

Rates of Crystallization of Copolyamides. II. Random Copolymers of Nylons 66 and 6

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Synopsis

Rates of crystallization of copolyamides of nylons 66 and 6 have been measured by a photometric technique using a hot-stage microscope. The copolymers all show some crystallinity, but the temperatures of crystallization are reduced as more comonomer is introduced. A close correlation between melting and crystallization behavior is observed. The copolymerized component is acting as a diluent rather than entering the homopolymer crystal.

INTRODUCTION

In part I,¹ random copolymers of nylon 11 with nylon 6 were shown to exhibit appreciable extents of crystallization, although they crystallized at lower temperatures. The crystallization kinetics were found to be related closely to the amount of supercooling from the melting points. There was no evidence of cocrystallization in the limited composition range (0–20% copolymerized) that was studied. In this work, crystallization rates have been measured for random copolymers of nylon 6 with nylon 66 covering a much wider range of composition.

Owing to the high melting temperatures required for these copolymers, and the possibility of reequilibration in the melt with the formation of water vapor, hot-stage microscopy was preferred to dilatometry. The differential thermal method² was insufficiently sensitive for copolymers of low crystallinity. Direct observation of spherulites during growth³ was impracticable for copolymers due to their small sizes (5 μ maximum). The photometric method of Magill⁴ fulfilled the experimental requirements, and a modified version gave an adequate response for the copolymer series.

EXPERIMENTAL

Apparatus

A Swift Model P polarizing microscope with Nicol prisms set at 90° was fitted with a 2¹/₂-in. diameter stainless-steel hot stage having a 300-watt heating coil. The stage was mounted in an asbestos block with a provision for supplying a nitrogen atmosphere. The eyepiece used was a double-demonstration ocular, one arm of which carried a cadmium sulfide photo-

resistor, leaving the other arm available for visual and photographic observations. A fitted illuminator was supplied from a constant voltage transformer.

Close temperature control of the stage to $\pm 0.1^\circ\text{C}$ was achieved by directing an amplified signal from a thermistor to the gate of a silicon controlled rectifier working a 0- to 110-volt mains supply. The stage temperature was monitored using analytical-quality chromel-alumel thermocouples including a crushed-ice 0°C reference junction. The measuring thermocouple potentiometer was standardized frequently against a reference Weston cell.

Copolymer samples were melted on a second hot plate that was coupled directly to the heated stage of the microscope. A rotary transformer gave a temperature control of $\pm 2^\circ\text{C}$, which was monitored using thermocouples connected to a millivoltmeter.

Polymer density measurements were obtained using a Davenport density gradient column at 23°C . The required gradation ($\rho = 1.10\text{--}1.17$) was constructed using solutions of carbon tetrachloride in xylene. The column was calibrated with standard glass floats.

Materials

The polymers and copolymers were prepared from the salt of hexamethylenediamine with adipic acid (66 salt) (B.A.S.F.) and 6-aminohexanoic acid (Koch-Light Laboratories). The latter was found to be more convenient for copolymerization than caprolactam. The mole unit for each monomer when calculating molar fractions was taken to be 131 g.

A two-stage process was normally used, with the formation of a prepolymer in a sealed tube followed by further polymerization in the molten state.

TABLE I
Limiting Viscosity Numbers and Molecular Weights of 66/6 Copolyamides

Molar composition, % nylon 66	Density, g/ml	$[\eta]_0$, ml/g	M_v^a	M_v^b
100	1.157	58	26,900	21,800
93	1.151	58	26,900	21,800
85	1.145	56	25,500	20,800
80	1.139	58	26,900	21,800
70	1.134	60	28,500	23,000
60	1.130	68	34,000	26,000
50	1.126	66	32,500	25,500
40	1.128	55	24,000	20,100
27	1.129	62	29,700	24,200
15	1.135	58	26,900	21,800
10	1.136	62	29,700	24,200
0	1.152	57	23,200	21,500

^a From Elias and Schumacher.⁵

^b From Burke and Orofino.⁶

This was carried out in a steam-nitrogen current at atmospheric pressure. A fluidized sand bed provided a temperature of $275^{\circ} \pm 5^{\circ}\text{C}$ for preparing nylon 66. Lower temperatures were used for preparing the copolymers. The materials were dried in a vacuum oven (60°C , 1 mm Hg, 48 hr) and kept in stoppered bottles.

