Thermally Induced Solid-State Polymerization in Nylon 66

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Synopsis

The thermally induced solid-state polymerization of 66 nylon was investigated. It was found that the rate-controlling step in the process is chemical reaction. A mechanism of the form, rate $= kt^n$ was shown to hold. The reaction rate constant was found to be $k = 1.53 \times 10^{10} \exp [-12,960/RT]$. Units of k are (hours)$^{-0.51}$. Activation energy determined in this work compared closely to that determined for nylon 6 solid-state polymerization.

It has been long noted in industry that it is possible to increase the degree of polymerization of certain solid condensation polymers by heating (but not melting) them in an inert gas atmosphere. This phenomenon has been termed solid-state polymerization or polymer build-up.

The phenomenon described above should be differentiated from that described in any of the studies done in the field of solid-state polymerization. Most of this work has dealt with addition polymerization. There are a considerable number of references in this area.[1–7]

Research on condensation polymers has chiefly involved nylon 6. References include the research of Cawthon and Smith,[8] Gunder and Livshits,[9] Kudryavtsev et al.,[10] and Matsuda et al.[11,12] The last investigators treated their data in a kinetic sense, determining an activation energy for the reaction.

Work on other polyamides has been limited to a patent by Monroe,[13] an article by Zimmerman[14] on equilibria in solid-phase polymerization, and some work by Matsuda and co-workers.[12] No investigations were found that examined the solid-state polymerization of nylon 66 for the mechanisms and chemical kinetics involved. The present work was, therefore, undertaken to evaluate these items.

The experimental apparatus is shown schematically in Figure 1. The procedure used was first to place 45 g. of nylon 66 chips (average diameter 0.073 in.) into the reactor and then to purge the sample with nitrogen to exclude oxygen. The exit valve was sealed, and the unit was then heated until the desired temperature was reached. Temperatures were measured

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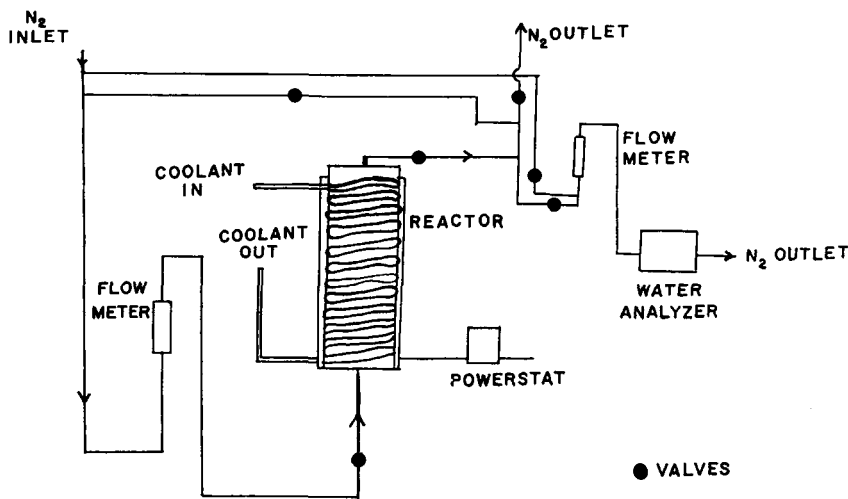
Fig. 1. Schematic of apparatus.

at the center and wall of the reactor.   Nitrogen was then trickled through
the unit and this stream was analyzed for moisture content.   When a pre-
arranged time had elapsed the unit was cooled with a water coil and a
sample taken for analysis.

A number of tests were taken for each sample at 1, 2, 4, and 10 hr. in-
tervals.   Three different nitrogen flow rates (1.5, 4.5, and 7.64 standard
ft.^{3}/hr.) and four temperatures (90, 105, 120, and 135°C.) were used.

