

# **Isothermal Crystallization of Copolyamides. I. Kinetics of Crystallization of Nylon 6-Piperazine Adipate and Nylon 6-Piperazine Terephthalate Random Copolyamides**

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## **Synopsis**

The kinetics of primary crystallization from the melt of nylon 6-piperazine adipate and nylon 6-piperazine terephthalate copolyamides were measured dilatometrically. It was found that the crystallization rate of the samples under investigation decreases with increase in the percentage comonomer content and rigidity of molecules over the entire temperature range investigated. The Avrami exponent  $n$  varied with temperature, values being from 2 to 4.

## **INTRODUCTION**

Previous papers<sup>1,2</sup> included the results of kinetic investigation of nylon 6 isothermal crystallization and the effect of molecular weight on it. The present work was carried out to examine how the crystallization rate of copolyamides of nylon 6 was affected by various comonomer content and consequently to determine the usability of these copolyamides for technologic purposes.

Except for the papers on the crystallization kinetics of nylon 6-11 and nylon 66-6 copolyamides recently published,<sup>3,4</sup> there is a lack of data on this problem in the literature.

## **EXPERIMENTAL**

Samples used for the investigations were copolyamides obtained by condensation of caprolactam and piperazine adipate or caprolactam and piperazine terephthalate in various molar proportion, as well as commercial nylon 6 homopolymer having no titanium dioxide and stabilized with acetic acid. Viscosities of the samples were measured in 98% sulfuric acid at 25°C using polymer solutions containing 0.35 to 0.117 g/100 ml. The results are given in Table I.

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TABLE I  
Materials Used for the Experiments

Sam- ple No.	Type of samples	Comono- mer con- tent, mole-%	Intrinsic viscosity, dl/g	Sample symbol	Mineral impurity content, wt-%
1	Nylon 6- piperazine adipate	2.5	1.06	PA-PPA 2.5	0.051
2	Nylon 6- piperazine adipate	4	1.08	PA-PPA 4	0.052
3	Nylon 6- piperazine adipate	6	1.07	PA-PPA 6	0.052
4	Nylon 6- piperazine terephthalate	4	1.13	PA-PPT 4	0.078
5	Nylon 6- piperazine terephthalate	6	1.05	PA-PPT 6	0.072
6	Nylon 6- piperazine terephthalate	8	1.08	PA-PPT 8	0.072
7	Nylon 6	0	1.10	PA	0.072

### Examination of the Effect of Annealing and Melting on Intrinsic Viscosity

The samples were introduced into glass ampoules and annealed under vacuum ( $10^{-6}$  mm Hg) at a temperature 5 degrees below their melting points for 1 to 7 hr. The samples were then melted in sealed ampoules under vacuum for 30 min at 270°C.

### Crystallization Conditions

The samples were dissolved in formic acid and filtered through a G-5 sintered filter. Films were cast from 2% solutions, extracted with water, and dried under vacuum ( $10^{-6}$  mm Hg). Dry samples were extruded from the melt. Crystallization measurements were carried out in dilatometers, using samples of 80 mg. Details on sample preparation, construction of dilatometers, and thermostats were given previously.<sup>1,5</sup>

### Selection of Melting Temperature and Time and Temperature of Crystallization

A Perkin-Elmer differential scanning calorimeter 1B was used to find the melting temperature, using 5-mg samples and a heating rate of 16°/min. The results are given in Table II. Samples were annealed before crystallization at different temperatures higher than  $T_m$  to find the optimum melting temperature. The effect of annealing on the crystallization rate

TABLE II  
Melting Parameters for Samples Listed in Table I

Sample No.	Sample symbol	$T_m$ , °K	$\Delta H_t$ , cal/g	$T_m$ (corrected), °K
1	PA-PPA 2.5	490	11.64	503
2	PA-PPA 4	482	11.02	497
3	PA-PPA 6	475	10.43	485
4	PA-PPT 4	I. max. 476 II. max. 482	11.32	492
5	PA-PPT 6	I. max. 461 II. max. 472	10.58	486
6	PA-PPT 8	I. max. 453 II. max. 464	10.20	473
7	PA	498	13.88	510

at a selected temperature and the effect of the annealing duration at a selected temperature higher than  $T_m$  on the crystallization rate were determined.