A measure of the molecular weights of the materials was obtained by solution viscosity measurements in aqueous formic acid (90%) containing sodium formate to suppress the polyelectrolyte effect (0.1 mole/liter). All the limiting viscosity numbers were in the range 55-68, measured at 25°C . To give some indication of the molecular weights of the polymers, the $[\eta]_0/M_v$ relations for nylon 66 were assumed for the copolymers. Details of the materials used for this study are shown in Table I. M_v values are calculated from expressions derived by Elias and Schumacher⁵ and Burke and Orofino.⁶ Inasmuch as the first workers used light scattering whereas Burke used osmometry, the discrepancy between the values is not surprising.

Methods

A piece of polymer was melted at 30°C above its melting point and pressed gently between cleaned glass cover slips, to give a uniform film of about $50\text{-}\mu$ thickness. After 5 min, the sample was rapidly transferred (<1 sec) to the microscope stage at the required constant temperature. The polymer crystallization was followed from the decreasing resistance of the photo-resistor, as the intensity of light falling on it increased. The signal was normally displayed on a time axis recorder.

To determine the melting point of a polymer sample, the sample was heated on the stage of the same apparatus, with a programmed heating rate of $2^{\circ}\text{C}/\text{min}$. The temperature at which the field of view became dark was recorded as the melting point.

The density of each copolymer (Table I) was determined after the samples had been crystallized from the melt to room temperature at a rate of $2^{\circ}\text{C}/\text{min}$.

RESULTS

Rates of Crystallization

Optical depolarization traces of polymer crystallization have the same general shape as dilatometric graphs. The crystallization process has been assumed to commence at the instant of transfer of the polymer melt to the heated stage of the microscope, and measurements were continued until no further crystallization could be detected. For the nylon 66/6 system of copolymers as with nylon 6/11 copolymers,¹ secondary crystallization occurs. Rates of crystallization of the copolymers were compared by using the time for one half of the complete crystallization, including the secondary process.

The effect of composition on the crystallization rate at various temperatures is shown in Figure 1 for nylon 66 and for copolymers with up to 50% nylon 6. The $t_{1/2}$ times for nylon 6 and copolymers containing up to 40% nylon 66 are shown in Figure 2. For each polyamide, copolymerization causes a reduction in the temperature required to produce a certain $t_{1/2}$

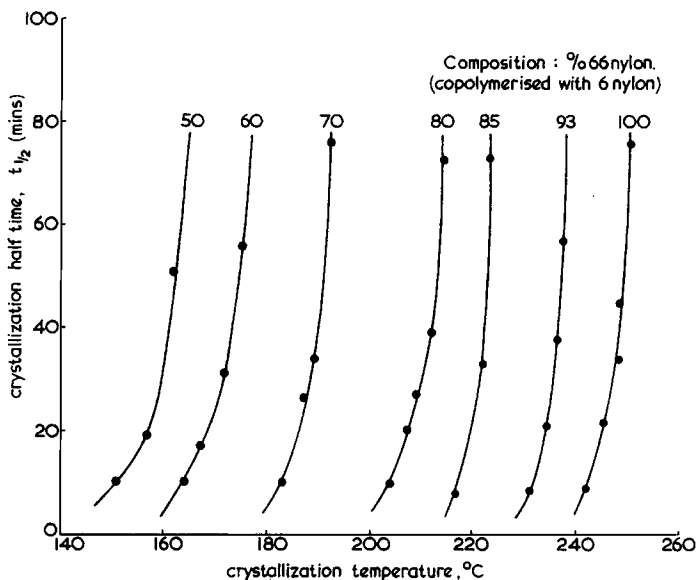


Fig. 1. Crystallization half-times at various temperatures for nylon 66 and its copolymers with up to 50% nylon 6.

