

# Poly( $\epsilon$ -caprolactam-co-hexamethylenediammonium adipate) 및 Poly( $\epsilon$ -caprolactam-co-p-xylylenediammonium adipate) 의 합성과 열적특성

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## Syntheses and Thermal Characteristics of Poly ( $\epsilon$ -caprolactam-co-hexamethylenediammonium adipate) and Poly( $\epsilon$ -caprolactam-co-p-xylylenediammonium adipate)

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**Abstract:** Caprolactam was copolymerized with hexamethylenediammonium adipate (6.6) and p-xylylenediammonium adipate (PXD. 6) salt to form two series of copolyamides. Pyrolysis-gas chromatography and nuclear magnetic resonance spectroscopy were used to determine copolymer compositions. Copolyamide 6/6.6 reveals reduced depression in  $T_m$  comparing with Flory's prediction which suggests that some amount of 6.6 units are incorporated in the crystalline lattice, however it is not apparent in copolyamide 6/PXD. 6. The melting thermogram, which showed multiple peaks in either isothermally or dynamically crystallized samples, is thought to be due to the melting and re-crystallization followed by remelting.

## 1. Introduction

Polyamide 6, one of the most common polyamides, has been extensively studied by many workers during past decades and the copolymerization has played an important role for the purpose of modification<sup>1-7</sup>.

Crystallization and melting behavior are important properties of polymer and have a close relationship to its structure and properties. The melting behavior of polyamide 6, which often appears as multiple endothermic peaks when annealed or drawn, has been under great controversy by many investigators. At present there are several interpretations of the origin of the multiple melting peaks. Naming three important explanations of them are (1) melting of morphologically different crystals<sup>8</sup>, (2) melting of recrystallized crystal from imperfect crystal during thermal analysis<sup>9-11</sup>, and (3) melting of crystals of a single morphological form differing in size and/or perfection<sup>12,13</sup>.

In this study it is attempted to clarify what are the most reasonable explanation on the multiple melting of poly (caprolactam-co-hexamethylenediammonium adipate) (denoted by copolyamide 6/6.6) and poly (caprolactam-co-p-xylylenediammonium adipate) (denoted by copolyamide 6/PXD.6) by examining the effects of crystallization conditions on the melting behavior of copolyamides.

## 2. Experimental

### 2-1. Polymerization

Copolyamides were prepared by ring-opening polymerization of  $\epsilon$ -caprolactam with hexamethylenediammonium adipate (6.6) or p-xylylenediammonium adipate (PXD. 6) salt. The salts were prepared by adding the ethanolic solution of diacid to an equimolar solution of diamine in ethanol with stirring. The salts formed were then filtered with suction, washed twice with ethanol, and dried in vacuo.

The condensation of salt with caprolactam was

carried out in autoclave by heating the mixture at 250-260°C for 3hr, followed by heating for 2hr under reduced pressure. Unreacted monomers were extracted by precipitation in water from formic acid solution. Intrinsic viscosities were measured at 25°C from dilute formic acid solution.

### 2-2. Copolymer Composition Determination

Monomer Composition in copolyamide 6/6.6 was determined by means of pyrolysis-gas chromatography (PGC). With respect to main chain of the polymer, scission at the C-N bond occurs in preference to that at the C-C bond, since the C-N bond (66 Kcal) is weaker than the C-C bond (82.5 Kcal). The resulting radicals are expected to yield carbon monoxide, cyclopentanone, and  $\epsilon$ -caprolactam, from polyamide 6.6 and 6, respectively. The quantitative analysis of the composition was carried out by measuring the relative yield between cyclopentanone and  $\epsilon$ -caprolactam obtained from PGC.

Nuclear magnetic resonance (NMR) spectroscopy was used for determining monomer composition in copolyamide 6/PXD.6 were quantitatively determined from the relative area of the proton peaks of aromatic group and methylene group.

