Thermally Induced Solid State Polycondensation of Nylon 66, Nylon 6-10 and Polyethylene Terephthalate

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The mechanism of solid state polycondensation has been subjected to a fundamental analysis. Equations were formulated for combined diffusion and chemical reaction for two separate situations. One was for solid state polycondensation in polymer flakes or chips. The other dealt with polymer powders. The resultant solutions related molecular weight changes to rate functions. A technique for deriving the rate functions from experimental data is described.

Solid state polycondensations were then studied for nylon 66, nylon 6-10, and polyethylene terephthalate. These data which ranged from 120 to 200°C. were tested with various mechanisms. The most appropriate one was found to be that developed in the present work. Chemical reaction was found to be the rate controlling step in solid state polycondensation in nylon 66, polyethylene terephthalate, powders of nylon 6-10 and larger particles of nylon 6-10 at and above 160°C. Diffusion of byproduct through the solid was the rate controlling step for larger particles of nylon 6-10 at temperatures below 160°C. Thermograms of nylon 6-10 indicated morphological changes which possibly influenced the behavior of the larger nylon 6-10 particles. The Arrhenius relation was fitted to the situations where chemical reaction controlled.

The thermally induced solid state polymerization of condensation polymers is a phenomenon that is well known in industry. The process is carried out by heating (but not melting) the condensation polymers in an inert gas atmosphere. In condensation polymers an equilibrium exists (*1, 2*)

$$P_1 + P_2 \rightleftharpoons P_3 + B$$

where P_1, P_2 are polymer chains which combine to form P_3 which is a longer chain, and B a byproduct which is small molecule such as water. In essence then, solid state polymerization actually involves taking off the byproduct and driving the reaction to the right. There then can be three possible rate determining steps:

1. Chemical reaction
2. Diffusion of byproduct molecules in the solid polymer
3. Diffusion of byproduct molecules from the solid polymer surface to the inert gas.

Most of the previous investigations (*2* to *9*) of solid state polymerization have generally neglected the mechanism aspect. One exception was the work of Lee and Griskey (*9*) who found that the rate controlling steps took place within the polymer itself. This was shown in two ways. First, varying the flow rate of nitrogen through the reactor had little effect on polymerization. This indicated that diffusion into the gas was not a rate controlling step. Furthermore, it was found that the rate of polymerization could be described by the equation

$$\text{rate} = kt^n \tag{1}$$

An equation of this type (*10*) indicates a process in a solid that involves both chemical reaction and diffusion within the material.

A recent study has treated this combined chemical reaction and diffusion in a more fundamental manner. The study first considered two possible geometric situations, polymer flakes and polymer powders. The latter material will more closely resemble spheres while the former is closer to the geometry of plane sheets (see Figures 1 and 2).

In the case of plane sheets (polymer flakes) the model of Figure 2 applies. For such a situation the following equation describes the diffusion

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

The diffusivity is assumed to depend on time. This in essence relates the diffusivity to the byproduct present and the chemical reaction. The initial and boundary conditions are listed below:

$$C = C_o, \quad -L < x < L, \quad t = 0 \tag{3}$$

$$C = C_s, \quad x = L \text{ and } x = -L, \quad t \geqq 0 \tag{4}$$

$$\frac{\partial C}{\partial x} = 0, \quad x = 0, \quad t > 0 \tag{5}$$

In order to solve Equation (2), the following variable transformations are made:

$$\theta = \frac{C_o - C}{C_o - C_s} \tag{6}$$

and

$$dT = D(t)\, dt \tag{7}$$

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Substituting into Equation (2) gives

$$\frac{\partial \theta}{\partial T} = \frac{\partial^2 \theta}{\partial x^2} \tag{8}$$

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

$$\theta = 0, \quad -L < x < L, \quad T = 0 \tag{9}$$

$$\theta = 1, \quad x = L \text{ and } x = -L, \quad T \geqq 0 \tag{10}$$

$$\frac{\partial \theta}{\partial x} = 0, \quad x = 0, \quad T > 0 \tag{11}$$

Equation (8) will be solved by the method of separation of variables. The techniques for doing this are given elsewhere (*11*).