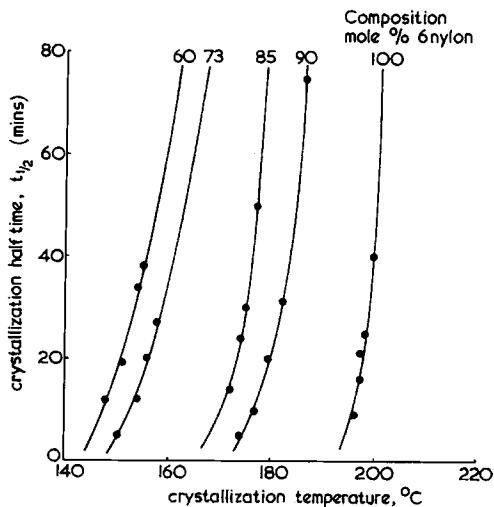


Fig. 2. Crystallization half-times at various temperatures for nylon 6 and its copolymers with up to 40% nylon 66.

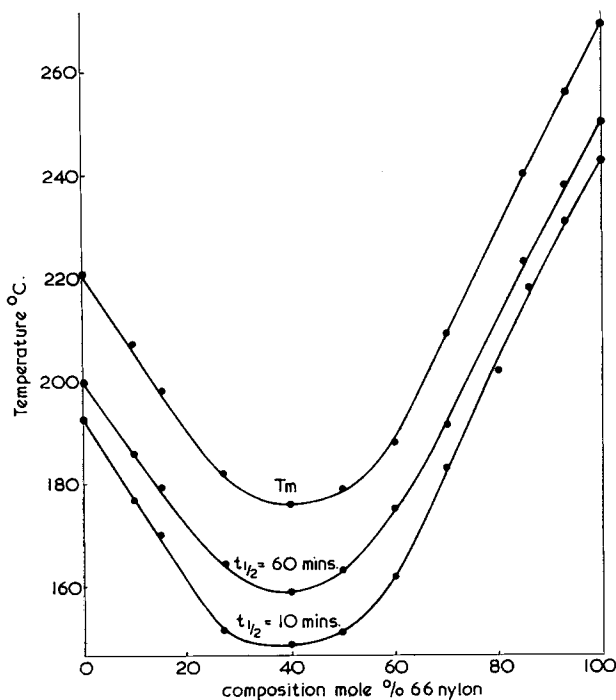


Fig. 3. Temperatures for melting and certain crystallization rates for nylon 66/6 copolymers.

time. As expected, the melting temperature of the copolymers is also reduced. Figure 3 shows a comparison of the melting points and the temperatures required to produce half-crystallization times of 10 and 60 min. The disappearance of the birefringence method gives high values for polymer melting points,⁷ and the results shown in Figure 3 are higher than those of Catlin, Czerwin, and Wiley⁸ using a Bloc Maquenne apparatus. An increased melting point is recorded for negatively birefringent spherulites, which are sometimes seen when nylon 66 is crystallized at low degrees of supercooling.⁹ Negatively birefringent spherulites are not observable for nylon 6.¹⁰ The results shown in Figure 3 were obtained from positively birefringent spherulites only.

Crystallinity of Copolymers

The densities of the polymers are shown in Figure 4. A conversion of density to percentage crystallinity is also shown in Figure 4, using the published densities¹¹ for amorphous and crystalline nylon 66 for the copolymers.

