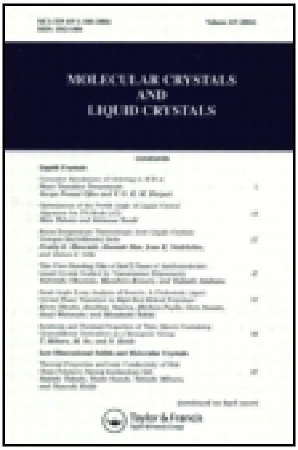

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The Polymerization of Crystalline Hexamethylenediammonium Adipate

P. D. FRAYER and J. B. LANDO

Abstract—Crystalline hexamethylenediammonium adipate (m.p. 197 °C), the one to one salt of hexamethylenediamine and adipic acid, polymerizes at temperatures below its melting point yielding the corresponding polyamide (Nylon 66). Although there is considerable disorientation of the resulting crystalline polymer, two preferred directions of chain growth have been established both tilted at least four degrees from the unique *b*-axis of the monoclinic monomer. It has been found that contact with hydrochloric acid vapor catalyzes the polymerization of the monomer, resulting in appreciable polymerization at temperatures as low as 70 °C and increased orientation of the polymer. Oriented reflections, attributable to the dimer and tetramer, are observed at all times in the acid catalyzed polymerization but not in the thermally polymerized material, indicating that continuous initiation is taking place in the former reaction.

The kinetics of the thermal polymerization have been investigated by TGA and IR analysis between 160 °C and 187 °C. The propagation reaction is zero order and has an activation energy of 46.5 kcal/mole. There appears to be a separable initiation process with an activation energy of 30.0 kcal/mole.

Introduction

Topotaxy is a phenomenon in which the molecular orientation of the product of a solid state chemical reaction is correlated to the molecular orientation in the reactant crystal. The polymerization of crystalline trioxane, the symmetric trimer of formaldehyde, is a good example of a topotactic reaction. Single crystals of trioxane yield regularly twinned crystals of polyoxymethylene.[1–4]

Since a solid state polycondensation reaction involves the removal of a small molecule and its diffusion out of the reacting crystal, it was not expected that reactions of this type could lead to oriented polymer. However, the topotactic intramolecular condensations of single crystals of phthalanilic acid,[5,6] and its parachloro[6] derivitive have been observed at 125 °C. Although these cyclization reactions yield the corresponding N-phenylphthalimide and are not polymerization reactions, they can be considered to be models of polycondensation reactions in the solid state. It should be noted that single crystals of phthalanilic acid, partially converted at 125 °C, contained oriented N-phenylphthalimide in a crystalline phase that was normally found to be unstable at that temperature. Apparently growing grains of this phase are stabilized by interaction with the remaining phthalanilic acid—an apparent epitaxial phenomenon.[6] These facts lead one to question whether or not there is a general relationship between epitaxial crystal growth and topotactic reactions. This problem is of particular interest in light of Adler's recent work, indicating that there are deviations from topotaxy in the early stages of the radiation polymerization of crystalline trioxane.[7]

Although many solid state condensation polymerizations have been reported, until recently no occurrence of topotaxy has been observed. However, in 1964 the solid state polymerization of ε-aminocaproic acid single crystals at 170 °C, yielding polymer (nylon 6) that was oriented in three dimensions, was observed.[8] Topotactic polymerization took place notwithstanding the fact that there was a contraction of 17% in the direction of chain growth and an 18% reduction of volume.

In the present work the solid state condensation polymerization of hexamethylenediammonium adipate (the one to one salt of hexamethylenediamine and adipic acid) to a polyamide (nylon 66) was investigated using X-ray, infrared (IR) and thermal gravametric analysis (TGA). The previously determined crystal structures of the monomer[9] and the polymer[10] were utilized in the interpretation of the experimental data.

Experimental

Monomer Preparation. Hexamethylenediammonium adipate (m.p. 197 °C) was prepared by adding a 60 to 80% solution of hexamethylenediamine in methanol to a 20% solution of adipic acid in hot methanol. As the solution cools the salt, which is only slightly soluble in methanol at room temperature, precipitates. Single crystals were grown by recrystallization from hot methanol or ethanol.

Powder samples used in the kinetic studies are recrystallized single crystals which were finely ground.

Polymerization. Single crystals of hexamethylenediammonium adipate were polymerized by annealing in vacuum or under nitrogen (to preclude oxidation) in a temperature controlled air oven. The polymerization temperatures investigated were between 135 °C and 160 °C. The polymerization of single crystals was also investigated in the presence of hydrochloric acid vapor at temperatures between 50 °C and 100 °C.

The kinetics of polymerization of powder samples was investigated by several methods in the absence of hydrochloric acid vapor over the temperature range 160 °C to 187 °C. Crude measurements were made in air, the weight loss as a function of time being measured subsequent to periods of heating. A Stanton Thermobalance (TGA) was used to measure the weight loss as a continuous function of time in a continuous flow of nitrogen at 160 °C, 180 °C and 187 °C. That virtually complete conversion was obtained, was verified by taking Debye Scherrer X-ray photographs using Cr $K\alpha$ radiation. Sublimation of monomer under these conditions of reaction was found to be less than one percent. Additional kinetic evidence was obtained by preparing KBr pellets containing monomer, heating for varying lengths of time, and following the appearance of polymer IR bands and the disappearance of monomer IR bands. For this purpose a Perkin-Elmer model 521 Infrared Spectrophotometer was used.

