

# Study on Crystallization of Nylon 6 (Polycapramide).

## III. Effect of "Crystalline Memory" on Crystallization Kinetics

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### Synopsis

The effect of the initial degree of crystallinity on the isothermal crystallization kinetics from the melt of nylon 6 has been examined. The investigations were carried out in the conditions which allow to maintain a "crystalline memory." For the investigations, dilatometric and microscopic methods were used depending on the temperature range used. It has been found that for samples of initial crystallinity up to 15% there exists a possibility of the growth of spherulites either from the sporadic or simultaneous nucleation depending on the crystallization temperature. For samples with initial degree of crystallinity higher than 15%, the growth of spherulites occurred always from the predetermined nuclei within the investigated range of the crystallization temperature. The crystallization rate of the samples increased with rise in initial degree of crystallinity of the samples.

### INTRODUCTION

One of the factors which influence the polymer crystallization process is a "crystalline memory" resulting from previous treatment of the samples. It is manifested by the formation of a definite degree of a macromolecular order in the sample, as well as by a rise of the melting temperature of the system.<sup>1-12</sup> Melting of such samples under conditions which do not completely destroy the "crystalline memory" may bring about a situation at which the crystallites with the highest degree of crystalline order remain in the melt and during cooling of the melt form the predetermined nuclei of crystallization.<sup>7-11</sup>

The effect of "crystalline memory" is probably observed during melt spinning of nylon 6. Fibers formed under practically "identical" conditions show along their length various tensile strengths, dyeabilities, etc. This effect was also noted during investigation of the isothermal crystallization kinetics of nylon 6.<sup>13-16</sup>

This phenomenon has not, however, been examined in details, since the works mentioned above had as their aim the determination of conditions in which the "crystalline memory" is destroyed, and carried out kinetic mea-

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surements from the homogeneous melt. This work was aimed to answer the question if, and to what extent, it is possible to obtain crystallization of nylon 6 from a sporadic nucleation in such a case, when in applied melting procedures before the crystallization some "crystalline memory" has to be preserved in the polymer melt. It was expected that the data obtained can have a practical use. The polymer under investigation was nylon 6, for which the kinetics of isothermal crystallization from the melt under conditions causing destruction of the "crystalline memory" have been examined previously.<sup>16</sup> Dilatometry and optical microscopy were used as measurement methods.

## EXPERIMENTAL

### Materials

du Pont commercial fiber-forming nylon 6 was used as base polymer. The polymer was free from titanium dioxide and was prepared by the hydrolytic polycondensation of caprolactam. The intrinsic viscosity of the samples was measured in 85% formic acid, using concentrations of 0.05–0.2 g/100 ml. The melting temperature assumed as temperature of melting peak was measured by means of DSC (Perkin-Elmer DSC 1B instrument). Samples were scanned at a heating rate of 8°C/min.

### Samples with Various Degrees of Crystallinity

The base polymer was extracted with water and dried to constant weight under a vacuum of  $10^{-6}$  mm Hg at 373°K in glass ampoules. Next, the ampoules were sealed by flame, and polymer was melted at 543°K for 30 min. These conditions, as has been previously reported,<sup>16</sup> are sufficient for obtaining a "homogeneous" melt. A few melted samples, immediately after melting, were quenched in acetone–solid carbon dioxide mixture and stored at a temperature of 208°K until they were used for kinetic investigations. The other samples, after melting, were quickly transferred to a thermostat set at 486°K and annealed for a period from 1 to 1680 hr. As a result of the above described procedure, samples with various degrees of crystallinity were obtained. For these samples, density, melting temperature, and mineral impurity content were determined. For all investigated samples, mineral impurity content was 0.06% by weight. The characteristics of the commercial sample and the samples with the various degrees of crystallinity are given in Table I. Samples listed in Table I were subjected to the crystallization experiments.

