticut. Distributed by Fisher Scientific Company, Silver Spring, Maryland. Used to regulate the power input to the primary heater and the speed of stirrers.

Recorder. Potentiometric, Speedomax H, 120 v, 60 cy, catalog no. 3-961-000-180-6-360-0, serial no. 62-54966-1-1. Manufactured by Leeds and Northrup Company, Philadelphia, Pennsylvania. Used to record the outputs of thermocouples installed on the reactors.

Regulator. Pressure, Oxweld type, R-7, 0-3,000 lb/sq in., gage, and 0-100 lb/sq in., gage. Manufactured by U. S. Gauge Company. Used to indicate and regulate nitrogen supply pressure.

Relay. Fisher Transister, model 30. Obtained from the Chemical Engineering Department stockroom. Used to control the oil bath temperature.

Rubber Bulb. Length 83 mm; diameter 46 mm. Obtained from the Chemical Engineering Department stockroom. Used in viscometry of polymer solutions.

Screen. U. S. Standard Sieve Series, A. S. T. M. Specifications. Manufactured by Fisher Scientific Company, Pittsburgh, Pennsylvania, and Eimer and Amend, New York, New York. Used in screen analyses of polymer resins.

Stirrer. Laboratory, electric, 115 v, 50-60 cy. Obtained from the Chemical Engineering Department stockroom. Used to circulate oil in the constant temperature bath.

Stirrer. Magnetic, Fisher Flexa-mix, catalog no. 14-511-2, 115 v. Obtained from Fisher Scientific Company, Silver Spring, Maryland. Used in dissolving polymers.

Stirring Bar. Sealed in glass, 1 in. long by $7/32$ in. in diameter. Obtained from the Chemical Engineering Department stockroom. Used in dissolving polymers.

Stopwatch. Electric, direct reading 0.1 second. Manufactured by Precision Scientific Company, Chicago, Illinois. Used to measure the efflux times of solvents and polymer solutions in the viscometers.

Support. Buret, Fisher Castaloy-R with white porcelain base. Obtained from the Chemical Engineering Department stockroom. Used to hold burets.

Thermometer. Beckman, differential, scale reading upward, graduated in 0.01 degree divisions, no. 2926. Fisher catalog no. 15-045. Obtained from the Chemical Engineering Department stockroom. Used to indicate temperature variation in the Cannon constant temperature bath for viscometry.

Thermometer. Glass, 0 to 200 °C, one degree divisions. Obtained from the Chemical Engineering Department stockroom. Used to measure the temperature in the oil bath.

Thermoregulator. Roto-stat, differential, -35 to 500 °F regulating range, ± 0.0005 °F sensitivity. Fisher catalog no. 15-180-15. Purchased from Fisher Scientific Company, Silver Spring, Maryland. Used to control the oil bath temperature.

Viscometer. Cannon-Ubbelohde dilution type for transparent liquids, sizes 75, 100, and 200. Manufactured by Cannon Instrument Company, P. O. Box 812, State College, Pennsylvania. Used to determine viscosities of polymer solutions.

Procedure

This section presents the procedures for performing the tests, characterizing the polymer resins, and calibrating the instruments.

Determination of Reactor Purge Time. The polymers used in this investigation degrade severely when heated in air. This degradation results in discoloration.

To determine the purge time required, polymer samples weighing approximately three grams were placed in each of the three reactors. Dry nitrogen (10 pounds per square inch, gage) was passed through each reactor at a fixed rate of 4,000 cubic centimeters per minute (measured at

14.7 pounds per square inch, absolute, 70 °F). Nitrogen was passed through one reactor for 1/2 hour, another for 1 hour, and the third for 1-1/2 hours. They were then sealed and immersed in an oil bath. The bath temperature was maintained at 200 °C. After 20 hours, the reactors were removed from the bath and their contents examined for discoloration. This approach was repeated for each polymer resin used in the investigation.

It was found that a purge time of 1-1/2 hours was adequate. But, for assurance, a two-hour purge time was employed for all of the tests conducted.

Procedure for Performing the Solid-Phase Reaction.

Four reactors were employed simultaneously at any given reaction temperature. Each reactor contained samples of two different particle sizes. One sample was put in a wire screen basket and the other on the bottom wire screen. To avoid mixing, the basket was set on spacers above the screen, so that the bottom of the basket would not touch the polymer sample retained by the screen. A chance process (tossing a coin) was used to decide whether the basket should contain large or small particles.

The reactors and their contents were purged. While purging was underway, the oil bath was heated to one of the five operating temperatures: 120, 140, 160, 180, and

200 °C. The maximum variation at any one of the temperatures was ± 1 °C.

After the two-hour purge, the reactors were sealed by closing the gas exhaust valves. The gas inlet valves remained open. The sealed reactors were immersed in the oil bath one at a time. A reactor was not introduced into the bath until the preceding one had reached bath temperature. Nitrogen flow was resumed when the temperature inside the reactor was the same as that of the oil bath. The rate of nitrogen flow, however, was reduced to 1,000 cubic centimeters per minute for the polyamides and 2,000 cubic centimeters per minute for the polyester. Again rates were measured at 14.7 pounds per square inch, absolute, 70 °F. Reaction was assumed to begin at the same time as the resumption of nitrogen flow. Reaction times of 5, 10, 15, and 20 hours were randomly assigned to each of the four reactors in the bath at each operating temperature.

To terminate the reaction, the reactor was removed from the bath, sealed, and air-cooled to room temperature. A 6-inch electric fan was used to accelerate cooling.

Polymer resins removed from the reactors were stored in plastic containers and kept in a desiccator.

To establish a reference point, a zero-hour reaction was conducted for each polymer at every temperature studied. The same procedure was used except that the reactor was removed as soon as it came to the bath temperature. The reactor was kept sealed during this entire operation.

Preparation of Polymer Solution for Viscometry.

Approximately 0.3 gram (weighed accurately to 0.1 milligram) of a polymer was added to 50 milliliters of solvent. Poly(hexamethylene adipamide) in formic acid required about 15 hours at room temperature to dissolve. Poly(hexamethylene sebacamide) in m-cresol required agitation for about 24 hours to dissolve at room temperature. To dissolve poly(ethylene terephthalate) in phenol/tetrachloroethane required heating to 130 °C for about 20 minutes.

Polymer solutions were filtered through Büchner funnels of medium grade porosity. The filtrates were collected for use in viscometry.

Determination of Intrinsic Viscosity. The intrinsic viscosity of a polymer was determined in a Cannon-Ubbelohde Dilution type viscometer. Ten milliliters of polymer solution were transferred into a viscometer positioned in a constant temperature bath. The 25 °C bath temperature

was controlled with a maximum variation of ± 0.01 °C. Twenty minutes were allowed for the polymer solution to reach thermal equilibrium. The efflux time was measured to 0.1 second using an electric stopwatch. Three efflux times were measured for every concentration of each solution. Three additional times were measured if the original three varied more than 0.2 second. If the additional readings failed to agree, the solution was discarded.

To obtain the intrinsic viscosity, it is necessary to measure the efflux time of a solution at several concentrations. This was achieved by successive dilutions of the solution in the viscometer. For the initial 10-milliliter solution, the volumes of solvent added over three dilutions were 3, 5, and 8 milliliters, respectively. Formic acid and phenol-tetrachloroethane were added from a 10 cubic centimeter hypodermic syringe. Because of its viscosity, m-cresol was added from a buret graduated in 0.1 milliliter divisions. Both the syringe and the buret were calibrated against a standard buret prior to use.

To compute the solution concentration after dilutions, the initial concentration was divided by 1.3, 1.8, and 2.6.

The intrinsic viscosities were calculated according to the procedure given on pages 129 through 133, in Sample Calculations.

Determination of Polymer Density. Polymer chips, flakes, or powders were dropped directly into the density gradient column. Their steady-state positions were noted and their densities were read from the calibration curve. Temperature of the column was controlled at 23 °C during the determination.

Screen Analysis of Polymer Resins. For each polymer the manufacturer supplied two batches, each cut to a different particle size. Screen analysis was made to determine the mean particle size of each batch. Approximately 500 grams of resin were analyzed using a series of U. S. sieves. An electrically powered mechanical shaker was employed for 20 minutes in each screening operation. The resin retained on each screen was weighed and its weight fraction calculated. The calculation of mean particle size is shown on page 127, Sample Calculations.

Determination of Polymer Pigment Content. Poly(hexamethylene adipamide) and poly(ethylene terephthalate) resins were delustered with a pigment, titanium dioxide. The amount of pigment was determined by burning a known quantity of polymer until the weight of ash remained unchanged. The ash content was taken to be the pigment content of the polymer.

Determination of Polymer Melting Point. The melting point of a polymer was determined by the differential thermal analysis (DTA) technique. Details of this technique are described in the section that follows.

Differential Thermal Analysis. Differential thermal analysis accurately measures the temperature difference between a sample and a reference material in the same controlled conditions. This temperature difference is plotted against the temperature increase of the reference material for interpretation. Powdered Al_2O_3 was used as the reference material. The amount of polymer sample varied to meet the requirement that the product of the weight of a substance with its heat capacity be approximately the same for both sample and reference material. Dry nitrogen was used to flood the measuring cell. The cut-off temperature was set at 300 °C. The rate of heating was 10 °C per minute. The differential temperature and the cell temperature were recorded on a thermogram.

Calibration of Temperature Recorder. The Speedomax H recorder was calibrated using a Rubicon potentiometer. A constant voltage of 10 millivolts was set on the potentiometer and the range of the recorder was adjusted to

read 100 per cent of the scale. Once the range was set, voltages were increased by 1-millivolt increments from 0 to 10 millivolts. Positions of the recorder pen were marked. A plot of the pen positions against the imposed voltages yielded a straight line.

Calibration of Thermocouples. Ten iron-constantan thermocouples were made. The cold junctions were kept in a water bath filled with crushed ice for calibration. The thermocouples were immersed in an oil bath, the temperature being initially maintained at 50 °C. The output voltage on each thermocouple was recorded. This procedure was repeated as the oil temperature was raised to 100, 150, and 200 °C. The output voltages of the four thermocouples selected for use, agreed within 0.1 millivolt at every calibration temperature.

Calibration of Density Gradient Column. Mixtures of carbon tetrachloride and xylene, in various volumetric proportions, were used in preparing the density gradient column. A 2,000-milliliter graduated cylinder was used to contain the mixtures. The cylinder was placed in a water bath kept at 23 °C. Four standard density floats (1.0000, 1.1000, 1.2000, and 1.3000 grams per cubic centimeter at 23 °C) were dropped into the column and their steady positions were noted on the graduated

cylinder. A plot of float positions against their densities provided a calibration curve for determining densities of polymers.

Calibration of Nitrogen Flowmeters. A Fisher Flowmeter Kit was employed to calibrate the nitrogen flowmeters (by Matheson). Dry nitrogen, supplied at 10 pounds per square inch, gage, was directed through a Matheson flowmeter and the Fisher flowmeter in series. Readings on both flowmeters were checked separately against the calibration curves provided by the manufacturers. The results were in good agreement, hence the calibration curve supplied with the Matheson flowmeters was accepted.

Selection of Viscometers. Cannon-Ubbelohde Dilution type viscometers were chosen for the viscometry work. They were designed for the determination of polymer intrinsic viscosities. Viscometer sizes were selected based on the kinematic viscosities of solvents used to dissolve the polymers. For formic acid, the solvent for poly(hexamethylene adipamide), size 75 viscometers were used. For m-cresol, the solvent for poly(hexamethylene sebacamide), size 200 viscometers were employed. Size 100 viscometers were chosen for poly(ethylene terephthalate) using a mixture of phenol and tetrachloroethane, 50/50 by weight, as the solvent.

Calibration of Viscometers. The Cannon-Ubbelohde viscometer calibration requires only the measurement of solvent efflux time when used to determine the intrinsic viscosity of polymers in dilute solutions (less than 1 gram per 100 milliliters of solvent). The efflux time of each solvent in the appropriate viscometer (two of each size) was determined by transferring 10 milliliters of solvent into the viscometer and recording the time for the solvent to flow across two marked lines. Four readings were taken for each solvent in each viscometer to obtain an average efflux time. Temperature of the water bath in which the viscometers were suspended was kept at 25 ± 0.01 °C.

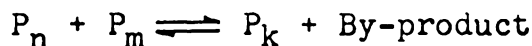
Method for Cleaning Viscometers. The viscometers used for poly(hexamethylene adipamide) were first rinsed with water followed, in order, with formic acid (about 10 milliliters), cleaning solution, distilled water, acetone, and finally dried with filtered air. The viscometers used for poly(hexamethylene sebacamide) and poly(ethylene terephthalate) were cleaned in a similar manner, with the exception that soapy water was used in place of formic acid.

IV. RESULTS

This section consists of the derivations of kinetic equations, data and results, and sample calculations.

Kinetic Equations

Each one of the condensation polymers used, as they were manufactured by a melt-phase process, contains polymer molecules of various sizes and the by-product molecules. Chemical equilibrium is maintained among these molecules as shown below:



where P_n , P_m , and P_k represent the polymer molecules having n , m , and k structural units. In order for the condensation reaction to take place in the solid polymer, removal of the by-product is necessary. When a molecule of the by-product is removed, a new molecule is formed if sufficient energy is available for the reaction to occur. It is assumed that the number of new by-product molecules produced from the solid-phase reaction is negligible in comparison with the number of by-product molecules initially present. Then, the kinetic problem

can be approximated as a case for drying solid polymers. Two particle geometries, plane sheet and sphere, are considered.

Formulation of Kinetic Equations. Matsuda and co-workers⁽⁸⁸⁾ gave an approximate relationship between the average molecular weight and the number of polymer molecules present during a condensation reaction.

$$\frac{\bar{M}_{n,o}}{\bar{M}_{n,t}} = \frac{N_t}{N_o} \quad (37)$$

where:

$\bar{M}_{n,o}$ = initial number-average molecular weight

$\bar{M}_{n,t}$ = number-average molecular weight at time t

N_o = total number of polymer molecules present initially

N_t = total number of polymer molecules present at time t.

Assume that the reaction is linear and bi-molecular in nature, then the expression given below relates the

the number of polymer molecules to the amount of by-product produced.

$$\frac{\bar{M}_{n,0}}{\bar{M}_{n,t}} = \frac{N_t}{N_0} = \frac{W_\infty - W_t}{W_\infty} = 1 - \frac{W_t}{W_\infty} \quad (38)$$

where:

W_t = number of by-product molecules released up to time t .

W_∞ = number of by-product molecules evolved if time extends to infinity.

To formulate the kinetic equations, flakes of polymers will be considered as plane sheets, whereas powders will be thought of as spherical particles. For a plane sheet of thickness $2L$ as illustrated in Figure 3, the following equation describes the one-dimensional diffusion problems.

$$\frac{\partial C}{\partial t} = D(t) \frac{\partial^2 C}{\partial x^2} \quad (39)$$

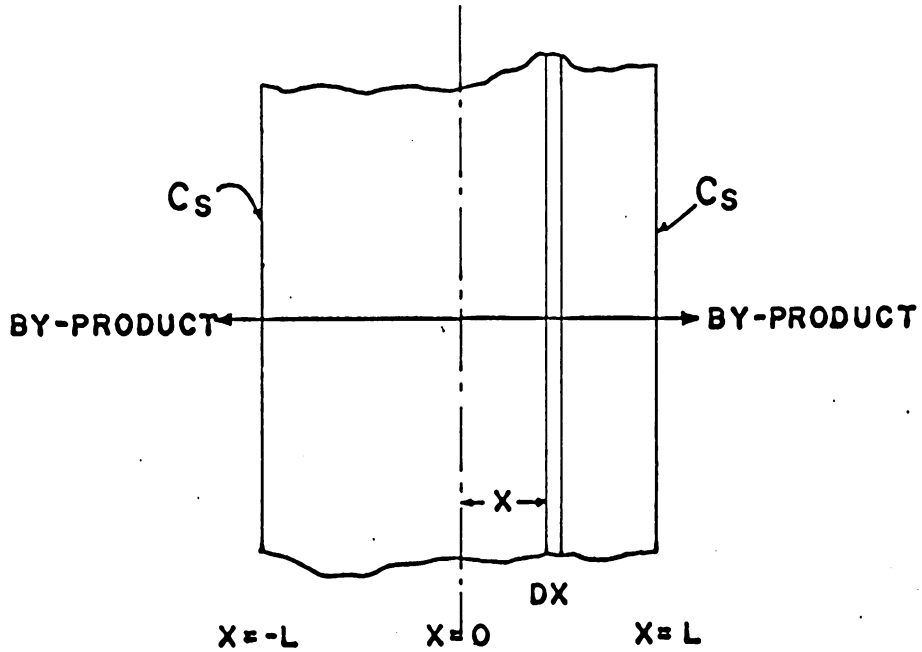
where:

C = concentration of by-product within the sheet, lb mole/cu ft

x = distance measured from the central plane in the sheet, ft

t = time, hr

$D(t)$ = diffusivity of the by-product, sq ft/hr.



EQUATION:

$$\frac{\partial C}{\partial t} = D(t) \frac{\partial^2 C}{\partial X^2}$$

INITIAL & BOUNDARY CONDITIONS:

$$C = C_0, \quad -L < X < L, \quad t = 0$$

$$C = C_s, \quad X = \pm L, \quad t \geq 0$$

$$\frac{\partial C}{\partial X} = 0, \quad X = 0, \quad t > 0$$

FIGURE 3. MATHEMATICAL MODEL FOR DIFFUSION IN
A PLANE SHEET

The diffusivity is assumed to depend on time. The initial and boundary conditions are listed below:

$$C = C_0, \quad -L < x < L, \quad t = 0 \quad (40)$$

$$C = C_s, \quad x = L \text{ and } x = -L, \quad t \geq 0 \quad (41)$$

$$\frac{\partial C}{\partial x} = 0, \quad x = 0, \quad t > 0 \quad (42)$$

in which C_0 and C_s represent the initial concentration and the concentration at the surface, respectively. Both are constants, however.

For a sphere of radius R as shown in Figure 4, the equation corresponding to equation 39 is

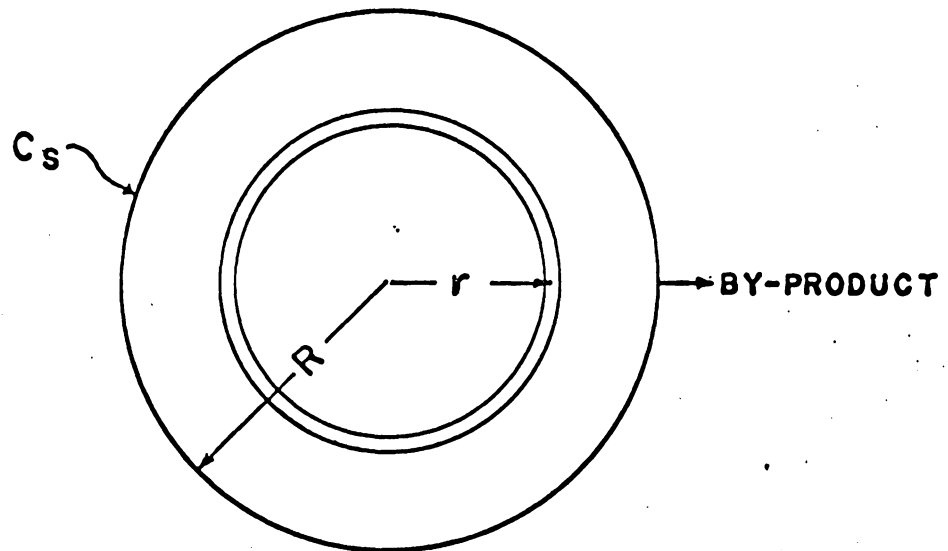
$$\frac{\partial C}{\partial t} = D(t) \left[\frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \frac{\partial C}{\partial r} \right] \quad (43)$$

for radial diffusion. The distance from the center of the sphere is denoted by r . The initial and boundary conditions are given as

$$C = C_0, \quad r < R, \quad t = 0 \quad (44)$$

$$C = C_s, \quad r = R, \quad t \geq 0 \quad (45)$$

$$\frac{\partial C}{\partial r} = 0, \quad r = 0, \quad t > 0 \quad (46)$$



EQUATION :

$$\frac{\partial C}{\partial t} = D(t) \left[\frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \frac{\partial C}{\partial r} \right]$$

INITIAL & BOUNDARY CONDITIONS:

$$C = C_0, \quad 0 < r < R, \quad t = 0$$

$$C = C_s, \quad r = R, \quad t \geq 0$$

$$\frac{\partial C}{\partial r} = 0, \quad r = 0, \quad t > 0$$

FIGURE 4. MATHEMATICAL MODEL FOR DIFFUSION IN A SPHERE

In order to solve equation 39, the following variable transformations are made.

$$\theta = \frac{C_0 - C}{C_0 - C_s}$$

and

$$dT = D(t) dt.$$

Substituting into equation 39 gives

$$\frac{\partial \theta}{\partial T} = \frac{\partial^2 \theta}{\partial x^2} \tag{47}$$

Suppose that a function can be found for $D(t)$ to permit direct exchange of t with T in specifying the initial and boundary conditions. Then, the initial and boundary conditions, after variable transformation, are

$$\theta = 0, \quad -L < x < L, \quad T = 0 \tag{48}$$

$$\theta = 1, \quad x = L \text{ and } x = -L, \quad T \geq 0 \tag{49}$$

$$\frac{\partial \theta}{\partial x} = 0, \quad x = 0, \quad T > 0 \tag{50}$$

Equation 44 will be solved by the method of separation of variables.

Writing:

$$\Theta = X(x) \psi (T) \quad (51)$$

where $X(x)$ is a function of x only and $\psi (T)$ is a function of T only. For convenience, X and ψ are to be used to indicate these two functions. Substituting in equation 47 yields

$$X \frac{\partial \psi}{\partial T} = \psi \frac{\partial^2 X}{\partial x^2} \quad (52)$$

which may be rewritten as

$$\frac{1}{\psi} \frac{d\psi}{dT} = \frac{1}{X} \frac{d^2 X}{dx^2} \quad (53)$$

In the above equation, the quantity on the left of the equal sign depends only on T , and that on the right varies only with x . In order for both sides of equation 53 to be equal, they must be equal to a constant. For convenience this constant is chosen to be $-\lambda^2$. Then equation 53 is written in two ordinary differential equations.

$$\frac{1}{\psi} \frac{d\psi}{dT} = -\lambda^2 \quad (54)$$

and

$$\frac{1}{X} \frac{d^2 X}{dx^2} = -\lambda^2 \quad (55)$$

The solution for equation 54 is

$$\psi = c_1 \exp(-\lambda^2 T) \quad (56)$$

and that for equation 55 is

$$X = c_2 \cos \lambda x + c_3 \sin \lambda x. \quad (57)$$

However, the constant λ may be zero. Thus, for $\lambda = 0$

$$\psi = c_1 \quad (58)$$

and

$$X = c_4 + c_5 x. \quad (59)$$

Equation 51 now becomes

$$\theta = c_6 + c_5 x + (c_7 \cos \lambda x + c_8 \sin \lambda x) \exp(-\lambda^2 T) \quad (60)$$

in which $c_6 = c_1 + c_4$, $c_7 = c_1 c_2$, and $c_8 = c_1 c_3$. In equations 56 through 60, c's are integration constants.

The physical situation dictates that, $\theta \rightarrow 1$ as $t \rightarrow \infty$. To satisfy this $c_6 = 1$ and $c_5 = 0$. Thus, equation 60 reduces to

$$\theta = 1 + (c_7 \cos \lambda x + c_8 \sin \lambda x) \exp (- \lambda^2 T) \quad (61)$$

More precisely, the above equation should be written as

$$\theta = 1 + \sum_{m=1}^{\infty} (A_m \cos \lambda_m x + B_m \sin \lambda_m x) \exp (- \lambda_m^2 T) \quad (62)$$

in which A_m , B_m , and λ_m will be determined by the initial and boundary conditions of the problem considered.

According to the condition stated in equation 50, one finds that $B_m = 0$. Furthermore, for

$$\theta = 1 \text{ at } x = L \text{ and } T = 0, \\ \sum_{m=1}^{\infty} A_m \cos \lambda_m L = 0 .$$

For the summation to be zero,

$$\lambda_m = \frac{m\pi}{2L} .$$

Then, equation 62 becomes

$$\theta = 1 + \sum_{m=1}^{\infty} \left(A_m \cos \frac{m\pi}{2L} x \right) \exp \left(- m^2 \pi^2 T / 4L^2 \right). \quad (63)$$

To evaluate A_m , the initial condition

$$\theta = 0, \quad -L < x < L, \quad T = 0$$

is applied to equation 63 which gives

$$-1 = \sum_{m=1}^{\infty} A_m \cos \frac{m\pi}{2L} x. \quad (64)$$

Multiplying both sides of equation 64 by $\cos \frac{m\pi}{2L} x \, dx$ and integrating the resulting equation from $-L$ to L yields

$$A_m = - \frac{4}{m\pi} (-1)^{\frac{m+3}{2}}$$

where m is an odd integer.

Substituting A_m in equation 63 and putting $m = 2n + 1$, one obtains

$$\theta = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)} \cos \frac{(2n+1)\pi}{2L} x \exp \left[- (2n+1)^2 \pi^2 T / 4L^2 \right]. \quad (65)$$

The number of by-products released up to time t , W_t , is computed below.

$$W_t = \int_0^t \left[-D(\tau) \frac{\partial C}{\partial x} \right]_{x=L} d\tau = \int_0^T \left[-\frac{\partial C}{\partial x} \right]_{x=L} dT. \quad (66)$$

Since $\theta = \frac{C_0 - C}{C_0 - C_s}$, from equation 65,

$$\left[-\frac{\partial C}{\partial x} \right]_{x=L} = \frac{2}{L} (C_0 - C_s) \sum_{n=0}^{\infty} \exp \left[- (2n + 1)^2 \pi^2 T / 4L^2 \right].$$

Substituting this into equation 66 and integrating, one gets

$$W_t = (C_0 - C_s) \frac{8L}{\pi^2} \left\{ \sum_{n=0}^{\infty} \frac{1}{(2n + 1)^2} - \sum_{n=0}^{\infty} \frac{1}{(2n + 1)^2} \exp \left[- (2n + 1)^2 \pi^2 T / 4L^2 \right] \right\}. \quad (67)$$

However,

$$\sum_{n=0}^{\infty} \frac{1}{(2n + 1)^2} = \frac{\pi^2}{8},$$

then

$$W_t = (C_o - C_s) \frac{8L}{\pi^2} \left\{ \frac{\pi^2}{8} - \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp \left[- (2n+1)^2 \pi^2 T/4L^2 \right] \right\} . \quad (68)$$

As $T \rightarrow \infty$,

$$W_{\infty} = (C_o - C_s) \frac{8L}{\pi^2} \frac{\pi^2}{8} \quad (69)$$

Thus,

$$1 - \frac{W_t}{W_{\infty}} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp \left[- (2n+1)^2 \pi^2 T/4L^2 \right] . \quad (70)$$

Equation 70 is also the expression for $\bar{M}_{n,0}/\bar{M}_{n,t}$.

For convenience, define

$$K_1(t) = \frac{\pi^2 T}{4L^2} \quad (71)$$

where:

$$T = \int_0^t D(t) dt .$$

Then, from equation 70 the resulting kinetic equation is

$$\frac{\bar{M}_{n,0}}{\bar{M}_{n,t}} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp [- (2n+1)^2 K_1(t)] \quad (72)$$

For a sphere equation 43 must be solved. It can be transformed into equation 73 by letting $u = Cr$.

$$\frac{\partial u}{\partial t} = D(t) \frac{\partial^2 u}{\partial r^2} \quad (73)$$

Since the above equation is identical to equation 39 for the case of a plane sheet, the same procedures used previously may be followed to solve equation 73. For brevity, the solution is given below.

$$\frac{\bar{M}_{n,0}}{\bar{M}_{n,t}} = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp [- n^2 K_2(t)] \quad (74)$$

where:

$$K_2(t) = \frac{\pi^2 T}{R^2} \quad (75)$$

The quantities $K_1(t)$ and $K_2(t)$ are dimensionless and are referred to as the rate functions.

Method for Obtaining $K(t)$. The quantities, $K_1(t)$ and $K_2(t)$, do not appear explicitly in equations 72 and 74. It would be inconvenient to compute $K(t)$ for an experimentally determined $\bar{M}_{n,0}/\bar{M}_{n,t}$ directly from the equations. However, a table consisting of the values of $K(t)$ and $\bar{M}_{n,0}/\bar{M}_{n,t}$ may be constructed to facilitate direct reading of $K(t)$ for a given ratio of molecular weights.

A digital computer program was developed to prepare the table in which an initial value of 0.0001 was assigned for $K(t)$ and incrementally increased by the quantity 0.0001 until it reached 0.8000. The values of $K(t)$ together with those of $\bar{M}_{n,0}/\bar{M}_{n,t}$ for a plane sheet and sphere were tabulated. The table, because of its volume is not included in this thesis; however, the computer program is shown in Appendix E, page 239, for those who wish to prepare such a table. An excerpt of the table is given in Table LXIV, page 241.

Data and Results

This section presents pertinent data and results.

Densities of Raw Polymers. Absolute and bulk densities of the three raw polymers are listed in Table III.

Mean Particle Diameters of Polymer Resins. Table IV shows the mean particle diameters of the three polymer resins. Screen analysis data are included in Appendix A.

Pigment Contents in Polymer Resins. Table V gives the pigment contents of poly(hexamethylene adipamide) and poly(ethylene terephthalate).

Reactor Temperature Profiles. Plotted in Figures 5 and 6 are the temperature profiles in the transient periods during heating and cooling from the controlled reaction temperatures. These figures were made using the data given in Appendix B.

Reynolds Number for Flow of Nitrogen through Polymer Beds. Table VI gives the Reynolds numbers computed for the flow of nitrogen through beds of polymers treated at various temperatures.

Differential Thermograms. Differential thermograms obtained for poly(hexamethylene adipamide),

poly(hexamethylene sebacamide), and poly(ethylene terephthalate) are shown in Figures 7, 8, and 9, respectively. Thermograms are included for each polymer for some selected samples generated in the reactions. Melting characteristics of raw resins are tabulated in Table VII.