All polymer samples were analyzed by intrinsic viscosity $[\eta]$ measure-
ments.   Number-average molecular weights $\bar{M}_n$ were calculated from the
relation[15]

$$\bar{M}_n = 12,000 \ [\eta]^{1.39}$$

Figure 2 is a plot of number-average molecular weight versus time for
given temperatures and nitrogen flow rates.   In order to evaluate these
data it is first necessary to consider the nature of the solid-state nylon 66
polymerization.   It has been pointed out elsewhere[14,16] that in condensa-
tion polymers an equilibrium exists.   This equilibrium can be depicted as

$$P_1 + P_2 \rightleftharpoons P_3 + H_2O$$
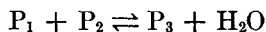
for nylon 66.   Hence, the solid-state polymerization actually involves
taking off the byproduct and thus driving this reaction to the right.
Therefore, there are two possible controlling steps: the diffusion of the
water from the solid polymer and the chemical reaction itself.

Consideration of Figure 2 with some literature information helps to
establish the rate-controlling step.   Walas[17] and Tu et al.[18] have noted
that when diffusion and chemical reaction are competing steps their relative
importance can be determined by considering whether gas flow rate or
temperature has a greater effect.   If the effect of the latter variable is

more pronounced, then chemical reaction controls. A greater effect of gas flow rate indicates that diffusion controls.

As can be seen from Figure 2 the effect of temperature is much more pronounced than the effect of nitrogen flow rate. This then indicates that chemical reaction is the controlling step in the process. The result is one that might have been perhaps predicted because of the small particle size of the nylon chips which accelerated mass transport of the byproduct.
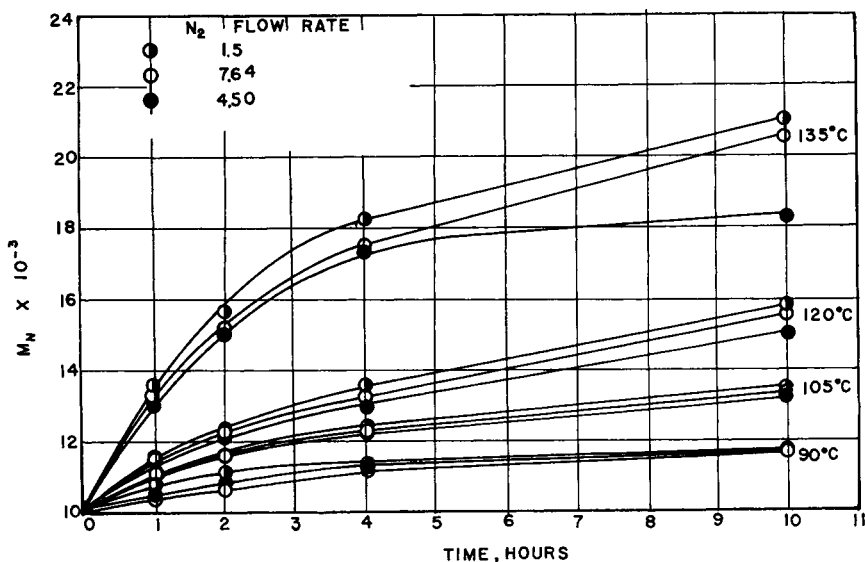

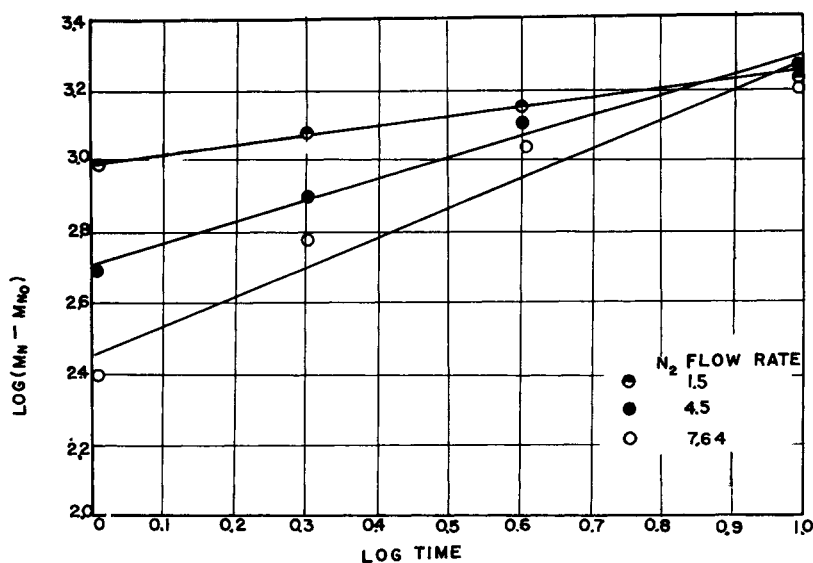Fig. 2. Number-average molecular weight vs. time.

