

## Copolyamide의 합성 - 구조 - 성질에 관한 연구 Ⅲ: Copolyamide 6/6.6, 6/6.T 및 6/6.I의 결정화에 공단량체가 미치는 영향

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### Synthesis-Structure-Property of Copolyamides. III. The Effect of Comonomer on the Crystallization Behavior of Copolyamides 6/6.6, 6/6.T and 6/6.I

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**Abstract:** The kinetics of isothermal crystallization from the melt of copolyamides 6/6.6, 6/6.T and 6/6.I was analyzed by differential scanning calorimetry at various degrees of supercooling. At the same degree of supercooling the rate of isothermal crystallization decreases in the order of copolyamides 6/6.T, 6/6.I and 6/6.6, which suggests that the rate decreases with the increase of structural rigidity of comonomer. Avrami exponent  $n$  values were somewhat larger for copolyamides 6/6.T and 6/6.I than for copolyamide 6/6.6. It is found from the melting temperature depression that the comonomer exclusion model is not always satisfied for the crystallization behavior of copolyamides.

#### INTRODUCTION

The nature of polymer crystal, which plays an important role for determining the properties of polymers, can be profoundly affected by rather small amounts of coconstituents such as comonomers, stereoisomers, branches, chain ends, etc. In copolymer, crystallization behavior and kinetics are affected by the content and structure of comonomer and subsequently the properties of copolymer are strongly dependent upon the chemical structure and content of comonomer as well as the crystallization conditions<sup>1-4</sup>.

In this study it is attempted to examine how the nature of comonomer affects the crystallization behaviors and kinetics of three kinds of random

copolyamides such as poly ( $\epsilon$ -caprolactam-co-hexamethylenediammonium adipate) (denoted by copolyamide 6/6.6), poly ( $\epsilon$ -caprolactam-co-hexamethylenediammonium terephthalate) (denoted by copolyamide 6/6.T) and poly ( $\epsilon$ -caprolactam-co-hexamethylenediammonium isophthalate) (denoted by copolyamide 6/6.I).

#### EXPERIMENTAL

**Polymerization** Three kinds of copolyamides were prepared by ring-opening polymerization of  $\epsilon$ -caprolactam with hexamethylenediammonium adipate (6.6), hexamethylenediammonium terephthalate (6.T) and hexamethylenediammonium isophthalate (6.I) salt, respectively. The prepara-

tion of amide salts and polymerization procedures were reported in the previous paper<sup>5</sup>.

**Characterization of Copolyamides** The method of determining 6.6 contents in copolyamide 6/6.6 was described in the previous report<sup>5</sup>. The contents of the corresponding 6.T and 6.I unit in copolyamide 6/6.T and 6/6.I, were determined from the relative area of the proton peaks of aromatic group and methylene group in the nuclear magnetic resonance (NMR) spectra.

Intrinsic viscosities were measured at 25°C from dilute formic acid solution, being found between 0.6 and 0.9.

Thermal properties were determined by Du Pont 910 differential scanning calorimeter (DSC) with a scan rate of 20°C/min unless otherwise specified.

**Isothermal Crystallization Kinetics** The isothermal crystallization rates were measured by DSC. The samples were melted at the temperatures of 30°C above their melting temperatures and then quickly cooled to the crystallization temperature ( $T_c$ ). At the crystallization temperature the samples were isothermally maintained for 10 to 20 min and the crystallization exotherms were recorded as a function of time.

## RESULTS AND DISCUSSION

The thermal properties of copolyamides are

listed in Table 1. The glass transition temperature ( $T_g$ ) of copolyamide 6/6.6 has no significant dependence on 6.6 contents, while it increases with 6.T or 6.I contents in copolyamide 6/6.T or 6/6.I since the inclusion of aromatic units into the main chain reduces the chain mobility. The melting temperature depression phenomenon is always observed and the depression is more prominent in copolyamide 6/6.T and 6/6.I than 6/6.6. The decreasing tendency of melt crystallization temperature,  $T_{cm}$ , is similar to that of melting temperature.