### 2-3. Thermal Analysis

Thermal analyses were performed using a Du Pont 1090 Thermal Analyzer with a Differential Scanning Calorimetry (DSC) 910 module under nitrogen gas purging. Thermal properties such as glass transition temperature ( $T_g$ ), melting temperature ( $T_m$ ), and melt crystallization temperature ( $T_{cm}$ ) were obtained from the first heating or cooling thermogram with a scanning rate of 20°C/min. Two types of melting thermograms were obtained: one is from the isothermally crystallized samples at various crystallization temperatures, the other from the dynamically crystallized samples at different cooling rates in DSC. In all the experiments the melting thermograms were obtained at a scan rate of 20°C/min. unless specified.

### 3. Results and Discussion

#### 3-1. Melting Point Depression in Copolyamides

The glass transition temperature ( $T_g$ ), melting temperature ( $T_m$ ), melt crystallization temperature ( $T_{cm}$ ), and heat of fusion ( $\Delta H_f$ ) are listed in Table 1. The intrinsic viscosities lie between 0.5-1.1, which indicates that these copolyamides have considerably high molecular weight.

The glass transition temperature ( $T_g$ ) of copolyamide 6/6.6 has no significant dependence on copolymer composition because polyamide 6 and polyamide 6.6 have very similar  $T_g$ . But, in the case of copolyamide 6/PXD.6,  $T_g$  increases with PXD.6 content since the inclusion of aromatic unit into the main chain reduces the chain mobility, thus  $T_g$  increases.

Changes in melting temperature with comonomer content show that these two copolyamides are random copolymers. From the theory of

equilibrium crystallization of random copolymer Flory proposed equation (1)<sup>14</sup>,

$$\frac{1}{T_m} - \frac{1}{T_m^0} = - \frac{R}{\Delta H^0} \ln(1-X) \quad (1)$$

where,  $T_m$  is the equilibrium melting temperature of homopolymer,  $T_m^0$  the equilibrium melting temperature of copolymer,  $\Delta H^0$  the heat of melting per mole of crystalline unit,  $R$  the gas constant, and  $X$  the mole fraction of noncrystallizable unit. Fig. 1 shows the plot of  $1/T_m$  vs.  $-\ln(1-X)$  and the straight lines are obtained at low concentration of comonomer, which means random copolymer. Although  $T_m$  and  $T_m^0$  in equation (1) are equilibrium melting temperatures the observed melting temperatures are tentatively used. By that reason the calculation of the heat of fusion  $\Delta H^0$  from the slope of Fig. 1 is not so meaningful, but the significance of initial straight line is still valid. Since the initial slope represents the proper-

**Table 1.** Thermal Properties of Copolyamides

(a) Copolyamide 6/6.6

copolymer code	mol%(6.6)	$[\eta]$ , dl/g	$T_g$ , °C	$T_m$ , °C	$T_{cm}$ , °C	$\Delta H_f$ , cal/g
6.A	4.4	0.72	35	213	180	12.12
6.B	8.2	0.95	36	207	171	9.66
6.C	17.5	0.98	36	189	150	9.41
6.D	26.7	0.92	33	182	146	6.39
6.E	33.3	0.98	36	176	140	7.17
6.F	66.7	1.03	34	210	175	5.43

(b) Copolyamide 6/PXD.6

copolymer code	mol%(PXD.6)	$[\eta]$ , dl/g	$T_g$ , °C	$T_m$ , °C	$T_{cm}$ , °C	$\Delta H_f$ , cal/g
P.A	2.0	0.82	33-37	209	175	13.74
P.B	4.1	0.51	"	200	165	12.07
P.C	7.6	0.90	"	184	145	8.43
P.D	13.5	0.72	49	174	130	6.48
P.E	19.6	0.70	55	162	98	4.94
P.F	30.6	0.59	61	—	143	—

ties of crystallizable homopolymer, it must be the same in either copolyamide 6/6.6 or 6/PXD.6, but the slopes of the two copolyamides are not the same as shown in Fig. 1. The difference of the initial slope are explained as follows: PXD.6 units may have the low possibility of fitting the crystal lattice of polyamide 6 because of the dissimilarity in structure and are assumed to be excluded from the crystallite. However, 6.6 units are very similar to polyamide 6 unit and may have relatively high possibility of inclusion in the crystalline lattice.