Intrinsic Viscosities and Average Molecular Weights of Polymers. Intrinsic viscosities and number-average molecular weights of polymers used in this investigation are included in Tables VIII through XIII. Confidence limits are also given for each intrinsic viscosity calculated. The original viscometric data are given in Appendix D.

Analysis of Variance. The results obtained from the analysis of variance of the intrinsic viscosity data are compiled in Tables XIV to XVI. Details involved in the analysis are shown in Appendix F.

Rate Functions and Extents of the Reactions. Temperature and time dependencies of the rate function $K(t)$ and the extent of reaction α are given in Tables XVII through XXII. The extent of reaction with each type of polymer is also illustrated as a function of reaction time and polymer particle size in Figures 10 to 12.

Arrhenius Equations of Specific Reaction Rates.

Temperature dependency of the specific reaction rates is shown as Arrhenius plots in Figures 13 to 15. The Arrhenius equations derived from these plots are summarized in Table XXIV.

Comparison of Calculated and Experimental Molecular Weights. The number-average molecular weights calculated from the derived kinetic equations are compared with the experimental values in Tables XXV to XXX. Deviations are expressed as per cent error in the same tables.

TABLE III

Densities of Raw Polymer Resins

Polymer	Mean Particle Diameter	Density ^a	Bulk Density
	in.	gm/cc	gm/ml
Poly(hexamethylene adipamide)	0.081	1.145	0.46 ^b
	0.139	1.145	0.56 ^b
Poly(hexamethylene sebacamide)	0.085	1.080	0.50 ^b
	0.134	1.080	0.51 ^b
Poly(ethylene terephthalate)	0.038	1.385	0.62 ^c
	0.084	1.385	0.49 ^c

^aDetermined at 23 °C in a density gradient column.

^bAverage of three determinations.

^cValues of single determination.

TABLE IV

Mean Particle Diameters of Polymer Resins

Polymer	Grade	Mean Particle Diameter
		in.
Poly(hexamethylene adipamide)	Fine	0.081
	Coarse	0.139
Poly(hexamethylene sebacamide)	Fine	0.085
	Coarse	0.134
Poly(ethylene terephthalate)	Fine	0.038
	Coarse	0.084

TABLE V

Pigment Contents of Polymer Resins

Polymer	Pigment Content % by weight
Poly(hexamethylene adipamide)	0.332 0.372 0.306 Average = 0.337
Poly(ethylene terephthalate)	0.356 0.330 Average = 0.337

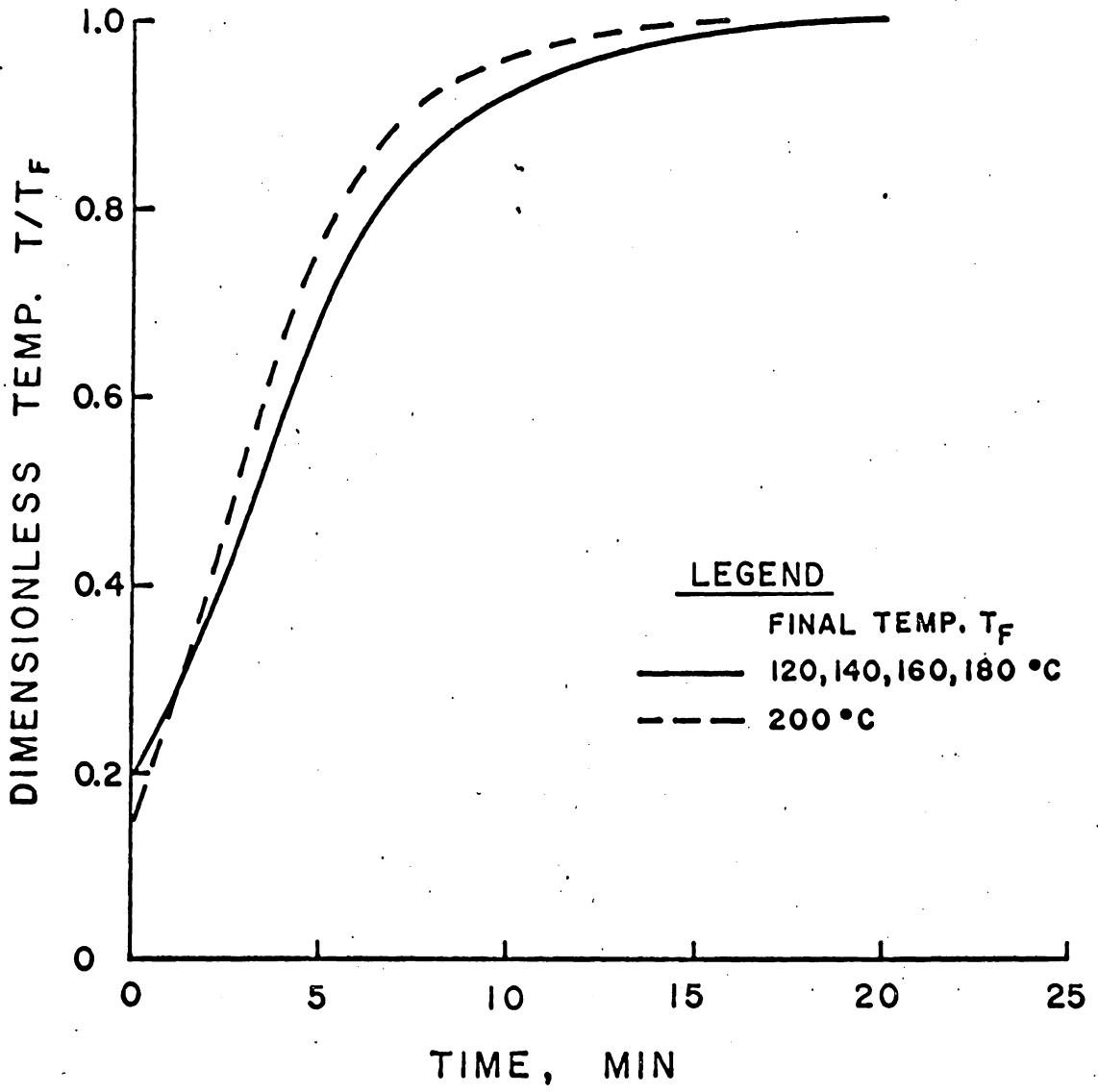


FIGURE 5. REACTOR TEMPERATURE DURING HEATING

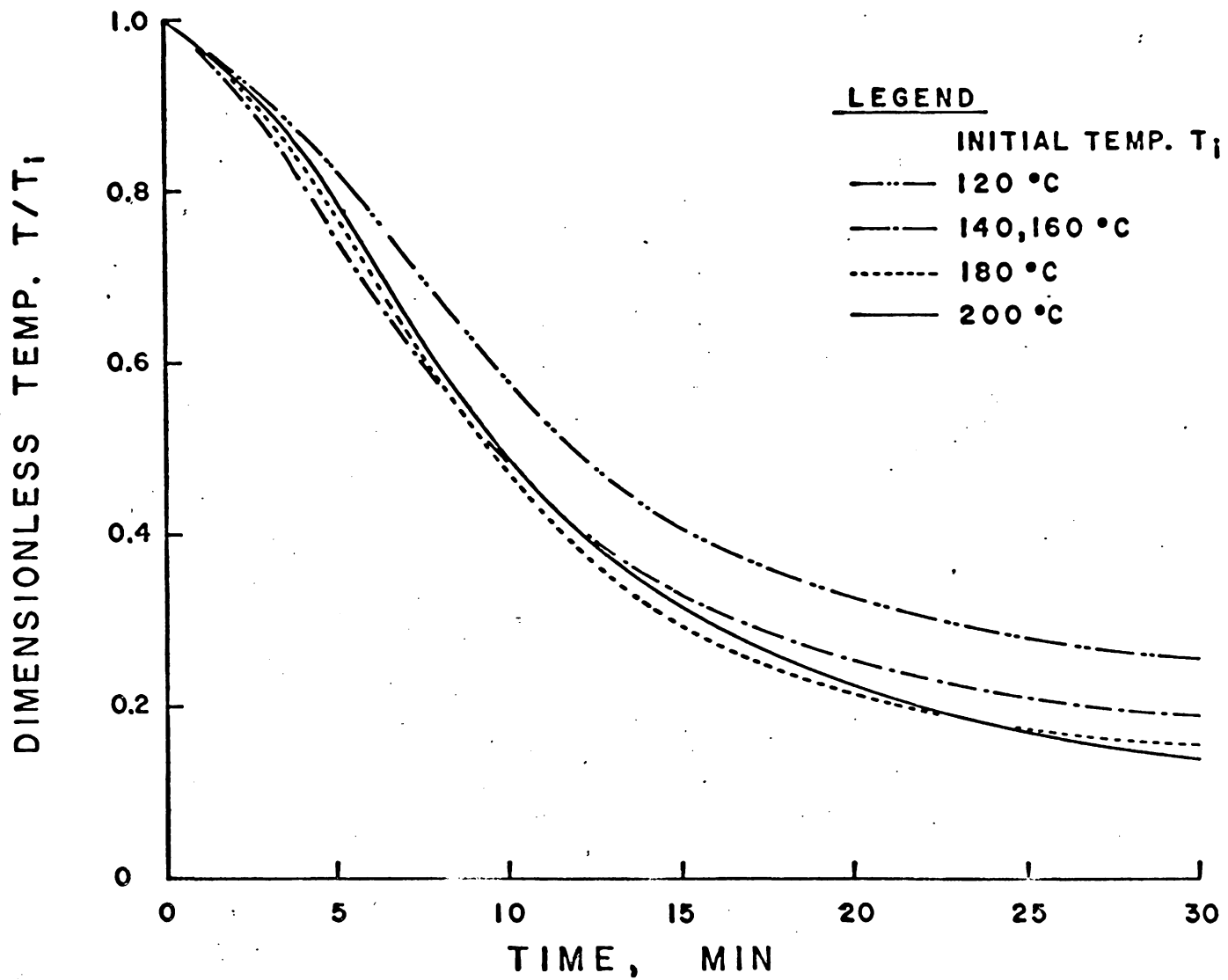


FIGURE 6. REACTOR TEMPERATURE DURING COOLING

TABLE VI

Reynolds Number for Flow of Nitrogen
through Beds of Polymers

Polymer	Mean Particle Diameter	Reaction Temperature	Re _p [*]
	in.	°C	
Poly(hexamethylene adipamide)	0.081	120	3.47
		140	3.40
		160	3.27
		180	3.16
	0.139	120	4.88
		140	4.80
		160	4.60
		180	4.46
Poly(hexamethylene sebacamide)	0.085	120	3.14
		140	3.08
		160	2.96
		180	2.86
	0.134	120	4.81
		140	4.72
		160	4.53
		180	4.39
Poly(ethylene terephthalate)	0.038	160	2.74
		180	2.66
		200	2.56
	0.084	160	7.60
		180	7.36
		200	7.10

*See Sample Calculations, page

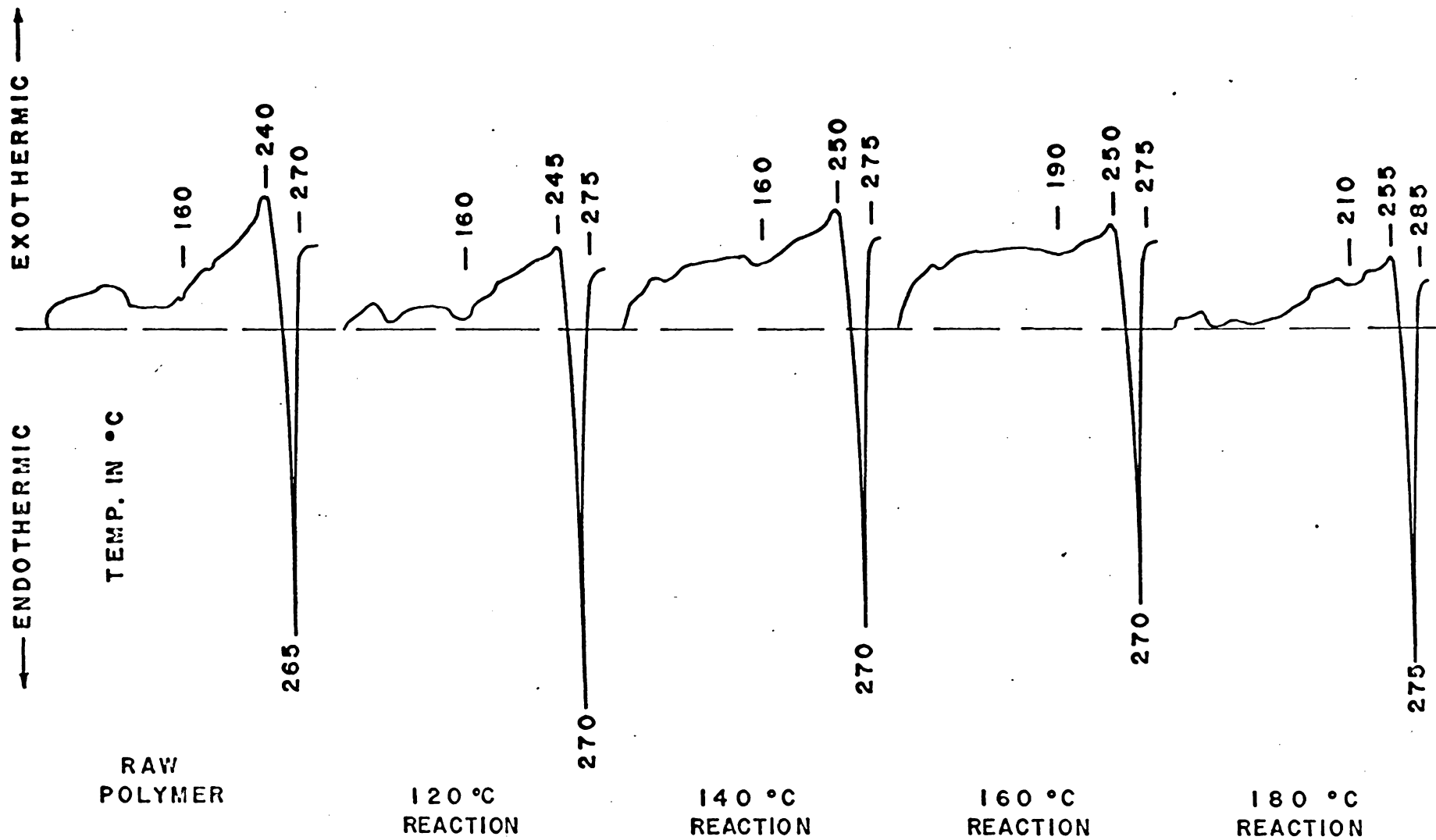


FIGURE 7. THERMOGRAMS OF POLY(HEXAMETHYLENE ADIPAMIDE)

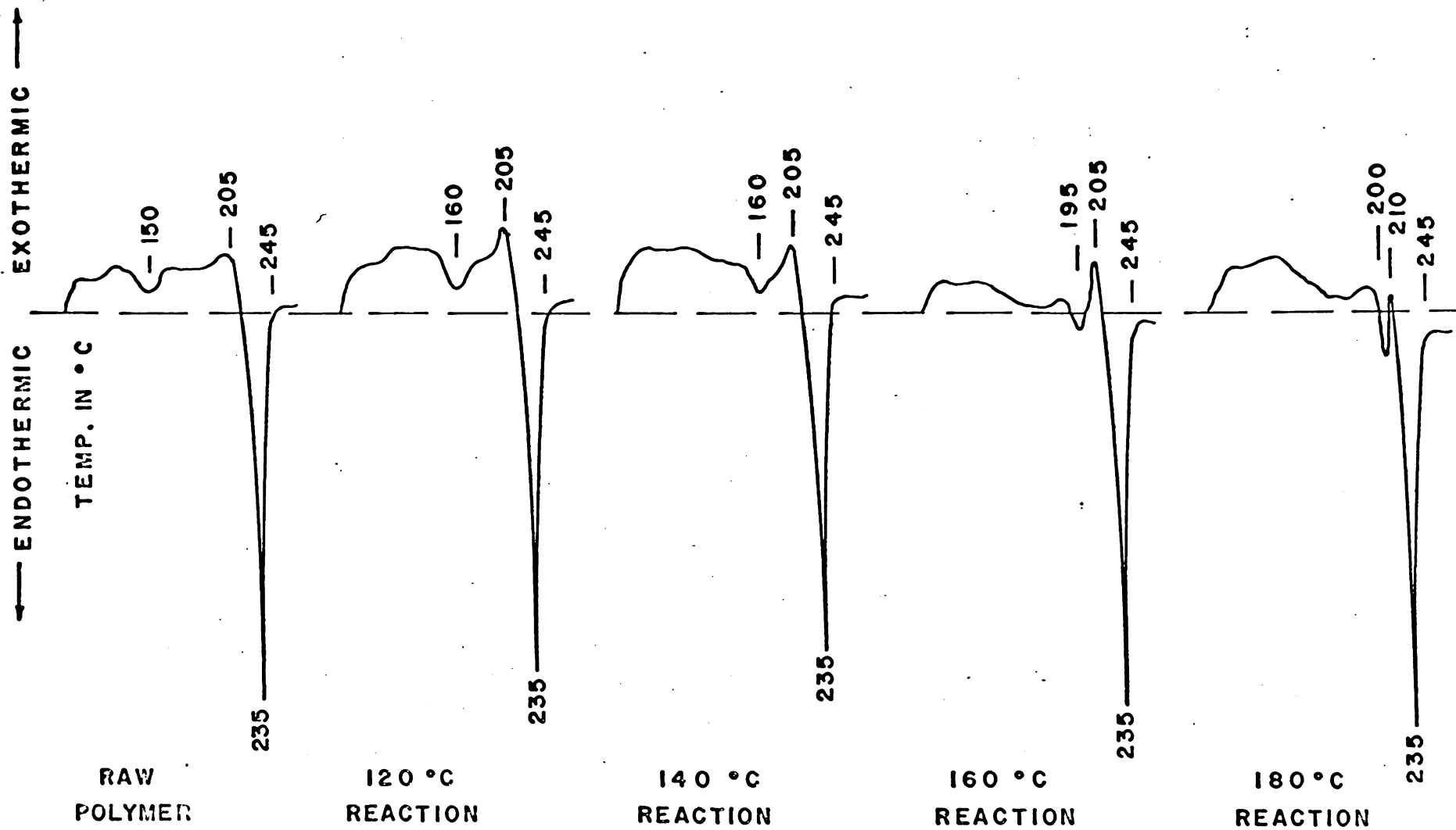


FIGURE 8. THERMOGRAMS OF POLY(HEXAMETHYLENE SEBACAMIDE)

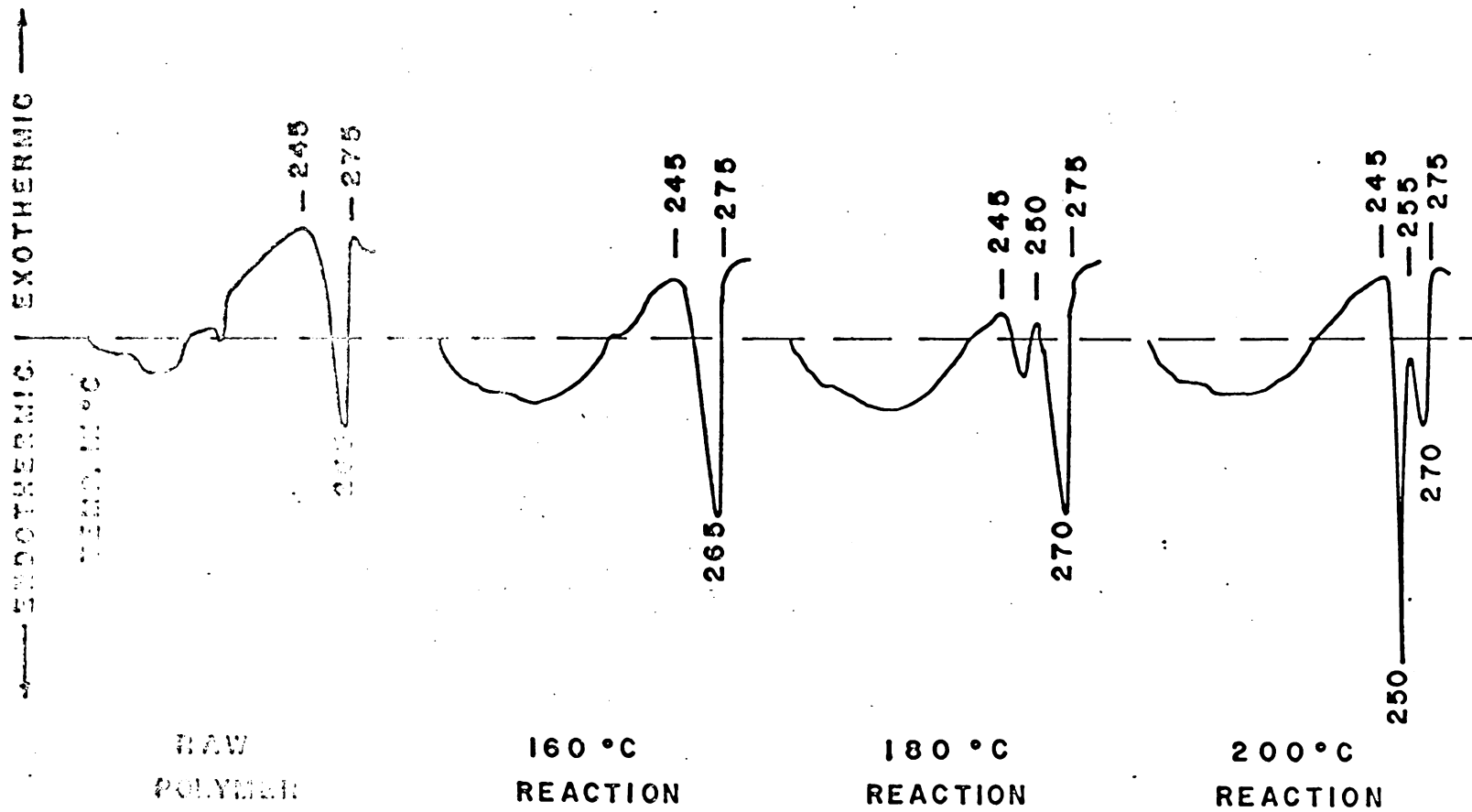


FIGURE 9. THERMOGRAMS OF POLY(ETHYLENE TEREPHTHALATE)

TABLE VII

Melting Temperatures of Raw Polymer Resins

Polymer	Melting Temperatures	
	Range °C	Peak °C
Poly(hexamethylene adipamide)	250-270	265
Poly(hexamethylene sebacamide)	210-240	235
Poly(ethylene terephthalate)	240-270	265

TABLE VIII

Effect of Reaction Temperature and Reaction Time
on Intrinsic Viscosity and Molecular Weight
of Poly(hexamethylene adipamide) of
0.081 in. Mean Particle Diameter

Temperature	Time	$[\eta]_1^a$	$[\eta]_2^b$	\bar{M}_n^c	Confidence Limits ^d
°C	hr	dl/gm	dl/gm		dl/gm
120	0	0.834	0.826	10100	0.0072
	5	0.952	0.933	12100	0.0033
	10	0.962	0.942	12300	0.0052
	15	0.973	0.953	12500	0.0053
	20	0.974	0.955	12500	0.0040
140	0	0.825	0.818	9900	0.0119
	5	0.973	0.955	12500	0.0264
	10	1.003	0.979	13100	0.0061
	15	1.042	1.016	13800	0.0054
	20	1.044	1.024	13800	0.1037
160	0	0.835	0.826	10100	0.0187
	5	1.045	1.025	13800	0.0046
	10	1.113	1.086	15100	0.0133
	15	1.161	1.127	16000	0.0139
	20	1.185	1.156	16500	0.0175
180	0	0.859	0.845	10500	0.0541
	5	1.160	1.137	16000	0.0418
	10	1.289	1.255	18500	0.0078
	15	1.357	1.317	19900	0.0108
	20	1.457	1.410	21900	0.0219

^aValue of $(\frac{\eta_r - 1}{C})_{C=0}$ in deciliters per gram (dl/gm).

^bValue of $(\frac{\ln \eta_r}{C})_{C=0}$.

^cComputed from $[\eta]_1$.

^d95% limits for $[\eta]_1$. Values shown are one-half of the limits.

TABLE IX

Effect of Reaction Temperature and Reaction Time
on Intrinsic Viscosity and Molecular Weight
of Poly(hexamethylene adipamide) of
0.139 in. Mean Particle Diameter

Temperature	Time	$[\eta]_1^a$	$[\eta]_2^b$	\bar{M}_n^c	Confidence Limits ^d
°C	hr	dl/gm	dl/gm		dl/gm
120	0	0.825	0.819	9900	0.0256
	5	0.950	0.933	12100	0.0081
	10	0.987	0.961	12800	0.0303
	15	0.967	0.945	12400	0.0069
	20	0.978	0.957	12600	0.0052
140	0	0.829	0.820	10000	0.0077
	5	0.972	0.954	12500	0.0272
	10	1.009	0.986	13100	0.0217
	15	1.017	0.994	13300	0.0125
	20	1.059	1.035	14100	0.0312
160	0	0.830	0.822	10000	0.0102
	5	1.063	1.038	14100	0.0089
	10	1.113	1.073	15100	0.0033
	15	1.171	1.145	16200	0.0182
	20	1.205	1.163	16900	0.0200
180	0	0.842	0.832	10200	0.0151
	5	1.173	1.150	16200	0.0089
	10	1.302	1.265	18800	0.0327
	15	1.396	1.351	20700	0.0201
	20	1.490	1.430	22600	0.0227

a, b, c, d See footnotes in Table VIII, page 98, for explanation.

TABLE X

Effect of Reaction Temperature and Reaction Time
on Intrinsic Viscosity and Molecular Weight
of Poly(hexamethylene sebacamide) of
0.085 in. Mean Particle Diameter

Temperature	Time	$[\eta]_1^a$	$[\eta]_2^b$	\bar{M}_n^c	Confidence Limits ^d
°C	hr	dl/gm	dl/gm		dl/gm
120	0	0.966	0.978	10300	0.0340
	5	1.005	1.015	10800	0.0244
	10	1.028	1.041	11000	0.0193
	15	1.036	1.053	11100	0.0227
	20	1.060	1.070	11400	0.0724
140	0	0.977	0.998	10400	0.0344
	5	1.048	1.056	11200	0.0214
	10	1.084	1.097	11600	0.0087
	15	1.102	1.112	11800	0.0173
	20	1.121	1.132	12100	0.0438
160	0	0.986	1.001	10500	0.0162
	5	1.094	1.108	11800	0.0064
	10	1.134	1.154	12200	0.0217
	15	1.163	1.178	12500	0.0278
	20	1.199	1.209	12900	0.0666
180	0	1.009	1.023	10800	0.0158
	5	1.165	1.180	12500	0.0139
	10	1.233	1.247	13300	0.0221
	15	1.267	1.278	13700	0.0161
	20	1.293	1.304	14000	0.0283

^{a,b,c,d}See footnotes in Table VIII, page 98, for explanation.

TABLE XI

Effect of Reaction Temperature and Reaction Time
on Intrinsic Viscosity and Molecular Weight
of Poly(hexamethylene sebacamide) of
0.134 in. Mean Particle Diameter

Temperature	Time	$[\eta]_1^a$	$[\eta]_2^b$	\bar{M}_n^c	Confidence Limits ^d
°C	hr	dl/gm	dl/gm		dl/gm
120	0	1.004	1.012	10700	0.0055
	5	1.020	1.036	10900	0.0366
	10	1.031	1.038	11000	0.0224
	15	1.035	1.050	11100	0.0434
	20	1.049	1.067	11200	0.0291
140	0	1.025	1.030	11000	0.0516
	5	1.081	1.093	11600	0.0091
	10	1.110	1.124	11900	0.0177
	15	1.121	1.136	12000	0.0166
	20	1.140	1.153	12300	0.0241
160	0	1.013	1.028	10800	0.0232
	5	1.133	1.141	12200	0.0245
	10	1.172	1.188	12600	0.0069
	15	1.204	1.217	13000	0.0151
	20	1.238	1.244	13400	0.0812
180	0	0.996	1.015	10700	0.0094
	5	1.184	1.205	12800	0.0109
	10	1.276	1.290	13800	0.0195
	15	1.304	1.320	14100	0.0438
	20	1.342	1.352	14500	0.0111

a, b, c, d See footnotes in Table VIII, page 98, for explanation.

TABLE XII

Effect of Reaction Temperature and Reaction Time
on Intrinsic Viscosity and Molecular Weight
of Poly(ethylene terephthalate) of
0.038 in. Mean Particle Diameter

Temperature	Time	$[\eta]_1^a$	$[\eta]_2^b$	\bar{M}_n^c	Confidence Limits ^d
°C	hr	dl/gm	dl/gm		dl/gm
160	0	0.660	0.659	18400	0.0178
	5	0.678	0.679	19000	0.0026
	10	0.685	0.685	19200	0.0026
	15	0.695	0.695	19600	0.0057
	20	0.709	0.710	20100	0.0092
180	0	0.643	0.644	17800	0.0106
	5	0.734	0.735	20900	0.0118
	10	0.797	0.796	23100	0.0049
	15	0.830	0.830	24300	0.0096
	20	0.849	0.849	25000	0.0028
200	0	0.645	0.647	17900	0.0046
	5	0.879	0.879	26100	0.0020
	10	0.978	0.979	29700	0.0224
	15	1.038	1.038	31900	0.0241
	20	1.084	1.083	33700	0.0103

a, b, c, d See footnotes in Table VIII, page 98, for explanation.