DISCUSSION

Microscopic observations confirm that spherulitic crystallization occurs readily throughout the copolymer series, but observations of the more

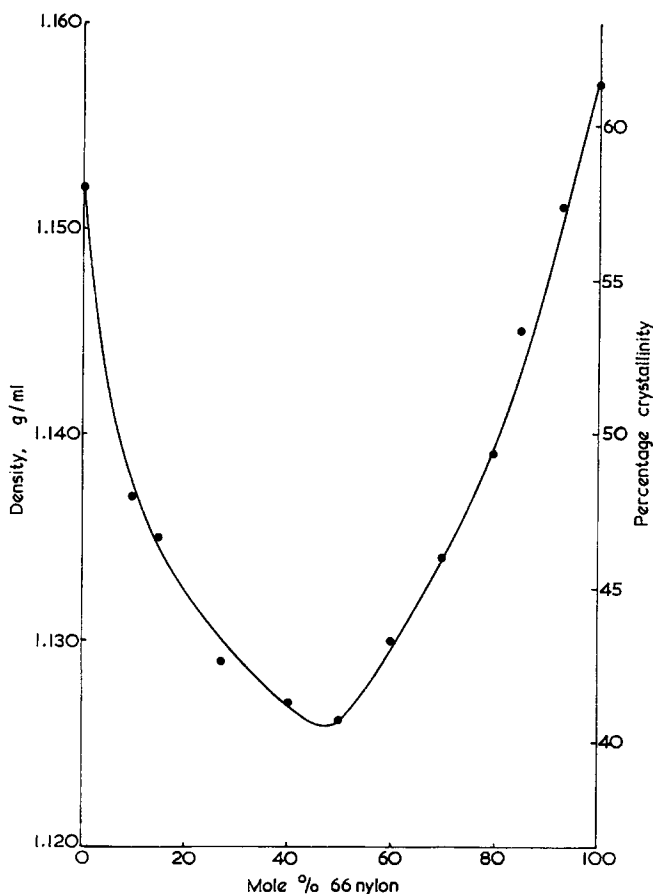


Fig. 4. Densities and percentage crystallinities for nylon 66/6 copolymers.

highly copolymerized samples (>30% copolymer) rarely showed aggregates of diameter larger than 1μ . The increased secondary crystallization period observed for the nylon 11/6 copolymers¹ is also pronounced with this series of copolyamides. No attempt was made to separate the secondary process from the primary process.

An increase in the proportion of comonomer added to nylon 66 or to nylon 6 leads to a decrease in the melting point T_m . As with the 6/11 system,¹ a certain rate of crystallization occurs at a lower temperature when a copolymer is compared with that of the homopolymer. However, the same rate of crystallization is obtained at the same value of ΔT (i.e., $T_m - T_c$). In this work, we are using the time of half-crystallization of the whole process as a measure of the rate of crystallization because we believe that the secondary crystallization is an important part. With this technique, any changes occurring within spherulites should be detectable by the change in intensity of light observed by the photocell.

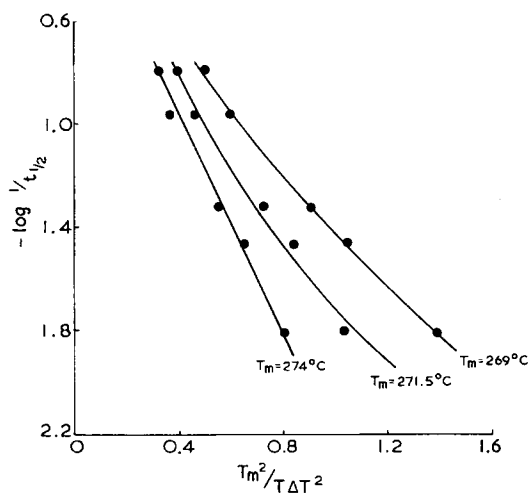


Fig. 5. Dependence of crystallization half-time on the extent of supercooling for nylon 66 using different values for T_m .

According to Mandelkern, Quinn, and Flory,^{12,13} plots of $\log 1/t_{1/2}$ versus $(T_m^2/T_c)(1/\Delta T)^2$ should be linear. If we take $t_{1/2}$ values for the crystallization, including the secondary crystallization, and use the measured value of T_m , we find curves for the homopolymers and for the copolymers.