The ultimate solution is:

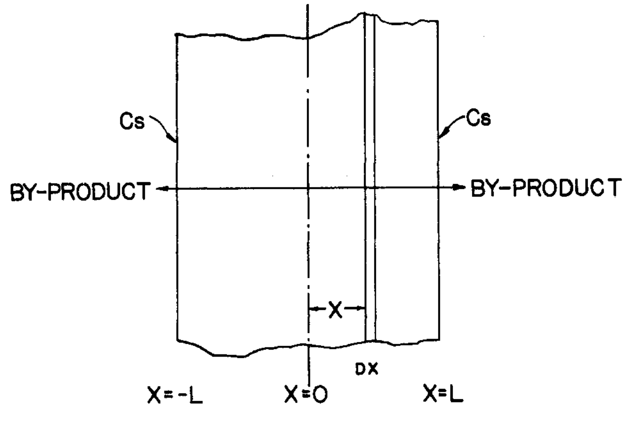
$$\theta = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)} \cos \frac{(2n+1)\pi}{2L} x \; \exp\left[-(2n+1)^2 \pi^2 T/4L^2\right] \tag{12}$$

The number of byproducts released up to time t, W_t, is computed

$$W_t = \int_o^t \left[-D(t) \frac{\partial C}{\partial x} \right]_{x=L} dt = \int_o^T \left[-\frac{\partial C}{\partial x} \right]_{x=L} dT \tag{13}$$

Since $\theta = \dfrac{C_o - C}{C_o - C_s}$, from Equation (6),

$$\left[-\frac{\partial C}{\partial x} \right]_{x=L} = \frac{2}{L} (C_o - C_s) \sum_{n=0}^{\infty} \exp\left[-(2n+1)^2 \pi^2 T/4L^2\right] \tag{14}$$



EQUATION:

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

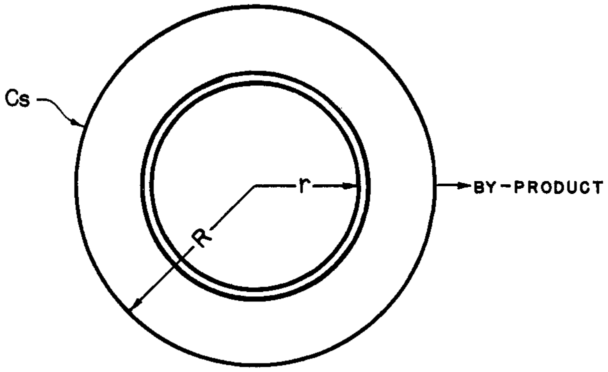
INITIAL & BOUNDARY CONDITIONS:

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

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

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

Fig. 1. Mathematical model for diffusion in a plane sheet.



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:

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

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

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

Fig. 2. Mathematical model for diffusion in a sphere.

Substituting this into Equation (13) and integrating, one gets

$$W_t = (C_o - C_s) \frac{8L}{\pi^2} \left\{ \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} - \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left[-(2n+1)^2 \pi^2 T/4L^2\right] \right\} \tag{15}$$

However,

$$\sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} = \frac{\pi^2}{8} \tag{16}$$

then

$$W_t = (C_o - C_s) \frac{8L}{\pi^2} \left\{ \frac{\pi^2}{8} - \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left[-(2n+1)^2 \pi^2 T/4L^2\right] \right\} \tag{17}$$

As $T \rightarrow \infty$,

$$W_\infty = (C_o - C_s) \frac{8L}{\pi^2} \frac{\pi^2}{8} \tag{18}$$

Thus,

$$1 - \frac{W_t}{W_\infty} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left[-(2n+1)^2 \pi^2 T/4L^2\right] \tag{19}$$

We can replace $1 - \dfrac{W_t}{W_\infty}$ by $\dfrac{\overline{Mn},0}{\overline{Mn},t}$

For convenience, define

$$K_1(t) = \frac{\pi^2 T}{4L^2} \tag{20}$$

where:

$$T = \int_o^t D(t)\, dt \tag{21}$$

Then, from Equation (33) the resulting kinetic equation is

$$\frac{\overline{Mn},0}{\overline{Mn},t} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left[-(2n+1)^2 K_1(t)\right] \quad (22)$$