TABLE XIII

Effect of Reaction Temperature and Reaction Time
on Intrinsic Viscosity and Molecular Weight
of Poly(ethylene terephthalate) of
0.084 in. Mean Particle Diameter

Temperature	Time	$[\eta]_1^a$	$[\eta]_2^b$	\bar{M}_n^c	Confidence Limits ^d
°C	hr	dl/gm	dl/gm		dl/gm
160	0	0.651	0.652	18100	0.0048
	5	0.662	0.661	18400	0.0103
	10	0.673	0.673	18800	0.0074
	15	0.690	0.690	19400	0.0026
	20	0.702	0.701	19800	0.0058
180	0	0.638	0.640	17600	0.0073
	5	0.706	0.707	20000	0.0057
	10	0.749	0.750	21400	0.0065
	15	0.783	0.784	22600	0.0031
	20	0.806	0.805	23400	0.0037
200	0	0.636	0.638	17500	0.0018
	5	0.825	0.825	24100	0.0126
	10	0.909	0.907	27100	0.0080
	15	0.980	0.976	29700	0.0146
	20	0.999	0.996	30500	0.0141

a,b,c,d See footnotes in Table VIII, page 98, for explanation.

TABLE XIV

Variance Analysis of Poly(hexamethylene adipamide)

Intrinsic Viscosity

Source	Degree of Freedom	Sum of Squares	Mean Squares	F-Ratio
Whole Plot:				
Temperature	3	0.510139	0.170046	12.945*
Time	4	0.569928	0.142482	10.847*
Temperature x Time	12	0.157634	0.013136	
Split Plot:				
Particle Size	1	0.000456	0.000456	4.035
Particle Size x Temperature	3	0.000399	0.000133	1.177
Particle Size x Time	4	0.000663	0.000166	1.469
Residual	12	0.001357	0.000113	
Total	39	1.240576		

*Probability of significance = 0.99.

TABLE XV

Variance Analysis of Poly(hexamethylene sebacamide)

Intrinsic Viscosity

Source	Degree of Freedom	Sum of Squares	Mean Squares	F-Ratio
Whole Plot:				
Temperature	3	0.182871	0.060957	15.991*
Time	4	0.164294	0.041074	10.775*
Temperature x Time	12	0.045745	0.003812	
Split Plot:				
Particle Size	1	0.006451	0.006451	
Particle Size x Temperature	3	0.001054	0.000351	
Particle Size x Time	4	0.000019	0.000005	
Residual	12	0.002294	0.000191	
Total	39	0.402728		
Regrouped Split Plot:				
Particle Size	1	0.006451	0.006451	44.490*
Particle Size x Temperature	3	0.001054	0.000351	2.421
Residual	16	0.002313	0.000145	

*Probability of significance = 0.99.

TABLE XVI

Variance Analysis of Poly(ethylene terephthalate)

Intrinsic Viscosity

Source	Degree of Freedom	Sum of Squares	Mean Squares	F-Ratio
Whole Plot:				
Temperature	2	0.243366	0.121683	11.768*
Time	4	0.172222	0.043055	4.164**
Temperature x Time	8	0.082711	0.010339	
Split Plot:				
Particle Size	1	0.008168	0.008168	68.067*
Particle Size x Temperature	2	0.002559	0.00128	10.667*
Particle Size x Time	4	0.001348	0.000337	2.808
Residual	8	0.000961	0.000120	
Total	29	0.511335		

*Probability of significance = 0.99.

**Probability of significance = 0.95.

TABLE XVII

Values of $K(t)$ for Poly(hexamethylene adipamide)
of Mean Particle Diameter, 0.081 in.

Temperature °C	Time hr	$\bar{M}_{n,o} / \bar{M}_{n,t}$	α^*	$K_1(t)$
120	5	0.832	0.168	0.0546
	10	0.820	0.180	0.0627
	15	0.807	0.193	0.0722
	20	0.806	0.194	0.0729
140	5	0.795	0.205	0.0814
	10	0.762	0.238	0.1097
	15	0.723	0.277	0.1487
	20	0.721	0.279	0.1058
160	5	0.732	0.268	0.1392
	10	0.671	0.329	0.2098
	15	0.632	0.368	0.2624
	20	0.615	0.385	0.2872
180	5	0.659	0.341	0.2253
	10	0.569	0.431	0.3601
	15	0.530	0.470	0.4284
	20	0.480	0.520	0.5256

$$* = 1 - \frac{\bar{M}_{n,o}}{\bar{M}_{n,t}}$$

TABLE XVIII

Values of K(t) for Poly(hexamethylene adipamide)
of Mean Particle Diameter, 0.139 in.

Temperature °C	Time hr	$\bar{M}_{n,o} / \bar{M}_{n,t}$	α^*	$K_1(6)$
120	5	0.822	0.178	0.0614
	10	0.779	0.221	0.0946
	15	0.802	0.198	0.0760
	20	0.789	0.211	0.0863
140	5	0.802	0.198	0.0759
	10	0.761	0.239	0.1107
	15	0.753	0.247	0.1183
	20	0.712	0.288	0.1607
160	5	0.709	0.291	0.1641
	10	0.665	0.334	0.2175
	15	0.620	0.380	0.2798
	20	0.596	0.404	0.3163
180	5	0.631	0.369	0.2639
	10	0.546	0.454	0.3996
	15	0.495	0.505	0.4953
	20	0.452	0.548	0.5851

$$* \alpha = 1 - \frac{\bar{M}_{n,o}}{\bar{M}_{n,t}}$$

TABLE XIX

Values of $K(t)$ for Poly(hexamethylene sebacamide)
of Mean Particle Diameter, 0.085 in.

Temperature °C	Time hr	$\bar{M}_{n,o} / \bar{M}_{n,t}$	α^*	$K_1(t)$
120	5	0.960	0.049	0.0031
	10	0.937	0.063	0.0077
	15	0.930	0.070	0.0095
	20	0.908	0.092	0.0164
140	5	0.930	0.070	0.0095
	10	0.898	0.102	0.0202
	15	0.882	0.118	0.0270
	20	0.867	0.133	0.0343
160	5	0.898	0.102	0.0202
	10	0.865	0.135	0.0353
	15	0.842	0.158	0.0483
	20	0.816	0.184	0.0656
180	5	0.861	0.139	0.0373
	10	0.812	0.188	0.0684
	15	0.789	0.210	0.0863
	20	0.773	0.227	0.1000

$$* \alpha = 1 - \frac{\bar{M}_{n,o}}{\bar{M}_{n,t}}$$

TABLE XX

Values of $K(t)$ for Poly(hexamethylene sebacamide)
of Mean Particle Diameter, 0.134 in.

Temperature °C	Time hr	$\bar{M}_{n,o} / \bar{M}_{n,t}$	α^*	$K_1(t)$
120	5	0.984	0.016	0.0005
	10	0.973	0.027	0.0014
	15	0.969	0.031	0.0019
	20	0.955	0.045	0.0039
140	5	0.946	0.054	0.0057
	10	0.920	0.080	0.0124
	15	0.911	0.089	0.0154
	20	0.895	0.105	0.0214
160	5	0.890	0.110	0.0234
	10	0.859	0.141	0.0385
	15	0.836	0.164	0.0521
	20	0.812	0.188	0.0685
180	5	0.835	0.165	0.0527
	10	0.773	0.227	0.0998
	15	0.756	0.244	0.1153
	20	0.733	0.267	0.1381

$$* \alpha = 1 - \frac{\bar{M}_{n,o}}{\bar{M}_{n,t}}$$

TABLE XXI

Values of K(t) for Poly(ethylene terephthalate)
of Mean Particle Diameter, 0.038 in.

Temperature °C	Time hr	$\bar{M}_{n,o} / \bar{M}_{n,t}$	α^*	$K_2(t)$
160	5	0.968	0.032	0.0009
	10	0.956	0.044	0.0017
	15	0.939	0.061	0.0033
	20	0.916	0.084	0.0063
180	5	0.851	0.149	0.0207
	10	0.770	0.230	0.0520
	15	0.732	0.268	0.0724
	20	0.712	0.288	0.0847
200	5	0.685	0.315	0.1033
	10	0.602	0.398	0.1754
	15	0.560	0.440	0.2217
	20	0.531	0.469	0.2581

$$* \alpha = 1 - \frac{\bar{M}_{n,o}}{\bar{M}_{n,t}}$$

TABLE XXII

Values of K(t) for Poly(ethylene terephthalate)
of Mean Particle Diameter, 0.084 in.

Temperature °C	Time hr	$\bar{M}_{n,o} / \bar{M}_{n,t}$	α^*	$K_2(6)$
160	5	0.980	0.020	0.0003
	10	0.960	0.040	0.0014
	15	0.931	0.069	0.0043
	20	0.912	0.089	0.0070
180	5	0.884	0.116	0.0123
	10	0.822	0.178	0.0302
	15	0.779	0.221	0.0477
	20	0.752	0.248	0.0612
200	5	0.728	0.272	0.0748
	10	0.647	0.353	0.1333
	15	0.590	0.410	0.1879
	20	0.576	0.424	0.2032

$$* \alpha = 1 - \frac{\bar{M}_{n,o}}{\bar{M}_{n,t}}$$

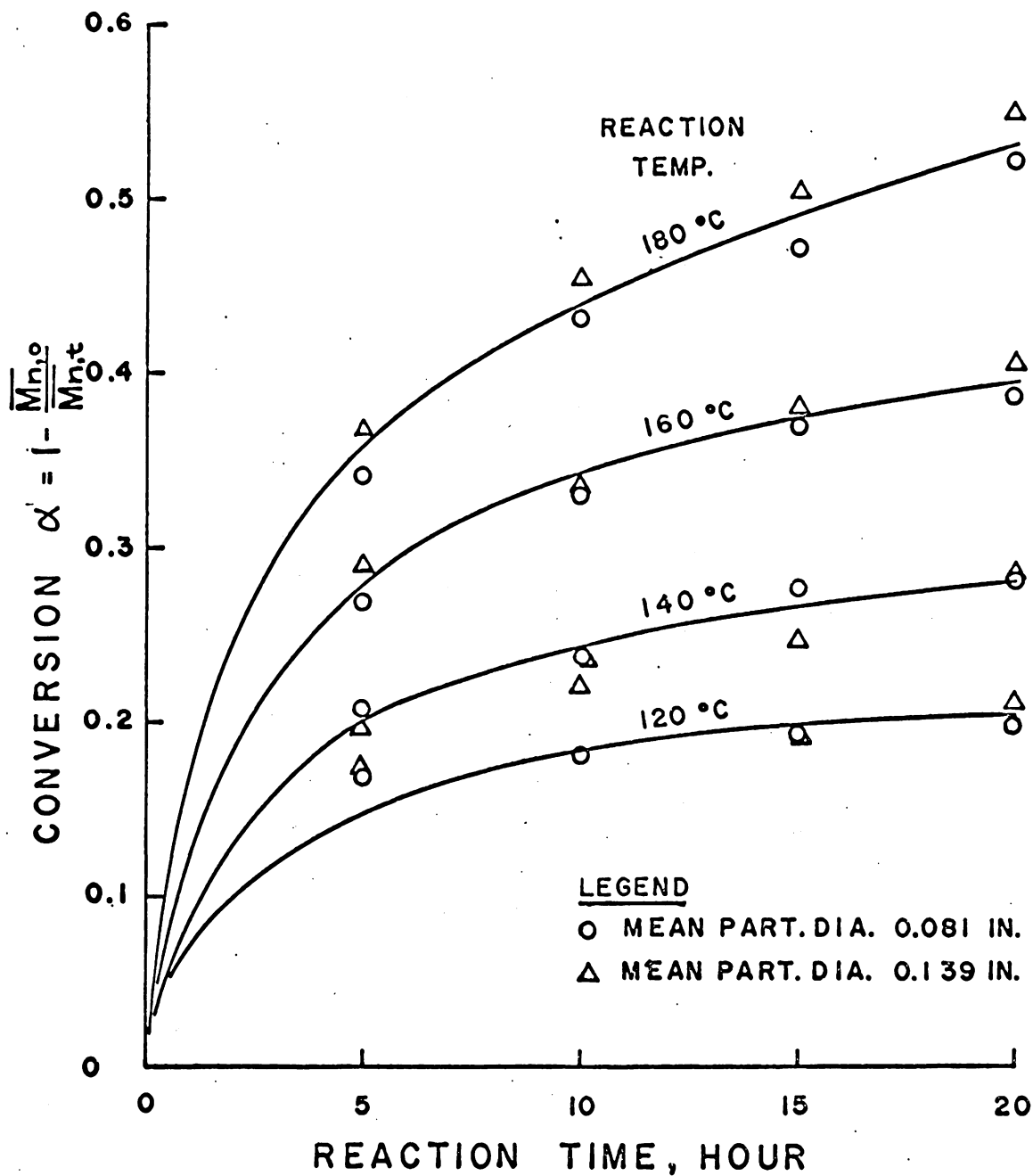


FIGURE 10. CONVERSION IN POLY(HEXAMETHYLENE ADIPAMIDE)

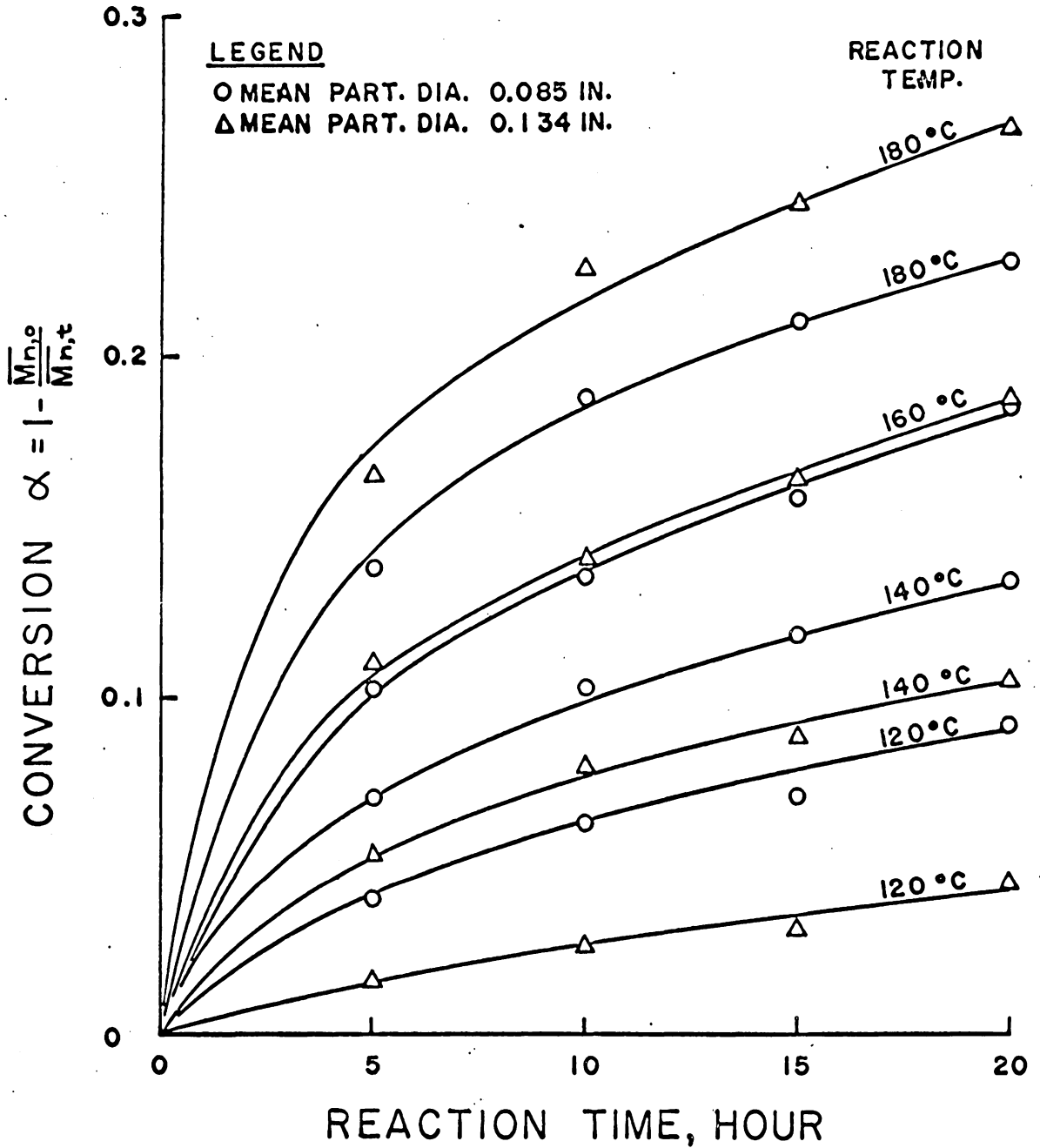


FIGURE 11. CONVERSION IN POLY(HEXAMETHYLENE SEBACAMIDE)

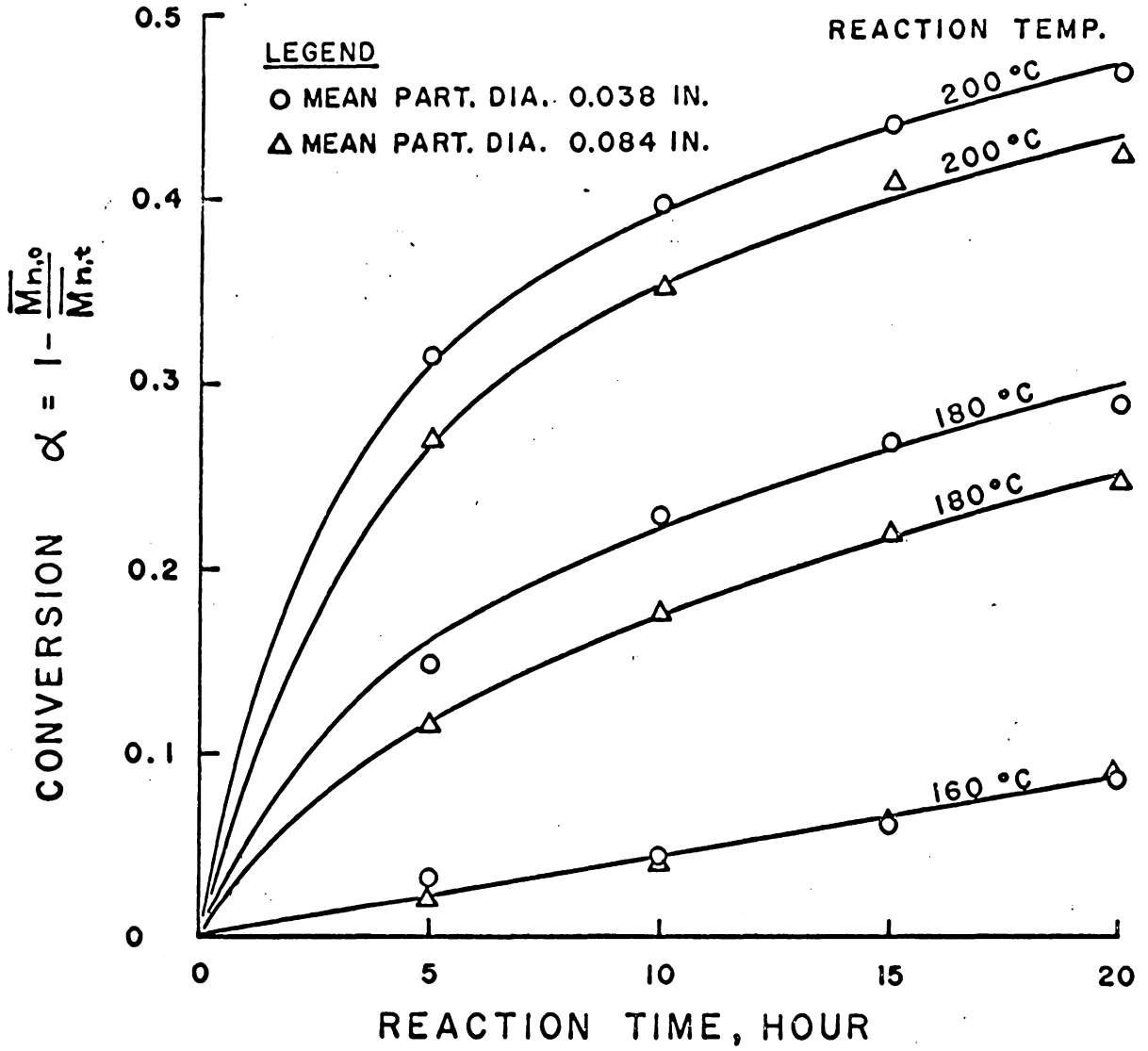


FIGURE 12. CONVERSION IN POLY(ETHYLENE TEREPHTHALATE)

TABLE XXIII

Specific Reaction Rate of Solid-Phase

Polycondensation

Polymer	Mean Particle Diameter	Temperature	Specific Reaction Rate		
	in.	°C	k*		
Poly(hexamethylene adipamide)	0.081	120	2 x 10 ⁻²		
		140	3.55 x 10 ⁻²		
	0.139	160	6.66 x 10 ⁻²		
		180	1.18 x 10 ⁻¹		
Poly(hexamethylene sebacamide)	0.085	120	7.11 x 10 ⁻⁴		
		140	1.86 x 10 ⁻³		
		160	3.52 x 10 ⁻³		
		180	6.27 x 10 ⁻³		
	0.134	120	1.41 x 10 ⁻⁴		
		140	1.12 x 10 ⁻³		
		160	3.86 x 10 ⁻³		
		180	8.78 x 10 ⁻³		
		Poly(ethylene terephthalate)	0.038	160	2.21 x 10 ⁻⁴
				180	4.60 x 10 ⁻³
200	1.65 x 10 ⁻²				
0.084	160		2.09 x 10 ⁻⁴		
	180	2.93 x 10 ⁻³			
	200	1.28 x 10 ⁻²			

*k's are expressed in (hr)^{-1/2} for poly(hexamethylene adipamide) and in (hr)⁻¹ for other polymers.

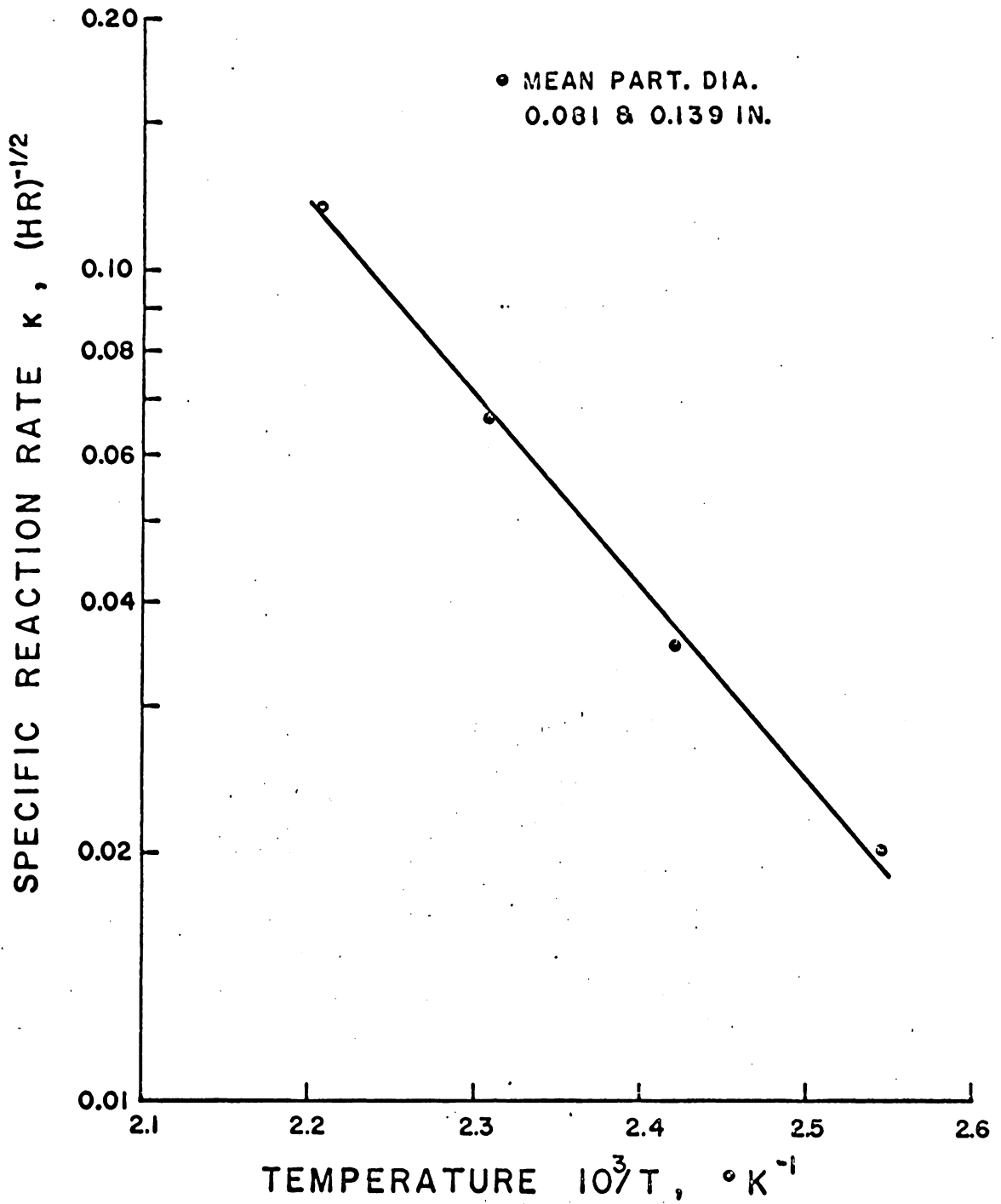


FIGURE 13. ARRHENIUS PLOT OF REACTION RATE FOR
POLY(HEXAMETHYLENE ADIPAMIDE)

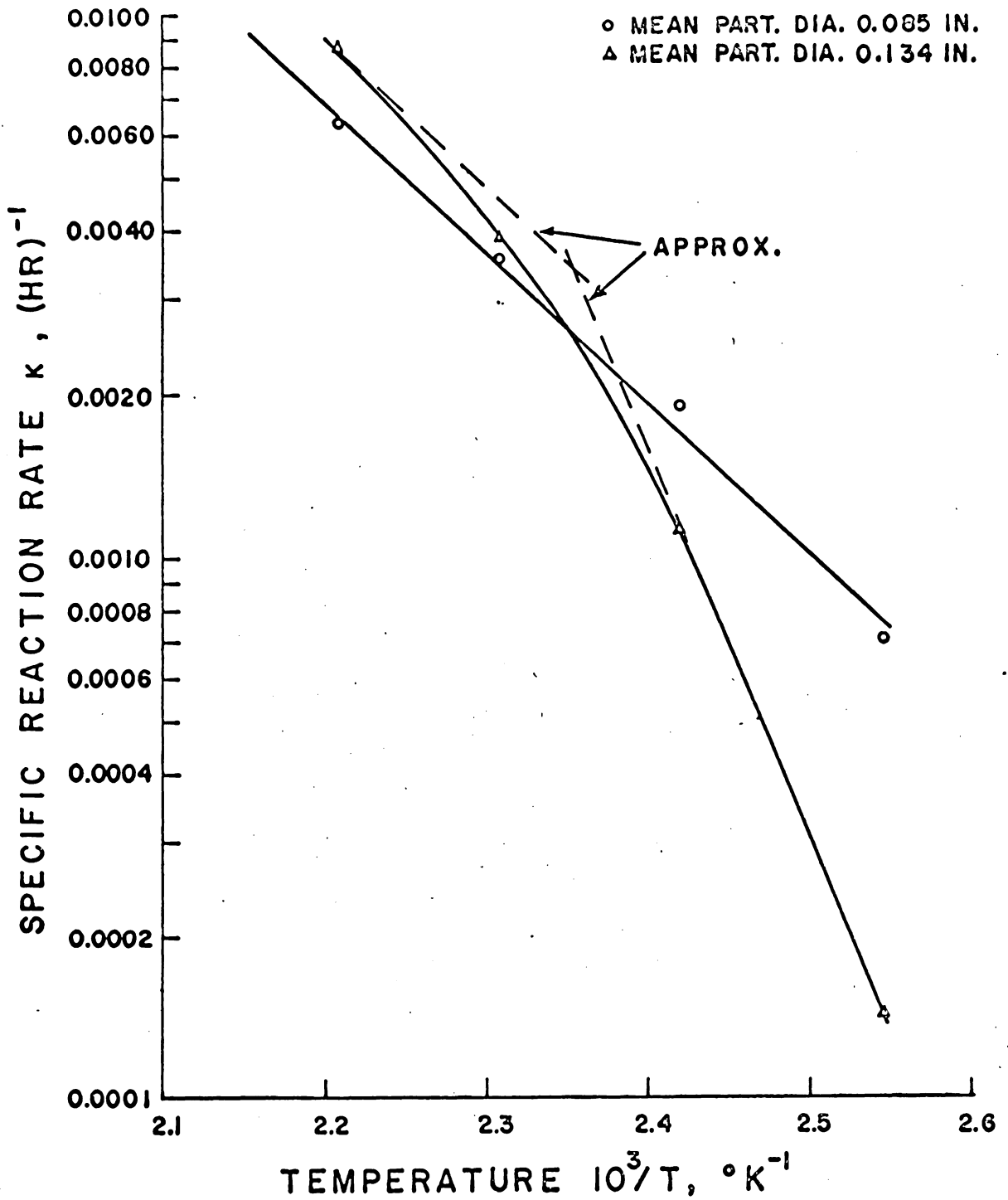


FIGURE 14. ARRHENIUS PLOT OF REACTION RATE FOR
POLY(HEXAMETHYLENE SEBACAMIDE)