According to the theory of random copolymer crystallization the melting point depression is lessened in copolymer which has noncrystallizable coint in crystalline lattice<sup>15,16</sup>. Therefore the reduced  $T_m$  depression in copolyamide 6/6.6 comparing with 6/PXD.6 indicates that the copolyamide 6/6.6 has some 6.6 units in the crystalline lattice and subsequently shows reduced  $T_m$  depression. At present it is not apparent whether PXD.6 units are completely excluded or not from the crystalline lattice, however it is safe to say that 6.6 units are included in crystalline lattice even though the amount is not so much.

The heat of fusion  $\Delta H_f$  would be another supplementary evidence to the explanation. Copolyamide 6/6.6 shows less depression in  $\Delta H_f$  than that

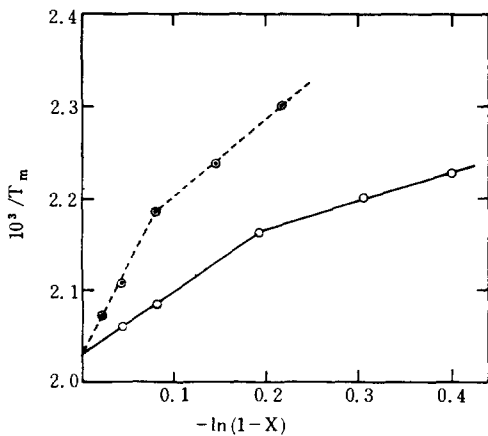


Fig. 1. The effect of copolymer composition of the measured melting points of copolyamides: (○) copolyamide 6/6.6; (●) copolyamide 6/PXD.6.

of 6/PXD.6 and is found to have remarkable crystallinity in all the compositions examined, while 6/PXD.6 loses its crystallinity when PXD.6 contents are greater than 20 mol%. The phenomenon implies that the significant amount of 6.6 unit may participate in the crystallization of 6/6.6

### 3-2. Multiple Melting Behavior of Copolyamides

Isothermally crystallized samples exhibit characteristic multiple melting endotherms as in Fig. 2. The lowest peak temperature ( $T_{m0}$ ), which is always observed at the temperature of about 10°C higher than the isothermal crystallization temperature ( $T_c$ ), is due to the melting of small and unstable crystal which was formed during annealing<sup>17-19</sup> (Figures 3, 4). This peak is known as the 'annealing peak'. However, the middle peak temperature ( $T_{m1}$ ) is highly dependent on the crystallization temperature and increases linearly with  $T_c$  as in Figures 5 and 6, while the highest peak temperature ( $T_{m2}$ ) is almost constant (Figures 7,8). If the double melting peaks ( $T_{m1}$ ) and ( $T_{m2}$ ) is assumed to reflect the melting of different crystal size and/or perfection<sup>8</sup>, they must vary with  $T_c$ . Therefore the assumption cannot explain this phenomena satisfactorily. If the double melting is assumed to be due to the difference in crystalline morphology<sup>12,13</sup>, both peak