Analysis of Samples. The melting points of monomer and polymer samples were obtained using a duPont model 900 Differential Thermal Analyzer at a scan rate of 10 °C/min. Viscosity average molecular weights were determined with a Ostwald viscometer using a 90% formic acid-water solution as the solvent.

Determination of the orientation of the polymer with respect to crystallographic directions in monomer single crystals was carried out using oscillation and Weissenberg X-ray photographs. These photographs were taken with Cu $K\alpha$ radiation using a Stoe Weissenberg camera.

Results

X-Ray Analysis of the Polymerization. The crystal structure of anhydrous hexamethylenediammonium adipate, a form stable above

24.1 °C, has been determined by Brown.[9] The monoclinic space group is $P2_{1/a}$ and the lattice constants are $a = 8.489$ Å, b (unique axis) $= 15.580$ Å, $c = 5.598$ Å, and the β angle $= 77.1°$. The X-ray density is 1.200 g/cc calculated for two molecules per unit cell.[9] The form of the polymer obtained in the solid state polymerization of this salt is the α form, which crystallizes in a triclinic unit cell, space group $P_{\bar{1}}$. The structure of α nylon 66 has been determined by Bunn and Garner.[10] The lattice constants are $a = 4.9$ Å, $b = 5.4$ Å, c (chain axis) $= 17.2$ Å, the α angle $= 48.5°$, $\beta = 77°$, and $\gamma = 63.5°$. The X-ray density is 1.24 g/cc calculated for one molecule per unit cell.

Figure 1 is a representation of the monomer structure projected onto the *ab* plane of the unit cell,[9] while Fig. 2 is a representation of the α unit cell of nylon 66.[10] It should be noted that the hydrogen bonds in the polymer structure are almost parallel to the *bc* plane while the " intrachain " hydrogen bonds in the monomer structure are essentially parallel to the *bc* plane of the monomer. Reaction would seem to be most likely along the hydrogen bonded chains parallel to the *b*-axis of the monomer. In this case the two " interchain " hydrogen bonds must be broken. In addition Fig. 1 demonstrates that the plane of the carbon atom zigzag of the diacid is not the same as the zigzag plane of the carbon atoms of the diamine. Furthermore, the carboxyl group is twisted by an angle of 69.8° with respect to the plane of carbon atoms of the diacid. In the crystal structure of adipic acid the twist is only 6°.[9] The hydrogen bonding to the diammonium ion apparently is the cause for the strained position of the carboxyl group. These points are important in considering the solid state polymerization since the resulting polymer takes on a planar zig-zag conformation.

When single crystals of the monomer are heated at 160 °C for 24 hours, complete conversion to polymer is obtained. Oscillation photographs indicate no obvious orientation of the polymer chains. When the temperature of polymerization is below 145°C, orientation is observable, but the samples had to be heated for longer and longer times (several months at a time) to get any conversion. Conversion and orientation appear to be optimized at approximately 145 °C. The (100), (010) and (110) reflections of the polymer appear to be oriented normal to the unique axis of the monomer. It should be noted that the (010) and (110) have virtually identical *d*-spacings.