The gap between melting temperature and melt crystallization temperature, which represents the driving force of melt crystallization, is different for each copolyamide system. In copolyamide 6/6.6 the difference is about 36°C, while it is above 50 and 40°C in copolyamide 6/6.T and 6/6.I, respectively. It means that crystallization rate of copolyamide 6/6.T and 6/6.I will be lower than that of copolyamide 6/6.6.

The heat of melting, which represents degree of crystallinity, decreases with increasing comonomer content and the decreasing tendency is more remarkable in copolyamide 6/6.T and 6/6.I than in copolyamide 6/6.6 (Fig. 1).

From the above results it is concluded that crystallization in copolyamide is affected by the existence of comonomer and that 6.T or 6.I units restrict copolymer crystallization more effectively

Table 1. Thermal Properties of Copolyamides

Copolymer code	Comonomer comp. {mol%}	$T_g, ^\circ\text{C}$	$T_m, ^\circ\text{C}$	$T_{cm}, ^\circ\text{C}$	$T_m - T_{cm}$	$\Delta H_f, \text{cal/g}$
6.A	4.4	35	213	180	33	12.12
6.B	8.2	36	207	171	36	9.66
6.C	17.5	36	189	150	39	9.41
6.D	26.7	33	182	146	36	6.39
T.A	1.1	49	213	163	50	11.68
T.B	3.0	52	198	147	51	7.87
T.C	4.5	55	192	141	51	7.17
T.D	6.1	59	181	115	66	6.67
T.E	7.2	62	176	117	59	6.52
I.A	1.4	48	214	173	41	10.84
I.B	3.8	52	203	158	45	10.45
I.C	5.3	56	197	152	45	9.32
I.D	8.6	61	180	124	56	5.26

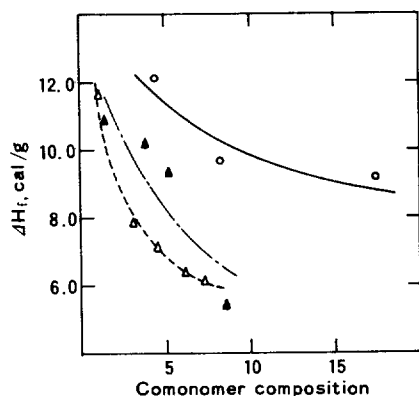


Fig. 1. Dependence of heat of melting on comonomer composition: (○) copolyamide 6/6.6; (△) copolyamide 6/6.T; (▲) copolyamide 6/6.I.

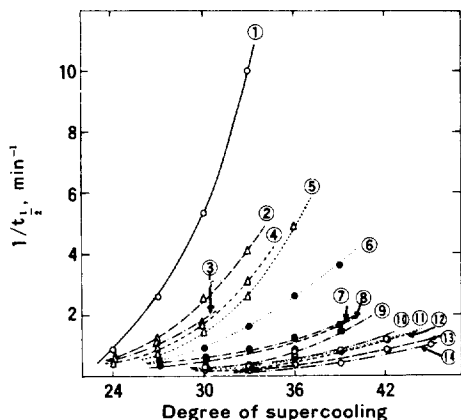


Fig. 2. The rate of crystallization ( $t_{1/2}^{-1}$ ) versus degree of supercooling: (1) polyamide 6; (5) 6.A; (2) 6.B; (3) 6.C; (4) 6.D; (11) T.A; (9) T.B; (12) T.C; (14) T.D; (13) T.E; (6) I.A; (7) I.B; (8) I.C; (10) I.D.

than 6.6.

The isothermal crystallization rate was determined at various degrees of supercooling from the crystallization thermogram of DSC under isothermal conditions. The weight fraction  $X_t$  of material that has been crystallized at time  $t$  and the half time  $t_{1/2}$  of conversion from amorphous to crystalline polymer at various crystallization temperatures were determined from the crystallization isotherms<sup>6-8</sup>. The kinetics of isothermal crystallization was analyzed by means of the