Fig. 3. Plots of log $(\bar{M}_n - \bar{M}_{n_0})$ vs. log t at 90°C.

The next stage of the present study was to carry out a kinetic analysis of the data. Walas[17b] has pointed out that the rate of reaction in solid materials usually varies as some power of the time, t, that is,
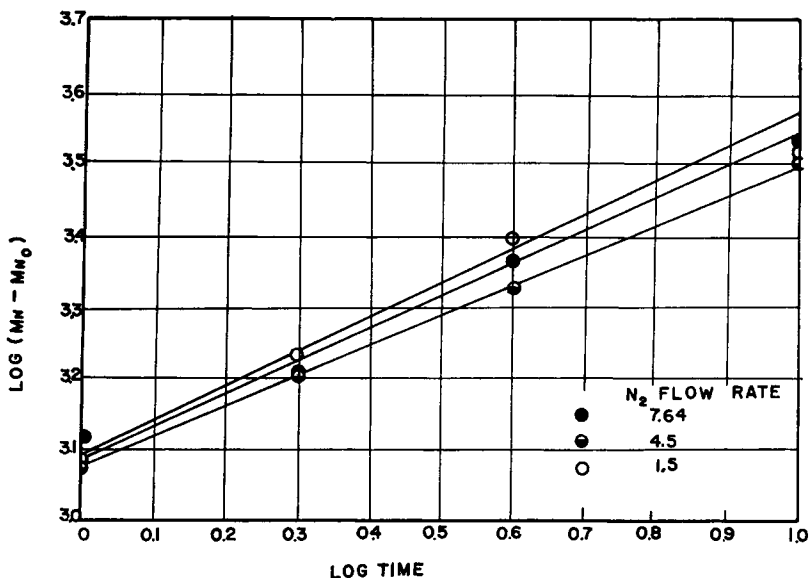
$$\text{rate} = kt^n \tag{1}$$

Fig. 4. Plots of log $(\bar{M}_n - \bar{M}_{n_0})$ vs. log t at 105°C.
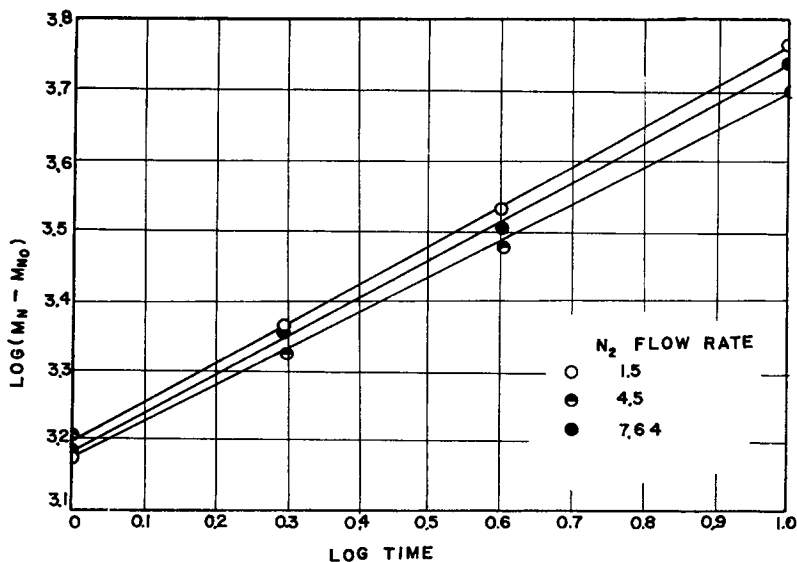