However, if the T_m values used in the expression are increased by successive increments, linear plots can be obtained, e.g., it is found that for nylon 66 the T_m value must be increased by 5°C and for nylon 66 containing 30% nylon 6, by 10°C. Similar results were obtained for the other copolymers (Table II). For crystalline polymers it has already been reported that the thermodynamic melting point of perfect crystallites is a good deal higher than the normal measured melting point, including that obtained when using the optical method. Values of 141°–142°C have now been given for the melting point of high-density polyethylene^{14,15} and 272.5°C for that of nylon 66.³ We believe that this corrected melting temperature approaches more closely the thermodynamic melting temperature of these substances.

The observed lowering in the melting point in this system is typical of copolymerization where only a single constituent of the copolymer is forming the crystals. The melting of the system follows the Flory treatment for polymer dilution¹⁶:

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{R}{\Delta H_u} \ln N_A$$

where ΔH_u is the heat of fusion of crystalline units and N_A is the mole fraction of the major constituent. Figure 7 shows that this treatment is applicable to nylon 66 containing up to 40% copolymerized nylon 6 and for nylon 6 containing up to 30% copolymerized nylon 66. The heats of fusion

TABLE II
Melting Points and Rates of Crystallization of Copolymers
of Nylon 66 and Nylon 6

Molar composition, % nylon 66	Measured melting temp, °C	Crystallization temp., °C	Crystallization half-time, min	Corrected melting point, °C
100	268	249.5	78.0	274
		248.8	43.3	
		246.5	32.0	
		245.0	22.0	
		242.0	8.7	
93	256	236.5	56.0	262
		234.8	38.0	
		234.0	21.0	
		233.5	13.3	
85	235	231.5	9.3	249
		223.2	73.0	
		221.8	33.3	
		219.2	24.0	
80	227	217.5	13.3	240
		211.0	4.0	
		212.0	47.3	
		211.5	37.3	
70	210	210.2	24.3	219
		207.2	20.0	
		204.2	10.7	
		191.7	94.6	
60	188	190.6	83.3	203
		189.2	36.6	
		187.0	26.6	
		183.0	10.6	
50	178	174.8	56.0	189
		171.2	32.0	
		169.5	26.7	
		167.5	17.3	
40	177	166.2	11.3	186
		160.2	52.0	
		157.2	37.3	
		155.8	19.3	
27	179	153.0	12.0	188
		151.5	9.7	
		155.2	38.6	
		154.0	34.3	
		150.8	18.7	
		148.5	11.7	
		146.0	5.3	
		157.0	27.3	
		156.5	20.0	
		153.5	12.0	
		150.5	6.3	

TABLE II (continued)

Molar composition, % nylon 66	Measured melting temp, °C	Crystallization temp., °C	Crystallization half-time, min	Corrected melting point, °C
15	195	176.8	49.0	205
		174.2	30.0	
		173.8	24.0	
		171.2	14.0	
		167.6	7.6	
10	201	185.2	79.0	212
		182.5	31.3	
		179.5	20.0	
		177.0	10.0	
		174.0	5.3	
0	221	199.5	44.7	226
		198.2	24.7	
		197.8	21.0	
		197.5	16.0	
		196.2	9.3	

for crystalline regions of the polymers when using the measured values of T_m are 28.1 cal/g for nylon 66 and 31.9 cal/g for nylon 6. Following the procedure shown in Figures 5 and 6, the thermodynamic melting points have been estimated for each copolymer, and the results are inserted into Figure 7. An increase in the crystalline heats of fusion is now obtained to 31.8 cal/g for nylon 66 and 32.0 cal/g for nylon 6. These values are still much lower than the results obtained by differential thermal analysis of polymers of known density.¹⁷ Low results for heats of fusion from copolymer melting point data have been reported previously.¹³