For a sphere of radius R as shown in Figure 1, the equation corresponding to Equation (2) is

$$\frac{\partial C}{\partial t} = D(t) \left[\frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \frac{\partial C}{\partial r} \right] \quad (23)$$

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

$$C = C_o, \quad r < R, \quad t = 0 \quad (24)$$

$$C = C_s, \quad r = R, \quad t > 0 \quad (25)$$

$$\frac{\partial C}{\partial r} = 0, \quad r = 0, \quad t > 0 \quad (26)$$

For a sphere, Equation (23) must be solved. It can be transformed into Equation (41) by letting $u = Cr$.

$$\frac{\partial u}{\partial t} = D(t) \frac{\partial^2 u}{\partial r^2} \quad (27)$$

Since the above equation is identical to Equation (2) for the case of a plane sheet, the same procedures used previously may be followed to solve Equation (41). For brevity, the solution is given below.

$$\frac{\overline{Mn},0}{\overline{Mn},t} = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left[-n^2 K_2(t)\right] \quad (28)$$

where:

$$K_2(t) = \frac{\pi^2 T}{R^2} \quad (29)$$

and

$$T = \int_0^t D(t)\, dt \quad (30)$$

The terms $K_1(t)$ and $K_2(t)$ are dimensionless and can be considered as rate functions. Computing these rate functions directly from experimental $\overline{Mn},0/\overline{Mn},t$ values is inconvenient since $K_1(t)$ and $K_2(t)$ do not appear explicitly in Equation (20) and (24). However, a table of values of $K_1(t)$, $K_2(t)$ and $\overline{Mn},0/\overline{Mn},t$ may be constructed. This was done by using a digital computer (*11*). The table, because of its volume, is not included in this paper. However, an excerpt is shown in Table 1.

TABLE 1. AN EXCERPT OF RATE FUNCTION VS. MOLECULAR WEIGHT RATIO TABLE

Rate Function $K_1(t)$ or $K_2(t)$	Molecular Weight Ratio $\frac{\overline{Mn},t}{\overline{Mn},o}$	
	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

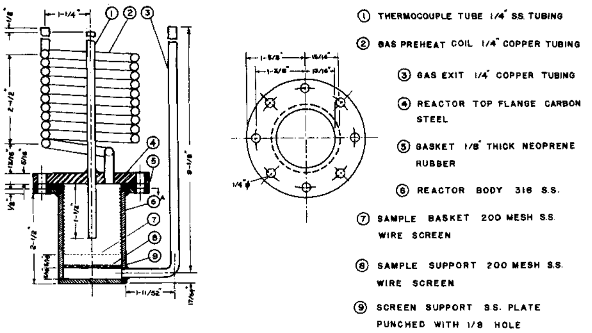


Fig. 3. Batch reactor.

Data of the type shown in Table 1 can be used to find the rate functions. These in turn can then be related to time and temperature, the determiners of the rate of polymerization. The computer program used in compiling Table 1 is given elsewhere (*11*).

The foregoing solutions were tested with experimental data for three separate polymer systems: 66 nylon, 6-10 nylon and polyethylene terephthalate.

A batch fixed bed reactor (Figure 3) was used to study the polymerizations. A wire screen supported by a punched plate was used to retain a given polymer sample of one average particle size. A screen basket was positioned above the wire screen to hold another sample of the same polymer of a different particle size. Ample space was provided above the samples for dispersing the incoming nitrogen which was introduced through a gas preheater. In addition to the reactors themselves, the apparatus consisted of a nitrogen supply, a constant temperature bath, and control devices (see Figure 4).

Four reactors were used simultaneously. Each reactor contained samples of two different particle sizes. A chance procedure was used to determine which sample was placed on the screen and which in the basket.

The reactors were first purged with nitrogen at room temperature for 2 hr. The oil bath was brought to temperature during the purge. After the conclusion of the purge, the reactors were sealed and immersed in the oil bath. A reactor was not introduced until the preceding one had reached bath temperature. Nitrogen flow was resumed when the reactor temperature reached the bath temperature. Reaction times of 5, 10, 15 and 20 hr were randomly assigned to the four reactors. The oil bath temperature was controlled to less than ±1°C. during a run.