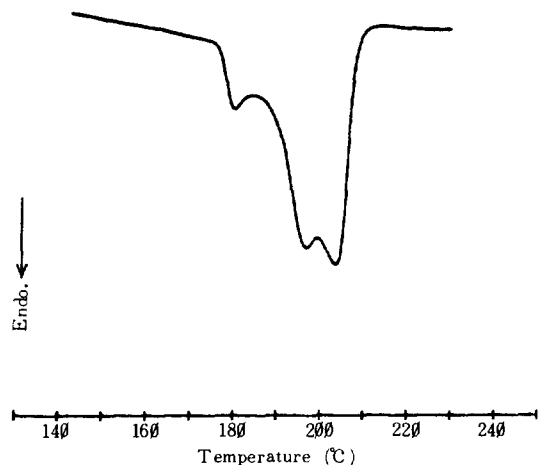
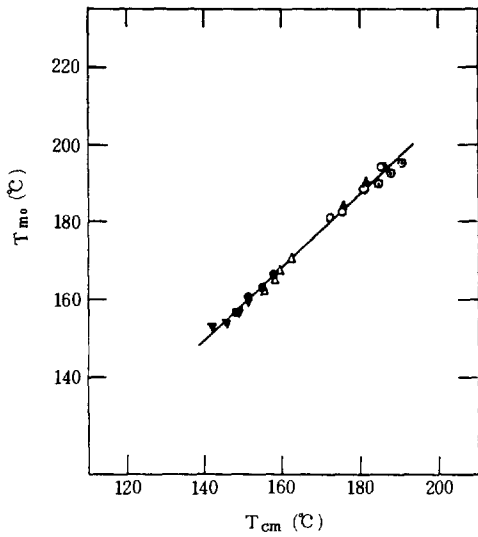
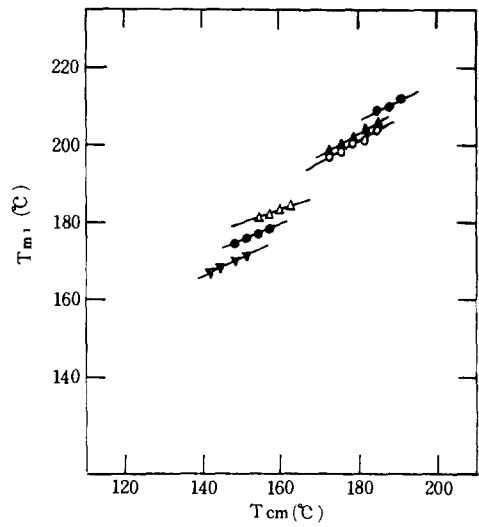


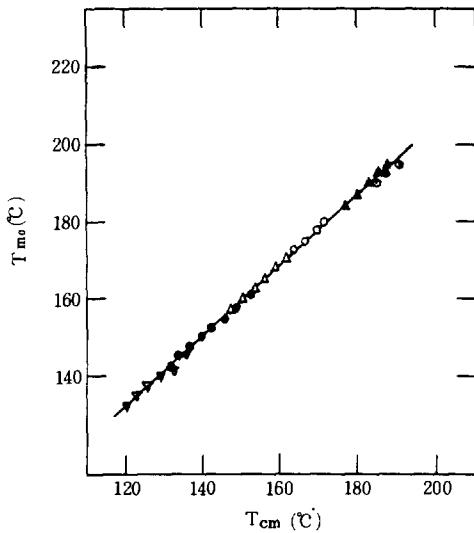
Fig. 2. Typical DSC thermogram of isothermally crystallized copolyamide 6/6.6.



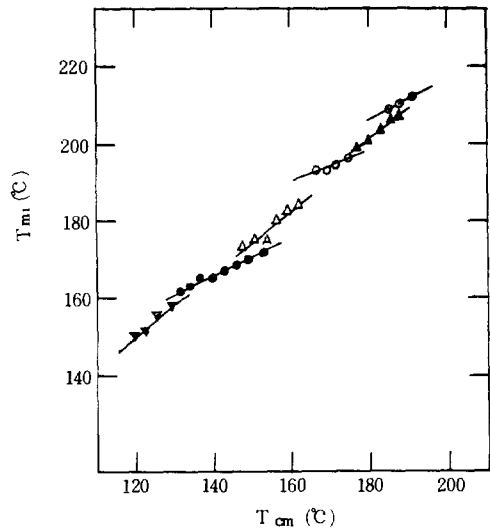
**Fig. 3.** The 'annealing peak' temperature ( $T_{m0}$ ) of copolyamide 6/6.6 as a function of crystallization temperature: (⊙) polyamide 6; (▲) 6.4; (○) 6.B; (△) 6.C; (●) 6.D; (▼) 6.E.