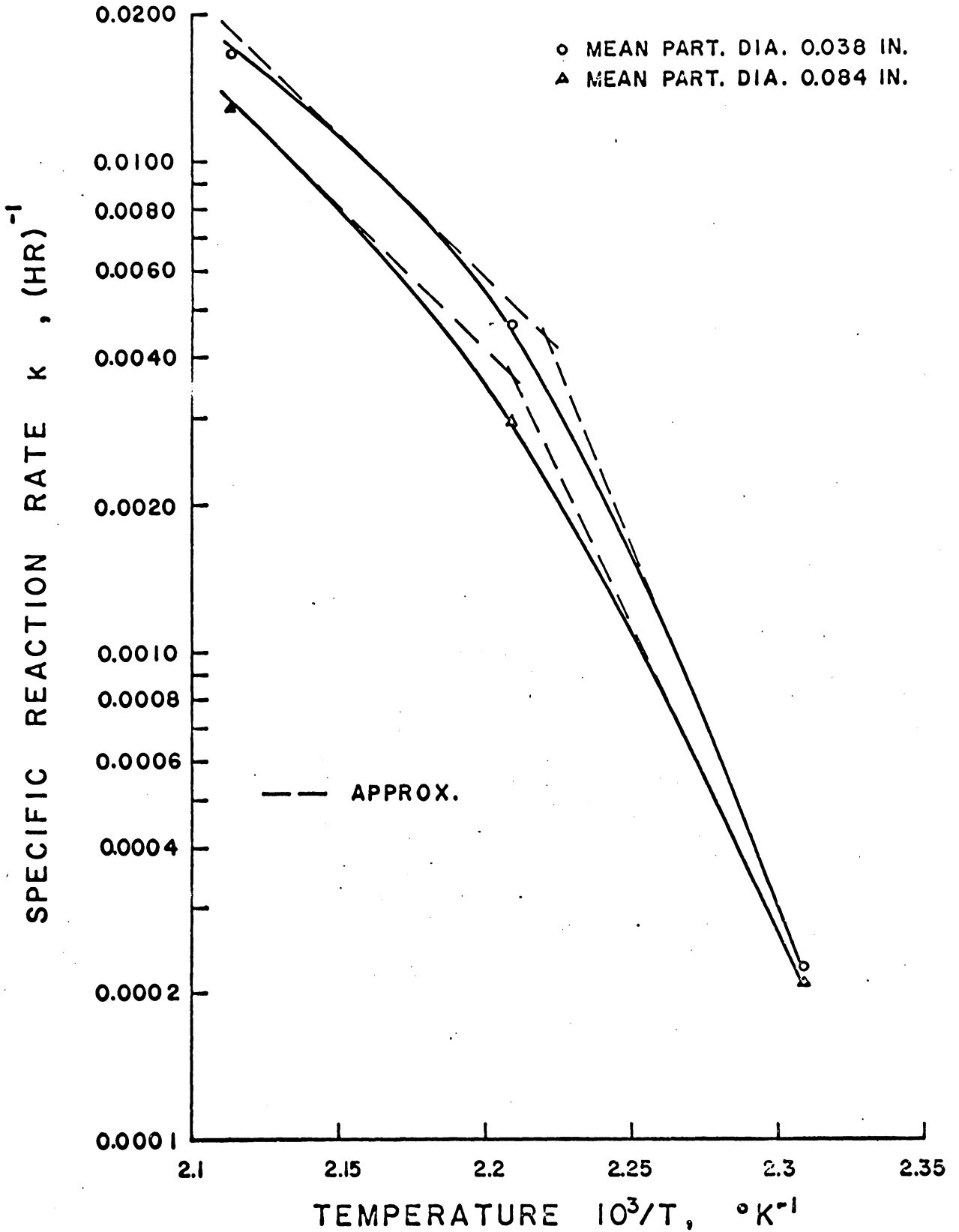


FIGURE 15. ARRHENIUS PLOT OF REACTION RATE FOR
POLY(ETHYLENE TEREPHTHALATE)

TABLE XXIV

Summary of Arrhenius Equations

Polymer	Arrhenius Equation	Remarks
Poly(hexamethylene adipamide)	$k = 1.39 \times 10^4 \exp\left(-\frac{10500}{RT}\right), \text{ hr}^{-1/2}$	For both particle sizes
Poly(hexamethylene sebacamide)	$k = 7.85 \times 10^3 \exp\left(-\frac{12600}{RT}\right), \text{ hr}^{-1}$	$\bar{D} = 0.085 \text{ in.}$
	$k = 1.05 \times 10^4 \exp\left(-\frac{12600}{RT}\right), \text{ hr}^{-1}$	$\bar{D} = 0.134 \text{ in.}$ $T > T_c$
	$k = 3.18 \times 10^{14} \exp\left(-\frac{33000}{RT}\right), \text{ hr}^{-1}$	$\bar{D} = 0.134 \text{ in.}$ $T < T_c$
Poly(ethylene terephthalate)	$k = 4.82 \times 10^{10} \exp\left(-\frac{26800}{RT}\right), \text{ hr}^{-1}$	$\bar{D} = 0.038 \text{ in.}$ $T > T_c$
	$k = 6.53 \times 10^{29} \exp\left(-\frac{66200}{RT}\right), \text{ hr}^{-1}$	$\bar{D} = 0.038 \text{ in.}$ $T < T_c$
	$k = 3.55 \times 10^{10} \exp\left(-\frac{26800}{RT}\right), \text{ hr}^{-1}$	$\bar{D} = 0.084 \text{ in.}$ $T > T_c$
	$k = 1.46 \times 10^{25} \exp\left(-\frac{57200}{RT}\right), \text{ hr}^{-1}$	$\bar{D} = 0.084 \text{ in.}$ $T < T_c$

TABLE XXV

Comparison of Calculated and Experimental Molecular Weights

Polymer: Poly(hexamethylene adipamide)

Mean Particle Diameter: 0.081 in.

Temperature °C	Time hr	K(t) _{cal}	$\left[\frac{\bar{M}_{n,o}}{\bar{M}_{n,t}} \right]_{cal}$	$\bar{M}_{n,cal}$	$\bar{M}_{n,exp}$	Error* %
120	5	0.043	0.851	11900	12100	- 1.7
	10	0.061	0.823	12300	12300	0
	15	0.074	0.804	12600	12500	0.8
	20	0.086	0.789	12800	12500	2.3
140	5	0.084	0.792	12500	12500	0
	10	0.119	0.752	13200	13100	0.8
	15	0.145	0.726	13600	13800	- 1.5
	20	0.168	0.705	14000	13800	1.4
160	5	0.152	0.720	14000	13800	1.4
	10	0.215	0.667	15100	15100	0
	15	0.263	0.631	16000	16000	0
	20	0.304	0.604	16700	16500	1.2
180	5	0.260	0.633	16600	16000	3.6
	10	0.367	0.565	18600	18500	0.5
	15	0.449	0.519	20200	19900	1.5
	20	0.519	0.483	21800	21900	- 0.5

$$*Error = \frac{\bar{M}_{n,cal} - \bar{M}_{n,exp}}{\bar{M}_{n,cal}} \times 100.$$

TABLE XXVI

Comparison of Calculated and Experimental Molecular Weights

Polymer: Poly(hexamethylene adipamide)

Mean Particle Diameter: 0.139 in.

Temperature °C	Time hr	$K(t)_{cal}$	$\left[\frac{\bar{M}_{n,o}}{\bar{M}_{n,t}} \right]_{cal}$	$\bar{M}_{n,cal}$	$\bar{M}_{n,exp}$	Error* %
120	5	0.043	0.851	11600	12100	- 4.3
	10	0.061	0.823	12000	12800	- 6.7
	15	0.074	0.804	12300	12400	- 0.8
	20	0.086	0.789	12600	12600	0
140	5	0.084	0.792	12600	12500	0.8
	10	0.119	0.752	13300	13100	1.5
	15	0.145	0.726	13800	13300	3.6
	20	0.168	0.705	14200	14100	0.7
160	5	0.152	0.720	14100	14100	0
	10	0.215	0.667	14900	15100	- 1.3
	15	0.263	0.631	15900	16200	- 1.9
	20	0.304	0.604	16500	16900	- 2.4
180	5	0.260	0.633	16100	16200	- 0.6
	10	0.367	0.565	18100	18800	- 3.9
	15	0.449	0.519	19700	20700	- 5.1
	20	0.519	0.483	21200	22600	- 6.6

$$*Error = \frac{\bar{M}_{n,cal} - \bar{M}_{n,exp}}{\bar{M}_{n,cal}} \times 100.$$

TABLE XXVII

Comparison of Calculated and Experimental Molecular Weights

Polymer: Poly(hexamethylene sebacamide)

Mean Particle Diameter: 0.085 in.

Temperature °C	Time hr	$K(t)_{cal}$	$\left[\frac{\bar{M}_{n,o}}{\bar{M}_{n,t}} \right]_{cal}$	$\bar{M}_{n,cal}$	$\bar{M}_{n,exp}$	Error* %
120	5	0.00385	0.955	10800	10800	0
	10	0.0077	0.937	11000	11000	0
	15	0.0115	0.923	11200	11100	0.9
	20	0.0154	0.911	11300	11400	- 0.9
140	5	0.00875	0.932	11200	11200	0
	10	0.0175	0.905	11500	11600	- 0.9
	15	0.0262	0.884	11800	11800	0
	20	0.0350	0.865	12000	12100	- 0.8
160	5	0.0175	0.904	11600	11800	- 1.7
	10	0.0350	0.865	12100	12200	- 0.8
	15	0.0525	0.835	12600	12500	0.8
	20	0.0700	0.809	13000	12900	0.8
180	5	0.0325	0.870	12400	12500	- 0.8
	10	0.0650	0.816	13200	13300	- 0.8
	15	0.0975	0.775	13900	13700	1.4
	20	0.1300	0.741	14600	14000	4.1

$$*Error = \frac{\bar{M}_{n,cal} - \bar{M}_{n,exp}}{\bar{M}_{n,cal}} \times 100.$$

TABLE XXVIII

Comparison of Calculated and Experimental Molecular Weights

Polymer: Poly(hexamethylene sebacamide)

Mean Particle Diameter: 0.134 in.

Temperature °C	Time hr	$K(t)_{cal}$	$\left[\frac{\bar{M}_{n,o}}{\bar{M}_{n,t}} \right]_{cal}$	$\bar{M}_{n,cal}$	$\bar{M}_{n,exp}$	Error* %
120	5	0.00070	0.981	10900	10900	0
	10	0.00141	0.973	11000	11000	0
	15	0.00212	0.967	11060	11100	- 0.4
	20	0.00282	0.961	11100	11200	- 0.9
140	5	0.0055	0.946	11600	11600	0
	10	0.0110	0.924	11900	11900	0
	15	0.0165	0.907	12100	12000	0.8
	20	0.0220	0.893	12300	12300	0
160	5	0.023	0.891	12100	12200	- 0.8
	10	0.046	0.845	12800	12600	1.6
	15	0.069	0.811	13300	13000	2.3
	20	0.092	0.782	13800	13400	2.9
180	5	0.0439	0.849	12600	12800	- 1.6
	10	0.0878	0.787	13600	13800	- 1.5
	15	0.1317	0.739	14500	14100	2.8
	20	0.1756	0.699	15300	14500	5.2

$$*Error = \frac{\bar{M}_{n,cal} - \bar{M}_{n,exp}}{\bar{M}_{n,cal}} \times 100.$$

TABLE XXIX

Comparison of Calculated and Experimental Molecular Weights

Polymer: Poly(ethylene terephthalate)

Mean Particle Diameter: 0.038 in.

Temperature °C	Time hr	$K(t)_{cal}$	$\left[\frac{\bar{M}_{n,o}}{\bar{M}_{n,t}} \right]_{cal}$	$\bar{M}_{n,cal}$	$\bar{M}_{n,exp}$	Error* %
160	5	0.001105	0.965	19100	19000	0.5
	10	0.00221	0.950	19400	19200	1.0
	15	0.00332	0.939	19600	19600	0
	20	0.00442	0.929	19800	20100	- 1.5
180	5	0.025	0.837	21200	20900	1.4
	10	0.050	0.774	23000	23100	- 0.4
	15	0.075	0.727	24500	24300	0.8
	20	0.100	0.689	25800	25000	3.1
200	5	0.092	0.701	25500	26100	- 2.4
	10	0.184	0.593	30100	29700	1.3
	15	0.276	0.517	34600	31900	7.8
	20	0.368	0.458	39000	33700	13.6

$$*Error = \frac{\bar{M}_{n,cal} - \bar{M}_{n,exp}}{\bar{M}_{n,cal}} \times 100.$$

TABLE XXX

Comparison of Calculated and Experimental Molecular Weights

Polymer: Poly(ethylene terephthalate)

Mean Particle Diameter: 0.084 in.

Temperature °C	Time hr	$K(t)_{cal}$	$\left[\frac{\bar{M}_{n,o}}{\bar{M}_{n,t}} \right]_{cal}$	$\bar{M}_{n,cal}$	$\bar{M}_{n,exp}$	Error* %
160	5	0.001045	0.966	18700	18400	1.6
	10	0.00209	0.951	19000	18800	1.1
	15	0.00314	0.940	19200	19400	- 1.0
	20	0.00418	0.931	19400	19800	- 2.1
180	5	0.018	0.860	20400	20000	2.0
	10	0.036	0.806	21800	21400	1.8
	15	0.054	0.766	23000	22600	1.7
	20	0.072	0.732	24000	23400	2.5
200	5	0.067	0.741	23600	24100	- 2.1
	10	0.134	0.646	27100	27100	0
	15	0.201	0.578	30300	29700	2.0
	20	0.268	0.523	33400	30500	8.7

$$*Error = \frac{\bar{M}_{n,cal} - \bar{M}_{n,exp}}{\bar{M}_{n,cal}} \times 100.$$

Sample Calculations

This section contains examples of the important calculations made in this investigation.

Mean Particle Diameter of Polymer Resin. Equations to compute the mean particle diameter of a polymer resin were taken from "Unit Operations of Chemical Engineering" by McCabe and Smith⁽⁸³⁾.

$$A_w = \frac{6\lambda}{\rho_p} \sum_{n=1}^{n_T} \frac{\Delta\phi_n}{\bar{D}_n} \quad (76)$$

Since \bar{D}_{vs} is defined as

$$\bar{D}_{vs} = \frac{6\lambda}{A_w \rho_p}, \quad (77)$$

\bar{D}_{vs} becomes

$$\bar{D}_{vs} = \frac{1}{\sum_{n=1}^{n_T} \frac{\Delta\phi_n}{\bar{D}_n}} \quad (78)$$

where:

- A_w = specific surface of mixture
- \bar{D}_{vs} = volume-surface mean diameter
- λ = geometric factor
- ρ_p = density of particles
- $\Delta\phi_n$ = fraction of the mixture retained on nth screen
- \bar{D}_n = average screen opening.

An example is given here to calculate the mean particle diameter of the fine grade poly(hexamethylene adipamide). Screen analysis data appear in Appendix A. Screen openings are listed in Perry's handbook⁽⁵⁾.

$$\bar{D}_{vs} = \frac{1}{\frac{0.171}{0.1129} + \frac{0.460}{0.0862} + \frac{0.242}{0.0724} + \frac{0.127}{0.0608}} = 0.081 \text{ in.}$$

Reynolds Number for Flow through a Packed Bed.

Reynolds number(Re_p) for flow in nitrogen through the polymer beds were calculated using Ergun's⁽¹³²⁾ definition of the Reynolds number.

$$Re_p = \frac{Du\rho}{\mu(1-\epsilon)} \quad (79)$$

where:

D = effective particle diameter

u = superficial velocity

ρ = density of fluid

μ = viscosity of fluid

ϵ = bed porosity = $\frac{\rho_p - \rho_B}{\rho_p}$; ρ_p is the density of the particle and ρ_B is the bulk density.

When consistent units are used, Re_p is dimensionless.

An example is given for 1000 cubic centimeters per minute of nitrogen (measured at 70 °F and 14.7 pounds per square inch, absolute) flowing through the reactor of cross-sectional area 0.0142 square feet. The reactor is packed with polymer of 0.081 inch particle size. Temperature of the reactor is maintained at 160 °C. Data given are:

$$D = 0.081 \text{ in.} = 0.00675 \text{ ft}$$

$$\rho = 0.0492 \text{ lb}_m/\text{cu ft at } 160 \text{ }^\circ\text{C and } 14.7 \text{ lb/sq in., abs}$$

$$\mu = 0.0232 \text{ cp} = 0.0000156 \text{ lb}_m/(\text{ft sec}) \text{ at } 160 \text{ }^\circ\text{C and } 14.7 \text{ lb/sq in., abs}$$

$$u = 0.0612 \text{ ft/sec at } 160 \text{ }^\circ\text{C and } 14.7 \text{ lb/sq in., abs}$$

$$\epsilon = (1.145 - 0.46)/1.145 = 0.599.$$

Then

$$\text{Re}_p = \frac{0.00675 \times 0.0612 \times 0.0492}{0.0000156(1 - 0.599)} = 3.27.$$

Intrinsic Viscosity. Polymer intrinsic viscosities were calculated from the data in Appendix D.

The intrinsic viscosity⁽²⁹⁾ is defined as

$$[\eta] = \lim_{C \rightarrow 0} \left(\frac{\eta_{sp}}{C} \right) = \lim_{C \rightarrow 0} \left(\frac{\ln \eta_r}{C} \right) \quad (80)$$

where:

$[\eta]$ = intrinsic viscosity, deciliters/gram,
or dl/gm

C = solution concentration, gm/dl

η_{sp} = specific viscosity = $(\eta_r - 1)$,
dimensionless

η_r = relative viscosity = (efflux time of
polymer solution)/(efflux time of
solvent), dimensionless.

Thus, plotting $\frac{\eta_{sp}}{C}$ or $\frac{\ln \eta_r}{C}$ versus C gives the value of $[\eta]$ at $C = 0$. For low solution concentrations ($C < 1$ gm/dl) the plot is a straight line.

In this investigation it was defined that

$$[\eta]_1 = \lim_{C \rightarrow 0} \left(\frac{\eta_{sp}}{C} \right)$$

and

$$[\eta]_2 = \lim_{C \rightarrow 0} \left(\frac{\ln \eta_r}{C} \right)$$

The disagreement between the values of $[\eta]_1$ and $[\eta]_2$ was an indication of the experimental error.

A digital computer program (Appendix E) was developed to calculate both $[\eta]_1$ and $[\eta]_2$ by the method of least squares. An example is given below to show the essential steps involved. Data were taken from Appendix D for poly(ethylene terephthalate), 0.038 inch particle size, treated at 200 °C for 20 hours. For the solution concentration $C = 0.6320$ gm/dl, the average efflux time was 369.77 seconds. Thus

$$\eta_r = \frac{369.77}{199.81} = 1.8506$$

where 199.81 was the solvent efflux time given in Appendix C. From the value of relative viscosity the quantities $\frac{\eta_{sp}}{C}$ and $\frac{\ln \eta_r}{C}$ were computed.

$$\frac{\eta_{sp}}{C} = \frac{1.8506 - 1}{0.6320} = 1.346 \text{ dl/gm}$$

$$\frac{\ln \eta_r}{C} = \frac{\ln 1.8506}{0.6320} = 0.974 \text{ dl/gm .}$$

The same procedure was repeated for the solution concentrations 0.4862, 0.3511, and 0.2431 gm/dl. The results were plotted against C in Figure 16. The straight lines

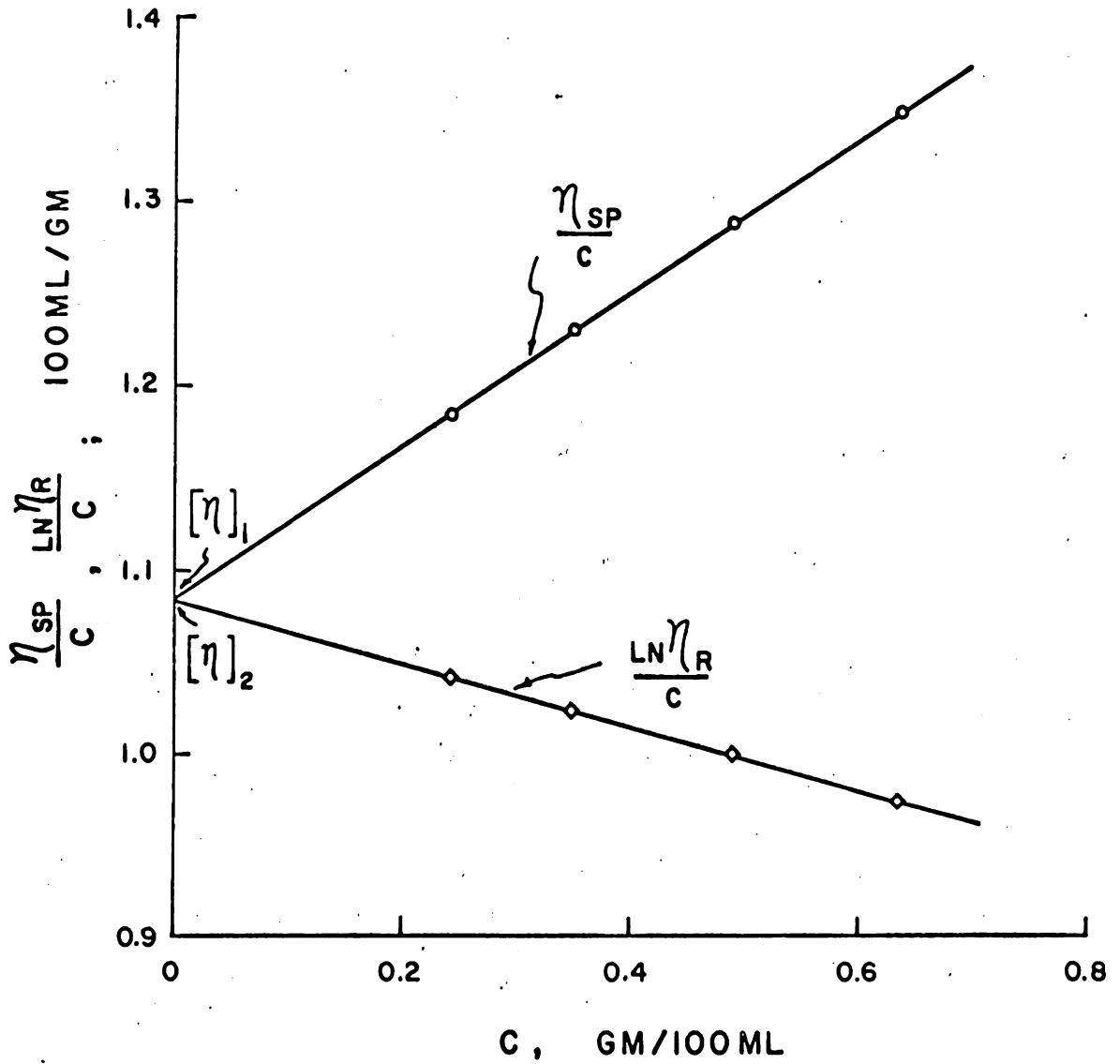


FIGURE 16. DETERMINATION OF INTRINSIC VISCOSITY

were obtained by least squares. Their intercepts on $C = 0$ were the values of $[\eta]_1$ and $[\eta]_2$.

$$[\eta]_1 = 1.084 \text{ dl/gm}$$

$$[\eta]_2 = 1.083 \text{ dl/gm.}$$

The 95 per cent confidence limits for $[\eta]_1$ were ± 0.0103 .

Number-Average Molecular Weights. The number-average molecular weights were computed from intrinsic viscosities using the empirical equations. For poly(hexamethylene adipamide) the equation by Taylor⁽¹¹⁹⁾ was used.

$$\bar{M}_n = 13,000 [\eta]^{1.39} \quad (2)$$

For poly(hexamethylene sebacamide) the equation by Morgan and Kwolek⁽⁹⁵⁾ was used.

$$\bar{M}_n = 10,700 [\eta]^{1.04} \quad (4)$$

For poly(ethylene terephthalate) the empirical equation by Conix⁽³³⁾ was employed.

$$\bar{M}_n = 30,500 [\eta]^{1.22} \quad (6)$$

Computations were made with the use of a digital computer. The program was actually part of the program developed to calculate the intrinsic viscosities. Values of $[\eta]_1$ were

used for computing the average molecular weights, because the constants appearing in the empirical equations were determined based on $[\eta]_1$. An example is given below to calculate the number-average molecular weight of poly(ethylene terephthalate) having an intrinsic viscosity of 1.084 dl/gm.

$$\bar{M}_n = 30,500 [1.084]^{1.22} = 33,652.$$

Since the confidence limits for the intrinsic viscosity were ± 0.0103 , the corresponding limits for the calculated molecular weight were ± 115 from the same equation. Hence, the molecular weight was reported to be 33,600.

Analysis of Variance. The technique of analysis of variance (Anova) for a split-plot design was used to examine the effects of reaction time, temperature, and polymer particle size on the polymer intrinsic viscosity. The model chosen was similar to that described in the book by Johnson and Leone⁽⁷³⁾.

$$X_{ijk} = \mu + A_i + C_k + (AC)_{ik} + B_j + (BA)_{ij} + (BC)_{jk} + (ABC)_{ijk} \quad (81)$$

where:

- X_{ijk} = intrinsic viscosity of a polymer of j th particle size, after reaction for k th duration at i th temperature
- μ = true mean of the intrinsic viscosity
- A_i = contribution to μ from i th temperature
- C_k = contribution to μ from k th reaction time
- $(AC)_{ik}$ = contribution to μ from A_i, C_k interaction
- B_j = contribution to μ from j th particle size
- $(BA)_{ij}$ = contribution to μ from B_j, A_i interaction
- $(BC)_{jk}$ = contribution to μ from B_j, C_k interaction
- $(ABC)_{ijk}$ = contribution to μ from A_i, B_j, C_k interaction
- i = 1, 2, ..., l reaction temperatures
- j = 1, 2, ..., m different particle sizes
- k = 1, 2, ..., n reaction durations.

The quantities, $(AC)_{ik}$ and $(ABC)_{ijk}$, were considered to be the whole-plot and split-plot errors, respectively, and were random variables in nature.

To compute the sum of squares(SS) the following equations were used. Let

$$T_{\dots} = \sum_i \sum_j \sum_k X_{ijk}$$

$$T_{i..} = \sum_j \sum_k X_{ijk}$$

$$T_{.j.} = \sum_i \sum_k X_{ijk}$$

$$T_{..k} = \sum_i \sum_j X_{ijk}$$

$$T_{ij.} = \sum_k X_{ijk}$$

$$T_{i.k} = \sum_j X_{ijk}$$

$$T_{.jk} = \sum_i X_{ijk}$$

Then

$$\text{Correction Factor(C.F.)} = \frac{T_{\dots}^2}{l mn}$$

$$SS_T = \sum_i \sum_j \sum_k X_{ijk}^2 - C.F.$$

$$SS_A = \sum_i \frac{T_{i..}^2}{mn} - C.F.$$

$$SS_B = \sum_j \frac{T_{.j.}^2}{ln} - C.F.$$

$$SS_C = \sum_k \frac{T_{..k}^2}{lm} - C.F.$$

$$SS_{AB} = \sum_i \sum_j \frac{T_{ij.}^2}{n} - SS_A - SS_B - C.F.$$

$$SS_{AC} = \sum_i \sum_k \frac{T_{i.k}^2}{m} - SS_A - SS_C - C.F.$$

$$SS_{BC} = \sum_j \sum_k \frac{T_{.jk}^2}{l} - SS_B - SS_C - C.F.$$

$$SS_{ABC} = \text{Residual} = SS_T - SS_A - SS_B - SS_C - SS_{AB} - SS_{AC} - SS_{BC} .$$

Table XXXI is a general format of the Anova table. Entries for poly(hexamethylene adipamide) were computed according to the procedures indicated below.

TABLE XXXI

Variance Analysis of a Split-Plot Design

Source	Degree of Freedom	Sum of Squares	Mean Square	Expected Mean Square
Whole Plot:				
A	$l-1$	SS_A	$\frac{SS_A}{l-1}$	$\sigma^2 + m \sigma_{Ac}^2 + \langle mn \sigma_A^2 \rangle$
C	$n-1$	SS_C	$\frac{SS_C}{n-1}$	$\sigma^2 + m \sigma_{Ac}^2 + \langle l m \sigma_C^2 \rangle$
AC	$(l-1)(n-1)$	SS_{AC}	$\frac{SS_{AC}}{(l-1)(n-1)}$	$\sigma^2 + m \sigma_{Ac}^2$
Split Plot:				
B	$m-1$	SS_B	$\frac{SS_B}{m-1}$	$\sigma^2 + \langle ln \sigma_B^2 \rangle$
BA	$(m-1)(l-1)$	SS_{AB}	$\frac{SS_{AB}}{(m-1)(l-1)}$	$\sigma^2 + \langle n \sigma_{AB}^2 \rangle$
BC	$(m-1)(n-1)$	SS_{BC}	$\frac{SS_{BC}}{(m-1)(n-1)}$	$\sigma^2 + \langle l \sigma_{BC}^2 \rangle$
Residual	$(l-1)(m-1)(n-1)$	SS_{ABC}	$\frac{SS_{ABC}}{(l-1)(m-1)(n-1)}$	σ^2
Total	$lmn-1$	SS_T		

$$T_{...} = 0.834 + 0.952 + \dots + 1.396 + 1.490 = 42.221$$

$$T_{i..} = 1.659 + 1.902 + \dots + 1.940 + 1.952 = 9.402, \text{ for}$$

$$A_i = 120 \text{ }^\circ\text{C}$$

$$T_{.j.} = 3.353 + 4.130 + \dots + 4.533 + 4.660 = 21.043, \text{ for}$$

$$B_j = 0.081 \text{ in.}$$

$$T_{..k} = 0.952 + 0.950 + \dots + 1.160 + 1.173 = 8.228, \text{ for}$$

$$C_k = 5 \text{ hr}$$

$$T_{ij.} = 0.834 + 0.952 + \dots + 0.973 + 0.974 = 4.695, \text{ for}$$

$$A_i = 120 \text{ }^\circ\text{C} \text{ and } B_j = 0.081 \text{ in.}$$

$$T_{i.k} = 0.952 + 0.950 = 1.902, \text{ for}$$

$$A_i = 120 \text{ }^\circ\text{C} \text{ and } C_k = 5 \text{ hr}$$

$$T_{.jk} = 0.952 + 0.973 + 1.045 + 1.160 = 4.130, \text{ for}$$

$$B_j = 0.081 \text{ in. and } C_k = 5 \text{ hr}$$

$$C.F. = 42.221^2 / 40 = 44.565321.$$

$$\begin{aligned}SS_T &= 0.834^2 + 0.973^2 + \dots + 1.396^2 + 1.490^2 - C.F. \\ &= 1.240576\end{aligned}$$

$$SS_A = (9.402^2 + \dots + 12.325^2)/10 - C.F. = 0.510139$$

$$SS_B = (21.043^2 + 21.178^2)/10 - C.F. = 0.000456$$

$$SS_C = (6.679^2 + \dots + 9.392^2)/8 - C.F. = 0.569928$$

$$\begin{aligned}SS_{AB} &= (4.695^2 + \dots + 6.203^2)/5 - SS_A - SS_B - C.F. \\ &= 0.000399\end{aligned}$$

$$\begin{aligned}SS_{AC} &= (1.659^2 + \dots + 2.947^2)/2 - SS_A - SS_C - C.F. \\ &= 0.157634\end{aligned}$$

$$\begin{aligned}SS_{BC} &= (3.353^2 + \dots + 4.732^2)/4 - SS_B - SS_C - C.F. \\ &= 0.000663\end{aligned}$$

$$SS_{ABC} = 0.001357, \text{ by difference.}$$

The mean square (MS) of A, for example, was calculated from

$$MS_A = \frac{SS_A}{1-1} = \frac{0.510139}{3} = 0.170046.$$

The F-ratio of A was calculated from

$$\frac{MS_A}{MS_{AC}} = \frac{0.170046}{0.013136} = 12.945.$$

Others were obtained in the same way.