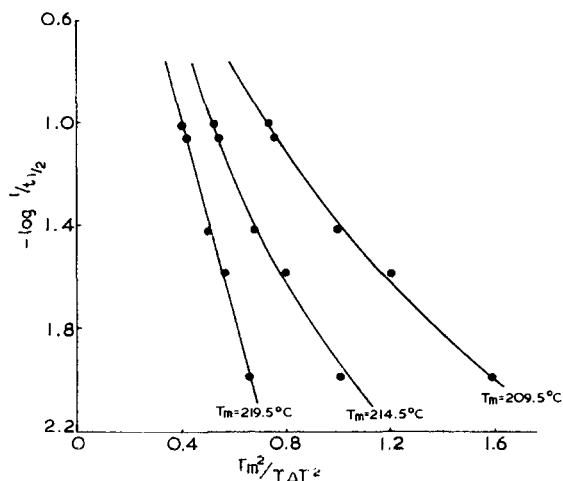


Fig. 6. Dependence of crystallization half-time on the extent of supercooling for 70/30 nylon 66/6 copolymer using different values for T_m .

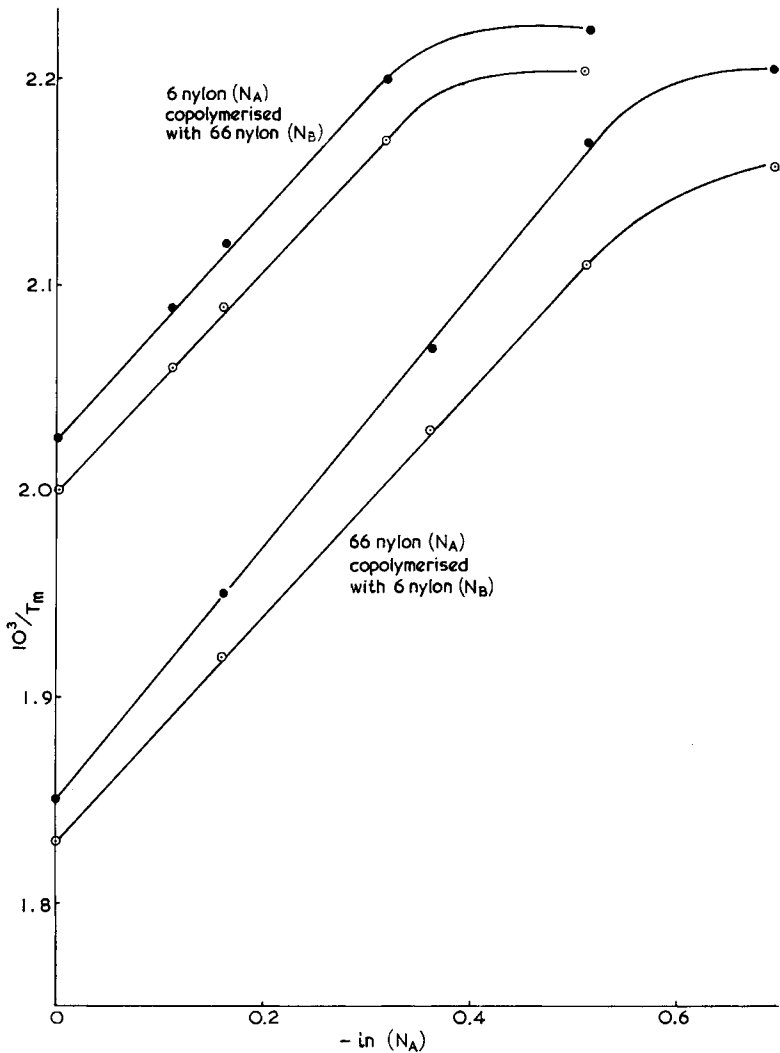


Fig. 7. Effect of copolymer composition on the measured and estimated melting points of nylon 66/6 copolymers: (●) measured melting points; (○) estimated melting points.

CONCLUSIONS

The optical depolarization technique provides a satisfactory method for the study of the crystallization of copolyamides of nylons 66 and 6 at temperatures up to 265°C. On increasing the amount of comonomers present, the extent of crystallization, and the melting temperatures are reduced. The copolymers crystallize at lower temperatures, but the same rate of crystallization is obtained with each copolymer at the same extent of supercooling below its melting temperature. The variation in crystal-

lization rate with temperature fits the expression of Mandelkern, Quinn, and Flory¹² if high values for the thermodynamic melting points are taken.

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