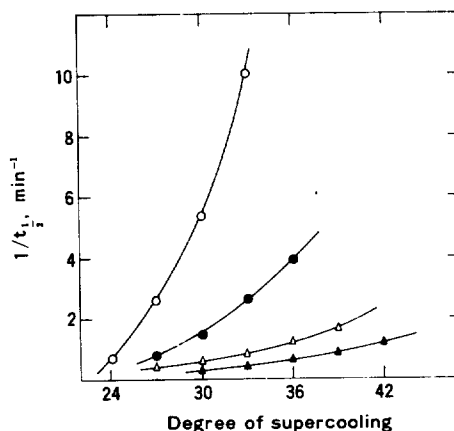


Fig. 3. The rate of crystallization ( $t_{1/2}^{-1}$ ) versus degree of supercooling: (○) polyamide 6; (●) 6.A; (△) I.C; (▲) T.C.

Avrami equation<sup>9</sup>.

As shown in Fig. 2, the isothermal crystallization rate represented by  $t_{1/2}^{-1}$  decreases with increasing crystallization temperature or decreasing degree of supercooling and decreases in the order of copolyamide 6/6.T, 6/6.I and 6/6.6 at the same degree of supercooling. Fig. 3 shows the rate of crystallization at various degrees of supercooling for the samples of almost the same comonomer contents (about 5 mol %). This considerable decrease in crystallization rate of the copolyamides as compared to that of polyamide 6 is due to the presence of non-crystallizable comonomer causing structural defects<sup>10-13</sup>.

The difference between the crystallization of copolyamide 6/6.6 and that of copolyamide 6/6.T or 6/6.I is due to the differences in chemical structure of the chains. The chains of copolyamide 6/6.T and 6/6.I are more rigid and thus those impart an additional restriction in crystalline lattice formation and consequently a decrease in crystallization rate.

The crystal growing mechanism of copolyamide depends on temperature and comonomer contents as known by the change in Avrami exponent ( $n$ )<sup>9</sup>. As shown in Figures 4 and 5, the Avrami exponent  $n$  decreases slightly with increasing degree of supercooling but remains nearly constant with the comonomer content. The  $n$  value

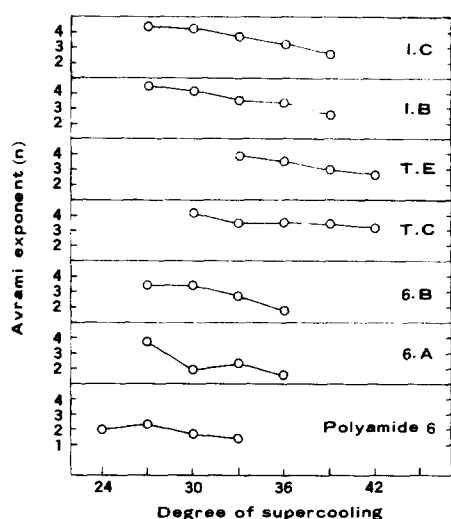


Fig. 4. Variation of Avrami exponent ( $n$ ) with degree of supercooling at various copolyamides.

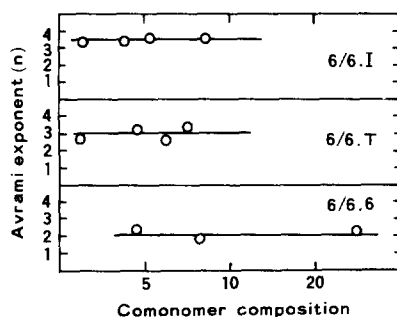


Fig. 5. Variation of Avrami exponent ( $n$ ) with comonomer composition at the degree of supercooling of 33.

shows somewhat larger value for copolyamide 6/6.T and 6/6.I than for copolyamide 6/6.6. For all the samples examined, the values of  $n$  are between 2 and 4, approximately being equal to 3, which corresponds to a three-dimensional growth and heterogeneous nucleation<sup>1</sup>.