Molecular Weight Ratio. The molecular weight ratios listed in Tables XVII to XXII, pages 107 to 112, were calculated from the following equations:

$$\frac{\bar{M}_{n,o}}{\bar{M}_{n,t}} = \left[\frac{[\eta]_{1,o}}{[\eta]_{1,t}} \right]^{1.39} \quad \text{for poly(hexamethylene adipamide)}$$

$$\frac{\bar{M}_{n,o}}{\bar{M}_{n,t}} = \left[\frac{[\eta]_{1,o}}{[\eta]_{1,t}} \right]^{1.04} \quad \text{for poly(hexamethylene sebacamide)}$$

$$\frac{\bar{M}_{n,o}}{\bar{M}_{n,t}} = \left[\frac{[\eta]_{1,o}}{[\eta]_{1,t}} \right]^{1.22} \quad \text{for poly(ethylene terephthalate)}.$$

For example, $[\eta]_{1,o} = 0.834$ and $[\eta]_{1,t} = 0.952$ for poly(hexamethylene adipamide) at 120 °C reaction from Table VIII, page 98. Then,

$$\frac{\bar{M}_{n,o}}{\bar{M}_{n,t}} = \left[\frac{0.834}{0.952} \right]^{1.39} = 0.832.$$

Specific Reaction Rate. Specific reaction rates were found by fitting a straight line to the values of $K(t)$ against t for every temperature. The equation used was

$$K(t) = kt^m \quad (82)$$

where:

$$K(t) = K_1(t) \text{ or } K_2(t) \text{ in equation 72 or 74}$$

$$k = \text{specific reaction rate, hr}^{-m}$$

$$t = \text{time, hr}$$

$$m = \text{constant, independent of temperature.}$$

As an example, plotting $K_1(t)$ of poly(hexamethylene adipamide) against $t^{1/2}$ yielded a straight line for every one of the four temperatures investigated (see Figure 17). The slope of these lines are the specific reaction rates. For example, at 120 °C the specific reaction rate $k = 0.02 \text{ hr}^{-1/2}$.

For poly(hexamethylene sebacamide) and poly(ethylene terephthalate) the ratios of $K(t)$ to t showed a small variation at a given temperature. An average of these ratios was taken to be the specific reaction rate. For example, the ratios for poly(hexamethylene sebacamide) of 0.085 inch average particle diameter, treated at 140 °C for 5, 10, 15, and 20 hours were 0.0019, 0.00202,

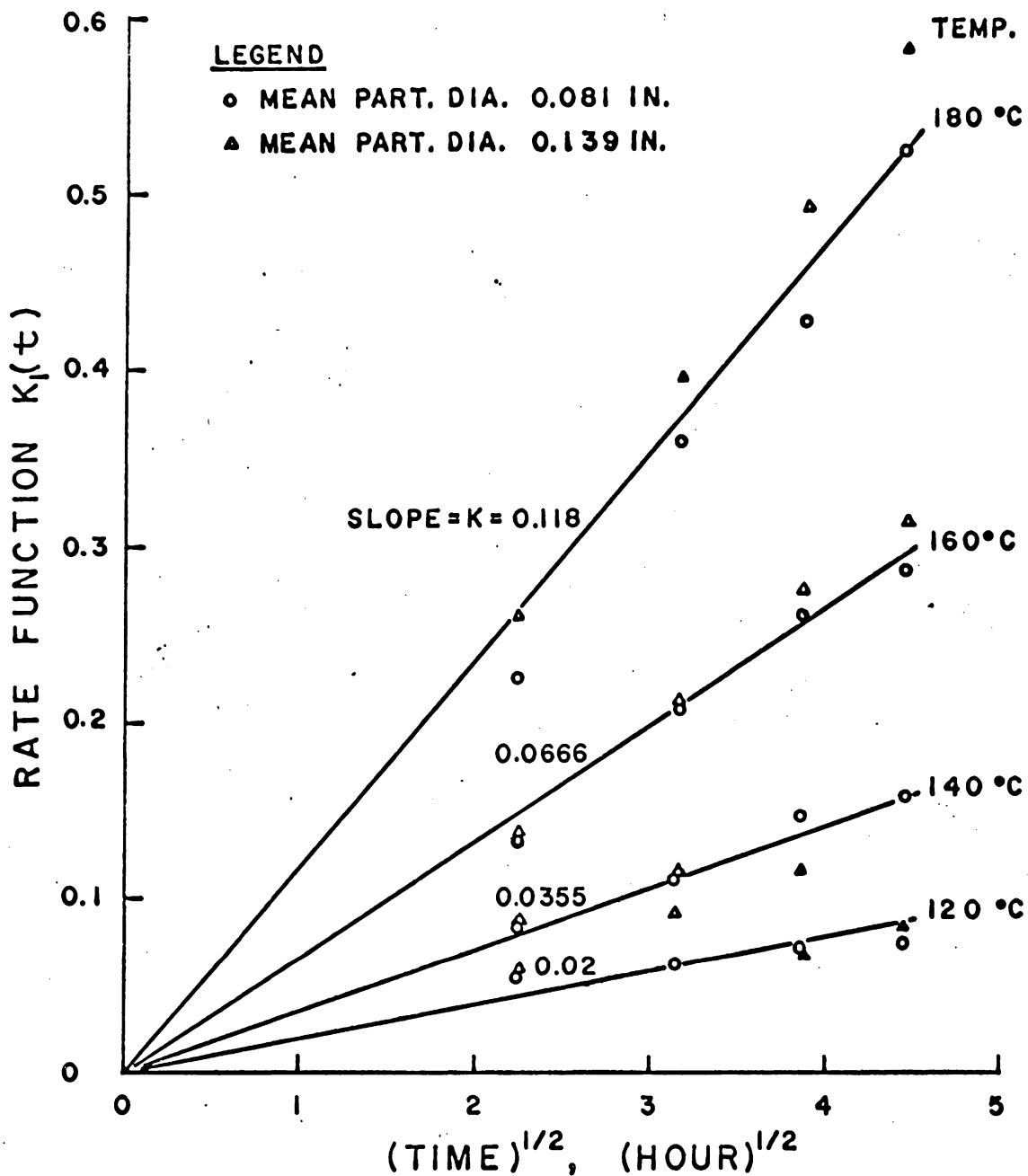


FIGURE 17. DETERMINATION OF SPECIFIC REACTION RATES FOR POLY(HEXAMETHYLENE ADIPAMIDE)

0.00180, and 0.00172, respectively. The value 0.0019, for instance, was computed from

$$\frac{K_1(t)}{t} = \frac{0.0095}{5} = 0.0019$$

in which 0.0095 was $K_1(t)$ tabulated in Table XIX, page 109.

The specific reaction rate was

$$k = \frac{0.0019 + 0.00202 + 0.00180 + 0.00172}{4} \\ = 0.00186.$$

In this case the rate function had an expression of

$$K_1(t) = kt, \text{ with } k \text{ in } (\text{hour})^{-1}.$$

Arrhenius Equation. The Arrhenius equation was used to express the temperature dependency of a specific reaction rate. The Arrhenius equation is written as

$$k = A \exp\left(-\frac{E}{RT}\right) \quad (83)$$

where:

- k = specific reaction rate, hr^{-m}
- A = frequency factor, hr^{-m}
- E = activation energy, cal/gm-mole
- R = gas constant, 1.987 cal/gm-mole
- T = temperature, °K.

As an example, from Figure 13, page 117, the slope of the straight line is

$$-\frac{E}{R} = \frac{\ln 1.87 \times 10^{-2} - \ln 1.2 \times 10^{-1}}{(2.55 - 2.2) \times 10^{-3}} = -5.3 \times 10^3;$$

hence,

$$E = 5.3 \times 10^3 \times 1.987 = 10,500 \text{ cal/gm-mole.}$$

From equation 83 the value of A is calculated from

$$\ln A = \ln k + E/(RT).$$

Since $k = 7 \times 10^{-2}$ at $(1/T) = 2.3 \times 10^{-3}$,

$$\ln A = \ln 7 \times 10^{-2} + 5.3 \times 10^3 \times 2.3 \times 10^{-3} = 9.541$$

and

$$A = 1.39 \times 10^4.$$

The resulting Arrhenius equation is

$$k = 1.39 \times 10^4 \exp \left(-\frac{10500}{RT} \right) \text{ hr}^{-1/2}.$$

Comparison of Calculated and Experimental Molecular Weights. The example given here shows the procedures used to obtain the calculated data in Tables XXV to XXX, pages 121 to 126.

For poly(hexamethylene adipamide) having 0.081 inch average particle diameter, treated at 180 °C, the specific reaction rate was read from the Arrhenius plot (Figure 13, page 117) to be $0.116 \text{ hr}^{-1/2}$. The rate function $K_1(t)$ was computed for a reaction time of 15 hours.

$$K_1(t)_{\text{cal}} = 0.116 (15)^{1/2} = 0.499.$$

The ratio of molecular weights was found from the table (an excerpt of the table is given in Table LXIV, page 241).

$$\left[\frac{\bar{M}_{n,o}}{\bar{M}_{n,t}} \right]_{\text{cal}} = 0.519 \quad \text{for } K_1(t) = 0.499.$$

Since $\bar{M}_{n,o} = 10500$ from Table VIII, page 103,

$$\bar{M}_{n,\text{cal}} = \frac{10500}{0.519} = 20200.$$

The difference between the calculated and the experimental molecular weights was expressed as per cent error of the calculated molecular weight.

$$\begin{aligned} \text{Error} &= \frac{\bar{Mn}_{\text{cal}} - \bar{Mn}_{\text{exp}}}{\bar{Mn}_{\text{cal}}} \times 100 = \frac{20200 - 19900}{20200} \times 100 \\ &= 1.5 \% \end{aligned}$$

in which $\bar{Mn}_{\text{exp}} = 19900$.

V. DISCUSSION

The results of the investigation are discussed in this section under the headings: literature review, experimental procedure, kinetic equations, and data and results. Recommendations for future study and limitations encountered in this investigation are presented at the end of the section.

Literature Review

The possibility of increasing the molecular weights of certain solid condensation polymers has been recognized for some time in the polymer industry. In 1939, Fenkel⁽⁵⁷⁾ and Pacsu⁽¹⁰⁰⁾ showed that continued polyamidation below the melting points of the polymers was feasible. Since then several patents^(38,40,50,91,124,125) have been assigned to various industrial firms for solid-phase polycondensation processes. Unfortunately, basic kinetic information is generally precluded from patent publication.

The kinetic studies^(65,66,88,127,131) were made primarily for the polyamidation reaction. Moreover, poly(hexamethylene adipamide), or nylon 66, was the

polymer most commonly chosen for the investigation. Aside from polyamides, no exploratory work was reported for the kinetics of solid-phase polycondensation of polyesters.

Among the studies on the solid-phase polycondensation of poly(hexamethylene adipamide) there was no general model to describe the reaction. Harding and MacNulty⁽⁶⁶⁾, in their study on the embrittlement of nylon 66, assumed a pseudo-unimolecular reaction and obtained the activation energy of 19.6 kilocalories per gram mole for the condensation reaction. Griskey and Lee⁽⁶⁵⁾, on the other hand, discovered that the reaction followed the power-law model⁽⁷²⁾ and obtained the activation energy of 12.9 kilocalories per gram mole. The power-law model,

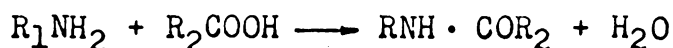
$$\text{Rate of change} = kt^n$$

in which k is the rate constant; t , time; and n , a constant, is frequently used to describe the nucleation step in the decomposition reaction of inorganic substances. The assumption followed in the derivation is that more than one event is necessary to form an active nucleus. With this assumption, it is shown that n is an integer^(72,116). Mathematically, this model dictates that at time zero, the rate should also be zero. The

value of n reported by Griskey and Lee⁽⁶⁵⁾ was -0.49 . There were finite rates at zero time for all temperatures in their study.

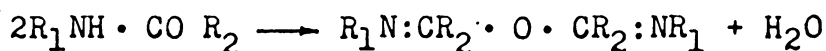
Volokhina et al.⁽¹²⁷⁾ investigated the polyamidation process in the solid state, but did not propose a kinetic model. Neither did they explain the mechanism of the reaction. Polyamidation of nylon 6 reported by Matsuda and co-workers^(87,88) could not be classified as a solid-phase process since the range of temperatures included the melting point of the polymer. They treated their data according to a second-order reaction and computed the activation energy to be 12.7 kilocalories per gram mole. However, the order of reaction was the same as that reported by Flory⁽⁴⁵⁾ for a melt-phase process.

While the kinetic models used varied from one investigation to another, the mechanism of reaction was generally accepted simply as continued condensation of the carboxyl and the amine end-groups^(65,66,88) identical to that observed in a melt-phase process.



Harding and MacNulty⁽⁶⁶⁾ also pointed out that a cross-linking reaction was unlikely to occur in view of the

continued solubility of the product in the solvent. A crosslinked material would be insoluble. Achhammer et al.⁽²⁾, on the contrary, proposed that the formation of water in the pyrolysis of polyamide in vacuo resulted from a crosslinking reaction.



The disagreement has not been rationalized.

Volokhina and co-workers⁽¹²⁷⁾ observed that the polyamidation in the solid state was an endothermic reaction. Ogata⁽⁹⁸⁾, Heikens et al.⁽⁶⁸⁾, and Tobolsky et al.⁽¹²⁰⁾ reported that polyamidation in melt or solution phases was exothermic.

The kinetic study of solid-state polymerization of poly(hexamethylene sebacamide), or nylon 610, was limited to the work by O'Connor⁽⁹⁶⁾. His exploratory work was rather qualitative. However, mass transfer was postulated to be the controlling factor rather than chemical kinetics. Griskey and Lee⁽⁶⁵⁾ concluded that chemical reaction was the rate controlling step since no pronounced effect was discerned by varying the flow of nitrogen from 1.5 to 7.64 standard cubic feet per hour. In a reaction involving solids, the rate governing step(s) may be one or more of

the three processes: mass transport through solid, mass transport through film, and chemical kinetics. Varying the flow of nitrogen primarily affects the film resistance. Hence, insignificance of this resistance as concluded in the investigation⁽⁶⁵⁾ would imply that either the mass transport through solid or chemical kinetics, or possibly both, could control the rate of reaction.

In addition to the increase of molecular weight observed in the solid-phase polyamidation reactions, Zimmerman⁽¹³¹⁾ found that there was a tendency to obtain broader than normal molecular weight distributions. This was explained to be the result of microscopic nonuniformity of the solid reagent.

Research on the solid-phase condensation polymerization was sporadic. No attempt was made to investigate the kinetics involved using a generalized approach.

Experimental Procedure

The experimental procedures in this investigation are examined for possible improvements and sources of error. Where possible, an order-of-magnitude of the error is estimated.

Apparatus. The reactor shown in Figure 1, page 47, was found to be adequate. Good temperature control was achieved through the use of preheated nitrogen. A maximum variation of ± 1 °C was noted at all temperature levels. Uniform heating of the polymer was believed to exist, since the body of the reactor was also maintained at the controlled temperature. The system used by Lee⁽⁸⁰⁾, however, showed a temperature gradient of as much as 15 °C across the bed of the polymer.

Determination of Purge Time. Discoloration of the polymer from degradation was the criterion used to determine the purge time. Solid polymers absorb moisture and air which are difficult to eliminate by a simple purging operation. Oxygen in air is detrimental to polymers at elevated temperatures. Since there was no serious discoloration noted under the conditions studied, it was believed that the purge time used was sufficient. In future studies a gas analyzer is suggested for determining optimum purge time.

Heating and Cooling of the Reactor Assembly. As shown in Figures 5 and 6, pages 91 and 92, the times required to heat the reactor assembly and to cool it from a controlled temperature were about 20 and 30 minutes, respectively.

Theoretically, it is desirable that absolutely no reaction occurs during these transient periods. But, this is difficult to realize in practice. In order to keep the reaction to a minimum, the flow of nitrogen was terminated and the reactor was pressurized (approximately 10 pounds per square inch, gage).

There remained a question as to whether or not the temperature at the center of the solid polymer reached the desirable reaction temperature at the end of the heat-up period. To check this, the equation given by Carslaw and Jaeger⁽²⁸⁾ for heat conduction through a slab with the surface temperature varying with time was used to compute the temperature at the center of the slab

after 20 minutes. The equation reduced from that given by Carslaw and Jaeger is

$$T = T_f - T_f e^{-\beta t} \frac{1}{\cos l (\beta / K)^{1/2}} - \frac{16 T_f l^2}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n e^{-K(2n+1)^2 \pi^2 t / 4l^2}}{(2n+1) [4\beta l^2 - K\pi^2 (2n+1)^2]} \quad (84)$$

where:

T = temperature at the center of the slab, °C

T_f = final temperature, °C

l = half thickness of the slab, cm

K = k/ρ , in which k is thermal conductivity and ρ density, cal, $\text{cm}^2/(\text{min})(\text{gm})(^\circ\text{C})$

β = a constant in $T_s = T_f(1 - e^{-\beta t})$ in which T_s is the surface temperature

t = time, min.

Thermal conductivities, k 's, of poly(hexamethylene adipamide) and poly(ethylene terephthalate) reported by Pickett⁽¹⁰³⁾ and Ringwald⁽¹⁰⁴⁾ are:

k = 0.035 cal/(min)(cm^2)(°C/cm) for poly(hexamethylene adipamide)

k = 0.0202 cal/(min)(cm^2)(°C/cm) for poly(ethylene terephthalate).

Since the thermal conductivity of poly(hexamethylene sebacamide) was not available in the literature, it was assumed to be the same as the value for poly(hexamethylene adipamide).

Densities of the polymers were taken from Table III, page 88.

The values of β determined from the data included in Appendix B, were 0.25 for 120 to 180 °C and 0.32 for 200 °C.

The mean particle diameters shown in Table IV, page 89, were taken as the thicknesses of the slabs.

In using equation 84, the first term in the summation was used since additional terms contributed little to the computed temperature. The results revealed that the temperature at the center of the polymer differed from the desired temperature by 1 °C in all cases.

Arrangement of Polymer in a Reactor. Two layers of polymers were placed in a reactor. Each layer contained a different average particle size. The choice of which polymer size occupied the upper layer was decided by a random process. Despite the outcome of this process, the upper layer would be constantly exposed to fresh nitrogen; whereas the lower layer would have to receive nitrogen containing the by-products released from the

polymer in the upper layer. Consequently, the driving force for removing the by-products from the polymer in the lower layer would be somewhat reduced. In order to assess the effect of the relative position on the extent of reaction, several tests were made using a single bed of poly(hexamethylene adipamide) at 160 °C for various reaction periods. No difference in intrinsic viscosity was detected between the polymers from the single-layer tests and those from the lower layers of the two-layer tests.

The advantage of the two-layer technique is that a polymer of two particle sizes is tested under identical conditions permitting a direct comparison of the results.

Determination of Intrinsic Viscosity. Extreme care was exercised in the preparation of polymer solutions for viscometry. Polymers were weighed accurately to 0.1 milligram. All volumetric measuring devices were calibrated against a standard unit. Fritted, medium-grade Büchner funnels were used to filter the reagents and the solutions prepared. Viscosity determinations were made at 25 °C with a maximum variation of ± 0.01 °C. The error most likely to occur in this work was the correction of solution concentration for pigment content. Since it was not practical to determine the pigment content for

every polymer sample prior to solution preparation, an average value (Table V, page 90) was used. Thus, non-uniform dispersion of the pigment in solid polymers would introduce error in computing the solution concentration. This error could not be assessed exactly. However, it was believed to be insignificant since, on the average, a difference of 0.003 deciliter per gram was found between the two intrinsic viscosities determined with and without corrections.

No correction was needed for samples of poly(hexamethylene sebacamide) because it contained no delustering agent.

Differential Thermal Analysis. Difficulties arose in conducting the differential thermal analysis of polymer samples. The major difficulty was the irregular shape of a polymer particle which did not permit uniform contact of the polymer with its support, an aluminum dish. As a result an accurate differential temperature was difficult to obtain. The support for the sample was not large enough to retain a coarse particle so that samples of large particle size were not examined. The rate of heating (10 °C per minute, unadjustable) was too fast to permit detection of the second-order transition

temperature. A 2 to 3 °C rise per minute is more desirable for polymer studies.

Kinetic Equations

The assumptions used in deriving the kinetic equations and the applications of these equations are discussed here.

Assumptions Used in the Derivations. The assumptions used in deriving the kinetic equations are listed below:

1. One-dimensional diffusion of by-products.
2. Omission of a source term in the diffusion equation.
3. Time dependency of the diffusion coefficient.
4. Time dependency of the rate function.

The validity of assuming a one-dimensional diffusion of the by-product depends on the geometry of the particle and the structural property of the polymer. If the polymer sample has a shape of a sheet of film or a spherical particle and if the polymer is isotropic, there is no ambiguity about this assumption. The polymers were considered to be isotropic in formulating the equations. This was necessary since a preferred direction of diffusion was not identifiable. The solid polymers used had irregular shapes; however, flakes or chips were

assumed to be plane sheets and powders were thought of as spherical particles in order to reduce the complexity of the mathematical model.

The raw polymer resins were the finished products of the melt-phase polymerization. The resins contained polymers of various molecular sizes and the by-products existing in an equilibrium state. In order to further the polymerization in the solid phase it is necessary to remove the by-products left from the melt process. Once a by-product molecule is removed a new by-product molecule is formed from the condensation of two active end groups. Thus, the diffusion equation should include a source term to account for the production of the by-product molecules.

$$\frac{\partial C}{\partial t} = D(t) \frac{\partial^2 C}{\partial x^2} + R$$

where R represents the rate of production. An appropriate expression for R is not obtainable, since condensation polymerization is reversible and the order of reaction in solid phase is unknown. For approximation the equation without the source term was used. It was expected that when the conversion was high such an approximation could be unsatisfactory.

The diffusivity was assumed to be time dependent. More precisely, it should be expressed as a function of concentration. In formulating the kinetic equations, the diffusivity was incorporated into a rate function $K(t)$ from which the rate constant was extracted. As pointed out by Laidler⁽⁷⁷⁾ and Taplin⁽¹¹⁸⁾ the concept of concentration has no significance in a solid-state reaction and the rate constant cannot be defined in the same way as for a homogeneous reaction. Therefore, as an alternative, the diffusivity and hence the rate function were assumed to be functions of time.

The expression for the rate function was kt^m in which k was the specific reaction rate; t , time; and m , a parameter. This expression is similar to the power law often used in describing the solid-state reactions of inorganic substances^(72,116,123). In solving the differential equations, this expression permitted transformation of time t into a new variable T without affecting the initial and boundary conditions.

The derived kinetic equations resemble the equations given by Serin and Ellickson⁽¹⁰⁸⁾. The equation for spherical particles is similar to the Dünwald-Wagner equation⁽⁶²⁾ widely applied to solid-state reactions.

Methods employed to solve the diffusion equations are discussed in detail by Crank^(34,35,36).

Applications. The kinetic equations satisfactorily describe the solid-phase polycondensation of the polymers investigated. Applications to other condensation polymers are believed to be valid.

Data and Results

The data and results obtained in this investigation are discussed in this section. Comparisons are made where data of similar nature are available from the literature.

Melting Temperatures of Raw Polymer Resins. The melting temperatures of the three polymer resins (Table VII, page 97) agreed with the reported values^(58,103,104). The softening points were higher than the maximum reaction temperatures by 70, 30, and 40 °C for poly(hexamethylene adipamide), poly(hexamethylene sebacamide), and poly(ethylene terephthalate), respectively. Hence the reactions were believed to take place in the solid phase.

Densities of Raw Polymer Resins. Starkweather⁽¹¹³⁾ determined the crystalline and amorphous densities of poly(hexamethylene adipamide) and poly(hexamethylene sebacamide) by the infrared method. With this information,

the amount of crystallinity may be estimated from the equation given by Frey and Knox⁽⁵⁹⁾ for the polyamide resins used.

$$x = \frac{V_a - V}{V_a - V_c}$$

where:

- x = volume fraction of crystallinity
- V_a = specific volume of amorphous material
- V_c = specific volume of pure crystalline material
- V = specific volume of sample.

The amounts of crystallinity calculated were 0.54 for poly(hexamethylene adipamide) and 0.38 for poly(hexamethylene sebacamide). It was reported that by proper annealing of polyamides crystallinities as high as 50 to 55 per cent could be obtained⁽⁵⁹⁾.

Crystallinity of polymers is still a controversial subject. To date, no absolute method of measurement has been adopted. Therefore, the crystallinities estimated here may have little or no significance.

Flow of Nitrogen through Polymer Beds. The Reynolds number tabulated in Table VI, page 93, indicate that a laminar flow of nitrogen was maintained during the reaction.

In laminar flow, a relatively stagnant gas film surrounds the polymer particles and presents an added resistance to the escape of by-products from the solids. Generally, the diffusivity of a gas through a stagnant gas film is of the order of 10^{-1} square centimeter per second and that of a gas through solids is about 10^{-8} square centimeter per second⁽¹⁷⁾. Therefore, the film resistance is negligible in comparison with the resistance within the solid. Mass transport in the solid or chemical kinetics, or even combinations of both, may control the rate of reaction.

Molecular Weight and Intrinsic Viscosity. Accurate determination of molecular weight is not possible for polymers because of the heterogeneous nature of the materials. Therefore, use of an average molecular weight becomes necessary. The number-average molecular weights of the polymers investigated were calculated from intrinsic viscosities using the empirical relationships given in the literature^(33,95,119). The accuracy of the computed molecular weight depended chiefly on the reliability of these empirical equations. An error of 10 per cent is not unusual.

From the analysis of variance the effect of particle size was concluded to be insignificant on the changes of poly(hexamethylene adipamide) intrinsic viscosity. For

poly(hexamethylene sebacamide) and poly(ethylene terephthalate) the influence of particle sizes was highly pronounced. It was realized later that the large particles of poly(hexamethylene adipamide) had a minor dimension comparable to the mean diameter of the small particles. Thus, the insensitivity of intrinsic viscosity to particle sizes is explained for this particular polymer.

Reaction temperatures and durations were shown to be highly significant in all cases according to the results of variance analysis (Tables XIV to XVI, pages 104 to 106).

Analysis of Kinetic Data. Flory's theory of the reactivity of large molecules⁽⁵²⁾ says that the reactivities of the functional groups are relatively unaffected by the viscosity of the medium. Although this theory has gained support from the studies of solution- and melt-phase polymerizations, it has not been tested for a solid-phase polymerization reaction. If this theory holds for a solid-phase process, the following equation can be derived from equation 9, page 25, to describe the changes in molecular weight with a second order reaction.

$$\bar{M}_{n,t} - \bar{M}_{n,0} = k_2 t \quad (85)$$

where k_2 is the specific reaction rate of a second-order reaction. Polyamidation⁽⁴⁵⁾ and un-catalyzed polyesterification⁽⁴⁴⁾ were found to be of second order. This equation states that plotting $(\bar{M}_n, t - \bar{M}_n, 0)$ against t yields a straight line. The slope of the straight line is the specific reaction rate for the temperature investigated. Furthermore, the intercept is zero at time zero. The molecular weight data presented in Tables VIII to XIII on pages 98 to 103 were plotted accordingly. It was found that not all of the data could be fitted with straight lines. Where straight lines were obtained, the intercepts were not zero. Therefore, the reaction observed in this investigation was not a second-order reaction. Attempts were also made to fit the data to a third-order reaction model, since catalyzed polyesterifications were reported to be of third-order. Results were unsatisfactory.

Since a second- and a third-order reaction could not successfully describe the reaction, subsequently the power law model used by Griskey and Lee⁽⁶⁵⁾ was tested. According to this model presented as equation 34, page 41, plotting $(\bar{M}_n, t - \bar{M}_n, 0)$ against time t on a log-log scale results in a straight line with a slope equal to $(n + 1)$. The intercept $\ln[k/(n + 1)]$ is used to calculate the

specific reaction rate k . In this model "n" is a constant independent of temperature for a given polymer.

The results of fitting a power law model to the data were not entirely satisfactory. A straight line relationship was obtained at all temperatures as well as for all three polymers investigated. Poly(hexamethylene sebacamide) of small particle size "n" showed a comparatively small variation between -0.44 to -0.54. However, "n" varied between a maximum of 3.0 and a minimum of -0.86 for the rest of the polymers studied. Since the values of "n" are inconsistent for a given polymer, the power law model is considered to be inadequate.

The kinetic equations derived in this investigation were then applied to the data. For poly(hexamethylene adipamide) the rate function $K_1(t)$ was found to be

$$K_1(t) = kt^{1/2}.$$

For poly(hexamethylene sebacamide) and poly(ethylene terephthalate) the rate functions were approximated by kt . It should be kept in mind that the expression kt^m was chosen empirically.