### Densities

The densities of the samples were measured using a density gradient column. The liquids used were toluene and carbon tetrachloride. The temperature of measurements was 493°K  $\pm$  0.02°K. The crystallinity of all the nylon 6 samples was calculated assuming  $d = 1.225$  g/cm<sup>3</sup> for a 100% crystalline material<sup>17</sup> and  $d = 1.084$  g/cm<sup>3</sup> for an amorphous polymer.<sup>18</sup>

### Crystallization Procedure

**Dilatometry.** The samples with a defined degree of crystallinity were placed in the dilatometers and melted at a temperature of 505°K for 30

TABLE I  
Materials Used for Experiments

Sample no.	Annealing time, hr	Intrinsic viscosity, dl/g	Density, g/cm <sup>3</sup>	Basic degree of crystallinity, %	T <sub>m</sub> , °K DSC (peak)	Notes
1	unknown	1.28	1.168	59.6	498	original sample
2	0	1.28	1.095	7.8	485	melted and quenched
3	0	1.28	1.097	9.2	485	melted and quenched
4	0	1.28	1.099	10.6	485	as above
5	0	1.28	1.100	13.5	486	as above
6	0	1.28	1.105	14.9	486	melted and quenched
7	1	1.28	1.115	22.0	487	
8	3	1.29	1.121	26.1	488	
9	12	1.29	1.151	47.5	490	
10	24	1.30	1.160	53.8	494	
11	48	1.31	1.165	57.4	496	
12	72	1.32	1.170	60.8	498	
13	96	1.33	1.176	65.2	498	
14	120	1.33	1.180	68.0	498	
15	168	1.35	1.188	73.7	498	
16	288	1.35	1.195	78.7	498	
17	360	1.35	1.197	80.2	498	
18	408	1.35	1.198	80.8	499	
19	624	1.35	1.198	80.8	499	
20	840	1.30	1.200	82.2	501	
21	1680	1.30	1.203	84.3	505	

min. After melting of the polymer, the dilatometers were quickly transferred to the crystallization bath, and samples were isothermally crystallized at temperatures in a range from 473° to 488°K  $\pm$  0.02°K. The changes in mercury height during the crystallization were read using a kathetometer. The measurements were repeated twice using differential dilatometry. The results were interpreted according to the Avrami equation. The construction and filling of the dilatometers has been previously described in detail.<sup>19</sup>

**Microscopy.** Microscopic observations of the crystallization process were done on sections of polymer chips mounted in degassed DC 550 silicone fluid between clean glass cover slides. The samples were melted at 505°K  $\pm$  0.05°K for 10 min on a special hot-stage and rapidly transferred next by a moving arm to the second hot-stage mounted on a polarizing microscope (Polish Optics Works, Warsaw, Poland). On this hot-stage samples were maintained within 0.05°K of the desired crystallization temperature. The crystallization runs were measured for various temperatures in the range of 393°K to 488°K by a cadmium sulfide photoresistor, mounted on one of the eyepieces of the binocular, and connected by a simple electrical circuit to a 0–150 mV chart recorder.<sup>20</sup> The measurements were repeated twice for each set of experimental conditions.

## RESULTS AND DISCUSSION

## Effect of Thermal Treatment on Degree of Crystallinity, Intrinsic Viscosity, and Melting Temperature of Nylon 6 Samples

As seen from Table I, for the applied conditions of the thermal treatment, the degree of crystallinity of the examined samples increased practically throughout the whole time of annealing, reaching a maximum value of 84.3%. This value is on about 27% higher than the ones reached by Wunderlich<sup>21</sup> for annealed nylon 6, and only 10% lower than the crystallinity found by him in zone-polymerized nylon 6, which crystallized in an extended-chain conformation.<sup>21</sup>

The melting peak temperature of the samples (Fig. 1) increased together with the rise in the degree of crystallinity up to 60%, and remained practically constant within 60% to 81% of crystallinity. After 1680 hr of annealing for a crystallinity of 84%,  $T_m = 505^\circ\text{K}$ , which is in an agreement with Burnett's data,<sup>22</sup> and is within the range reported by Arakawa<sup>23</sup> for double-oriented nylon 6 films heat treated under vacuum.