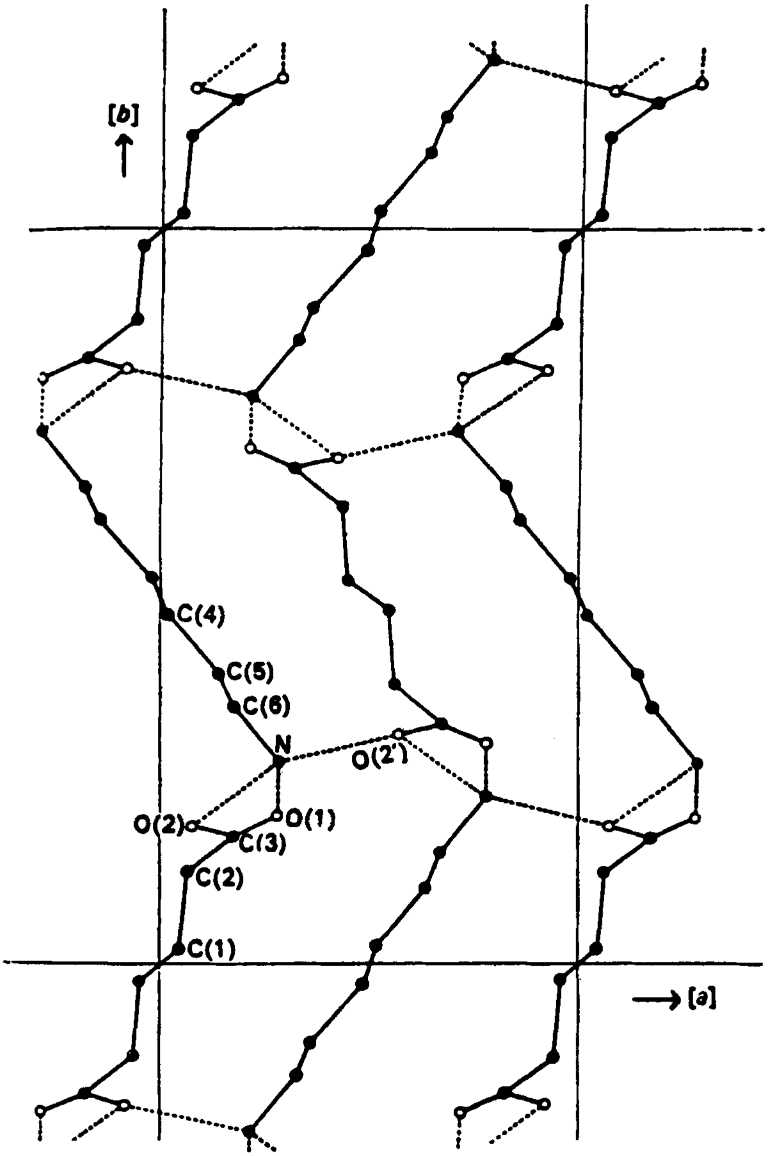

Figure 1. Diagram of the unit cell of the monomer showing the hydrogen bonding with broken lines (9).

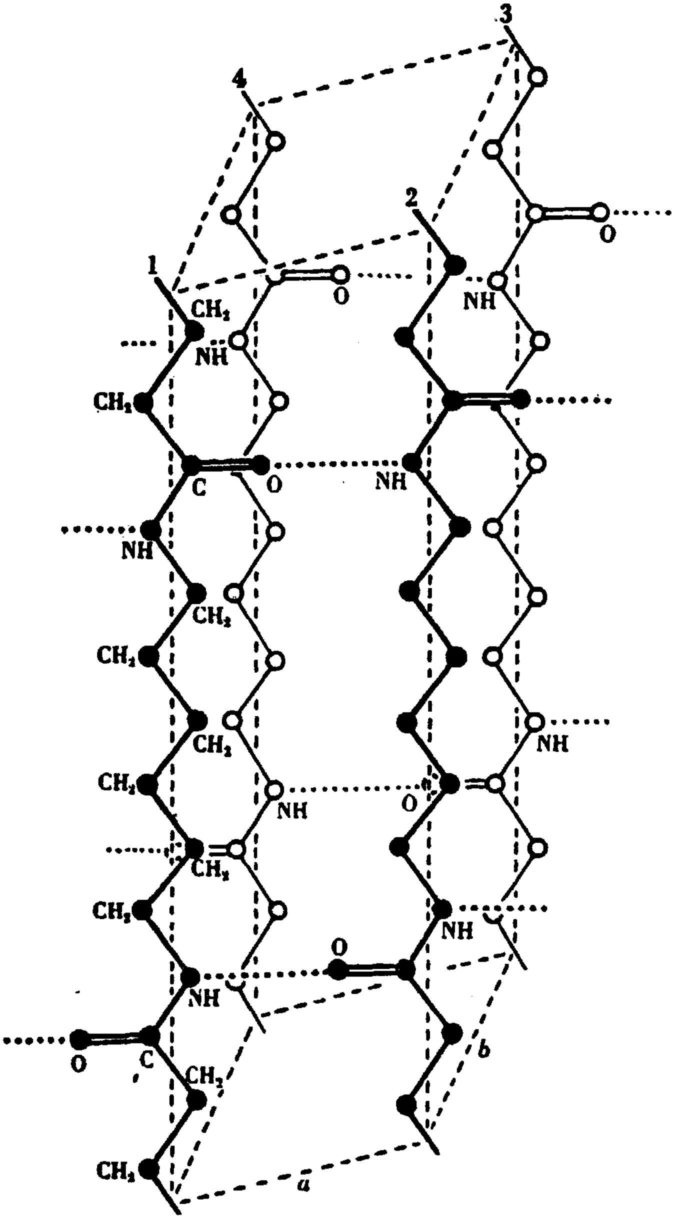

Figure 2. The triclinic unit cell for the alpha form of nylon 66 (10).

Since acids have been used as catalysts for the solution polymerization (11), it was thought that acid vapors might catalyze the solid state polymerization at lower temperatures. By using HCl vapor as a catalyst, reasonable conversions and improved orientation were obtained at lower temperatures as shown in Fig. 3, a 60° oscillation photograph of a monomer crystal partially converted to polymer at 70 °C (three days) and aligned around the monomer *b*-axis. The orientation of the (100), (010) and (110) polymer reflections (two strongest rings), although not distinguishable in Fig. 3, is similar to that observed from crystals polymerized at 145 °C in the absence of HCl. However clear orientation of two polymer reflections, near the meridian above the monomer sixth layer line is observed in Fig. 3. In relative intensity and in position they fit the superimposed (117) and (027) reflections of the polymer given by Bunn and Garner[10] for the α form. They appear on what would be the seventh layer line of a fiber pattern of the polymer. Since the superimposed ($\bar{1}17$) and (227) reflections are also observed on this layer line in Fig. 3, there appears to be a preferred orientation of the polymer chains approximately along the monomer *b*-axis. The symmetry of these seventh layer reflections indicate twinning of polymer crystallites lateral to the chain axis. It should be noted that, although there is preferred orientation, there is considerable disorientation of polymer crystallites indicated by the powder rings in Fig. 3.