Table XXIII, page 116, presents the specific reaction rates at various temperatures for the three types of polymers. The temperature dependency of the specific

reaction rate is shown as Arrhenius plots in Figures 13 to 15, pages 117 to 119. The Arrhenius equations for the specific reaction rates were derived from the plots and were summarized in Table XXIV, page 120. In order to verify the fit, the Arrhenius equations were used to calculate the average molecular weights which were then compared with the experimental results. Deviations were expressed in terms of per cent error as indicated in Tables XXV through XXX, pages 121 through 126. The maximum deviation was found to be 13.6 per cent. An error of this magnitude is not unusual in this type of experiment. Therefore, the kinetic equations derived are considered to be sufficient.

Solid-Phase Polycondensations in Poly(hexamethylene adipamide) and Poly(hexamethylene sebacamide). From Figures 10 and 11, pages 113 and 114, it is noted that the reaction proceeded at about the same rate (slope of curve) for both the large and the small polymer particles after five hours of reaction. Furthermore, while the rate varied with temperature, it did not seem to change with time once the polymers had been treated for ten hours. The conversion rate being independent of time suggests that the reaction proceeds analogously to the thermal decomposition of inorganic crystalline salts in which

overlapping processes of nucleation and growth are evidenced^(72,116). Generally, it is satisfactory to assume that the rate of growth of the nuclei is constant once they are formed. Magill showed that the mechanisms of nucleation and growth agreed with the morphology of the crystallized nylon 66⁽⁸⁵⁾. Fuller, Baker, and Pape⁽⁶⁰⁾ observed a considerable rotational freedom of the polyamide chain molecules in the solid state. Rotational motion of the molecules will promote bringing two active end groups together, so that if sufficient energy is acquired by these groups, annihilation takes place. The process of bringing two end groups into an adjacent position may be considered as the nucleation step, whereas the process of annihilation may be thought of as the growth of nuclei.

Temperature was found to have some peculiar effects on the reaction. Samples of large particles resulted in a higher conversion than those of small particles at 150 °C and above. At lower temperatures, an opposite situation was noted. This phenomenon was discernible with poly(hexamethylene adipamide), although the influence of particle sizes was concluded to be insignificant from the analysis of variance as well as from the geometry of

the particles. With poly(hexamethylene sebacamide) the phenomenon was definitely significant.

The peculiar temperature effect may result from polymer degradation, the exothermic nature of the reaction, or a combination of both factors. Degradation was probably a minor factor since no discoloration was noted. There was a possibility that some degradation could have occurred without discoloration of the polymer. If this was the case, the polymer of small particles because of larger specific surface would be more severely affected than the polymer of large particles.

The polymerization between linear poly(hexamethylene adipamide) was reported to be exothermic by Ogata⁽⁹⁸⁾. He determined the heat of reaction to be -26.4 kilocalories per gram mole. No similar information was available from the literature for the formation of poly(hexamethylene sebacamide). By analogy, the reaction is believed to be an exothermic one. Polymers are in general poor heat conductors. It is more difficult for a large particle to dissipate the heat of reaction than for a small particle. As a result, the large particle experiences a higher temperature than the small particle. A higher conversion with the large particles is thus

expected since the reaction rate increases exponentially with temperature.

The heat of reaction and the thermal conductivity of poly(hexamethylene sebacamide) are not available for computing the solid temperatures of this polymer. However, from the Arrhenius plot shown in Figure 18, the estimates of internal temperature in the large particles are obtainable with the assumption that reaction rates are independent of particle size above 160 °C. The temperature inside the small particles is assumed to be the same as the surrounding temperature. The temperatures in the large particles were estimated to be approximately 164 and 190 °C when the surrounding temperatures were 160 and 180 °C. The self-heating behavior is common in solid-state reactions of inorganic materials as indicated by Cohen⁽³²⁾.

The relationship between the specific reaction rate and temperature of poly(hexamethylene sebacamide) was not a straight line in the case of large particles. A high energy of activation (33.0 kilocalories per gram mole) was required to initiate the reaction at 120 and 140 °C, suggesting that the diffusion of by-products was governing the reaction. The activation energy decreased as the temperature increased. This behavior indicates that at

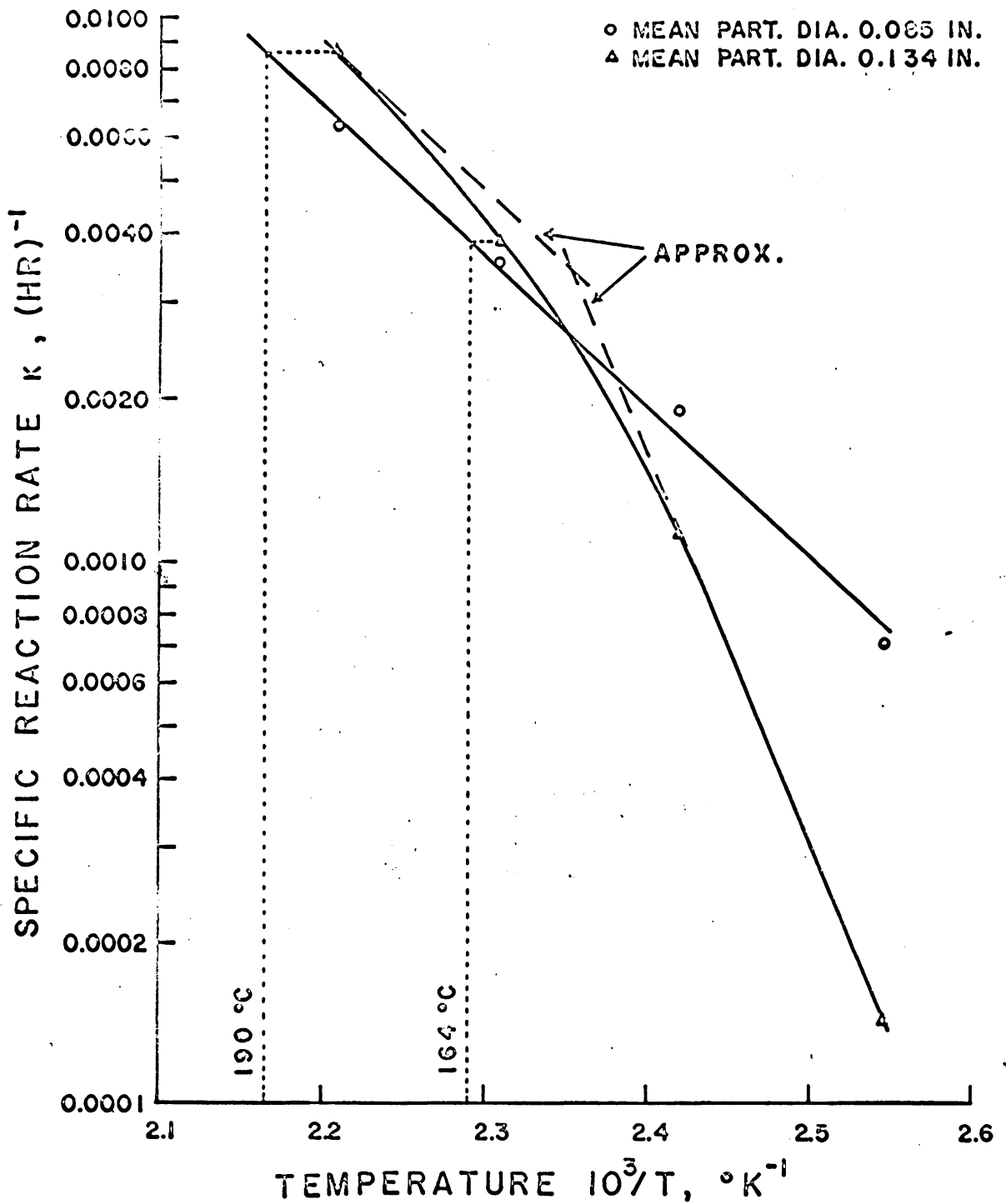


FIGURE 18. ESTIMATION OF POLY(HEXAMETHYLENE SEBACAMIDE) INTERNAL TEMPERATURES

high temperatures, some type of disorder of the molecules becomes responsible for the reaction⁽⁷⁴⁾.

Changes of the polyamide structure were reported by several investigators. Brill⁽²¹⁾ observed that the monoclinic lattice of poly(hexamethylene adipamide) became hexagonal at about 161 °C. Fuller, Baker, and Pape⁽⁶⁰⁾ found that rearrangements of molecules occurred at about 160 °C in annealing poly(hexamethylene adipamide) and poly(hexamethylene sebacamide). In this investigation, the thermograms in Figures 7 and 8, pages 94 and 95, of the two polyamides studied reveal an endothermic peak at 160 °C for the samples treated at 120 and 140 °C. The thermograms also show the disappearance of the 160 °C endothermic peak for polymers obtained from 160 and 180 °C reactions. The exact nature of the structural disorder cannot be determined based on the information obtained in this investigation. However, according to the study on the crystalline behavior of linear polyamide by Fuller, Baker, and Pape⁽⁶⁰⁾ it is reasonable to assume that the diffusion of by-product in a large particle becomes a less important factor in comparison with chemical kinetics at elevated temperatures. When chemical reaction controls, the activation energy for the reaction should not vary with polymer particle sizes.

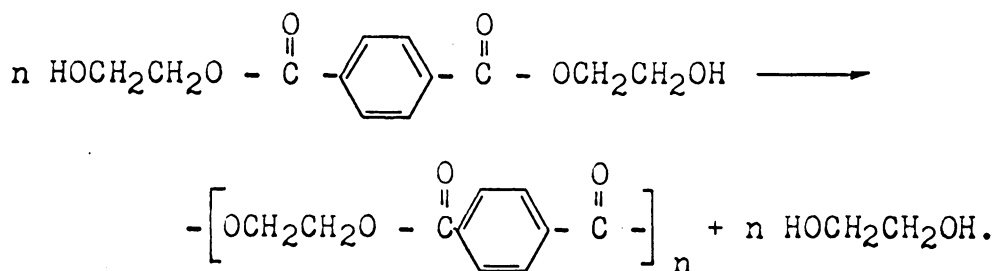
The activation energies were computed to be 10.5 kilocalories per gram mole of poly(hexamethylene adipamide), 12.6 kilocalories per gram mole of poly(hexamethylene sebacamide) when chemical reaction was the primary rate controlling factor, and 33.0 kilocalories per gram mole of poly(hexamethylene sebacamide) when diffusion was the rate governing step. The activation energies of poly(hexamethylene sebacamide) having large particles were obtained from straight line approximation as shown in Figure 14, page 118. Griskey and Lee⁽⁶⁵⁾ reported a value of 12.96 kilocalories per gram mole for the solid-state reaction of poly(hexamethylene adipamide). The disagreement with the 10.5 kilocalories per gram mole obtained in this investigation is not unusual in view of the nature of kinetic studies.

It is interesting to note from Figure 14, page 118, that a characteristic temperature may be located to indicate the relative significance of diffusion and chemical kinetics in the progress of solid-phase polycondensation. A characteristic temperature of 426 °K (153 °C) was found for poly(hexamethylene sebacamide). The ratio of this characteristic temperature to the polymer crystalline melting point was 0.84. For poly(ethylene terephthalate) this ratio was also found to be about 0.84. Further

discussion is deferred to the section describing the solid-phase polymerization of poly(ethylene terephthalate).

Solid-Phase Polycondensation in Poly(ethylene terephthalate). Figure 12, page 115, indicates that the rate of conversion was relatively independent of particle sizes after five hours of reaction. It also shows that the conversion increased linearly with time after ten hours. These behaviors are similar to those found with the polyamides and, hence, are explained by the mechanisms of nucleation and growth of the nuclei.

The effects of temperature on the reaction were somewhat different from those observed with the polyamides. At 160 °C, the polymer of both particle sizes exhibited approximately an equal rate of reaction as shown in Figures 12 and 15, pages 115 and 119. This indicates that the reaction was principally governed by the diffusion of excess glycol in the finished polymer when it was manufactured. The by-product from the reaction is also glycol as indicated below⁽¹¹²⁾.



The removal of glycol was slow at 160 °C reaction since the normal boiling point of the glycol is 197.4 °C. The process could be imagined as the evaporation from a film of liquid glycol which was replenished from the solids by capillary action. Thus, the reaction rate being independent of particle sizes is conceivable.

As temperature increases the phenomenon of film evaporation diminishes. Chemical reaction and the diffusion of by-product from the interior to the surface of the solids may become rate controlling. The conversion curves in Figure 12, page 115, and the Arrhenius plot in Figure 15, page 119, confirm the above reasoning.

The differential thermogram shown in Figure 9, page 96, reveals a structural change at elevated temperatures. The polymer treated at 160 °C exhibited a broad melting peak. On the other hand, the polymers reacted at 180 and 200 °C had two melting peaks. White⁽¹²⁹⁾ attributed the two melting peaks to the loss of preferred orientation. The temperature at which disorientation took place is not clearly indicated in the differential thermogram. However, with the method used in the analysis of polyamide data, the disorientation occurred at about 177 °C for the small particles and at about 179 °C for the large particles. For the convenience of discussion these

temperatures are referred to as characteristic temperatures. Above the characteristic temperatures the activation energy was 26.8 kilocalories per gram mole for both particle sizes. No information is available in the literature for comparison. However, Flory⁽⁴³⁾ reported that 25 kilocalories per gram mole was the activation energy for the reaction of ethylene glycol with succinic acid. Below the characteristic temperatures the activation energies were 66.2 and 57.2 kilocalories per gram mole for the small and large particles, respectively.

The ratios of the characteristic temperatures to the polymer melting point were 0.83 and 0.84 for the small and large particles, respectively. It is interesting to know that the ratio is also 0.84 for poly(hexamethylene sebacamide) of large particles. For all practical purposes, an average of 0.84 is suggested for the two different polymers. Table XXXII lists the characteristic temperatures, the melting points, and the ratios computed.

The significance of this ratio in a solid-phase polycondensation awaits further verification from studies similar to this investigation. It is postulated that when both chemical kinetics and diffusion control the reaction their relative importance depends on whether the reaction

TABLE XXXII

Characteristic Temperature of Polymer

Polymer*	Mean Particle Diameter in.	Characteristic Temperature T_c °K	Melting Temperature T_m °K	T_c/T_m
Poly(hexamethylene sebacamide)	0.134	426	508	0.84
Poly(ethylene terephthalate)	0.038 0.084	450 452	538 538	0.83 0.84

*Poly(hexamethylene adipamide) did not show a characteristic temperature on the Arrhenius plot.

temperature is higher or lower than 0.84 of the polymer melting point T_m . At temperatures above 0.84 T_m chemical kinetics controls; whereas at temperatures below 0.84 T_m diffusion governs the reaction. It is expected that when the reaction is carried out at temperatures high above the characteristic temperature, but slightly below the polymer melting point, the solid-phase polycondensation would resemble the melt-phase process.

Recommendations

The following recommendations are made on the basis of this investigation for future studies.

By-product Analysis. The by-products from the reactions should be analyzed both qualitatively and quantitatively in order to understand the chemical aspects of the reactions. This investigation considered primarily the physical aspects of the reactions.

By-product Removal. The reaction kinetics should be studied by removal of the by-products with vacuum. The pressure gradient together with the concentration gradient will promote the rate of reaction.

Polymer Characteristics. Polymer molecular weight distributions should be determined since they relate

closely with the physical and chemical properties of polymers. It is recommended that such investigation be conducted on one particular type of polymer. Determinations of molecular weight distributions are quite involved and time-consuming.

Reaction Temperature. It would be interesting to conduct the experiments at temperatures higher than those attained in this investigation. Such a study would reveal more about the contribution of molecular motion to the rate of reaction.

Other Condensation Polymers. Extension of this investigation to other condensation polymers should be made in order to verify the observed phenomena. The derived kinetic equations can be applied when using linear condensation polymers. Non-linear condensation polymers may be used to test the suitability of the kinetic equations.

Polymer Morphology. Polymers of various morphological properties should be used as raw materials. This would be of particular interest since molecular structure was found to play a significant role in the solid-phase polycondensation.

Method of Heat Treatment. Dielectric heating is suggested as a method for treating the polymers. This

method will provide uniform temperature within the solid particles. The polymer molecules because of their dielectric properties will become highly excited so that a high rate of reaction may be obtainable.

Limitations

This section contains a list of the limitations encountered in the experiments.

Polymer Resins. The polymer resins received from the manufacturer were not uniform in particle size and shape. As a result, particle size was not incorporated as a variable into the Arrhenius rate equations.

Reaction Temperature. The maximum reaction temperature was limited by either the system or the procedure used. The flash point of the oil used in the constant temperature bath was about 200 °C. This determined the highest reaction temperature for the polyester. The procedure for purging the reactors was not adequate for preventing degradation of the polyamides at 200 °C.

Reaction Time. The reaction time was limited to 20 hours. The lowest reaction temperatures required this much time to show changes in the polymers and the large quantity of nitrogen would have made the cost

prohibitive to extend the time. A cylinder of dry nitrogen with the supply pressure of 2400 pounds per square inch, gage, was just enough to complete a test for one polymer at a given temperature. A significant increase in molecular weight was observed at the lowest reaction temperatures after 20 hours of reaction.

Differential Thermal Analysis. The geometry of the polymer particles as well as the fixed rate of heating (10 °C per minute) impaired the results of differential thermal analysis. The irregularity of the particles reduced the accuracy of the recorded differential temperatures. The high rate of heating prevented the equipment from sensing the second-order transition temperatures of the polymers.

VI. CONCLUSIONS

The kinetic studies of polycondensations in solid poly(hexamethylene adipamide) and poly(hexamethylene sebacamide) at temperatures varying from 120 to 180 °C, and in solid poly(ethylene terephthalate) at temperatures varying from 160 to 200 °C led to the following conclusions:

1. Poly(hexamethylene adipamide) reacted at 180 °C for 20 hours showed an increase of the number-average molecular weight from about 10,000 to 22,000.

2. Poly(hexamethylene sebacamide) reacted at the same conditions as above yielded an increase in the number-average molecular weight from approximately 10,000 to 14,000.

3. Poly(ethylene terephthalate) reacted at 200 °C for 20 hours resulted in an increase in the number-average molecular weight from about 18,000 to 34,000.

4. For the three polymers investigated the rate of conversion was sensitive to particle size up to five hours of reaction. After five hours the rate of conversion became relatively insensitive to the particle size up to the 20 hours studied. At a given temperature the

conversion of all samples tested increased at a constant rate after ten hours.

5. A substantial reduction in the activation energy occurred at temperatures approximately 0.84 of the polymer melting points of poly(hexamethylene sebacamide) and poly(ethylene terephthalate).

6. The transport of by-products and chemical kinetics explained the behavior of the reaction.

7. The derived kinetic equations successfully described the reactions.

VII. SUMMARY

Kinetic studies of the polymerization reaction in solid condensation polymers are very limited. Two publications were available in the literature. However, in both investigations no generalized kinetic model was proposed and the mechanisms of the reaction were not explored.

The objective of this study was to investigate the factors affecting the kinetics of thermally-induced polymerization in solid poly(hexamethylene adipamide), poly(hexamethylene sebacamide), and poly(ethylene terephthalate), and to propose a generalized kinetic equation to describe the reaction. The factors considered were polymer particle size, reaction temperature, and time.

The reactions were conducted isothermally at four temperatures ranging from 120 to 180 °C for the polyamides and at three temperatures ranging from 160 to 200 °C for the polyester. Dry nitrogen was used to provide an inert atmosphere. The maximum reaction time was 20 hours.

The polymer intrinsic viscosities were determined and the number-average molecular weights were calculated.

The thermal behavior of some selected samples was examined by differential thermal analysis.

Two kinetic equations were derived. One equation is applicable to particles which can be approximated as plane sheets, and the other to particles which can be thought of as spheres. These two equations described the observed reactions successfully. Arrhenius rate equations were used to express the temperature dependency of the reaction rates.

The results of this investigation led to the following conclusions: the number-average molecular weight of poly(hexamethylene adipamide) increased from approximately 10,000 to 22,000 when reacted at 180 °C for 20 hours; poly(hexamethylene sebacamide) showed an increase from about 10,000 to 14,000 at the same reaction conditions; the change in the number-average molecular weight of poly(ethylene terephthalate) was from approximately 18,000 to 34,000 when reacted at 200 °C for 20 hours; a substantial reduction in the activation energy occurred at temperatures about 0.84 of the melting points of poly(hexamethylene sebacamide) and poly(ethylene terephthalate); the transport of by-products through the solids and chemical kinetics explained the behavior of the reaction.

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Addenda

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Appendix A

Data of Screen Analyses for the Polymer Resins

TABLE XXXIII

Screen Analysis of Poly(hexamethylene adipamide)

U. S. Sieve No.	Average Opening in.	Weight Fractions	
		Fine	Coarse
	+4		0.000
-4	+6	0.000	0.664
-6	+8	0.171	0.318
-8	+10	0.460	0.018
-10	+12	0.242	0.000
-12	+14	0.127	
-14		0.000	
	Total	1.000	1.000

TABLE XXXIV

Screen Analysis of Poly(hexamethylene sebacamide)

U. S. Sieve No.	Average Opening in.	Weight Fractions	
		Fine	Coarse
	+4		0.000
-4	+6	0.000	0.531
-6	+8	0.092	0.467
-8	+10	0.744	0.002
-10	+12	0.149	0.000
-12	+14	0.015	
-14		0.000	
	Total	1.000	1.000

TABLE XXXV

Screen Analysis of Poly(ethylene terephthalate)

U. S. Sieve No.	Average Opening in.	Weight Fractions	
		Fine	Coarse
+6	0.1595		0.000
-6 +8	0.1129		0.318
-8 +10	0.0862	0.000	0.324
-10 +12	0.0724	0.050	0.227
-12 +14	0.0608	0.294	0.105
-14 +16	0.0512	0.007	0.026
-16 +18	0.0432	0.165	0.000
-18 +20	0.0363	0.212	
-20 +25	0.0306	0.135	
-25 +30	0.0256	0.065	
-30 +35	0.0215	0.038	
-35 +40	0.0181	0.019	
-40 +45	0.0152	0.015	
-45	0.0128	0.000	
Total		1.000	1.000

Appendix B

Reactor Temperatures During the
Heating and Cooling Periods

TABLE XXXVI

Reactor Temperatures During Heating to
and Cooling from 120 °C

Time min	Temperature	
	Heating °C	Cooling °C
0	28.5	120.0
2.5	49.0	112.5
5.0	80.0	97.8
7.5	98.5	82.5
10.0	109.0	69.5
12.5	114.0	58.2
15.0	118.0	50.0
17.5	119.0	43.8
20.0	119.5	39.0
22.5	120.0	36.0
25.0	120.0	34.0
27.5	120.0	32.0
30.0	120.0	31.0

TABLE XXXVII

Reactor Temperatures During Heating to
and Cooling from 140 °C

Time min	Temperature	
	Heating °C	Cooling °C
0	28.5	140.0
2.5	59.5	125.5
5.0	99.5	104.0
7.5	120.5	84.0
10.0	130.5	67.5
12.5	134.5	55.5
15.0	136.5	46.5
17.5	138.0	40.0
20.0	139.0	35.5
22.5	140.0	32.5
25.0	140.0	30.5
27.5	140.0	29.0
30.0	140.0	28.5

TABLE XXXVIII

Reactor Temperatures During Heating to
and Cooling from 160 °C

Time	Temperature	
	Heating	Cooling
min	°C	°C
0	30.0	160.0
2.5	61.0	146.0
5.0	106.5	120.5
7.5	132.5	97.0
10.0	146.0	78.0
12.5	152.5	63.5
15.0	156.0	53.0
17.5	158.0	45.5
20.0	159.0	40.5
22.5	160.0	37.0
25.0	160.0	34.5
27.5	160.0	33.0
30.0	160.0	31.5

TABLE XXXIX

Reactor Temperatures During Heating to
and Cooling from 180 °C

Time	Temperature	
	Heating	Cooling
min	°C	°C
0	26.5	180.0
2.5	72.5	168.0
5.0	127.0	137.0
7.5	154.5	109.0
10.0	168.5	84.0
12.5	175.0	66.0
15.0	177.5	52.5
17.5	179.0	44.5
20.0	180.0	38.0
22.5	180.0	34.5
25.0	180.0	32.0
27.5	180.0	30.0
30.0	180.0	29.0

TABLE XL

Reactor Temperatures During Heating to
and Cooling from 200 °C

Time min	Temperature	
	Heating °C	Cooling °C
0	29.0	200.0
2.5	89.5	190.5
5.0	153.0	158.0
7.5	181.5	124.0
10.0	195.0	98.5
12.5	197.0	77.0
15.0	198.5	63.0
17.5	199.5	52.5
20.0	200.0	44.5
22.5	200.0	41.0
25.0	200.0	35.0
27.5	200.0	29.0
30.0	200.0	28.0

Appendix C

Efflux Times of Solvents in Viscometers

TABLE XLI

Efflux Time of Solvent in Cannon-Ubbelohde Viscometer

Viscometer		Solvent	Efflux Time, ^b seconds				
Size	Number		1	2	3	4	Average
75	D548	90% Formic Acid	187.2	187.3	187.2	187.1	187.20
	D549		186.3	186.2	186.3	186.2	186.25
100	D445	Phenol/TCE, ^a 50/50 by wt	199.9	199.8	199.7	199.85	199.81
	D446		203.0	203.0	202.95	203.1	203.01
200	D162	m-Cresol	116.4	116.4	116.4	116.35	116.39
	D164		112.9	112.9	112.95	112.8	112.89

^a Tetrachloroethane.

^b Determined at 25 °C ± 0.01 °C.

Appendix D

Viscometric Data of Polymer Solutions

TABLE XLII

Viscometry Data of Poly(hexamethylene adipamide) of Mean Particle
Diameter, 0.081 in., Reacted at 120 °C

Reaction Time	Viscometer	Solution Concentration	Efflux Time				Relative Viscosity	Reduced Specific Viscosity	Inherent Viscosity
			1	2	3	Ave.			
hr		gm/dl	sec					dl/gm	dl/gm
0	D 548	0.6225	294.85	295.00	295.00	294.95	1.5756	0.925	0.730
		0.4788	268.30	268.45	268.35	268.37	1.4336	0.906	0.752
		0.3458	244.55	244.50	244.40	244.48	1.3060	0.885	0.772
		0.2394	226.10	226.10	226.20	226.13	1.2080	0.869	0.789
5	D 548	0.6127	304.20	304.00	304.20	304.13	1.6246	1.019	0.792
		0.4713	275.70	275.70	275.70	275.70	1.4728	1.003	0.821
		0.3404	250.40	250.20	250.20	250.27	1.3369	0.990	0.853
		0.2357	230.30	230.30	230.40	230.33	1.2304	0.978	0.880
10	D 549	0.6187	305.00	304.95	305.10	305.02	1.6377	1.031	0.797
		0.4757	276.00	276.00	276.15	276.05	1.4821	1.013	0.827
		0.3437	250.25	250.35	250.20	250.27	1.3437	1.000	0.860
		0.2380	230.10	230.00	230.05	230.05	1.2352	0.988	0.888
15	D 548	0.6177	307.40	307.35	307.45	307.40	1.6421	1.040	0.803
		0.4752	278.30	278.45	278.35	278.37	1.4870	1.025	0.835
		0.3432	252.05	252.15	252.25	252.15	1.3470	1.011	0.868
		0.2376	231.65	231.55	231.60	231.60	1.2372	0.998	0.896
20	D 548	0.6067	305.80	306.00	306.00	305.93	1.6342	1.045	0.810
		0.4667	277.10	277.05	277.10	277.03	1.4799	1.028	0.840
		0.3371	251.20	251.15	251.25	251.20	1.3419	1.014	0.872
		0.2333	230.90	230.95	230.95	230.93	1.2336	1.001	0.900

TABLE XLIII

Viscometry Data of Poly(hexamethylene adipamide) of Mean ParticleDiameter, 0.081 in., Reacted at 140 °C

Reaction Time	Viscometer	Solution Concentration	Efflux Time				Relative Viscosity	Reduced Specific Viscosity	Inherent Viscosity
			1	2	3	Ave.			
hr		gm/dl	sec					dl/gm	dl/gm
0	D 549	0.6039	289.25	289.30	289.20	289.25	1.5530	0.916	0.729
		0.4645	263.90	263.80	264.00	263.90	1.4169	0.898	0.750
		0.3355	240.95	241.00	241.10	241.02	1.2941	0.877	0.768
		0.2323	223.40	223.35	223.50	223.42	1.1996	0.859	0.783
5	D 549	0.6241	309.70	309.60	309.75	309.68	1.6627	1.062	0.815
		0.4801	278.70	278.90	278.75	278.78	1.4968	1.035	0.840
		0.3467	252.30	252.30	252.30	252.30	1.3546	1.023	0.875
		0.2400	231.30	231.25	231.20	231.25	1.2416	1.007	0.902
10	D 549	0.6906	327.50	327.55	327.50	327.51	1.7585	1.098	0.817
		0.5312	292.90	292.80	292.90	292.90	1.5725	1.078	0.852
		0.3837	261.80	261.75	261.75	261.77	1.4055	1.057	0.887
		0.2656	237.65	237.60	237.75	237.67	1.2761	1.040	0.918
15	D 549	0.6568	324.60	324.50	324.60	324.57	1.7427	1.131	0.846
		0.5052	290.60	290.70	290.80	290.70	1.5608	1.110	0.881
		0.3649	260.45	260.50	260.50	260.48	1.3986	1.092	0.919
		0.2526	236.90	236.80	236.85	236.85	1.2717	1.076	0.952
20	D 548	0.5870	311.70	311.90	311.80	311.80	1.6656	1.134	0.869
		0.4515	280.80	280.80	280.70	280.77	1.4908	1.087	0.884
		0.3261	254.05	254.00	254.00	254.02	1.3569	1.094	0.936
		0.2258	232.75	232.70	232.80	232.75	1.2433	1.078	0.964

TABLE XLIV

Viscometry Data of Poly(hexamethylene adipamide) of Mean ParticleDiameter, 0.081 in., Reacted at 160 °C