During the annealing of the samples, an undesirable phenomenon of increase in molecular weight, caused probably by the further polycondensation of the polymer, was observed (Fig. 1). This observation is in agreement with previous experiments performed on nylon 6 from du Pont.<sup>16</sup> In a

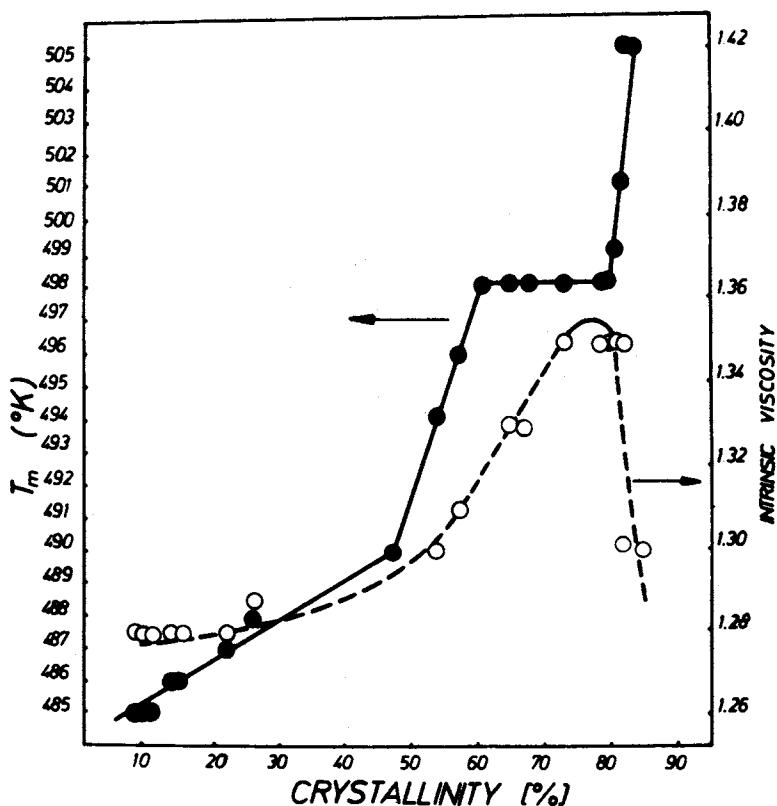


Fig. 1. Melting peak temperature and intrinsic viscosity as a function of the degree of crystallinity.

case of prolonged annealing of the samples for 840 and 1680 hr, a lowering of the intrinsic viscosity was observed. It is probably caused by the simultaneous occurrence of two processes—further polycondensation and degradation. This possibility is underlined by the fact that the measured intrinsic viscosity of these samples is still higher than the viscosity of the base sample; but at the same time, a free caprolactam is evident from an additional absorption band at 11.2 and 11.5  $\mu\text{m}$  of the infrared spectrum.<sup>24</sup>

It seems also probable that in the case of prolonged annealing, the transamidation reaction between free caprolactam which appeared in the sample as a product of degradation and polymer chains can take place, which results in an additional decrease in chain length.

As results from Figure 1, the observed changes in molecular weight caused by the thermal treatment of the polymer have a negligible effect on the melting temperature of the samples. One can see that for the samples annealed for 840 and 1680 hr for which decrease in the molecular weight is especially evident, the temperature of the melting peak is still high. It should be noted, however, that on the DSC thermograms of these samples a long, low-temperature tail was observed. This tail can be due to the melting of the low molecular weight material which was rejected by the growing crystalline front, but also to the presence of products of partial degradation of nylon 6.

### Effect of "Crystalline Memory" on Rate of Crystallization

It has been found that together with growth of the degree of crystallinity of the samples, there appeared an increase in the crystallization rate, which is shown in a diagram where the dependence of the logarithm of the half-times of crystallization is plotted versus the reciprocal of the crystallization temperature  $1/T_c$  (Fig. 2). It has been observed, however, that for values of degree of crystallinity higher than 70% (curves 9 to 15) in Arrhenius plots instead of a straight line, there appeared two intersecting lines; and, at the same time, for the higher crystallinities the intersection points of the lines moved toward higher crystallization temperatures (curves 16 to 20).

Figure 3 shows the dependence of the reciprocal of the half-time of crystallization versus the degree of initial crystallinity of the samples. The dependence shows, in principle, a rectilinear character. The crystallization rate  $1/t_{0.5}$  increases monotonically together with the rise in the initial crystallinity. However, for a higher degree of crystallinity for which a reduction in molecular weight was observed (Figs. 1 and 3), a substantial increase in slope is recorded. It is probably due to the fact that reduction of the molecular weight reduces the viscosity of the melt and thus enhances the crystallization.