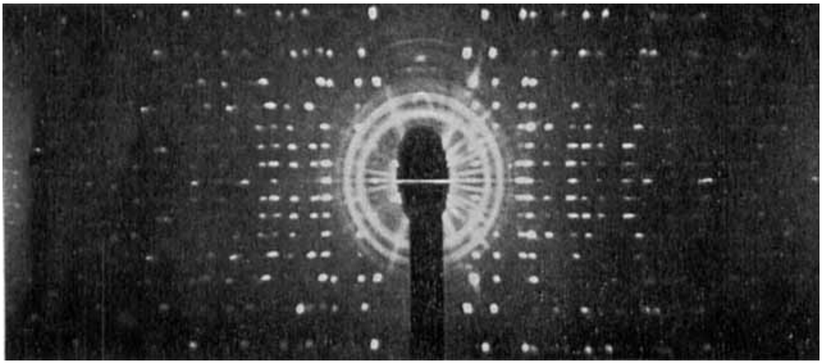

Figure 3. A 60 degree oscillation photograph of monomer reacted in HCl at 70 °C for 3 days (aligned around the *b*-axis of the monomer and using Cu $K\alpha$, camera dia. 57.3 mm).

The zero layer Weissenberg photograph, shown in Fig. 4, of a partially converted monomer crystal aligned around the *b*-axis, is a superposition of polymer reflections on the ($h0l$) layer of the monomer. The polymer reflections, although elongated, indicate orientation of polymer crystallites lateral to the *b*-axis of the monomer. As expected, there are two distinct orientations as demonstrated by the multiplicity of the (100) and (010) polymer reflections. Figure 5 is a schematic representation of the position of the polymer reflections with respect to the a^*- and c^*-axes of the monomer as seen in Fig. 4. The subscript $_t$ is used to distinguish the two polymer orientations. As can be seen the angle between the twinned orientations is approximately 68°, while the angle between the (010) and (100) reflections or the $(010)_t$ and $(100)_t$ is approximately 64° (or 116°), which is in agreement with the angle between the a^*- and b^*-axes of the α form of the polymer. These data are consistent with chain orientation approximately along the monomer *b*-axis.

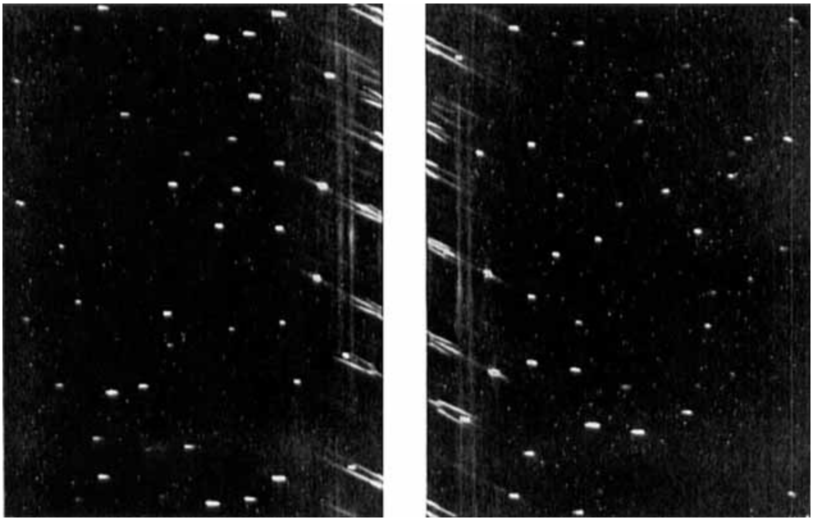

Figure 4. A zero-layer Weissenberg photograph of monomer reacted in HCl at 70 °C for 3 days (aligned around the monomer *b*-axis and using Cu $K\alpha$, camera dia. 57.3 mm.).

If one assumes exact alignment of the polymer chains along the *b*-axis of the monomer for both lateral orientations, then it is possible to represent the orientation of the real and reciprocal axes of the monomer and polymer in terms of a rectangular coordinate system

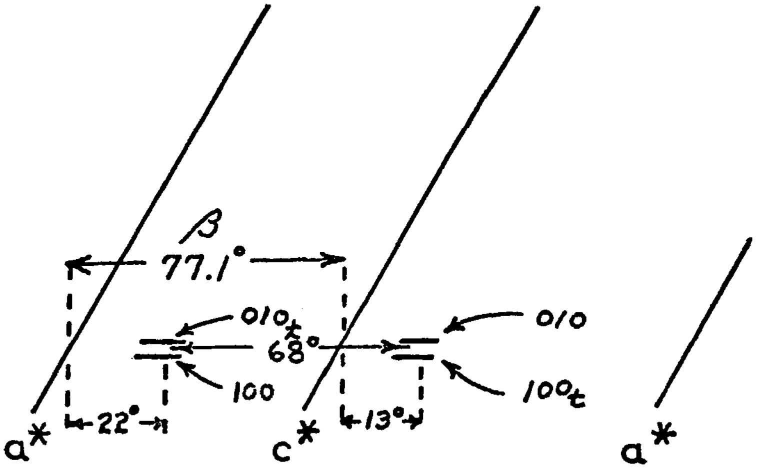

Figure 5. An illustration of the placement of the polymer (100) and (010) reflections with respect to the monomer reciprocal lattice axes, a^* and c^* in Fig. 4.

XYZ as shown in Fig. 6a and 6b. In these figures the subscript 1 refers to the polymer real and reciprocal axes, while the subscript $_t$ in Fig. 6b refers to the second orientation of the polymer.

