

Rates of Crystallization of Copolyamides. I. Random Copolymers of Nylons 6 and 11

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Synopsis

Rates and extents of crystallization of nylon 11 and nylon 6/11 copolymers have been measured by dilatometry. As the amount of copolymerization increased there was a decrease in the extent of crystallization and in the rates of crystallization for any degree of supercooling below the melt.

INTRODUCTION

Isothermal crystallization rates for polyamides have been reported using dilatometry,¹⁻⁶ microscopy,⁷⁻¹² and differential thermal analysis.^{13, 14} No measurements on copolyamides have been reported. It is well known that the introduction of another monomer produces a reduction in the melting point and in the extent of crystallization, but no information is available on the rates of crystallization of copolyamides. In this study random copolyamides of nylon 11 with up to 20% (molar) nylon 6 have been prepared and studied. Crystallization rates have been determined by dilatometry.

EXPERIMENTAL

Materials

All the copolymers were prepared from the amino acid monomers, ω -aminoundecanoic acid and ω -aminocaproic acid, to ensure the production of truly random copolymers. This assumes that the functional groups NH_2 and COOH will have the same reactivity and that lactam formation does not affect the composition of the copolymers.

The requisite amounts of amino acid (based on molar composition) were carefully mixed and made into a paste with distilled benzene. On heating this mixture slowly, the benzene evaporated removing air from the fine particles. Nitrogen was passed over the surface of the monomers as the temperature was slowly raised to 220°C. When the monomers had

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melted, nitrogen was passed through the melt to assist the removal of moisture formed in the condensation reaction. Polymerization was continued for 10 hr after which the product was allowed to solidify under nitrogen. The use of small quantities of benzene was found to be a convenient method for the removal of air from the amino acids to prevent oxidation. Very white products were obtained. The melting points of each sample were measured at a heating rate of $10^{\circ}\text{C}/\text{min}$ using the du Pont 900 differential thermal analyzer.

Dilatometry

Rates of crystallization were measured using a dilatometric technique. The dilatometer consisted of a small bulb (8 mm diameter) containing the polymer attached horizontally to a vertical measuring stem of Veridia capillary tubing (0.4 mm bore).

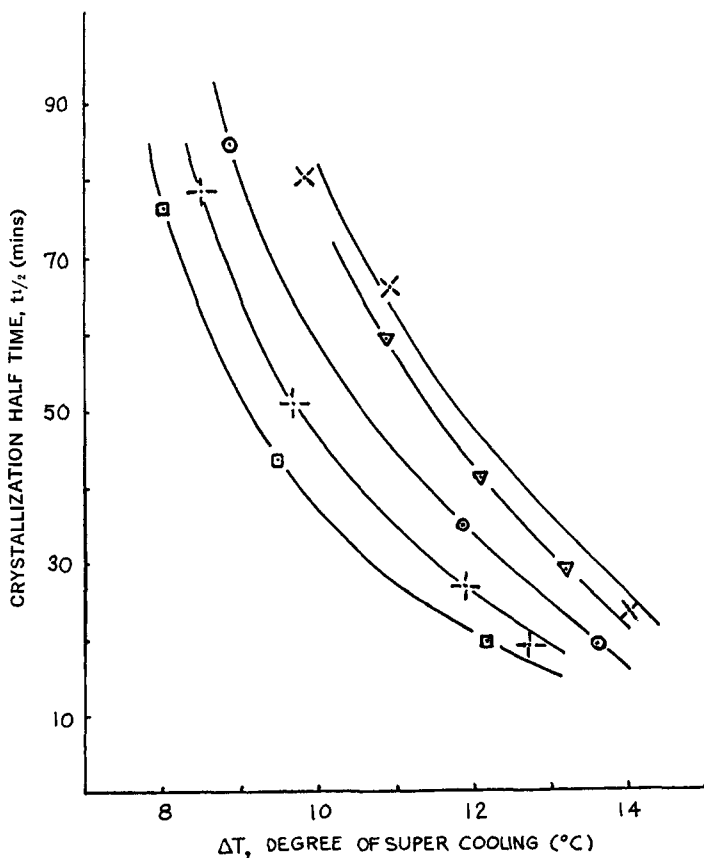


Fig. 1. Crystallization half-times for copolyamides 11/6 at different amounts of super-cooling: (\square) nylon 11; ($-|-$) 5% copolymer; (\odot) 10% copolymer; (∇) 15% copolymer; ($>-<$) 2% copolymer.