Reaction Time	Viscometer	Solution Concentration	Efflux Time				Relative Viscosity	Reduced Specific Viscosity	Inherent Viscosity
			1	2	3	Ave.			
hr		gm/dl	sec					dl/gm	dl/gm
0	D 549	0.5986	288.49	288.30	288.35	288.35	1.5482	0.916	0.730
		0.4605	263.60	263.50	263.60	263.57	1.4151	0.901	0.754
		0.3326	240.90	240.90	240.85	240.88	1.2933	0.882	0.773
		0.2302	223.25	223.35	223.40	223.33	1.1991	0.865	0.789
5	D 549	0.6035	315.00	315.00	314.90	314.97	1.6911	1.145	0.871
		0.4642	283.35	283.35	283.30	283.33	1.5212	1.123	0.904
		0.3353	255.15	254.95	255.00	255.03	1.3693	1.101	0.937
		0.2321	233.15	233.05	233.05	233.08	1.2514	1.083	0.966
10	D 548	0.6416	334.35	334.10	334.30	334.22	1.7854	1.224	0.903
		0.4935	298.20	298.15	298.10	298.15	1.5927	1.201	0.943
		0.3564	265.55	265.45	265.45	265.48	1.4182	1.173	0.980
		0.2468	240.65	240.65	240.65	240.65	1.2855	1.157	1.018
15	D 548	0.6225	332.60	332.40	332.50	332.50	1.7762	1.247	0.923
		0.4688	297.40	297.30	297.40	297.37	1.5885	1.229	0.967
		0.3458	265.25	265.40	265.30	265.32	1.4173	1.207	1.009
		0.2394	240.75	240.70	240.80	240.75	1.2861	1.195	1.051
20	D 549	0.6133	336.00	336.10	336.05	336.05	1.8043	1.311	0.962
		0.4718	299.30	299.35	299.30	299.32	1.6071	1.287	1.006
		0.3407	266.00	265.90	265.95	265.95	1.4279	1.256	1.046
		0.2359	240.45	240.40	240.50	240.45	1.2910	1.234	1.083

TABLE XLV

Viscometry Data of Poly(hexamethylene adipamide) of Mean Particle
Diameter, 0.081 in., Reacted at 180 °C

Reaction Time hr	Viscometer	Solution Concentration gm/dl	Efflux Time				Relative Viscosity	Reduced Specific Viscosity dl/gm	Inherent Viscosity dl/gm
			1	2	3	Ave.			
0	D 549	0.6302	296.10	296.10	296.20	296.13	1.5810	0.922	0.727
		0.4848	269.40	269.35	269.35	269.37	1.4463	0.921	0.761
		0.3501	244.95	244.90	244.80	244.88	1.3148	0.899	0.782
		0.2424	226.05	226.05	226.00	226.03	1.2136	0.881	0.799
5	D 548	0.6045	339.00	338.90	339.00	338.97	1.7933	1.312	0.966
		0.4650	302.10	302.10	302.20	302.13	1.5984	1.287	1.009
		0.3358	267.85	267.85	267.90	267.87	1.4172	1.242	1.038
		0.2325	242.70	242.70	242.50	242.63	1.2836	1.220	1.074
10	D 549	0.5914	344.30	344.25	344.40	344.32	1.8487	1.435	1.039
		0.4549	305.05	305.20	305.00	305.08	1.6380	1.403	1.085
		0.3286	270.15	270.10	269.90	270.05	1.4499	1.369	1.131
		0.2275	243.30	243.25	243.30	243.28	1.3062	1.346	1.174
15	D 549	0.5972	355.70	355.60	355.50	355.60	1.9093	1.523	1.083
		0.4594	313.50	313.40	313.50	313.47	1.6831	1.487	1.133
		0.3318	275.90	275.90	275.70	275.83	1.4810	1.450	1.184
		0.2297	247.00	247.00	247.00	247.00	1.3262	1.420	1.229
20	D 549	0.6009	307.50	370.60	370.50	370.53	1.9894	1.647	1.145
		0.4622	324.10	324.20	324.15	324.15	1.7404	1.602	1.199
		0.3338	283.20	283.05	283.10	283.12	1.5201	1.558	1.255
		0.2311	252.30	252.20	252.10	252.20	1.3541	1.532	1.312

TABLE XLVI

Viscometry Data of Poly(hexamethylene adipamide) of Mean Particle
Diameter, 0.139 in., Reacted at 120 °C

Reaction Time	Viscometer	Solution Concentration	Efflux Time				Relative Viscosity	Reduced Specific Viscosity	Inherent Viscosity
			1	2	3	Ave.			
hr		gm/dl	sec					dl/gm	dl/gm
0	D 549	0.5976	289.05	289.10	289.10	289.08	1.5521	0.924	0.736
		0.4597	263.55	263.65	263.60	263.60	1.4153	0.903	0.756
		0.3320	241.00	240.90	240.95	240.95	1.2937	0.885	0.776
		0.2298	223.05	223.10	223.05	223.07	1.1077	0.860	0.785
5	D 549	0.5718	293.60	293.55	293.65	293.60	1.5764	1.008	0.796
		0.4398	267.80	267.85	267.75	267.80	1.4379	0.996	0.826
		0.3177	244.30	244.40	244.20	244.30	1.3117	0.981	0.854
		0.2199	226.20	226.10	226.00	226.10	1.2140	0.973	0.882
10	D 548	0.6711	319.90	320.10	320.00	320.00	1.7094	1.048	0.792
		0.5208	288.00	287.90	287.90	287.93	1.5381	1.033	0.827
		0.3762	258.70	258.70	258.60	258.67	1.3818	1.015	0.860
		0.2604	236.60	234.70	236.50	236.60	1.2639	1.013	0.899
15	D 549	0.6721	317.50	317.40	317.60	317.50	1.7047	1.049	0.794
		0.5170	285.60	285.50	285.55	285.55	1.5332	1.031	0.827
		0.3734	256.60	256.70	256.60	256.63	1.3779	1.012	0.858
		0.2585	234.35	234.30	234.30	234.32	1.2581	0.998	0.888
20	D 549	0.6203	307.00	306.90	306.90	306.93	1.6479	1.044	0.805
		0.4772	277.70	277.65	277.70	277.68	1.4909	1.029	0.837
		0.3446	251.50	251.45	251.45	251.45	1.3501	1.016	0.871
		0.2386	230.90	230.80	230.80	230.83	1.2394	1.003	0.900

TABLE XLVII

Viscometry Data of Poly(hexamethylene adipamide) of Mean Particle
Diameter, 0.139 in., Reacted at 140 °C

Reaction Time	Viscometer	Solution Concentration	Efflux Time				Relative Viscosity	Reduced Specific Viscosity	Inherent Viscosity
			1	2	3	Ave.			
hr		gm/dl	sec					dl/gm	dl/gm
0	D 548	0.6382	297.20	297.25	297.20	297.22	1.5877	0.921	0.724
		0.4909	270.00	270.10	270.05	270.05	1.4426	0.902	0.746
		0.3546	245.75	245.60	245.50	245.62	1.3121	0.880	0.766
		0.2455	226.95	226.95	226.90	226.93	1.2122	0.864	0.784
5	D 548	0.6275	311.75	311.80	311.85	311.80	1.6656	1.061	0.813
		0.4827	280.60	280.60	280.70	280.63	1.4991	1.034	0.839
		0.3486	253.60	253.60	253.70	253.63	1.3540	1.018	0.871
		0.2413	232.70	232.70	232.70	232.70	1.2431	1.007	0.902
10	D 548	0.6444	319.30	319.10	319.20	319.20	1.7051	1.094	0.828
		0.4957	287.50	287.30	287.30	287.37	1.5351	1.079	0.865
		0.3580	258.00	257.90	257.80	257.90	1.3777	1.055	0.895
		0.2478	235.55	234.50	234.60	235.55	1.2583	1.042	0.927
15	D 549	0.6785	328.10	328.00	328.00	328.03	1.7612	1.122	0.834
		0.5219	292.80	292.70	292.80	292.77	1.5719	1.096	0.867
		0.3769	261.85	261.90	261.80	261.85	1.4059	1.077	0.904
		0.2610	237.55	237.65	237.60	237.60	1.2757	1.056	0.933
20	D 548	0.6344	324.70	324.85	324.70	324.75	1.7348	1.158	0.868
		0.4880	290.10	290.20	290.30	290.20	1.5502	1.127	0.898
		0.3524	260.60	260.65	260.50	260.58	1.3920	1.112	0.939
		0.2440	237.35	237.40	237.30	237.35	1.2679	1.098	0.973

TABLE XLVIII

Viscometry Data of Poly(hexamethylene adipamide) of Mean Particle
Diameter, 0.139 in., Reacted at 160 °C

Reaction Time	Viscometer	Solution Concentration	Efflux Time				Relative Viscosity	Reduced Specific Viscosity	Inherent Viscosity
			1	2	3	Ave.			
hr		gm/dl	sec					dl/gm	dl/gm
0	D 548	0.5976	289.15	289.15	289.10	289.13	1.5445	0.911	0.727
		0.4597	264.25	264.10	264.20	264.18	1.4112	0.894	0.749
		0.3320	241.80	241.65	241.65	241.70	1.2911	0.877	0.770
		0.2298	224.25	224.20	224.25	224.23	1.1978	0.861	0.785
5	D 548	0.6175	320.70	320.70	320.75	320.72	1.7132	1.155	0.872
		0.4750	287.90	287.70	287.95	287.85	1.5377	1.132	0.906
		0.3431	258.85	258.80	258.75	258.80	1.3825	1.115	0.944
		0.2470	238.00	238.15	237.90	238.02	1.2715	1.099	0.972
10	D 548	0.7052	347.55	347.55	347.50	347.53	1.8565	1.215	0.877
		0.5425	308.10	308.30	308.30	308.23	1.6465	1.192	0.919
		0.4148	278.20	278.30	278.30	278.27	1.4865	1.173	0.956
		0.3205	256.70	256.80	256.70	256.73	1.3714	1.159	0.985
15	D 549	0.5838	326.30	326.50	326.30	326.37	1.7523	1.289	0.961
		0.4491	291.40	291.50	291.40	291.43	1.5647	1.257	0.997
		0.3243	260.80	260.80	260.80	260.80	1.4003	1.234	1.038
		0.2245	237.25	237.10	237.10	237.15	1.2733	1.217	1.076
20	D 548	0.7068	364.40	364.30	364.30	364.33	1.9462	1.339	0.942
		0.5437	321.00	320.80	320.70	320.83	1.7138	1.313	0.991
		0.3927	281.25	281.25	281.25	281.25	1.5024	1.279	1.037
		0.2827	253.80	253.80	253.90	253.83	1.3559	1.259	1.077

TABLE XLIX

Viscometry Data of Poly(hexamethylene adipamide) of Mean ParticleDiameter, 0.139 in., Reacted at 180 °C

Reaction Time	Viscometer	Solution Concentration	Efflux Time				Relative Viscosity	Reduced Specific Viscosity	Inherent Viscosity
			1	2	3	Ave.			
hr		gm/dl	sec					dl/gm	dl/gm
0	D 548	0.6191	294.15	294.10	294.15	294.13	1.5712	0.923	0.730
		0.4762	268.05	268.10	268.10	268.08	1.4321	0.907	0.754
		0.3439	244.45	244.40	244.40	244.42	1.3057	0.889	0.776
		0.2381	226.15	226.00	226.10	226.08	1.2077	0.872	0.793
5	D 549	0.5882	332.70	332.65	332.70	332.68	1.7757	1.319	0.976
		0.4525	296.20	296.10	296.00	296.10	1.5805	1.283	1.012
		0.3268	264.00	264.20	264.20	264.13	1.4098	1.254	1.051
		0.2262	239.40	239.40	239.50	239.43	1.2780	1.229	1.084
10	D 549	0.6097	351.25	351.20	351.35	351.27	1.8860	1.453	1.041
		0.4690	310.70	310.75	310.80	310.75	1.6685	1.425	1.092
		0.3387	273.95	273.95	273.95	273.95	1.4709	1.390	1.139
		0.2345	245.60	245.60	245.50	245.57	1.3185	1.358	1.179
15	D 548	0.5986	361.80	361.60	361.60	361.67	1.9320	1.557	1.100
		0.4605	318.30	318.45	318.35	318.32	1.7007	1.522	1.153
		0.3326	279.40	279.40	279.60	279.47	1.4929	1.482	1.205
		0.2302	250.10	250.15	250.05	250.10	1.3360	1.460	1.258
20	D 548	0.6528	393.55	393.45	393.60	393.53	2.1022	1.688	1.138
		0.5022	342.10	342.25	342.00	342.12	1.8276	1.648	1.201
		0.3627	295.70	295.80	295.80	295.77	1.5800	1.599	1.261
		0.2511	260.85	260.85	260.85	260.85	1.3934	1.567	1.321

TABLE I

Viscometry Data of Poly(hexamethylene sebacamide) of Mean ParticleDiameter, 0.085 in., Reacted at 120 °C

Reaction Time	Viscometer	Solution Concentration	Efflux Time				Relative Viscosity	Reduced Specific Viscosity	Inherent Viscosity
			1	2	3	Ave.			
hr		gm/dl	sec					dl/gm	dl/gm
0	D 164	0.6060	198.40	198.45	198.30	198.38	1.7573	1.250	0.930
		0.4662	175.60	175.50	175.45	175.52	1.5548	1.190	0.947
		0.3367	155.80	155.80	155.80	155.80	1.3801	1.129	0.957
		0.2331	141.00	141.20	141.10	141.10	1.2499	1.072	0.957
5	D 164	0.6404	206.85	206.85	206.80	206.83	1.8327	1.300	0.946
		0.4926	181.10	181.10	181.10	181.10	1.6042	1.227	0.959
		0.3558	159.75	159.70	159.75	159.73	1.4149	1.166	0.975
		0.2463	144.05	144.00	144.05	144.03	1.2758	1.120	0.989
10	D 162	0.6222	213.90	214.00	213.10	214.00	1.8386	1.348	0.978
		0.4786	187.10	187.05	187.15	187.10	1.6075	1.269	0.992
		0.3457	164.90	164.85	165.00	164.82	1.4161	1.204	1.006
		0.2393	148.45	148.50	148.45	148.47	1.2756	1.152	1.017
15	D 164	0.6332	212.10	212.05	212.15	212.10	1.8788	1.388	0.996
		0.4871	185.05	185.05	184.95	185.02	1.6389	1.312	1.014
		0.3518	161.90	161.95	161.90	161.92	1.4343	1.235	1.025
		0.2435	145.00	145.10	145.05	145.05	1.2849	1.170	1.029
20	D 164	0.6444	213.20	213.25	213.15	213.20	1.8886	1.379	0.987
		0.4957	185.75	185.55	185.50	185.60	1.6441	1.299	1.003
		0.3580	162.30	162.30	162.40	162.33	1.4379	1.223	1.014
		0.2478	146.15	146.25	146.10	146.17	1.2948	1.190	1.043

TABLE LI

Viscometry Data of Poly(hexamethylene sebacamide) of Mean ParticleDiameter, 0.085 in., Reacted at 140 °C

Reaction Time	Viscometer	Solution Concentration	Efflux Time				Relative Viscosity	Reduced Specific Viscosity	Inherent Viscosity
			1	2	3	Ave.			
hr		gm/dl	sec					dl/gm	dl/gm
0	D 162	0.6408	215.10	215.15	215.20	215.15	1.8484	1.324	0.959
		0.4929	188.00	188.00	188.00	188.00	1.6153	1.248	0.973
		0.3560	165.20	165.20	165.10	165.13	1.4188	1.176	0.983
		0.2465	148.20	148.15	148.15	148.17	1.2730	1.108	0.979
5	D 164	0.6392	210.25	210.25	210.25	210.25	1.8624	1.349	0.973
		0.4917	183.65	183.80	183.60	183.68	1.6271	1.275	0.990
		0.3551	161.50	161.45	161.45	161.48	1.4304	1.212	1.008
		0.2458	145.10	145.30	145.20	145.20	1.2864	1.165	1.025
10	D 162	0.6552	226.10	225.90	226.00	226.00	1.9417	1.437	1.013
		0.5040	195.60	195.85	195.90	195.88	1.5830	1.355	1.033
		0.3640	170.55	170.55	170.60	170.57	1.4655	1.279	1.050
		0.2520	152.20	152.15	152.25	152.20	1.3077	1.221	1.065
15	D 164	0.6498	218.90	218.90	218.90	218.90	1.9391	1.445	1.019
		0.4998	189.75	189.75	189.70	189.73	1.6807	1.362	1.039
		0.3610	165.50	165.50	165.50	165.50	1.4660	1.291	1.060
		0.2499	147.70	147.80	147.70	147.73	1.3086	1.235	1.076
20	D 164	0.6326	218.35	218.45	218.50	218.43	1.9349	1.478	1.043
		0.4866	189.70	189.70	189.70	189.70	1.6804	1.398	1.067
		0.3514	165.60	165.60	165.50	165.57	1.4666	1.328	1.090
		0.2433	147.30	147.35	147.35	147.33	1.3051	1.254	1.094

TABLE LII

Viscometry Data of Poly(hexamethylene sebacamide) of Mean Particle
Diameter, 0.085 in., Reacted at 160 °C

Reaction Time	Viscometer	Solution Concentration	Efflux Time				Relative Viscosity	Reduced Specific Viscosity	Inherent Viscosity
			1	2	3	Ave.			
hr		gm/dl	sec					dl/gm	dl/gm
0	D 164	0.6385	207.00	207.00	206.95	206.98	1.8335	1.306	0.950
		0.4911	181.10	181.05	181.10	181.08	1.6040	1.230	0.962
		0.3547	159.60	159.50	159.65	159.58	1.4136	1.166	0.976
		0.2455	143.60	143.60	143.55	143.58	1.2719	1.108	0.980
5	D 164	0.6175	213.80	213.70	213.75	213.75	1.8934	1.447	1.034
		0.4750	186.00	186.05	186.05	186.03	1.6479	1.364	1.052
		0.3431	163.00	162.80	162.80	162.87	1.4427	1.290	1.068
		0.2375	145.85	145.90	145.85	145.82	1.2921	1.230	1.079
10	D 164	0.6100	218.95	219.00	219.00	218.98	1.9398	1.541	1.086
		0.4692	189.60	189.60	189.50	189.57	1.6792	1.448	1.105
		0.3389	165.10	165.15	165.00	165.08	1.4623	1.364	1.121
		0.2346	147.10	146.95	147.00	147.00	1.3022	1.288	1.126
15	D 164	0.6360	225.10	225.25	225.15	225.17	1.9946	1.564	1.086
		0.4892	194.05	193.90	194.10	194.02	1.7187	1.469	1.107
		0.3533	168.30	168.45	168.30	168.35	1.4913	1.391	1.131
		0.2446	149.15	149.15	149.30	149.20	1.3216	1.315	1.140
20	D 164	0.6044	220.65	220.60	220.65	220.63	1.9544	1.579	1.109
		0.4649	191.05	191.15	190.95	191.05	1.6924	1.489	1.132
		0.3358	166.85	166.85	166.75	166.82	1.4777	1.423	1.163
		0.2325	147.95	148.05	148.05	148.02	1.3112	1.338	1.165

TABLE LIII

Viscometry Data of Poly(hexamethylene sebacamide) of Mean ParticleDiameter, 0.085 in., Reacted at 180 °C

Reaction Time	Viscometer	Solution Concentration	Efflux Time				Relative Viscosity	Reduced Specific Viscosity	Inherent Viscosity
			1	2	3	Ave.			
hr		gm/dl	sec					dl/gm	dl/gm
0	D 162	0.6376	215.10	215.20	215.15	214.15	1.8485	1.331	0.964
		0.4905	188.20	188.30	188.10	188.20	1.6170	1.258	0.980
		0.3542	165.50	165.45	165.45	165.47	1.4217	1.191	0.993
		0.2452	148.80	148.60	148.60	148.67	1.2773	1.131	0.998
5	D 164	0.6228	222.60	222.60	222.65	222.62	1.9720	1.561	1.090
		0.4791	192.60	192.45	192.45	192.50	1.7052	1.472	1.114
		0.3460	167.10	167.05	167.05	167.07	1.4799	1.387	1.133
		0.2395	148.55	148.50	148.40	148.47	1.3152	1.316	1.144
10	D 162	0.6400	240.90	240.90	240.80	240.87	2.0695	1.671	1.136
		0.4923	206.20	206.10	206.10	206.13	1.7710	1.566	1.161
		0.3556	117.60	177.60	177.60	177.60	1.5259	1.479	1.188
		0.2426	156.50	156.60	156.40	156.50	1.3446	1.400	1.203
15	D 164	0.6402	236.25	236.30	236.25	236.27	2.0929	1.707	1.154
		0.4925	201.95	202.05	201.95	201.98	1.7892	1.602	1.181
		0.3557	173.65	173.65	173.65	173.65	1.5382	1.513	1.211
		0.2462	152.85	152.70	152.75	152.67	1.3533	1.435	1.229
20	D 164	0.6334	237.55	237.55	237.50	237.53	2.1041	1.743	1.174
		0.4872	203.00	203.00	203.00	203.00	1.7982	1.638	1.204
		0.3519	174.45	174.35	174.40	174.40	1.5449	1.548	1.236
		0.2436	153.15	153.10	153.15	153.13	1.3565	1.463	1.252

TABLE LIV

Viscometry Data of Poly(hexamethylene sebacamide) of Mean ParticleDiameter, 0.134 in., Reacted at 120 °C

Reaction Time	Viscometer	Solution Concentration	Efflux Time				Relative Viscosity	Reduced Specific Viscosity	Inherent Viscosity
			1	2	3	Ave.			
hr		gm/dl	sec					dl/gm	dl/gm
0	D 162	0.6022	205.70	205.75	205.70	205.72	1.7675	1.274	0.946
		0.4632	181.80	181.70	181.80	181.77	1.5617	1.213	0.962
		0.3346	161.30	161.25	161.35	161.30	1.3859	1.153	0.975
		0.2316	146.20	146.30	146.30	146.27	1.2567	1.108	0.987
5	D 162	0.6654	222.10	222.15	221.95	222.07	1.9080	1.365	0.971
		0.5118	193.50	193.45	193.55	193.50	1.6625	1.294	0.993
		0.3697	168.50	168.55	168.60	168.55	1.4481	1.212	1.001
		0.2559	150.80	150.60	150.75	150.72	1.2950	1.153	1.010
10	D 162	0.6580	218.45	218.25	218.40	218.37	1.8762	1.332	0.956
		0.5062	190.65	190.50	190.55	190.57	1.6373	1.259	0.974
		0.3656	167.50	167.60	167.40	167.50	1.4391	1.201	0.996
		0.2531	150.10	150.10	150.10	150.10	1.2897	1.145	1.005
15	D 164	0.6538	214.90	214.85	214.95	214.90	1.9036	1.382	0.985
		0.5029	187.20	187.10	187.00	187.10	1.6574	1.307	1.005
		0.3632	163.60	163.60	163.50	163.57	1.4489	1.236	1.021
		0.2515	145.90	145.95	146.00	145.95	1.2929	1.165	1.021
20	D 162	0.6010	214.40	214.25	214.30	214.32	1.8414	1.400	1.016
		0.4523	187.45	187.40	187.35	187.40	1.6101	1.320	1.030
		0.3339	164.85	165.00	165.00	164.95	1.4172	1.249	1.044
		0.2312	148.20	148.15	149.15	148.17	1.2730	1.181	1.044

TABLE LV

Viscometry Data of Poly(hexamethylene sebacamide) of Mean Particle
Diameter, 0.134 in., Reacted at 140 °C

Reaction Time	Viscometer	Solution Concentration	Efflux Time				Relative Viscosity	Reduced Specific Viscosity	Inherent Viscosity
			1	2	3	Ave.			
hr		gm/dl	sec					dl/gm	dl/gm
0	D 162	0.6054	207.10	207.10	207.00	207.07	1.7791	1.287	0.952
		0.4657	183.60	183.50	183.60	183.57	1.5772	1.239	0.978
		0.3363	162.30	162.40	162.30	162.33	1.3947	1.174	0.989
		0.2328	146.80	146.85	146.90	146.85	1.2617	1.124	0.999
5	D 162	0.6308	220.60	220.50	220.40	220.50	1.8945	1.418	1.013
		0.4852	192.00	192.10	192.10	192.07	1.6502	1.340	1.032
		0.3504	168.15	168.20	168.20	168.18	1.4450	1.270	1.051
		0.2426	150.55	150.55	150.55	150.55	1.2935	1.210	1.061
10	D 162	0.6356	225.70	225.55	225.55	225.60	1.9383	1.476	1.041
		0.4889	195.45	195.55	195.50	195.50	1.6797	1.390	1.061
		0.3531	170.50	170.50	170.50	170.50	1.4649	1.317	1.081
		0.2445	151.95	151.95	151.95	151.95	1.3055	1.249	1.090
15	D 164	0.6190	217.25	217.40	217.20	217.28	1.9247	1.494	1.058
		0.4762	188.65	188.55	188.65	188.62	1.6708	1.409	1.078
		0.3439	164.60	164.60	164.50	164.57	1.4578	1.331	1.096
		0.2381	146.80	146.80	146.90	146.83	1.3006	1.262	1.104
20	D 164	0.6532	225.25	225.40	225.25	225.30	1.9957	1.524	1.058
		0.5025	194.10	194.00	194.10	194.07	1.7191	1.431	1.078
		0.3629	168.25	168.20	168.10	168.18	1.4898	1.350	1.098
		0.2512	149.45	149.40	149.50	149.45	1.3239	1.289	1.117

TABLE LVI

Viscometry Data of Poly(hexamethylene sebacamide) of Mean Particle
Diameter, 0.134 in., Reacted at 160 °C

Reaction Time	Viscometer	Solution Concentration	Efflux Time				Relative Viscosity	Reduced Specific Viscosity	Inherent Viscosity
			1	2	3	Ave.			
hr		gm/dl	sec					dl/gm	dl/gm
0	D 162	0.6232	213.50	213.50	213.50	213.50	1.8344	1.339	0.974
		0.4794	187.35	187.15	187.15	187.22	1.6086	1.270	0.992
		0.3462	164.65	164.55	164.50	164.57	1.4140	1.196	1.001
		0.2397	148.20	148.10	148.10	148.13	1.2727	1.138	1.006
5	D 162	0.6024	218.85	218.75	218.90	218.83	1.8802	1.461	1.048
		0.4634	190.85	190.85	190.65	190.78	1.6391	1.379	1.066
		0.3347	167.60	167.60	167.60	167.60	1.4400	1.315	1.089
		0.2317	150.30	150.40	150.35	150.35	1.2918	1.259	1.105
10	D 162	0.6042	226.75	226.70	226.60	226.68	1.9476	1.568	1.103
		0.4648	196.25	196.10	196.25	196.20	1.6857	1.475	1.123
		0.3357	170.75	170.80	170.75	170.77	1.4672	1.392	1.142
		0.2324	152.15	152.25	152.30	152.23	1.3079	1.325	1.155
15	D 162	0.6298	234.55	234.60	234.65	234.60	2.0156	1.613	1.113
		0.4845	202.05	202.05	201.90	202.00	1.7355	1.518	1.138
		0.3499	174.75	174.85	174.75	174.78	1.5017	1.434	1.162
		0.2422	154.75	154.70	154.70	154.72	1.3293	1.360	1.175
20	D 162	0.6102	231.35	231.55	231.35	231.42	1.9883	1.620	1.126
		0.4694	199.20	199.35	199.35	199.30	1.7123	1.517	1.146
		0.3390	174.00	173.95	174.00	173.98	1.4948	1.460	1.186
		0.2347	154.10	154.10	153.95	154.05	1.3236	1.379	1.195

TABLE LVII

Viscometry Data of Poly(hexamethylene sebacamide) of Mean Particle
Diameter, 0.134 in., Reacted at 180 °C

Reaction Time	Viscometer	Solution Concentration	Efflux Time				Relative Viscosity	Reduced Specific Viscosity	Inherent Viscosity
			1	2	3	Ave.			
hr		gm/dl	sec					dl/gm	dl/gm
0	D 162	0.6374	215.90	216.10	216.00	216.00	1.8558	1.343	0.970
		0.4903	188.40	188.45	188.50	188.45	1.6191	1.263	0.983
		0.3541	165.30	165.30	165.30	165.30	1.4202	1.187	0.991
		0.2452	148.65	148.70	148.60	148.65	1.2771	1.130	0.998
5	D 164	0.6660	236.60	236.60	236.50	236.57	2.0956	1.645	1.111
		0.5123	201.70	201.75	201.80	201.75	1.7871	1.536	1.133
		0.3700	173.10	173.10	173.05	173.08	1.5332	1.441	1.155
		0.2562	152.35	152.20	152.20	152.20	1.3487	1.361	1.168
10	D 162	0.6540	249.80	249.60	249.80	249.73	2.1456	1.752	1.167
		0.5031	212.60	212.60	212.65	212.68	1.8268	1.643	1.198
		0.3633	181.60	181.70	181.70	181.67	1.5609	1.544	1.226
		0.2515	159.10	159.00	159.00	159.03	1.3664	1.457	1.241
15	D 164	0.6046	233.80	233.50	233.65	233.65	2.0697	1.769	1.203
		0.4651	200.60	200.80	200.80	200.73	1.7781	1.673	1.237
		0.3359	172.15	172.15	172.10	172.13	1.5248	1.562	1.256
		0.2325	151.75	151.90	151.85	151.83	1.3449	1.483	1.274
20	D 164	0.6776	254.25	254.25	254.15	254.22	2.2519	1.848	1.198
		0.5212	214.75	214.65	214.60	214.67	1.9016	1.730	1.233
		0.3764	181.90	181.90	182.00	181.93	1.6116	1.625	1.268
		0.2606	158.10	158.10	158.00	158.07	1.4002	1.536	1.292

TABLE LVIII

Viscometry Data of Poly(ethylene terephthalate) of Mean ParticleDiameter, 0.038 in., Reacted at 160 °C