Since the (100) and $(010)_t$ reflections occur approximately 99° from the *c*-axis of the monomer, a zero layer Weissenberg photograph aligned around the monomer *c*-axis should register the tails of these reflections and not the $(100)_t$ and (010) reflections. This has been observed experimentally, thus confirming the approximate validity of the above analysis.

It must be emphasized that this previous analysis is based on the assumption of exact alignment of the polymer chain axis with the unique axis of the monomer. If this assumption were true, then the relative intensities would be the same for the a^* and b^* reflections with respect to the a^* twin and b^* twin reflections observed in Fig. 4. This is not observed. The (100) and $(010)_t$ reflections are cut off which means that these axes are tilted slightly out of the sphere of reflection. Furthermore, if these reflections are cut off on the same

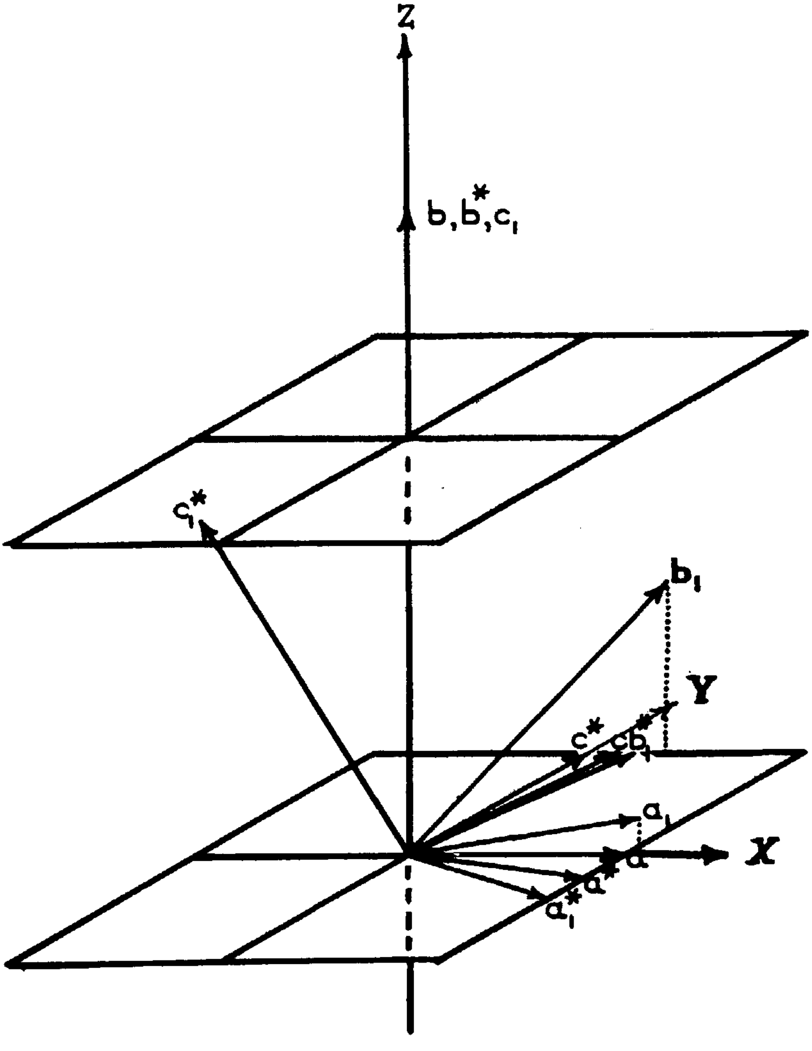

Figure 6(a). One orientation of the monomer and polymer real and reciprocal lattice axes with respect to the orthogonal axes *XYZ*.

side, then the tilt for each axis is in the same direction with respect to the monomer a^* c^* net. However, these reflections appear to be cut off on opposite sides. Thus, the a^*-axis of the polymer in Fig. 6b should be slightly above the *XY* plane and the b_t^*-axis of the polymer in Fig. 6a should be tilted slightly below the *XY* plane. The tilt