The reaction was terminated by removing the reactor, sealing it, and then air cooling it to room temperature. Polymers removed from the reactors were stored in plastic containers and kept in a desiccator.

Intrinsic viscosities of the samples were measured in a Cannon-Ubbelohde dilution type of viscometer. The solvents used were formic acid (nylon 66), meta cresol (nylon 6-10) and phenol/tetrachloroethane (polyethylene terephthalate). Number average molecular weights were calculated from relations given for nylon 66 by Taylor (*12*), for nylon 6-10 by Morgan (*13*), and polyethylene terephthalate by Conix (*14*).

Figures 5, 6, and 7 are plots of $\overline{Mn},t - \overline{Mn},0/\overline{Mn},0$ (that is, conversion) *vs.* reaction time for the polymers studied. As can be seen, particle size appears to be unimportant for nylon 66 but does seem to have an effect in the cases of nylon 6-10 and polyethylene terephthalate.

$K_1(t)$ and $K_2(t)$ values for the polymers were then determined for the polymers. These values were then used to calculate specific reaction rate values for the polymers from the relation

$$K(t) = k' t^m$$

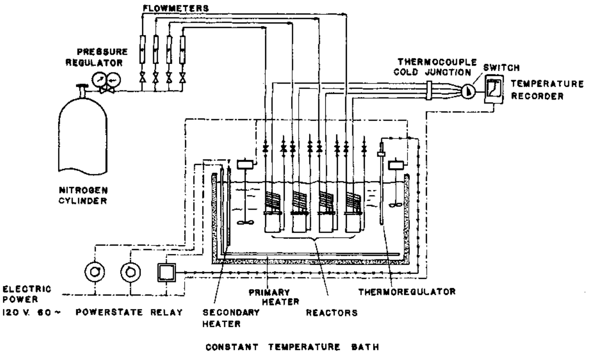


Fig. 4. Overall apparatus.

Note that k' is not the same as the specific reaction rate k given earlier in Equation (1). The latter item has units of (hr.) $^{-n-1}$ while the former item's units are (hr.)$^{-m}$.

TABLE 2. SPECIFIC REACTION RATE OF SOLID-PHASE POLYCONDENSATION

Polymer	Mean particle diameter in.	Temperature °C.	Specific reaction rate k*
poly(hexamethylene adipamide)	0.081 and 0.139	120	2×10^{-2}
		140	3.55×10^{-2}
		160	6.66×10^{-2}
		180	1.18×10^{-1}
poly(hexamethylene sebacamide)	0.085	120	7.11×10^{-4}
		140	1.86×10^{-3}
		160	3.52×10^{-3}
		180	6.27×10^{-3}
	0.134	120	1.41×10^{-4}
		140	1.12×10^{-3}
		160	3.86×10^{-3}
		180	8.78×10^{-3}
poly(ethylene terephthalate)	0.038	160	2.21×10^{-4}
		180	4.60×10^{-3}
		200	1.65×10^{-2}
	0.084	160	2.09×10^{-4}
		180	2.93×10^{-3}
		200	1.28×10^{-2}

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

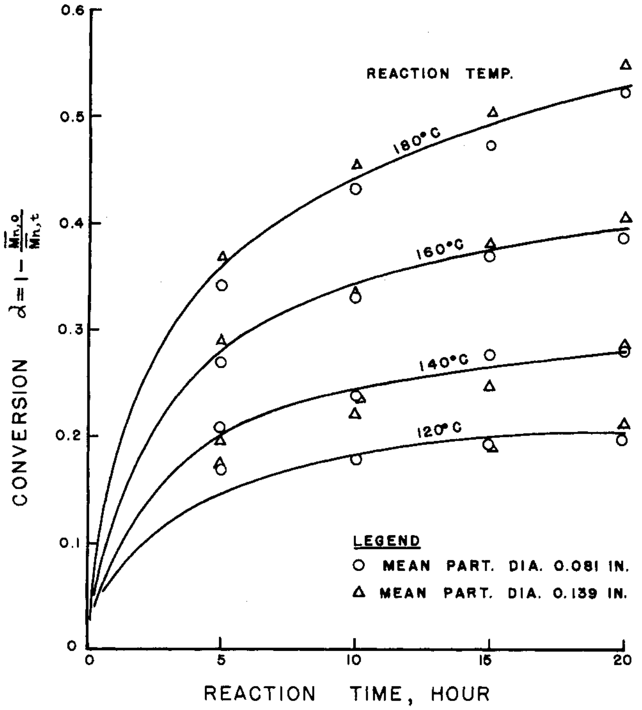


Fig. 5. Conversion vs. reaction time for nylon 66.