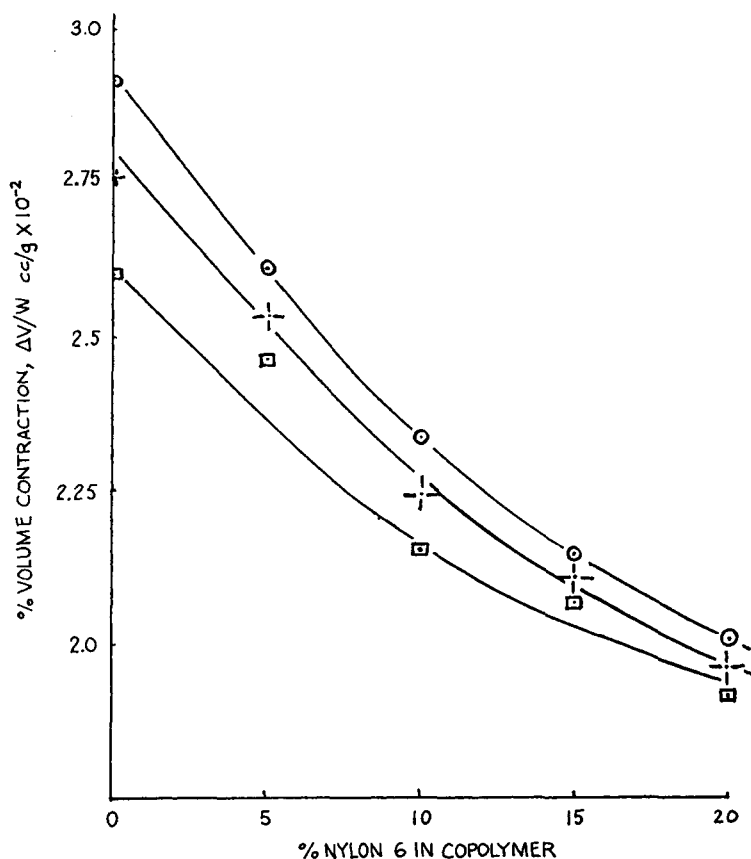


Fig. 2. Volume contractions for copolyamides 11/6 of different compositions: (○) ΔT 13.0°C; (—+—) ΔT 11.5°C; (□) ΔT 10.0°C.

A polymer sample was heated under vacuum for 4 hr at 20°C above the melting point to remove residual moisture. It was cooled and a small plug (0.15–0.20 g) was cut and sealed into the dilatometer bulb. Care was taken during the sealing operation to leave as little free space as possible and yet avoid degradation. The dilatometer was then evacuated to 10^{-5} mm Hg. Triple-distilled Hg was then introduced into a side arm in the dilatometer which was then sealed. The required quantity of Hg could be transferred into the dilatometer. When this was adjusted correctly the vessel was opened. All measurements reported here were made at atmospheric pressure.

The polymer samples were heated at 20°C above their melting temperature for 30 min and then rapidly transferred to the crystallization bath the temperature of which was controlled to 0.3°C. The crystallization was followed by observing the contraction in volume with a cathetometer. It was found that the dilatometer and sample achieved the temperature of the

TABLE I
Volume Contractions and Rates of Crystallization
of Nylon 11 and Nylon 11/6 Copolymers

Polymer	DTA melting point, °C	Crystallization temp., °C	Degree of supercooling, °C	Crystallization half-life, min	Volume contraction, cc/g	Rate constant k for crystallization, min^{-4}
nylon 11	187.5	179.5	8.0	76.5	.0238	1.0×10^{-6}
		178.0	9.5	43.5	.0275	1.9×10^{-7}
		175.3	12.2	19.5	.0283	1.5×10^{-8}
95/5 nylon 11/6 copolymer	180.0	171.5	8.5	79.0	.0235	4.8×10^{-6}
		170.3	9.7	51.0	.0248	7.7×10^{-7}
		168.1	11.9	26.8	.0254	9.6×10^{-8}
		167.3	12.7	19.3	.0260	1.4×10^{-8}
90/10, nylon 11/6 copolymer	174.0	165.1	8.9	85.0	.0210	5.7×10^{-6}
		162.1	11.9	39.5	.0223	2.8×10^{-7}
		160.4	13.6	18.5	.0239	1.2×10^{-8}
85/15 nylon 11/6 copolymer	166.0	155.1	10.9	59.0	.0210	1.1×10^{-6}
		153.9	12.1	40.5	.0213	2.8×10^{-7}
		152.8	13.2	28.5	.0216	4.3×10^{-8}
80/20 nylon 11/6 copolymer	159.0	149.1	9.9	80.0	.0189	3.2×10^{-6}
		148.0	11.0	65.5	.0195	4.8×10^{-8}
		145.0	14.0	23.0	.0204	9.5×10^{-9}

crystallization bath in less than 3 min. In each case the time for commencement of crystallization was taken to be 3 min after the transfer.