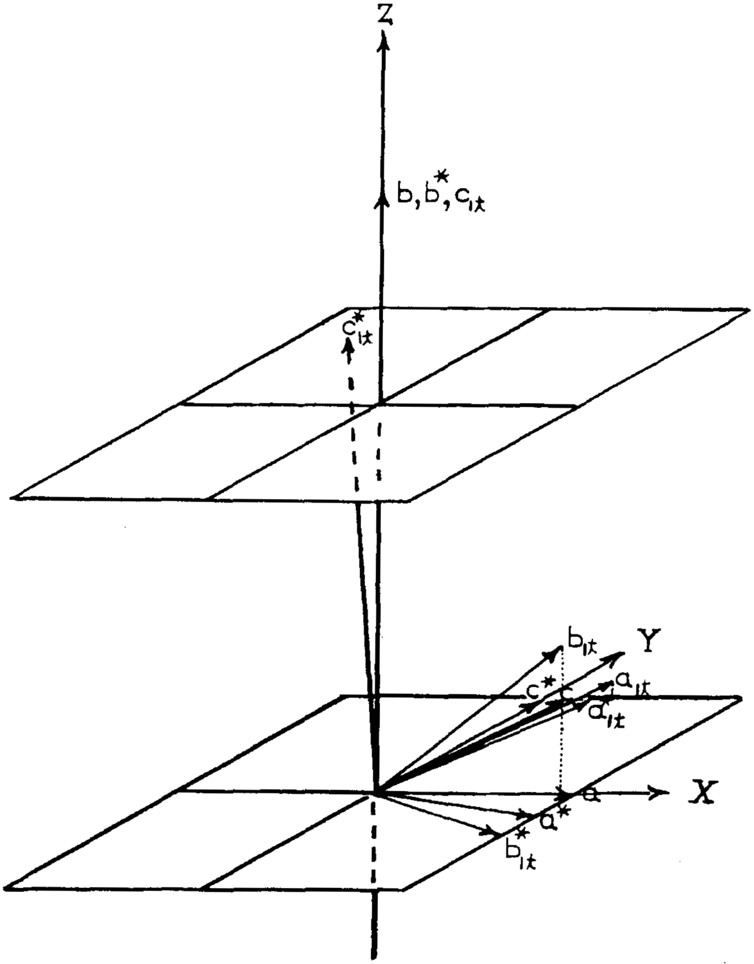

Figure 6(b). The second orientation of the monomer and polymer real and reciprocal lattice axes with respect to the orthogonal axes *XYZ*.

involving the chain axis in both orientations must be at least 4°. Consideration of the polymer (110) reflection yields further evidence for the proposed tilt. In the Fig. 4 Weissenberg photograph the (110) reflection should occur at a rotation angle of about 35.5 degrees from the (100) reflection toward the (010) reflection in both orientations and at the same 2θ value as the (010) reflection. The (110) reflection is barely observed as a result of the tilt and its weaker intensity relative to the (100) and (010) reflections. Thus, the polymer chains in the two orientations are not coaxial.

In addition to the X-ray reflections already considered, several other reflections were observed which could not be indexed as polymer reflections, alpha or beta forms, or as monomer, the anhydrous or the dihydrate forms. Most extra reflections were found to fit well the data of Zahn and Lauer[12] who reported Debye-Scherrer data for the dimer and tetramer of nylon 66. Only the *d*-spacings were reported and these were not indexed.

Table 1 lists the reflections of the polymer and the two oligomers, dimer and tetramer. All strong oligomer reflections were found in the oscillation X-ray photograph of Fig. 3 and the Weissenberg X-ray photograph of Fig. 4. The first reflection listed was found to be the strongest and was observed only when a very small beam stop was used. In the Weissenberg X-ray photographs this reflection was also found to be twinned in the same manner as the polymer reflections. These oligomer reflections were observed in all samples partially polymerized in the presence of HCl gas but never in thermally polymerized samples. Of course, other oligomers are probably present. Although two major polymer orientations are present, there is also some disorientation or powdering (still crystalline) of both the polymer and the oligomer reflections.

TABLE 1 A Comparison of the X-ray Data for the Polymer and Two Oligomers (12)

d-spacings in Angstroms		
Nylon 66	dimer	tetramer
—	7.87	7.87
6.55	6.55	6.55
—	—	4.95
4.44	4.44	4.44
3.70	3.70	3.70
—	3.42	3.35
3.18	3.08	3.10
—	2.88	—
2.64	2.65	2.67
—	1.77	—
—	1.72	1.72

The Kinetics of the Polymerization. Preliminary semiquantitative analysis of the polymerization of the crystalline monomer of 160 °C in air without HCl catalyst showed that the rate of polymerization strongly depended upon the surface area of the samples. The polymerization proceeds more rapidly in ground samples than in large single crystals. Because of this all samples in the kinetic studies were taken from the same lot of finely ground crystals.

The rate of polymerization was investigated at 160 °C, 180 °C and 187 °C by TGA in flowing nitrogen in the absence of O_2 and HCl. Figure 7 shows the conversion with time at the three temperatures. All samples polymerized essentially to completion as determined by X-ray analysis. At each temperature an induction period is observed. Since the rate is much slower at 160 °C, Fig. 7 contains only the

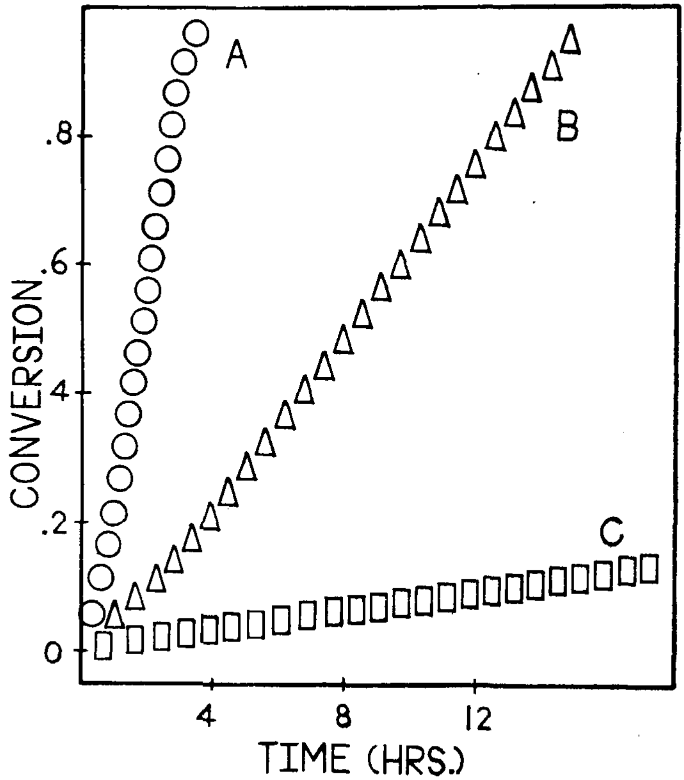

Figure 7. The conversion with time for powder samples heated at *A*—187 °C, *B*—180 °C, and *C*—160 °C in TGA.

induction portion of the kinetic curve. Because of the time scale in Fig. 7, the induction period is not clearly shown (see Fig. 8). All curves show a deviation from linearity at short and long times.