Reaction Time	Viscometer	Solution Concentration	Efflux Time				Relative Viscosity	Reduced Specific Viscosity	Inherent Viscosity
			1	2	3	Ave.			
hr		gm/dl	sec					dl/gm	dl/gm
0	D 446	0.6091	295.75	295.65	295.70	295.70	1.4566	0.750	0.617
		0.4685	272.75	272.70	272.80	272.75	1.3435	0.733	0.630
		0.3384	251.90	251.80	251.80	251.87	1.2407	0.711	0.637
		0.2343	236.05	236.05	236.00	236.03	1.1625	0.694	0.643
5	D 445	0.6485	302.50	302.40	302.40	302.43	1.5136	0.792	0.639
		0.4989	276.15	276.15	276.25	276.18	1.3822	0.766	0.649
		0.3603	253.15	253.20	253.15	253.17	1.2671	0.741	0.657
		0.2495	235.70	235.80	234.80	235.77	1.1800	0.721	0.663
10	D 446	0.6306	304.65	304.75	304.65	304.68	1.5008	0.794	0.644
		0.4851	278.70	278.75	278.85	278.77	1.3732	0.769	0.654
		0.3503	256.15	255.90	256.10	256.05	1.2613	0.746	0.663
		0.2425	238.80	238.80	238.75	238.78	1.1762	0.727	0.669
15	D 445	0.6197	299.85	299.90	299.90	299.88	1.5008	0.808	0.655
		0.4767	274.40	274.45	274.35	274.40	1.3733	0.783	0.665
		0.3443	251.90	251.90	251.90	251.90	1.2607	0.757	0.673
		0.2383	234.90	234.90	235.00	234.97	1.1760	0.739	0.680
20	D 446	0.6101	304.80	304.75	304.70	304.75	1.5012	0.822	0.666
		0.4693	279.00	279.00	279.05	279.02	1.3744	0.798	0.678
		0.3389	256.20	256.20	256.05	256.15	1.2618	0.772	0.686
		0.2347	238.90	238.85	238.80	238.85	1.1765	0.752	0.693

TABLE LIX

Viscometry Data of Poly(ethylene terephthalate) of Mean ParticleDiameter, 0.038 in., Reacted at 180 °C

Reaction Time	Viscometer	Solution Concentration	Efflux Time				Relative Viscosity	Reduced Specific Viscosity	Inherent Viscosity
			1	2	3	Ave.			
hr		gm/dl	sec					dl/gm	dl/gm
0	D 446	0.5874	290.90	290.80	290.90	290.87	1.4328	0.737	0.612
		0.4518	268.90	268.70	268.80	268.80	1.3241	0.717	0.621
		0.3262	249.10	249.10	249.20	249.13	1.2272	0.696	0.627
		0.2259	234.10	234.05	234.20	234.12	1.1532	0.678	0.631
5	D 445	0.6023	302.90	303.00	302.95	302.95	1.5162	0.857	0.691
		0.4633	276.25	276.25	276.20	276.23	1.3825	0.826	0.699
		0.3346	253.50	253.40	253.40	253.43	1.2684	0.802	0.711
		0.2317	235.95	236.00	236.00	235.98	1.1810	0.781	0.718
10	D 445	0.5954	310.05	309.95	310.00	310.00	1.5515	0.926	0.738
		0.4580	281.80	281.80	281.70	281.77	1.4102	0.896	0.751
		0.3308	257.30	257.30	257.20	257.27	1.2876	0.869	0.764
		0.2290	238.45	238.55	238.60	238.53	1.1938	0.846	0.774
15	D 446	0.5902	315.10	315.00	315.05	315.03	1.5767	0.977	0.771
		0.4540	285.30	285.30	285.35	285.32	1.4280	0.943	0.785
		0.3279	259.70	259.65	259.60	259.65	1.2995	0.913	0.799
		0.2270	240.00	239.90	240.05	239.98	1.2010	0.885	0.807
20	D 446	0.6209	330.10	330.10	330.00	330.07	1.6259	1.008	0.783
		0.4776	297.20	297.30	297.10	297.20	1.4640	0.972	0.798
		0.3449	268.70	268.55	268.80	268.68	1.3235	0.938	0.813
		0.2388	247.20	247.10	247.10	247.13	1.2173	0.910	0.823

TABLE LX

Viscometry Data of Poly(ethylene terephthalate) of Mean Particle
Diameter, 0.038 in., Reacted at 200 °C

Reaction Time	Viscometer	Solution Concentration	Efflux Time				Relative Viscosity	Reduced Specific Viscosity	Inherent Viscosity
			1	2	3	Ave.			
hr		gm/dl	sec					dl/gm	dl/gm
0	D 445	0.5984	288.95	289.00	289.00	288.98	1.4463	0.746	0.617
		0.4603	266.30	266.30	266.20	266.27	1.3326	0.723	0.624
		0.3324	246.50	246.40	246.40	246.43	1.2333	0.702	0.631
		0.2302	231.20	231.25	231.30	231.25	1.1573	0.683	0.635
5	D 446	0.5952	328.80	328.70	328.75	328.75	1.6194	1.041	0.810
		0.4578	296.20	296.25	296.30	296.25	1.4593	1.003	0.826
		0.3307	268.10	268.10	268.00	268.07	1.3205	0.969	0.841
		0.2289	246.70	246.70	246.80	246.73	1.2154	0.941	0.852
10	D 445	0.6006	342.50	342.50	342.45	342.48	1.7140	1.189	0.897
		0.4620	305.40	305.50	305.50	305.47	1.5288	1.145	0.919
		0.3337	272.70	272.65	272.70	272.68	1.3647	1.093	0.932
		0.2310	248.75	248.75	248.75	248.75	1.2449	1.060	0.948
15	D 446	0.6125	361.40	361.30	361.35	361.35	1.7800	1.273	0.941
		0.4712	319.50	319.45	319.40	319.45	1.5736	1.217	0.962
		0.3403	283.40	283.50	283.40	283.43	1.3961	1.164	0.981
		0.2356	257.10	257.10	257.10	257.10	1.2664	1.131	1.002
20	D 445	0.6320	369.80	369.80	369.70	369.77	1.8506	1.346	0.974
		0.4862	325.10	324.90	324.80	324.93	1.6262	1.288	1.000
		0.3511	286.15	286.20	286.00	286.12	1.4320	1.230	1.023
		0.2431	257.40	257.30	257.30	257.33	1.2879	1.184	1.041

TABLE LXI

Viscometry Data of Poly(ethylene terephthalate) of Mean ParticleDiameter, 0.084 in., Reacted at 160 °C

Reaction Time	Viscometer	Solution Concentration	Efflux Time				Relative Viscosity	Reduced Specific Viscosity	Inherent Viscosity
			1	2	3	Ave.			
hr		gm/dl	sec					dl/gm	dl/gm
0	D 446	0.5914	293.30	293.20	293.30	293.27	1.4446	0.752	0.622
		0.4549	270.30	270.15	270.25	270.23	1.3311	0.728	0.629
		0.3286	250.20	250.00	250.10	250.10	1.2320	0.706	0.635
		0.2275	234.90	234.90	234.85	234.88	1.1570	0.690	0.641
5	D 445	0.6306	294.60	294.75	294.55	294.63	1.4746	0.753	0.616
		0.4851	270.80	270.80	270.75	270.78	1.3552	0.732	0.627
		0.3503	249.90	249.80	249.70	249.80	1.2502	0.714	0.637
		0.2425	233.50	233.50	233.55	233.52	1.1687	0.696	0.643
10	D 445	0.6302	297.20	297.30	297.30	297.27	1.4878	0.774	0.630
		0.4848	272.45	272.40	272.40	272.42	1.3634	0.750	0.639
		0.3501	250.85	250.90	250.90	250.88	1.2556	0.730	0.650
		0.2424	234.30	234.25	234.20	234.25	1.1724	0.711	0.656
15	D 446	0.6273	303.60	303.70	303.75	303.68	1.4959	0.791	0.642
		0.4825	278.20	278.10	278.10	278.13	1.3700	0.767	0.652
		0.3485	225.80	225.80	225.70	225.77	1.2599	0.746	0.663
		0.2413	238.65	238.70	238.80	238.72	1.1759	0.729	0.672
20	D 445	0.6211	299.10	299.05	299.10	299.08	1.4968	0.800	0.649
		0.4778	274.10	274.10	274.00	274.07	1.3717	0.778	0.661
		0.3451	251.80	251.90	252.00	251.90	1.2607	0.755	0.671
		0.2389	235.10	235.10	235.20	235.13	1.1768	0.740	0.681

TABLE LXII

Viscometry Data of Poly(ethylene terephthalate) of Mean Particle
Diameter, 0.084 in., Reacted at 180 °C

Reaction Time	Viscometer	Solution Concentration	Efflux Time				Relative Viscosity	Reduced Specific Viscosity	Inherent Viscosity
			1	2	3	Ave.			
hr		gm/dl	sec					dl/gm	dl/gm
0	D 445	0.5964	287.30	287.35	287.40	287.35	1.4381	0.735	0.609
		0.4588	265.00	265.00	265.00	265.00	1.3263	0.711	0.616
		0.3313	245.70	245.70	245.60	245.67	1.2295	0.693	0.624
		0.2294	230.70	230.80	230.75	230.75	1.1548	0.675	0.627
5	D 445	0.6197	301.20	301.15	301.20	301.18	1.5073	0.819	0.662
		0.4767	275.35	275.50	275.35	275.40	1.3783	0.794	0.673
		0.3443	252.60	252.65	252.65	252.63	1.2644	0.768	0.681
		0.2383	235.55	235.50	235.50	235.52	1.1787	0.750	0.690
10	D 446	0.5926	307.60	307.50	307.40	307.50	1.5147	0.869	0.701
		0.4558	280.60	280.75	280.70	280.68	1.3826	0.839	0.711
		0.3292	257.50	257.45	257.60	257.52	1.2685	0.816	0.722
		0.2279	239.80	239.80	239.80	239.80	1.1812	0.795	0.731
15	D 445	0.6065	311.20	311.15	311.10	311.15	1.5572	0.919	0.730
		0.4665	282.45	282.50	282.45	282.47	1.4137	0.887	0.742
		0.3369	257.60	257.65	257.60	257.62	1.2893	0.859	0.754
		0.2333	238.75	238.80	238.60	238.72	1.1948	0.835	0.763
20	D 446	0.5992	316.55	316.50	316.70	316.58	1.5594	0.934	0.741
		0.4609	287.50	287.50	287.55	287.52	1.4163	0.903	0.755
		0.3329	262.20	262.35	262.25	262.27	1.2919	0.877	0.769
		0.2305	243.10	243.00	243.00	243.03	1.1971	0.855	0.780

TABLE LXIII

Viscometry Data of Poly(ethylene terephthalate) of Mean ParticleDiameter, 0.084 in., Reacted at 200 °C

Reaction Time	Viscometer	Solution Concentration	Efflux Time				Relative Viscosity	Reduced Specific Viscosity	Inherent Viscosity
			1	2	3	Ave.			
hr		gm/dl	sec					dl/gm	dl/gm
0	D 446	0.5850	290.40	290.40	290.30	290.37	1.4303	0.736	0.612
		0.4500	268.20	268.00	268.10	268.10	1.3206	0.712	0.618
		0.3250	248.50	248.65	248.60	248.58	1.2245	0.691	0.623
		0.2250	233.80	233.75	233.85	233.80	1.1517	0.674	0.628
5	D 446	0.5956	320.00	320.00	319.90	319.97	1.5761	0.967	0.764
		0.4582	290.00	290.00	290.05	290.02	1.4286	0.935	0.778
		0.3309	263.80	263.90	263.90	263.87	1.3000	0.907	0.793
		0.2291	243.90	243.90	243.80	243.87	1.2013	0.879	0.801
10	D 445	0.6025	328.85	328.80	328.85	328.83	1.6457	1.072	0.827
		0.4635	295.80	295.65	295.80	290.75	1.4802	1.036	0.846
		0.3347	266.60	266.70	266.70	266.67	1.3346	1.000	0.862
		0.2317	244.70	244.80	244.80	244.77	1.2250	0.971	0.876
15	D 446	0.5934	343.00	343.10	343.00	343.03	1.6897	1.162	0.884
		0.4565	307.00	307.15	307.00	307.05	1.5125	1.123	0.906
		0.3297	275.50	275.60	275.50	275.53	1.3572	1.083	0.926
		0.2282	251.55	251.65	251.60	251.60	1.2393	1.049	0.940
20	D 446	0.6023	349.35	349.35	349.20	349.30	1.7206	1.196	0.901
		0.4633	311.50	311.50	311.35	311.45	1.5342	1.153	0.924
		0.3346	278.50	278.40	278.55	278.48	1.3718	1.111	0.945
		0.2317	253.50	253.45	253.60	253.52	1.2488	1.074	0.959

Appendix E

Digital Computer Fortran Source Lists

Fortran Source List for Construction of Molecular
Weight Ratio versus KT Table

```
PRINT 10
10 FORMAT(8X,2HKT,16X,4HSLAB,16X,6HSPHERE)
   AKT=0.0001
23 SUM1=0.
   SUM2=0.
   AN=1.
22 ASLAB=((2.*AN+1.)**2)*AKT
   ASPHE=(AN**2)*AKT
   SUM1=SUM1+1./(((2.*AN+1.)**2)*EXP(ASLAB))
   SUM2=SUM2+1./((AN**2)*EXP(ASPHE))
   IF(AKT-0.007)25,25,26
26 IF(AKT-0.01)27,27,28
28 IF(AKT-0.02)29,29,30
30 IF(AKT-0.04)31,31,32
32 IF(AKT-0.08)33,33,34
34 IF(AKT-0.16)35,35,36
36 IF(AKT-0.30)37,37,38
38 IF(AKT-0.80)39,39,40
25 IF(AN-50.)20,20,21
27 IF(AN-40.)20,20,21
29 IF(AN-30.)20,20,21
31 IF(AN-20.)20,20,21
33 IF(AN-14.)20,20,21
35 IF(AN-8.)20,20,21
37 IF(AN-6.)20,20,21
39 IF(AN-3.)20,20,21
20 AN=AN+1.
   GO TO 22
21 ALPHA1=(8./(3.14159**2))*((1./EXP(AKT))+SUM1)
   ALPHA2=(6./(3.14159**2))*SUM2
   PRINT 11,AKT,ALPHA1,ALPHA2
11 FORMAT(F15.6,5X,F15.10,5X,F15.10)
   AKT=AKT+0.0001
   GO TO 23
40 STOP
   END
```

TABLE LXIV

An Excerpt of Rate Function Versus
Molecular Weight Ratio Table

Rate Function $K_1(t)$ or $K_2(t)$	Molecular Weight Ratio	
	Sheet	Sphere
0.046000	0.84593293	0.78288079
0.046100	0.84576556	0.78266015
0.046200	0.84559836	0.78243976
0.046300	0.84543134	0.78221961
0.046400	0.84526451	0.78199978
0.046500	0.84509786	0.78178018
0.046600	0.84493140	0.78156087
0.046700	0.84476509	0.78134183
0.046800	0.84459898	0.78112304
0.046900	0.84443303	0.78090452
0.047000	0.84426728	0.78068630

Fortran Source List for Computations of Intrinsic Viscosity
and Average Molecular Weight

```
        DIMENSION X(5),Y(5),YSP(5),YLN(5)
61 READ 51,L
        READ 1,SK,SA
50 READ 51,K
        READ 2,TEMP,TIME,N
        READ 3,(X(I),Y(I),I=1,N)
        DO 4 I=1,N
            YSP(I)=(Y(I)-1.)/X(I)
4      YLN(I)=(ALOG(Y(I)))/X(I)
C      LEAST SQUARES FIT TO DATA
        SX=0.
        SSX=0.
        SYSP=0.
        SSYSP=0.
        SKYSP=0.
        SYLN=0.
        SSYLN=0.
        SKYLN=0.
        DO 5 I=1,N
            SX=SX+X(I)
            SSX=SSX+X(I)*X(I)
            SYSP=SYSP+YSP(I)
            SSYSP=SSYSP+YSP(I)*YSP(I)
            SKYSP=SKYSP+X(I)*YSP(I)
            SYLN=SYLN+YLN(I)
            SSYLN=SSYLN+YLN(I)*YLN(I)
```

(Continued on page 243)

Fortran Source List for Computations of Intrinsic Viscosity
and Average Molecular Weight

(Continued from page 242)

```
5 SXYLN=SXYLN+X(I)*YLN(I)
  AN=N
  CORXLN=SXYLN-SX*SYLN/AN
  CORXSP=SXYSP-SX*SYSP/AN
  CORSSX=SSX-SX*SX/AN
  TSYSP=SSYSP-SYSP*SYSP/AN
  TSYLN=SSYLN-SYLN*SYLN/AN
  BSP=CORXSP/CORSSX
  BLN=CORXLN/CORSSX
  ASP=SYSP/AN-BSP*SX/AN
  ALN=SYLN/AN-BLN*SX/AN
  RESSP=TSYSP-BSP*BSP*CORSSX
  RESLN=TSYLN-BLN*BLN*CORSSX
  EMSSP=RESSP/(AN-2.)
  EMSLN=RESLN/(AN-2.)
C  CONFIDENCE LIMITS FOR INTERCEPT
  CFLTSP=4.303*SQRT(EMSSP*(1./AN+(SX/AN)*(SX/AN)/CORSSX))
  CFLTLN=4.303*SQRT(EMSLN*(1./AN+(SX/AN)*(SX/AN)/CORSSX))
C  CALCULATION OF HUGGINS CONSTANT
  HKLN=BLN/(ALN*ALN)
  HKSP=BSP/(ASP*ASP)
```

(Continued on page 244)

Fortran Source List for Computations of Intrinsic Viscosity
and Average Molecular Weight

(Continued from page 243)

```
C      CALCULATION OF MOLECULAR WEIGHT
      AMOLSP=SK*(ASP**SA)
      AMOLLN=SK*(ALN**SA)
      CLMOSP=SK*(CFLTSP**SA)
      CLMOLN=SK*(CFLTLN**SA)
      PRINT 10,TEMP,TIME
      PRINT 11
      PRINT 12,(X(I),Y(I),YSP(I),YLN(I),I=1,N)
      PRINT 13
      PRINT 14,ASP,CFLTSP,AMOLSP,CLMOSP,BSP
      PRINT 20,HKSP
      PRINT 15
      PRINT 14,ALN,CFLTLN,AMOLLN,CLMOLN,BLN
      PRINT 20,HKLN
      IF(K-1)50,50,52
52 IF(L-1)61,61,62
      1 FORMAT(2F10.2)
51 FORMAT(I2)
      2 FORMAT(2F10.0,I1)
      3 FORMAT(2F10.5)
```

(Continued on page 245)

Fortran Source List for Computations of Intrinsic Viscosity
and Average Molecular Weight

(Continued from page 244)

```
10 FORMAT(5X,14HREACTION TEMP=,F5.0,5X,14HREACTION TIME=,F5.0)
11 FORMAT(10X,4HCONC,6X,2HRV,5X,5HSPV/C,3X,5HLRV/C)
12 FORMAT(9X,F6.4,3X,F6.4,3X,F5.3,3X,F5.3)
13 FORMAT(20X,4HIVSP,4X,4HCLIV,4X,6HMOL WT,3X,4HCLMW,5X,5HSLOPE)
14 FORMAT(19X,F5.3,3X,F6.4,3X,F6.0,3X,F6.0,3X,F5.3)
20 FORMAT(20X,17HHUGGINS CONSTANT ,F5.3)
15 FORMAT(20X,4HIVLN,4X,4HCLIV,4X,6HMOL WT,3X,4HCLMW,5X,5HSLOPE)
62 STOP
   END
```


APPENDIX F

Variance Analyses of Intrinsic Viscosity Data

(Nomenclature are defined in
Sample Calculations, pages
135 through 138.)

Analysis of Variance for Split-Plot Experiment

Polymer: Poly(hexamethylene adipamide)

X - Table: Entries are X_{ijk} 's

A_i	B_j	C_k					T_{ij}
		0	5	10	15	20	
120	b1	0.834	0.952	0.962	0.973	0.974	4.695
	b2	0.825	0.950	0.987	0.967	0.978	4.707
140	b1	0.825	0.973	1.003	1.042	1.044	4.887
	b2	0.829	0.972	1.009	1.017	1.059	4.886
160	b1	0.835	1.045	1.113	1.161	1.185	5.339
	b2	0.830	1.063	1.113	1.171	1.205	5.382
180	b1	0.859	1.160	1.289	1.357	1.457	6.122
	b2	0.842	1.173	1.302	1.396	1.490	6.203
$T_{..k}$		6.679	8.288	8.778	9.084	9.392	42.221 = $T_{...}$

AC - Table: Entries are $T_{i.k}$'s

A_i	C_k					$T_{i..}$
	0	5	10	15	20	
120	1.659	1.902	1.949	1.940	1.952	9.402
140	1.654	1.945	2.012	2.059	2.103	9.773
160	1.665	2.108	2.226	2.332	2.390	10.721
180	1.701	2.333	2.591	2.753	2.947	12.325

BC - Table: Entries are $T_{.jk}$'s

B_j	C_k					$T_{.j}$
	0	5	10	15	20	
b1	3.353	4.130	4.367	4.533	4.660	21.043
b2	3.326	4.158	4.411	4.551	4.732	21.178

(Continued on page 248)

Analysis of Variance for Split-Plot Experiment

Polymer: Poly(hexamethylene adipamide)

(Continued from page 247)

Computation of Sum of Squares

$$\text{Correction Factor (C.F.)} = \frac{T^2_{\dots}}{40} = \frac{42.221^2}{40} = 44.565321$$

$$SS_T = \sum_i \sum_j \sum_k X^2_{ijk} - \text{C.F.} = 45.805897 - \text{C.F.} = 1.240576$$

$$SS_A = \sum_i \frac{T^2_{i..}}{10} - \text{C.F.} = 45.075460 - \text{C.F.} = 0.510139$$

$$SS_B = \sum_j \frac{T^2_{.j.}}{20} - \text{C.F.} = 44.565777 - \text{C.F.} = 0.000456$$

$$SS_C = \sum_k \frac{T^2_{..k}}{8} - \text{C.F.} = 45.135249 - \text{C.F.} = 0.569928$$

$$SS_{AB} = \sum_i \sum_j \frac{T^2_{ij.}}{5} - SS_A - SS_B - \text{C.F.} = 45.076315 - SS_A - SS_B - \text{C.F.} \\ = 0.000399$$

$$SS_{AC} = \sum_i \sum_k \frac{T^2_{i.k}}{2} - SS_A - SS_C - \text{C.F.} = 45.803022 - SS_A - SS_C - \text{C.F.} \\ = 0.157634$$

$$SS_{BC} = \sum_j \sum_k \frac{T^2_{.jk}}{4} - SS_B - SS_C - \text{C.F.} = 45.136368 - SS_B - SS_C - \text{C.F.} \\ = 0.000663$$

Analysis of Variance for Split-Plot Experiment

Polymer: Poly(hexamethylene sebacamide)

X - Table: Entries are X_{ijk} 's

A_i	B_j	C_k					T_{1j}
		0	5	10	15	20	
120	b1	0.966	1.005	1.028	1.036	1.060	5.095
	b2	1.004	1.020	1.031	1.035	1.049	5.139
140	b1	0.977	1.048	1.084	1.102	1.121	5.332
	b2	1.025	1.081	1.110	1.121	1.140	5.477
160	b1	0.986	1.094	1.134	1.163	1.199	5.576
	b2	1.013	1.133	1.172	1.204	1.238	5.760
180	b1	1.009	1.165	1.233	1.267	1.293	5.967
	b2	0.996	1.184	1.276	1.304	1.342	6.102
$T_{..k}$		7.976	8.730	9.068	9.232	9.442	44.448 = $T_{...}$

AC - Table: Entries are $T_{i.k}$'s

A_i	C_k					$T_{i..}$
	0	5	10	15	20	
120	1.970	2.025	2.059	2.071	2.109	10.234
140	2.002	2.129	2.194	2.223	2.261	10.809
160	1.999	2.227	2.302	2.367	2.437	11.336
180	2.005	2.349	2.509	2.571	2.635	12.069

BC - Table: Entries are $T_{.jk}$'s

B_j	C_k					$T_{.j}$
	0	5	10	15	20	
b1	3.938	4.312	4.479	4.568	4.673	21.970
b2	4.038	4.418	4.589	4.664	4.769	22.478

(Continued on page 250)

Analysis of Variance for Split-Plot Experiment

Polymer: Poly(hexamethylene sebacamide)

(Continued from page 249)

Computation of Sum of Squares

$$\text{Correction Factor (C.F.)} = \frac{T^2_{\dots}}{40} = \frac{44.448^2}{40} = 49.390618$$

$$SS_T = \sum_i \sum_j \sum_k X^2_{ijk} - \text{C.F.} = 49.793346 - \text{C.F.} = 0.402728$$

$$SS_A = \sum_i \frac{T^2_{i..}}{10} - \text{C.F.} = 49.573489 - \text{C.F.} = 0.182871$$

$$SS_B = \sum_j \frac{T^2_{.j.}}{20} - \text{C.F.} = 49.397069 - \text{C.F.} = 0.006451$$

$$SS_C = \sum_k \frac{T^2_{\dots k}}{8} - \text{C.F.} = 49.554912 - \text{C.F.} = 0.164294$$

$$SS_{AB} = \sum_i \sum_j \frac{T^2_{ij.}}{5} - SS_A - SS_B - \text{C.F.} = 49.580994 - SS_A - SS_B - \text{C.F.}$$

$$= 0.001054$$

$$SS_{AC} = \sum_i \sum_k \frac{T^2_{i.k}}{2} - SS_A - SS_C - \text{C.F.} = 49.783528 - SS_A - SS_C - \text{C.F.}$$

$$= 0.045745$$

$$SS_{BC} = \sum_j \sum_k \frac{T^2_{.jk}}{4} - SS_B - SS_C - \text{C.F.} = 49.561382 - SS_B - SS_C - \text{C.F.}$$

$$= 0.000019$$

Analysis of Variance for Split-Plot Experiment

Polymer: Poly(ethylene terephthalate)

X - Table: Entries are X_{ijk} 's

A_i	B_j	Ck					$T_{ij.}$
		0	5	10	15	20	
160	b1	0.660	0.678	0.685	0.695	0.709	3.427
	b2	0.651	0.662	0.673	0.690	0.702	3.378
180	b1	0.643	0.734	0.797	0.830	0.849	3.853
	b2	0.638	0.706	0.749	0.783	0.806	3.682
200	b1	0.645	0.879	0.978	1.038	1.084	4.624
	b2	0.636	0.825	0.909	0.980	0.999	4.349
$T_{..k}$		3.873	4.484	4.791	5.016	5.149	23.313 = $T_{...}$

AC - Table: Entries are $T_{i.k}$'s

A_i	Ck					$T_{i..}$
	0	5	10	15	20	
160	1.311	1.340	1.358	1.385	1.411	6.805
180	1.281	1.440	1.546	1.613	1.655	7.535
200	1.281	1.704	1.887	2.018	2.083	8.973

BC - Table: Entries are $T_{.jk}$'s

B_j	Ck					$T_{.j.}$
	0	5	10	15	20	
b1	1.948	2.291	2.460	2.563	2.642	11.904
b2	1.925	2.193	2.331	2.453	2.507	11.409

(Continued on page 252)

Analysis of Variance for Split-Plot Experiment

Polymer: Poly(ethylene terephthalate)

(Continued from page 251)

Computation of Sum of Squares

$$\text{Correction Factor (C.F.)} = \frac{T^2 \dots}{30} = \frac{23.313^2}{30} = 18.116532$$

$$SS_T = \sum_i \sum_j \sum_k X^2_{ijk} - \text{C.F.} = 18.627867 - \text{C.F.} = 0.511335$$

$$SS_A = \sum_i \frac{T^2_{i..}}{10} - \text{C.F.} = 18.359898 - \text{C.F.} = 0.243366$$

$$SS_B = \sum_j \frac{T^2_{.j.}}{15} - \text{C.F.} = 18.124700 - \text{C.F.} = 0.008168$$

$$SS_C = \sum_k \frac{T^2_{..k}}{6} - \text{C.F.} = 18.288754 - \text{C.F.} = 0.172222$$

$$SS_{AB} = \sum_i \sum_j \frac{T^2_{ij.}}{5} - SS_A - SS_B - \text{C.F.} = 18.370625 - SS_A - SS_B - \text{C.F.} \\ = 0.002559$$

$$SS_{AC} = \sum_i \sum_k \frac{T^2_{i.k}}{2} - SS_A - SS_C - \text{C.F.} = 18.614831 - SS_A - SS_C - \text{C.F.} \\ = 0.082711$$

$$SS_{BC} = \sum_j \sum_k \frac{T^2_{.jk}}{3} - SS_B - SS_C - \text{C.F.} = 18.298270 - SS_B - SS_C - \text{C.F.} \\ = 0.001348$$

ABSTRACT

Kinetic Studies of Solid-Phase Polycondensation in Two Polyamides and a Polyester

by Fen C. Chen

The effects of polymer particle size, temperature, and time on the continued condensation of two polyamides: poly(hexamethylene adipamide) and poly(hexamethylene sebacamide), and a polyester, poly(ethylene terephthalate), were studied experimentally.

The polyamides were held at elevated temperatures from 120 to 180 °C for periods of 5 to 20 hours in a nitrogen atmosphere. A similar procedure was followed with the polyester except that the range of temperature was 160 to 200 °C. The number-average molecular weights of the polymers before and after treatment were calculated from the polymer intrinsic viscosities. The thermal behavior of selected polymers was also examined by differential thermal analysis.

Poly(hexamethylene adipamide) showed an increase in the number-average molecular weight from approximately 10,000 to 22,000 when treated at 180 °C for 20 hours. Under the same conditions, poly(hexamethylene sebacamide)

showed a change from about 10,000 to 14,000. Poly-(ethylene terephthalate) treated at 200 °C for 20 hours exhibited an increase from approximately 18,000 to 34,000.

Two kinetic equations were derived and were successfully applied to the experimental data. From these equations the specific reaction rates were obtained. The temperature dependency of the reaction rates was expressed in the form of the Arrhenius equation.

The effect of particle size on the reaction was noted. Also noted were changes in polymer thermal behavior as the reaction temperature was raised. At low temperatures the transport of reaction by-products from the interior to the surface of solids controlled the reaction. At high temperatures chemical kinetics determined the reaction.