RESULTS AND DISCUSSION

The data shown in Table I was collated from the crystallization curves that were obtained for 11 nylon and for the copolymers. The crystallization half-time was taken as the time for one half of the primary crystallization from the time of attaining the temperature of the crystallization bath. Three min was allowed from the time of transfer for equilibrium. Any additional induction period was included as part of the crystallization process. Some error may arise in the choice of the end of the primary crystallization since this was determined by visual inspection. Secondary crystallization effects were found to become more pronounced as larger amounts of ω -aminocaproic acid were incorporated into the copolymers.

As expected, an increase in the amount of comonomer resulted in a decrease in the melting temperature. In Figure 1, $t_{\frac{1}{2}}$ (in min) for crystallization has been plotted against the degree of supercooling below the melting point for nylon 11 and for the copolymers. A trend can be seen for slightly more supercooling to be necessary to produce a given rate of crystallization as the amount of ω -aminocaproic acid in the copolymer is increased.

In Figure 2, the total extent of crystallization (as the volume contraction per g) has been plotted against copolymer composition. Increasing the extent of copolymerization results in a drop in the total crystallizability.

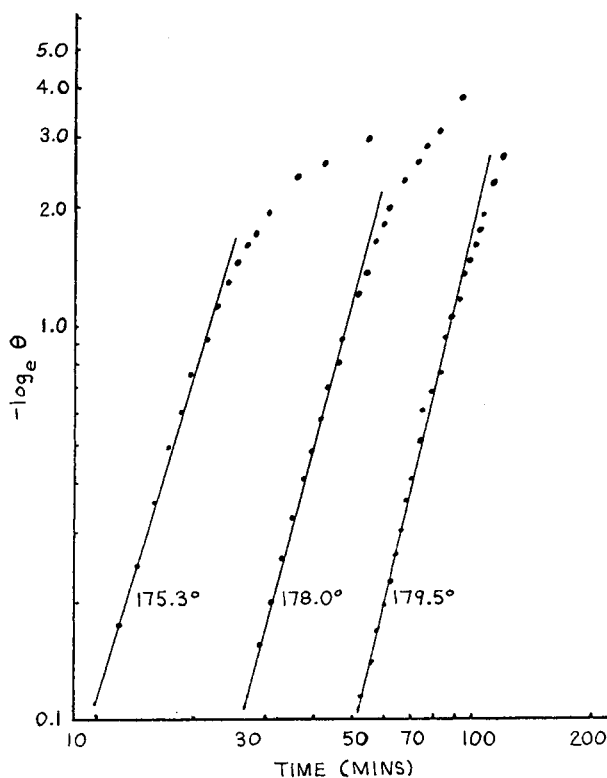


Fig. 3. Avrami plots for nylon 11.

Greater extents of crystallization are observed for the copolymers and for nylon 11 when crystallizing at greater amounts of supercooling (i.e., at faster crystallization rates at lower crystallization temperatures). According to Keith and Padden's mechanism¹⁵ for spherulite growth, imperfect material is rejected as the spherulite grows outward. At faster growth rates, this selection procedure is not as efficient and more imperfect material is included within the spherulites. This could lead to greater amounts of crystallization at faster growth rates for those copolyamides and for nylon 11 itself since all of these materials are only partially crystalline (i.e., they are only 60% or 70% crystalline).

When Avrami plots were made on the dilatometric data for nylon 11 and for the copolyamides, a line with integer 4 could be drawn through a considerable part of the data at the early stages of crystallization. There was more departure from this line for polymers crystallizing quickly than for those crystallizing slowly. Figure 3 shows Avrami plots for nylon 11. Similar plots were obtained for the copolyamides. From these data the values for k shown in Table I have been determined from extrapolations of t when $-\ln \theta = 0.1$ and assuming $n = 4$.

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