According to Mandelkern, Quinn, and Flory<sup>14</sup>, plots of  $\log t_{1/2}^{-1}$  versus  $T_m^2/T_c(T_m - T_c)^2$  should be linear. If the measured values of  $T_m$  are used, the plots do not constitute a straight line as shown in Fig. 6. However, by successive increments of  $T_m$  until linear plots are obtained, the corrected melting temperature ( $T_m^*$ ) can be determined. The

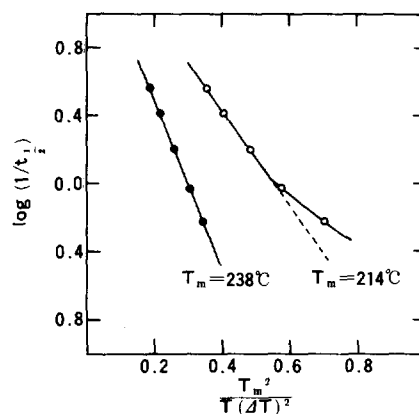


Fig. 6. Temperature dependence of  $t_{1/2}^{-1}$  for the sample I.A. for the measured (open circles) and the corrected (solid circles) values of  $T_m$ .

corrected value can be treated as the equilibrium melting temperature. As illustrated in Fig. 6 the corrected melting temperature of the sample I.A. is 238°C. Similar results were obtained for the other copolymers (Table 2).

From the theory of equilibrium crystallization of random copolymer Flory proposed the equation<sup>15</sup>:  $1/T_m - 1/T_m^0 = -(R/m\Delta H^0) \ln(1-X)$ , where,  $T_m$  is the equilibrium melting temperature of copolymer,  $T_m^0$  the equilibrium melting temperature of homopolymer,  $\Delta H^0$  the heat of melting per mole of crystalline unit,  $R$  the gas constant and  $X$  the mole fraction of noncrystallizable unit. The equation is based on complete co-

Table 2. Corrected Melting Temperatures of Copolyamides

copolymer code	comonomer comp. (mol%)	$T_m^*$ , °C
6.A	4.4	237
6.B	8.2	233
6.C	17.5	217
T.A	1.0	237
T.B	3.0	222
T.C	4.5	216
T.D	6.1	205
T.E	7.2	200
I.A	1.4	238
I.B	3.8	227
I.C	5.8	221
I.D	8.6	204

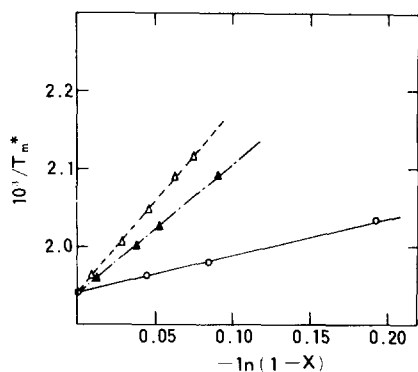


Fig. 7. Plots of  $1/T_m^*$  against  $-\ln(1-X)$ : (○) copolyamide 6/6.6; (△) copolyamide 6/6.T; (▲) copolyamide 6/6.I.

monomer exclusion from the crystalline lattice and the plots of  $1/T_m$  versus  $\ln(1-X)$  should be straight lines whose slopes are identical irrespective of comonomer characteristics. Fig. 7 shows the plots of  $1/T_m^*$  versus  $-\ln(1-X)$  and straight lines are obtained at low concentration of comonomer, which means random copolymers. As shown in Fig. 7 the slopes of the three copolyamides are not the same, that is, the melting temperature depression is more serious in copolyamide 6/6.T and 6/6.I than in 6/6.6, which suggests that these copolymers do not always follow a comonomer exclusion model<sup>2,3</sup>. According to the previous paper<sup>5</sup> the reduced melting temperature depression in copolyamide 6/6.6 was thought to be due to the partial inclusion of 6.6 unit in the crystalline lattice. However, copolyamide 6/6.T seems to follow a comonomer exclusion model. Copolyamide 6/6.I, whose slope lies between copolyamide 6/6.T and 6/6.6 in Fig. 7, is considered to follow roughly a comonomer exclusion model.

## CONCLUSIONS

The rate of isothermal crystallization decreases with increasing comonomer content and the decreasing tendency is in the order of copolyamide 6/6.T, 6/6.I and 6/6.6.

The Avrami exponent  $n$  decreases slightly with increasing degree of supercooling but remains nearly constant with the comonomer content.

It is found from the melting temperature depression that the comonomer exclusion model is not always satisfied for the crystallization behaviors of copolyamides.

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