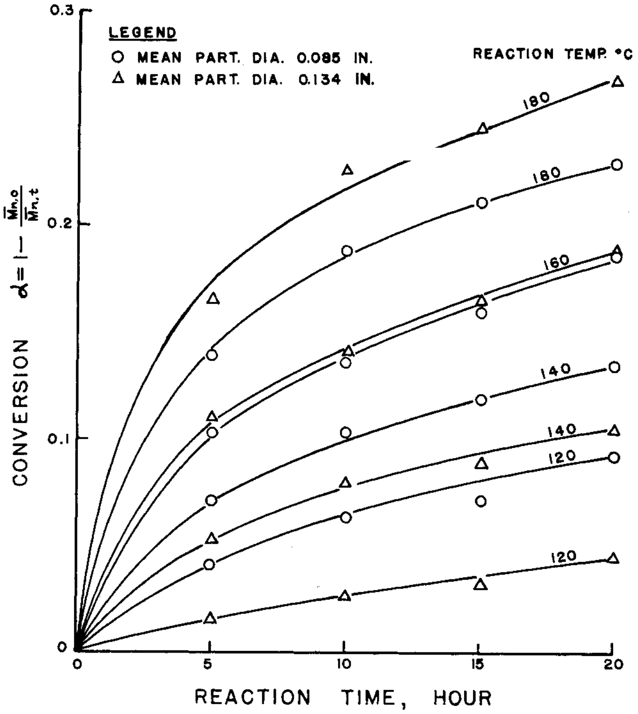


Fig. 6. Conversion vs. reaction time for nylon 6-10.

Figure 8 is a plot of $K_1(t)$ *vs.* $t^{1/2}$ for nylon 66. The slopes of the resultant lines are the k values for each temperature. The exponents for nylon 6-10 and polyethylene terephthalate were both unity. The specific reaction rate data for all samples are listed in Table 2.

The behavior of specific reaction rate with temperature was evaluated using the Arrhenius equation.

$$k' = A \exp(-E/RT)$$

Figures 9 and 10 are the Arrhenius equation plots for the various polymers. As can be seen, the data for both particle sizes of nylon 66 and polyethylene terephthalate yield common straight lines. This behavior indicates that chemical reaction is the rate determining step for solid state polymerizations in nylon 66 and polyethylene terephthalate.

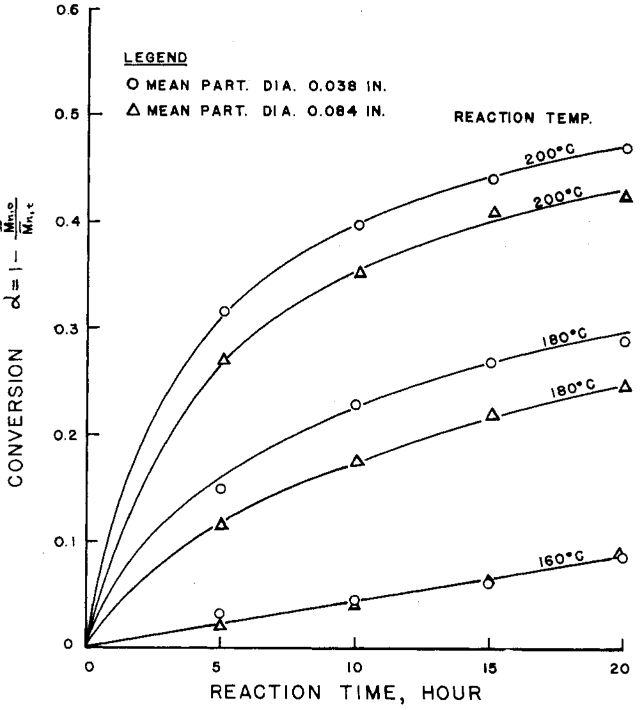


Fig. 7. Conversion vs. reaction time for polyethylene terephthalate.