### "Crystalline Memory" and Mechanism of Crystallization

As shown in Figure 4, the mechanism of crystallization described by the Avrami exponent  $n$  is different for the two different ranges of the degree of initial crystallinity. Within the range of 7.5% to 15% crystallinity, a temperature range has been observed which differentiates two mechanisms of crystallization. At a temperature of crystallization from 483° to 488°K, nucleation of spherulites is sporadic in time and  $n$  is equal to 4.

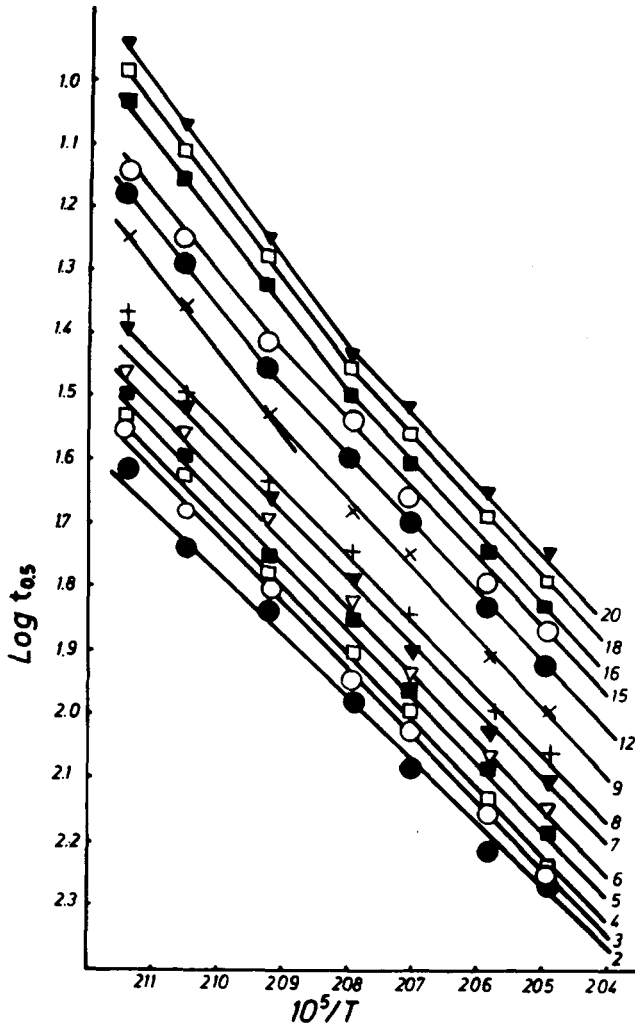


Fig. 2. Arrhenius plots. (Numbers of curves correspond to numbers of samples listed in Table I.)

In the crystallization temperature range from  $473^\circ$  to  $481^\circ\text{K}$ , the nucleation of spherulites is simultaneous or predetermined in time, and  $n$  is equal to 3. A similar phenomenon has previously been observed for nylon 6 crystallized from a homogeneous melt (without "crystalline memory").<sup>14,16</sup>

At the region of the crystallinity from 20% to 84%, for the whole examined range of temperature, exponent  $n$  reached a value close or equal to 3. The obtained dilatometric data were verified by microscopic observations of crystallized films. For samples of initial crystallinity within 7.5% to 15%, the spherulites appeared sporadically in time,  $n = 4$ , while for samples of crystallinity within 20% to 84%, the spherulites appeared simultaneously in time,  $n = 3$ .

Thus, it seems that in some specific cases for samples with low crystallinity, melted under conditions which do not destroy the "crystalline memory" and crystallized at a low supercooling (close to the melting temperature), the growth of crystals from either sporadic or simultaneous