The polymerization can be considered to consist of two stages, initiation and propagation. The initiation or nucleation stage follows an exponential equation which goes to zero when a steady state or a maximum number of initiation sites is reached. Thereafter the reaction appears to be zero order almost to complete conversion. This scheme can be represented mathematically in the following way. Let A be the number of initiation sites at any time and A_0 be the maximum number of initiation sites, then

$$dA/dt = k(A_0 - A). \tag{1}$$

At steady state A reaches A_0 and the initiation stage is completed. The value of A at any time, t, can be obtained by integration of Eq. (1) to yield

$$A = A_0(1 - e^{-kt}) \tag{2}$$

It is believed that the initiation or nucleation process can occur either on the surface of crystallites or at internal surfaces (defects) within the crystallites.

Since the propagation step has been found to follow zero-order kinetics with respect to monomer concentration after a constant concentration of growth nuclei (A_0) is reached, the decrease in the fraction unreacted, θ, with time will be some constant, k_1, times the number of growth nuclei at any time or

$$-d\theta/dt = k_1 A. \tag{3}$$

Using the value of A at any time found previously, Eq. (3) becomes

$$-d\theta/dt = k_1 A_0(1 - e^{-kt}). \tag{4}$$

Integration of this equation yields the fraction converted, X, as

$$X = 1 - \theta = k_1 A_0 t + k_1 A_0/k(e^{-kt}) - k_1 A_0/k. \tag{5}$$

At short reaction times the exponential term is important. At longer times the exponential goes to zero and the conversion X should be proportional to t. In Fig. 8 is shown a plot of Eq. (5) for the 187 °C data. The constants for the equation are determined from the slope of the linear portion ($k_1 A_0$) and the extrapolated intercept

$(-k_1A_0/k)$. The experimental points are shown to agree very well with the theoretical equation. The fit at 180 °C and 160 °C is similar.

A reasonable mechanism for the propagation stage is sheath-like growth of the polymer chains which are restricted by the molecular orientation of the monomer. Directional sheath-like growth would be expected to follow zero-order kinetics.

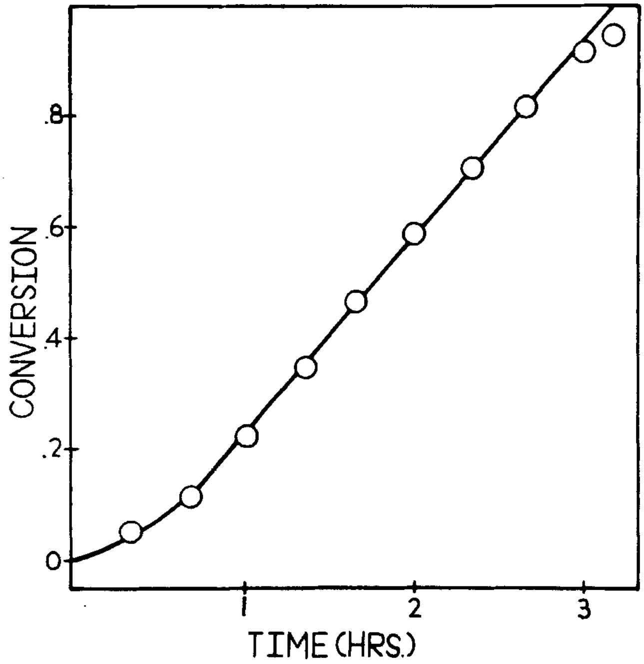

Figure 8. The agreement of experiment (○) with the theoretical equation (——) at 187 °C.

Since the experimental data yield only (k_1A_0) and the $(-k_1A_0/k)$, k can be obtained, but k_1 and A_0 cannot be separated. These constants for each reaction are listed in Table 2. An Arrhenius plot of the k_1A_0 values at the three temperatures gives an apparent activation energy of 46.5 kcal/mole for the propagation stage. Similarly, an Arrhenius plot of the k values at the three temperatures gives an activation energy of 30 kcal/mole for the initiation or nucleation process. These plots are shown in Fig. 9. Thus, the data obtained can be explained by a reasonable mathematical model that yields

TABLE 2 The Values of the Constants for Eq. (5)

Constants	187 °C	180 °C	160 °C
k_1A_0	0.3615	0.0691	0.00873
$-k_1A_0/k$	− 0.1330	− 0.0650	− 0.0400
k	2.7200	1.0620	0.2183

an equation which fits both the initiation and propagation stages of the polymerization.