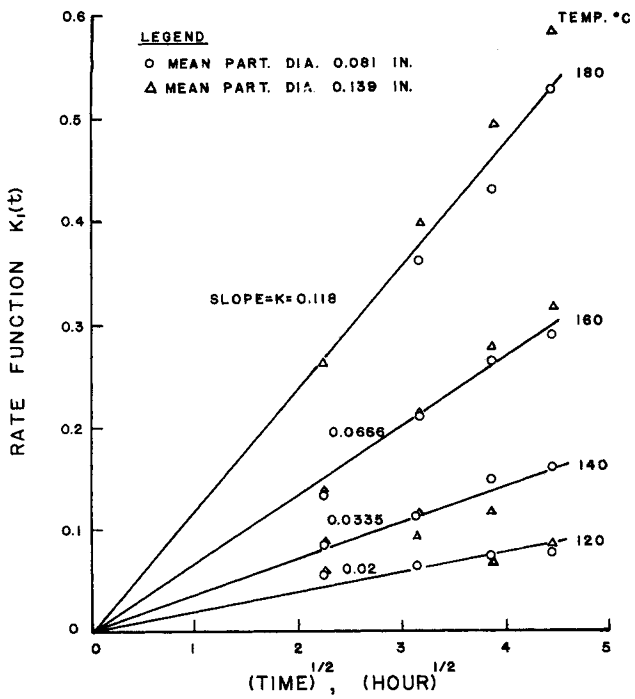


Fig. 8. $K_1(t)$, rate function, vs. (time)$^{1/2}$ for nylon 66.

On the other hand, some of the nylon 6-10 data do not appear to follow the Arrhenius relation. Test of other relations such as collision theory and the Eyring activated rate theory yielded the same behavior as Figure 10. In this figure the large particle data at 120 and 140°C. deviate from the line of log *k vs.* 1/*T*. This apparent effect of particle size suggests that diffusion through the solid polymer is the rate controlling step for these data (large particles at 120 and 140°C.) rather than chemical reaction. The small particle data and the remainder of the large particle data indicate that chemical reaction controls in these cases for nylon 6-10.

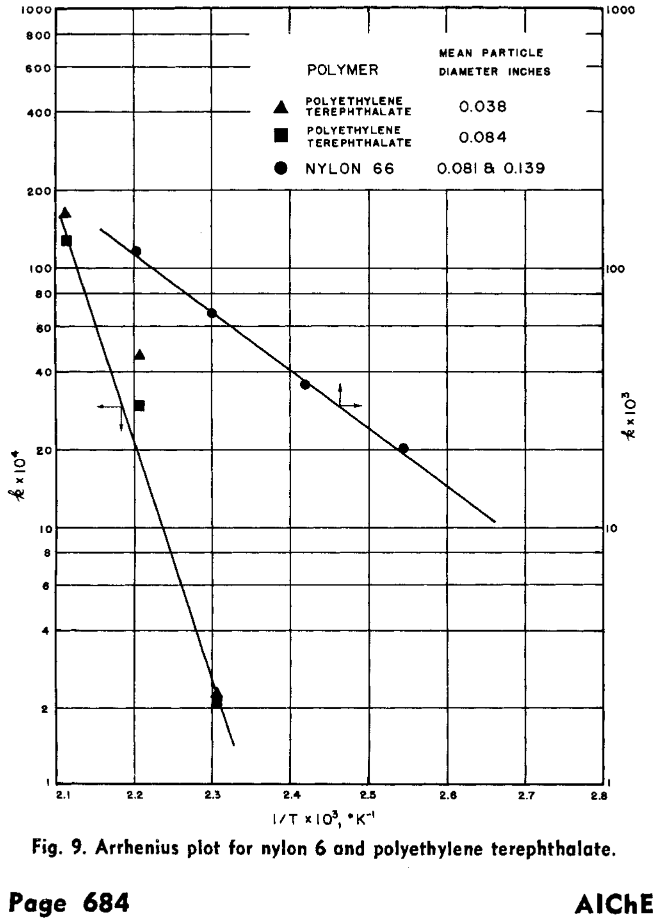


Fig. 9. Arrhenius plot for nylon 6 and polyethylene terephthalate.