#### Calculation of Kinetic Data

The values of  $\theta = (h_t - h_\infty)/(h_0 - h_\infty)$  indispensable for kinetic plots were calculated from the dilatometric data. Kinetic parameters were calculated from the Avrami equation adapted for dilatometric measurements:

$$\frac{h_t - h_\infty}{h_0 - h_\infty} = \exp [-Kt^n] \quad (1)$$

where  $h_0$ ,  $h_t$ , and  $h_\infty$  represents the mercury height during the induction period, at time  $t$ , and after the isotherms has leveled off, respectively. The exponent  $n$  was calculated by the method proposed by Hay,<sup>6</sup> and the rate constant  $K$ , from half-times of crystallization according to the equation

$$K = \frac{\ln 2}{t_{0.5}^n} \quad (2)$$

assuming  $n$  equal to 3.

## RESULTS AND DISCUSSION

The annealed homopolymer did not show any change in intrinsic viscosity, but there was some increase in the viscosity of copolyamides within the first 1 to 3 hr of annealing, the value thereafter being constant. For these reasons, all the copolyamides were first annealed under vacuum for appropriate times.

#### Melting Temperature and Time Before Crystallization and Temperature of Crystallization

Nylon 6 was melted for 30 min at 270°C, the condition, as was previously<sup>1</sup> found, being sufficient to obtain practically "amorphous" melt. The

crystallization rate of copolyamides increased with lowering of the annealing temperature to below 250°C. Annealing at 270°C for a period longer than 15 min did not affect the shape of the kinetic curves.

Based on the results obtained, all the samples were melted at 270°C for 30 min, and the crystallization of homopolymer and copolyamides was carried out by supercooling at 7° to 19°C and 6° to 38°C, respectively. At a higher extent of supercooling, the crystallization began even before the samples reached the temperature of the crystallization bath.

It was found that in nylon 6-piperazine terephthalate copolyamides, a separation of the melt took place into two layers of different volumes, divided by a layer of mercury. The layers were cut up to determine their melting point by means of a polarizing microscope provided with a hot-stage. The melting point of the lower layers was on the average higher than that of the upper layers by 6° to 7°C for all the samples under investigation. There were also two maxima on the DSC thermograms taken with these samples, independent of weight and shapes of the samples. Homogenization of the melt and consequent disappearance of the layers was accomplished after repeated melting of the given sample.

As follows from Table II in accordance with theoretical assumptions,<sup>7,8</sup> the melting points of the copolyamides were dropping with increase in comonomer content. The value of the heat of fusion of the copolyamides behaved in similar fashion. The values of  $T_m$  and  $\Delta H_f$  obtained for nylon 6 were similar to those given by Inoue.<sup>9</sup>

### Isothermal Crystallization

Figure 1 shows an exemplary plot in the Avrami system for nylon 6-piperazine adipate, 4 mole-%, copolyamide. Similar plots were obtained for the rest of the copolyamides and for nylon 6.

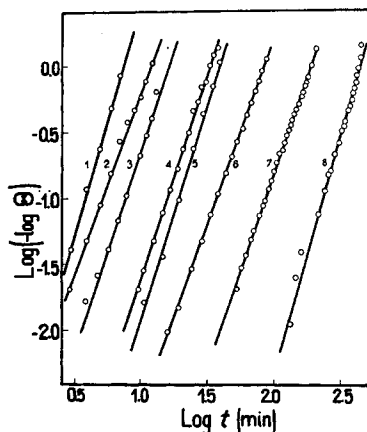


Fig. 1. Avrami plots for PA-PPA 4 copolyamide at various crystallization temperatures: (1) 451°K; (2) 454°K; (3) 457°K; (4) 460°K; (5) 463°K; (6) 466°K; (7) 469°K; 472°K.

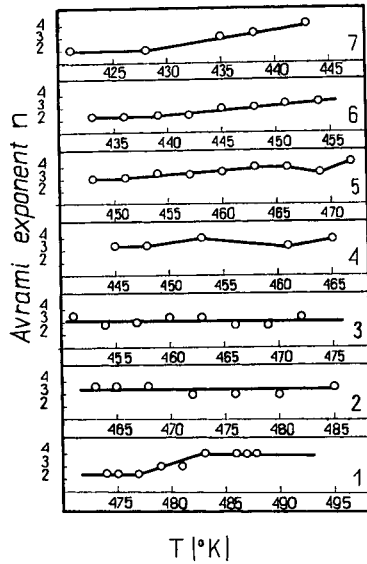


Fig. 2. Plot of Avrami exponent  $n$  vs. crystallization temperatures: (1) PA; (2) PA-PPA 2.5; (3) PA-PPA 4; (4) PA-PPA 6; (5) PA-PPT 4; (6) PA-PPT 6; (7) PA-PPT 8.