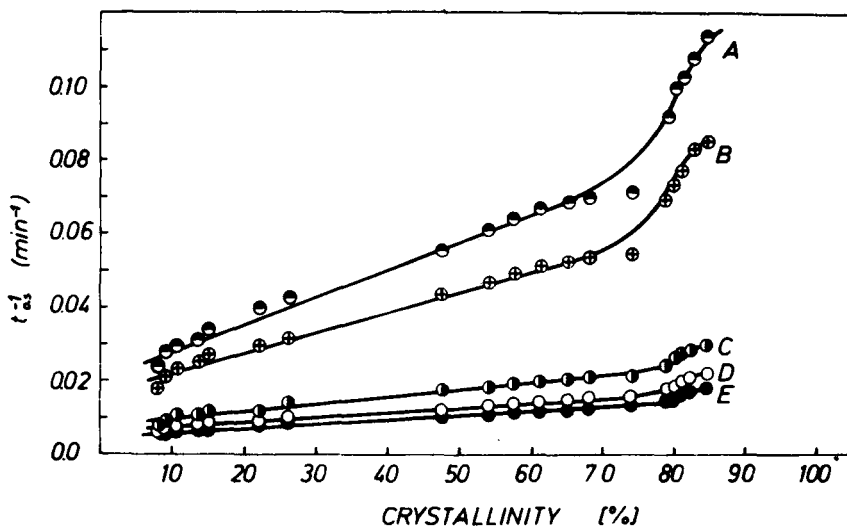


Fig. 3. Reciprocal of half-times of crystallization vs. degree of crystallinity for selected temperatures of crystallization: (A) 473°K; (B) 478°K; (C) 483°K; (D) 486°K; (E) 488°K.

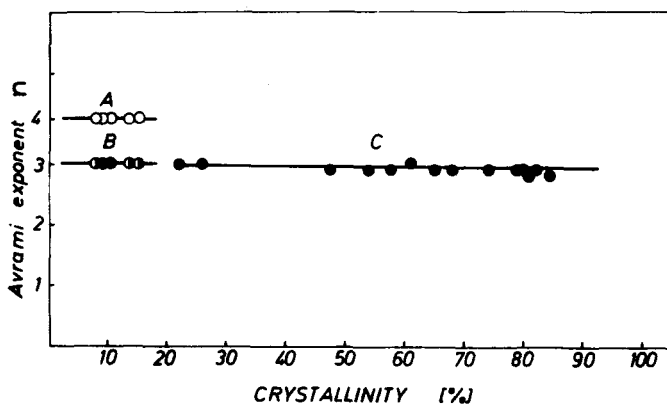


Fig. 4. Avrami exponent  $n$  vs. degree of crystallinity of investigated samples: (A) crystallization temperature 483°–488°K; (B) crystallization temperature 473°–481°K; (C) crystallization temperature 473°–488°K; for samples with degree of crystallinity within 20% to 84%.

nucleation, depending on the crystallization temperature,<sup>11</sup> is possible. This phenomenon may be explained by the fact that melting of the samples with low crystallinity, even at a temperature which does not totally destroy this crystallinity, causes however considerable lowering of the number and size of crystallites which had previously existed in the sample. Then, in some temperature range near  $T_m$ , for which the size of critical nuclei is relatively small and the rate of their formation is high, newly formed critical nuclei soon predominate the number of nuclei remaining from the melt, and nucleation occurs sporadically<sup>11</sup> ( $n = 4$ , for 483°–488°K). At somewhat lower crystallization temperatures, the critical nuclei are so small that the nuclei which are left in the melt will build up and nucleation is predetermined in time ( $n = 3$ , for 473°–481°K). Melt-

ing of samples of higher crystallinity (20%-84%) under conditions described above causes a considerable number of undestroyed aggregates to remain in the melt so that they allways outweigh in number the newly formed critical nuclei, and nucleation is predetermined in time for the whole temperature range.

In the light of the above observations, it seems possible that both the crystallization rate and the final degree of crystallinity (nonequilibrium) obtained in the definite technological conditions may depend on the degree of crystallinity of nylon 6 pellets used for the melt spinning of fibers. If the degree of crystallinity of the pellets is lower than 15%, which is not very probable under technological conditions, then the original state of the polymer pellets has practically no influence on the fiber structure. Yet in the usual industrial practice, the degree of crystallinity of the pellets is considerable higher than 15%. In these cases, the final properties of the melt-spun fibers of nylon 6 will depend to a great extent on the distribution of crystallinity of the pellets, the distance from the melting grids of bars, etc. For a large distribution of crystallinity of pellets melted under the same conditions, after-spinning crystallization leads to the growth of fibers—the spherulites of various dimensions that result in inhomogeneity of mechanical properties and different behavior at dyeing and ageing along their length. All these speculations are pertinent, however, only in the case when, under the applied technological conditions, the melting grid of the bars does not totally destroy the “crystalline memory.”

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