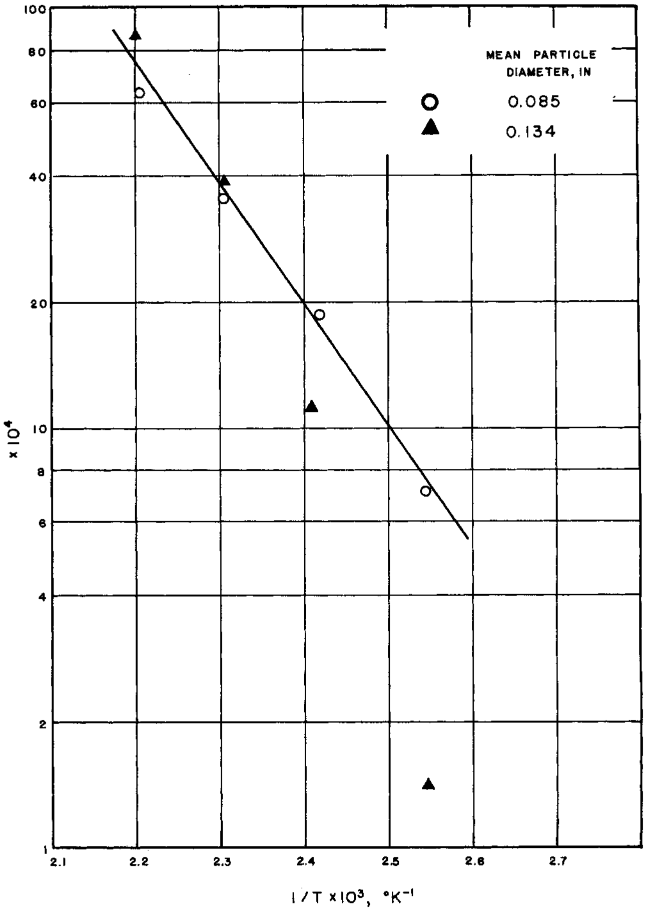


Fig. 10. Arrhenius plot for nylon 6-10.

The various nylon 6-10 samples were also subjected to differential thermal analysis to determine if any morphological changes had occurred. These thermograms are given in Fig. 11. As can be seen for the unreacted (raw) polymer, and those samples reacted at 120 and 140°C. there is an endothermic peak at approximately 160°C. This peak has been reported by Fuller, Baker, and Pape (*15*) as an occurrence of molecular rearrangements in nylon 6-10. In the samples reacted at 160 and 180°C., however, the 160°C. endothermic peak appears to be missing. In addition a melting peak appears at 195 to 200°C. for the 160 and 180°C. reaction samples.

The foregoing indicates that some morphological change has probably occurred in the samples reacted at higher temperature. The exact nature of this change is not known. It is conceivable, however, that this change possibly is related to the agreement of the higher temperature data with the Arrhenius relation (Figure 10) for nylon 6-10. In other words, the alteration of morphology reduced the resistance to diffusion within the solid polymer.

Rate equations for the specific reaction rates are presented in Table 3. It is of interest to compare these data

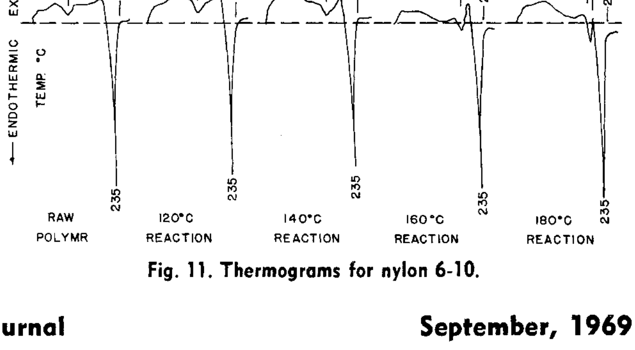


Fig. 11. Thermograms for nylon 6-10.

to energy of activation data found elsewhere. Lee and Griskey (*9*) found an activation energy of 12.96 kcal./g. mole for solid state polymerization of nylon 66. Matsuda and co-workers (*6*) determined a value of 12.7 kcal./g. mole for nylon 6 solid state polymerization. No solid state data were available for polyethylene terephthalate. However, Challa (*16*) did report an activation energy of about 31 kcal./g. mole for its melt polymerization.