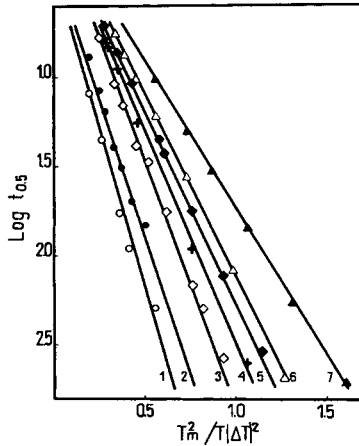


Fig. 3. Temperature dependence of half-times of crystallization for investigated samples calculated for corrected values of  $T_m$  listed in Table II: (1) PA-PPT 8; (2) PA-PPT 6; (3) PA-PPT 4; (4) PA-PPA 6; (5) PA-PPA 4; (6) PA-PPA 2.5; (7) PA.

Figure 2 illustrates the relationship between the exponent  $n$  and the temperatures of crystallization for the investigated copolyamides and nylon 6.

The dependence of  $\log t_{0.5}$  (half-time of crystallization) on  $T_m^2 / T(\Delta T)^2$  for corrected values of  $T_m$  is given in Figure 3.

### Crystallization Mechanism

As is seen from Figure 2, the mechanism of copolyamide and nylon 6 crystal growth depends on temperature, as confirmed by the varying values of  $n$ . There is a range of temperature, 482° to 483°K, which separates two different nucleation mechanisms in nylon 6. At higher temperatures, the growth proceeds three-dimensionally from sporadic nuclei, while at lower temperatures, the growth proceeds from instantaneous nuclei, as observed previously.<sup>1,2</sup>

For copolyamides, the values of  $n$  are between 4 and 2, practically being equal to 3, which corresponds to a three-dimensional growth and heterogeneous nucleation. This is confirmed by the appearance of well-developed spherulites always at the same points of samples, as observed under a polarizing microscope. It is obvious that the Avrami theory has a limited application for copolyamides, the value of  $n$  being only approximate.

According to the theory,<sup>10,11</sup> the relationship between log half-times of crystallization and  $T_m/T(\Delta T)$  and  $T_m^2/T(\Delta T)^2$  should have a rectilinear character of crystal growth from two-dimensional and three-dimensional secondary nuclei, respectively. However, in all cases investigated, curved lines were obtained assuming constant values of  $T_m$  from DSC measurements. Straight lines are obtained when higher values of  $T_m$  are taken for the calculations. It follows that values of  $T_m$  found by the differential scanning calorimetry method do not correspond with the equilibrium melting points. Corrected values of  $T_m$  are given in Table II.

### Rate of Crystallization

The crystallization rate within the studied temperature range decreases with rise in temperature. According to theory,<sup>7,8</sup> the crystallization rate of copolyamides is considerably lower than that of nylon 6, the value being significantly affected by both the chemical composition of comonomer and its content in the samples under examination.

At the same percentage comonomer content (4 mole-%), samples of nylon 6-piperazine terephthalate crystallized considerably slower than those of nylon 6-piperazine adipate. Samples of nylon 6-piperazine terephthalate (6 mole-%) crystallized about four times slower than samples of nylon 6-piperazine terephthalate (4 mole-%) under the same conditions of supercooling. This considerable decrease in the copolyamide crystallization rate as compared to that of nylon 6 is due to the presence of a noncrystallizing comonomer in copolyamides causing structural defects.<sup>10</sup> Because of low comonomer content, these defects can be considered as impurities which in the melt-crystal transition are rejected from ordered regions and deposited within intercrystalline regions, thus limiting further free growth of spherulites.

The difference between the crystallization rate of samples of nylon 6-piperazine adipate and that of nylon 6-piperazine terephthalate is due to differences in chemical structure of the chains. The chain of nylon 6-

piperazine terephthalate copolyamide is more rigid, with side groups having greater volume. This brings an additional restriction in free network formation and, consequently, a decrease in crystallization rate.

It was further observed that in the nylon 6-piperazine terephthalate copolyamides in which a separation of layers was observed after melting, crystallization proceeded in two stages. The lower layer crystallized first, showing turbidity in a shorter time than the upper layer. The kinetic curves taken for the entire sample had two distinct bending points, which was particularly pronounced at a low extent of supercooling. At greater supercooling, although the lower layer also crystallized faster than the upper layer, the crystallization of both layers overlapped, and the curve had only one bending point.

This two-stage crystallization is due to differences in the melting points of the two layers. At the same crystallization temperature, the lower layer, having a higher melting point, reaches a higher extent of supercooling and crystallizes faster than the upper layer, having a lower melting point.

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