**Fig. 5.** The first melting peak temperature ( $T_{m1}$ ) of copolyamide 6/6.6 as a function of crystallization temperature: (⊙) polyamide 6; (▲) 6.A; (○) 6.B; (△) 6.C; (●) 6.D; (▼) 6.E.



**Fig. 4.** The 'annealing peak' temperature ( $T_{m0}$ ) of copolyamide 6/PXD.6 as a function of crystallization temperature: (⊙) polyamide 6; (▲) P.A; (○) P.B; (△) P.C; (●) P.D; (▼) P.E.



**Fig. 6.** The first melting peak temperature ( $T_{m1}$ ) of copolyamide 6/PXD.6 as a function of crystallization temperature: (⊙) polyamide 6; (▲) P.A; (○) P.B; (△) P.C; (●) P.D; (▼) P.E.

temperatures must vary with  $T_c$ . Hence the assumption cannot apply to the case too. Finally, let us examine the theory based on

recrystallization<sup>9-11</sup>. If the double melting is due to the melting and subsequent recrystallization followed by remelting,  $T_{m2}$  may be independent

of  $T_c$  since it is the melting of recrystallized material. On the other hand,  $T_{m1}$  which is due to the melting of lamellar crystal from the melt at  $T_c$

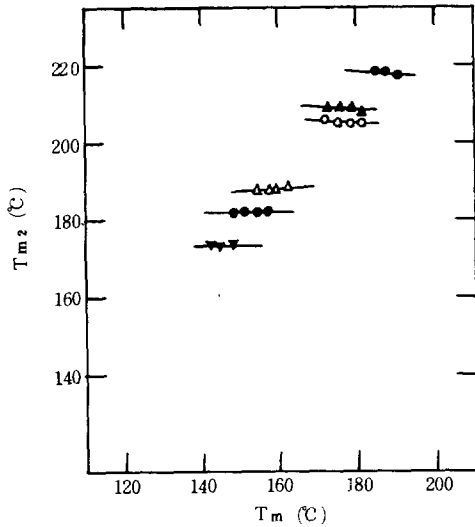


Fig. 7. The second melting peak temperature ( $T_{m2}$ ) of copolyamide 6/6.6 as a function of crystallization temperature:  
 (○)polyamide 6;(▲)6.A;(○)6.B;(△)6.C;(●)6.D;(▼)6.E.

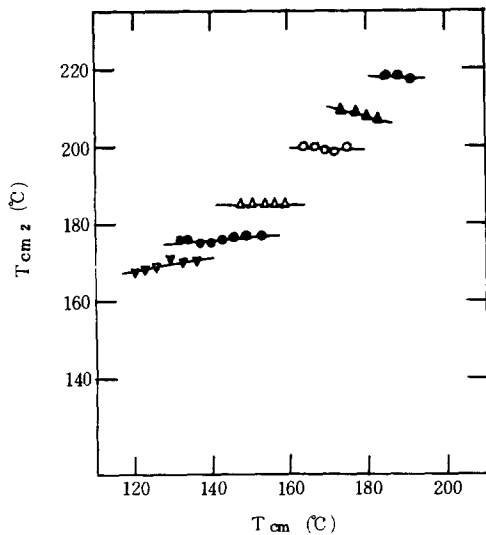


Fig. 8. The second melting peak temperature ( $T_{m2}$ ) of copolyamide 6/PXD.6 as a function of crystallization temperature:  
 (○)polyamide 6;(▲)P.A;(○)P.B;(△)P.C;(●)P.D;(▼)P.E.

must increase as  $T_c$  increases. This is in accord with the experimental results as shown in Figures 5-8. Lamellar crystal formed at high  $T_c$  must have larger and more perfect crystal than the crystal formed at low  $T_c$  and consequently have higher melting temperature.