TABLE 3. SUMMARY OF ARRHENIUS EQUATIONS

Polymer	Equation	Temperature Range
nylon 66	$k = 1.39 \times 10^4 \exp\left\{\frac{-10{,}500}{RT}\right\}, \text{hr.}^{-1/2}$	120-180°C.
nylon 6-10*	$k = 1.68 \times 10^4 \exp\left\{\frac{-13{,}200}{RT}\right\}, \text{hr.}^{-1}$	120-180°C.
polyethylene terephthalate	$k = 6.6 \times 10^{17} \exp\left\{\frac{-42{,}500}{RT}\right\}, \text{hr.}^{-1}$	160-200°C.

* For data only where chemical reaction controls.

It should be pointed out that the solid state data from other sources were obtained by using kinetic models different from the one of the present work. In spite of this, it is instructive to compare these data to those of the present study.

The nylon 6-10 activation energy value was quite close to those found for nylon 66 (*9*) and nylon 6 (*6*) elsewhere. The nylon 66 value of the present study was somewhat different (10.6 *vs.* 12.96 kcal./g. mole), but still close enough to indicate no radical disagreement. In addition, the polyethylene terephthalate value of 42.5 kcal./g. mole seems reasonable in light of the 31 kcal./g. value for melt polymerization.

CONCLUSIONS

1. Chemical reaction is the rate controlling step for solid state polycondensations in nylon 66, polyethylene terephthalate, for powders of nylon 6-10 (average diameter 0.085 in.) and larger nylon 6-10 particles (average diameter 0.134 in.) at temperatures of 160°C. and higher. The equations for specific reaction rate were $k = 1.39 \times 10^4 \exp(-10{,}500/RT)$, $\text{hr.}^{-1/2}$ for nylon 66; $k = 1.68 \times 10^4 \exp(-13{,}200/RT)$, hr.^{-1} for nylon 6-10; and $k = 6.60 \times 10^{17} \exp(-42{,}500/RT)$, hr.^{-1} for polyethylene terephthalate.

2. Diffusion through the solid polymer appears to be the rate controlling step for particles of nylon 6-10 as large or larger than 0.134 in. in diameter at temperatures of 140°C. or less.

3. Changes in polymer morphology appear to influence solid state polycondensation in nylon 6-10.

4. The Arrhenius relation can be applied to the cases noted above in the first conclusion.

5. The solution of the equation of continuity of species developed by Chen (*11*) can be used to describe solid state polycondensations.

NOTATION

A = frequency factor in Arrhenius equation, $(\text{hr.})^{-m}$
C = byproduct concentration, g. mole/cc.
C_o = initial byproduct concentration, g. mole/cc.
C_s = surface byproduct concentration, g. mole/cc.
$D(t)$ = byproduct diffusivity sq.cm./hr.
E = activation energy, kcal./g. mole
$k_1(t)$ = dimensionless rate function for plane sheets
$K_2(t)$ = dimensionless rate function for spheres
L = length, cm.
$\overline{Mn},t$ = polymer number average molecular weight at time, t
$\overline{Mn},0$ = polymer number average molecular weight at time $t = 0$
R = gas constant, kcal./g. mole °K.
T = temperature, ok
T' = variable defined by $dT' = D(t)\,dt$
Wt = number of byproduct molecules diffused at time of t
W_∞ = number of byproduct molecules diffused at time of ∞
k = specific reaction rate
k' = specific reaction rate
m = exponent
r = radius, cm.
t = time, hr.
u = Cr
x = thickness, cm.
θ = $C_o - C/C_o - C_s$

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