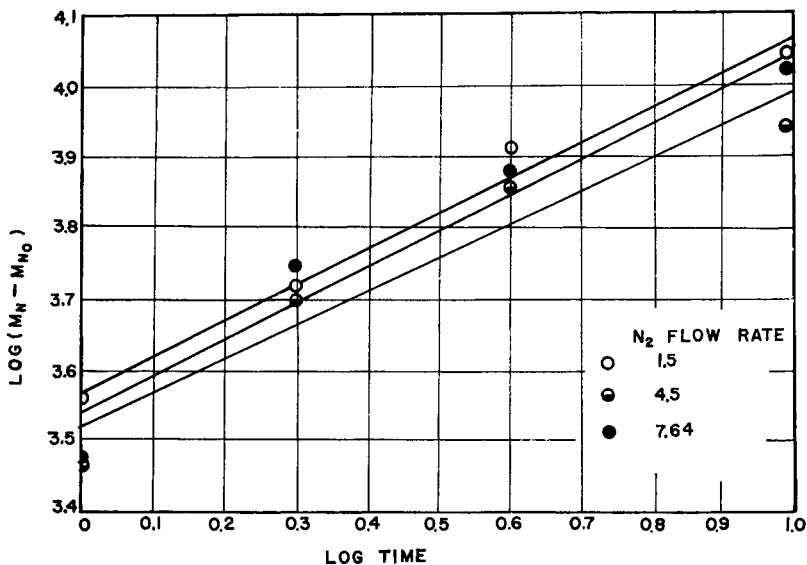Fig. 5. Plots of log $(\bar{M}_n - \bar{M}_{n_0})$ vs. log t at 120°C.

Fig. 6. Plots of log $(\bar{M}_n - \bar{M}_{n0})$ vs. log at 135°C.

Assuming such a relation to hold gives us for the case at hand

$$d\bar{M}_n/dt = kt^n \tag{2}$$

If we integrate eq. (2) by applying the limits

$$t = 0 \ \bar{M}_n = \bar{M}_{n_0}$$

$$t = t \ \bar{M}_n = \bar{M}_n$$

where $\bar{M}_{n_0}$ is initial number-average molecular weight, we then get

$$(\bar{M}_n - \bar{M}_{n0}) = [k/(n + 1)]t^{n+1} \tag{3}$$

or

$$\ln (\bar{M}_n - \bar{M}_{n_0}) = \ln [k/(n + 1)] + (n + 1) \ln t \tag{4}$$

Thus, if we plot $\ln (\bar{M}_n - \bar{M}_{n_0})$ versus $\ln t$ we should get straight lines with a slope of $(n + 1)$. Plots at each of the temperatures studied are shown in Figures 3–6. All lines were fit by the method of least squares. As can be seen, the data in Figures 4, 5, and 6 give straight lines of nearly the same slope. The data of Figure 3 are not quite as well behaved. This scatter is due most likely to the fact that this was the lowest reaction temperature where effects not noticed at the higher reaction temperatures became apparent.