In the TGA experiments the total weight loss exceeded the calculated amount by a few percent. Although the diamine is most likely to sublime first, the excess weight loss might also include loss of the diacid (Tm 153 °C, pure acid), loss of any solvent which could not be removed by drying at 100 °C, and especially any adsorbed water from the atmosphere. Even if all the excess weight loss was due to sublimation of the diamine, the amount lost would be less than 1 mole %. When the reaction is followed by IR, the sample is pressed in a KBr pellet and the effect of any loss of amine should be eliminated. The IR dat; was taken at 160 °C by following the decrease in the 775 cm^{-1} band of the monomer (presently unassigned and not present in the polymer) and the increase in the 1190 cm^{-1} band of the polymer (torsional CH_2CO vibration) (13). The TGA and IR results

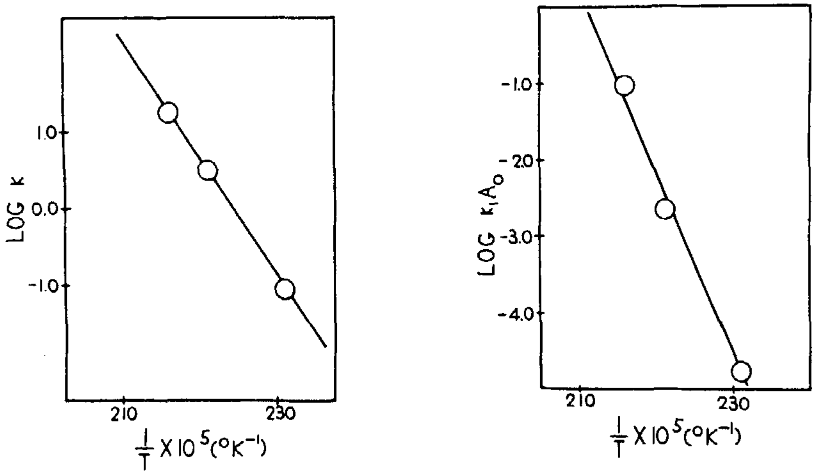

Figure 9. The Arrhenius plots for the propagation and initiation stages.

yield curves of the same shape, although they are measuring different aspects of the reaction. IR measures the reaction as it occurs and TGA measures an additional time lag associated with the loss of water from the sample by diffusion.

The effect of excess water on the reaction was also investigated in a semiquantitative manner. It was found that if the excess water was not eliminated by flowing nitrogen that the rate of polymerization was decreased by 50%, indicating that the polymerization in the solid state may be an equilibrium reaction as suggested for the melt polymerization (14, 15).

The viscosity average molecular weights of the samples polymerized in N_2 at 160, 180, and 187 °C were determined. The viscosity average molecular weights were calculated from the intrinsic viscosities by the following equation verified by light scattering for the molecular weight range 150 to 50 000:

$$(\text{intrinsic viscosity}) = 0.025 + 13.2 \times 10^{-5}(M^{0.873}) . \qquad (16)$$

Thus, the calculated viscosity average molecular weights are as follows:

Polymerization Temperature	molecular weight
160 °C	10500
180 °C	8100
187 °C	6400 .

The melting points of samples of polymer obtained at 160 °C, 180 °C, and 187 °C were determined by DTA. During initial heating endotherms were observed at 235–7 °C and 250–252 °C for all samples. Recrystallization and subsequent reheating yielded a single endotherm at 252 °C. The lower endotherm in the first pass increased in intensity relative to the higher endotherm the lower the original polymerization temperature. Since the molecular weight and the degree of orientation is greater at lower polymerization temperatures, the 235–7 °C endotherm may be related to a change in morphology (decrease in orientation) similar to that suggested by Ke.[17]

Discussion

The X-ray analysis shows that a partially topotactic reaction has occurred and therefore that the disposition of the monomer molecules at least partially restricts the solid state polymerization to specific directions of chain growth. It was mentioned previously that when the polymer is formed, the monomer methylene units must rearrange themselves into the planar zig-zag conformation. The tilting of the polymer chain axis probably occurs as a result of the change in the length of the repeat distance from 15.8 Å for the monomer to 17.2 Å for the polymer. Furthermore, all hydrogen bonds must be broken since the reformation of hydrogen bonds and the change to the planar zig-zag conformation probably are the main determining factors for the twinning which occurs. If the hydrogen bond along the monomer *a*-axis were not broken, then the polymer *a*- and *b*-axes probably would not be twinned, since the hydrogen bonding in the polymer is nearly along the polymer *a*-axis as seen in Fig. 2.

The limitation on the degree of orientation with respect to crystallographic directions in the monomer is probably related to the 10.3% decrease in the molecular volume of a monomer unit in going from crystalline monomer to crystalline polymer. The resulting large amount of available volume should increase the probability of disorientation of the polymer during the polymerization, although growth could remain directional. Since it also should facilitate the diffusion of water out of the reacting crystals it would be expected to facilitate polymerization.

The polymerization without a catalyst has been shown to consist of two stages. The number of growing chains apparently reaches a steady state or a maximum number. The reaction with HCl as a catalyst undoubtably follows different kinetics. X-ray analysis has shown the presence of oligomers throughout the polymerization with HCl, indicating continuous initiation. Thus the number of growth nuclei is sporadic in time and does not reach a steady state value. The oligomer reflections (dimer and tetramer) were never observed in the thermal polymerization without HCl as a catalyst.

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