It is interesting to note that the average slope of the lines in Figure 3, in spite of the scatter, gives an n of -0.47 as compared to average n values of -0.55, -0.45, and -0.50, respectively, for Figures 4, 5, and 6. Hence, it appears that a n value of -0.49 (average of all the results) would be appropriate for the solid-state polymerization of nylon 66.
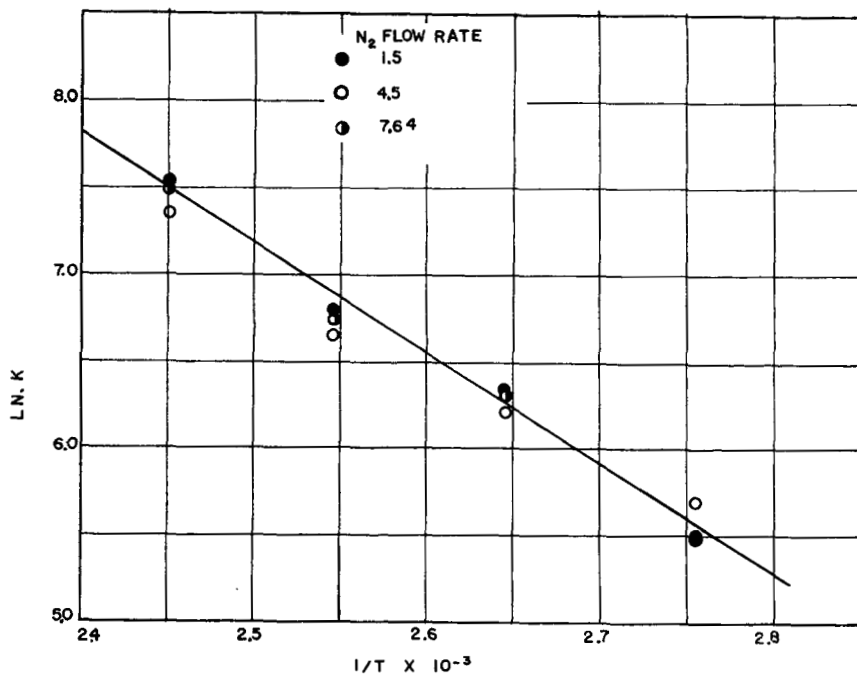
Fig. 7. Plot of log k vs. reciprocal of temperature.

Average values of k determined from the intercepts at log $t = 0$ are plotted against the reciprocal of temperature in Figure 7. The slope of this line yielded an activation energy of 12.96 kcal./g.-mole. This result is interesting, since the data of Matsuda et al.[12] gave an activation energy of 12.7 kcal./g.-mole for the solid-state polymerization of nylon 6.

The Arrhenius frequency factor determined from Figure 7 was 1.53 × 10^{10}. Units of frequency factor are (hours)$^{-0.51}$.

The conclusions derived from this investigation can be summarized as follows.

(1) Chemical reaction is the controlling step in the solid-state polymerization of nylon 66 chips.

(2) The kinetic formula

$$d\bar{M}_n/dt = kt^n$$

appropriately described the rate of molecular weight change in the solid-state polymerization of nylon 66.

(3) A value of $n = -0.49$ was found for nylon 66 solid-state polymerization.

(4) The Arrhenius equation for the solid-state polymerization of 66 nylon was found to be

$$k = 1.53 \times 10^{10} \exp\{-12,960/RT\} \text{ Units of } k \text{ are (hours)}^{-0.51}.$$

(5) The Arrhenius activation energy for nylon 66 solid-state polymerization was found to be 12.96 kcal./g.-mole as compared to 12.7 kcal./g.-mole for nylon 6.

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Résumé

La polymérisation à l'état solide induite thermiquement du nylon-66 a été étudiée. On a trouvé que l'étape determinante de la vitesse de ce processus est une réaction chimique. Un mécanisme de la forme, vitesse = kt^n a été proposé. (La constante de vitesse de la réaction est indiquée dans la résumé anglais.) L'énergie d'activation déterminée dans ce travail est voisine de celle de la polymérisation à l'état solide du nylon-6.

Zusammenfassung

Die thermisch induzierte Polymerisation von Nylon 66 im festen Zustand wurde untersucht. Als geschwindigkeitbestimmender Sehritt dieses Prozesses erwies sich die chemische Reaktion. Ein Geschwindigkeitsgesetz von der Form Geschwindigkeit = kt^n erwies sich als gültig. (Wert der Geschwindigkeitskonstanten siehe englische Zusammenfassung.) Die in der vorliegenden Arbeit bestimmte Aktivierungsenergie stimmt eng mit der für die Polymerisation von Nylon 6 im festen Zustand bestimmten überein.