Double melting due to recrystallization can also be confirmed by investigating the heating rate dependency of relative peak area. As shown in Fig. 9, at slow heating rates the original crystal has enough time to reorganize and the overall melting behavior will contain a relatively large contribution of recrystallization and remelting. The resultant behavior will then be a composite of the peaks due to the melting of the original crystal, the recrystallization exotherm and the melting of the recrystallized material. As the heating rate is increased, the crystals will have

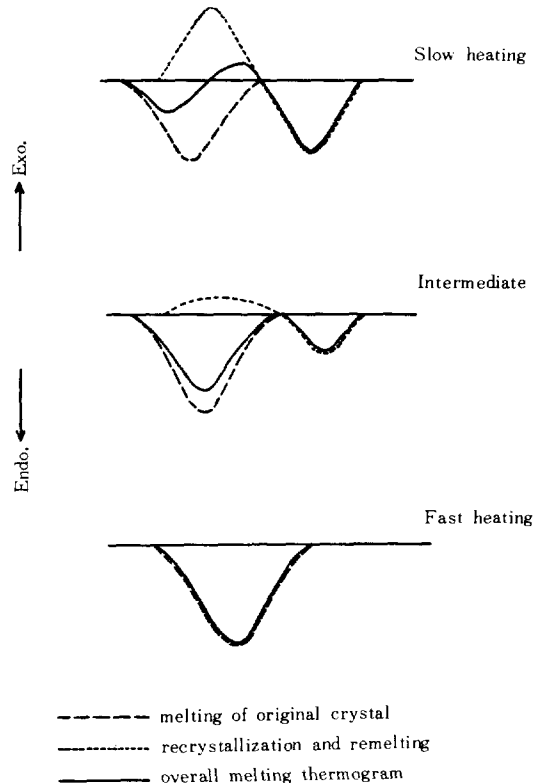


Fig. 9. Schematic representation of heating rate dependency of melting thermogram.

less time to reorganize and the recrystallization and remelting will decrease in magnitude<sup>20</sup>. Hence the relative amount of original crystal, which can be approximately represented by peak height ratio ( $H_1/H_2$ ), must be increase with heating rate. Fig. 10 shows the heating rate

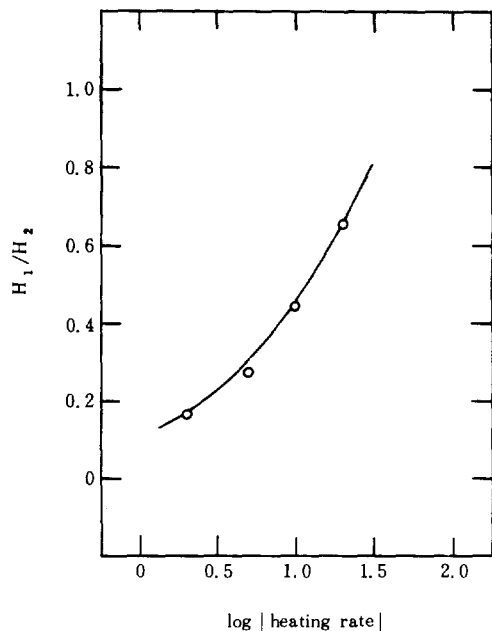


Fig. 10. The plot of the melting peak height ratio ( $H_1/H_2$ ) of polyamide 6 against  $\log | \text{heating rate} |$ .

dependency of relative peak height ratio and a good agreement with the statement described above.

In order to extract more evidences, we have investigated the melting behavior of samples crystallized at various cooling rates. The results are shown in Table 2 and Fig. 11. At slow cooling rate the sample may have sufficient time to

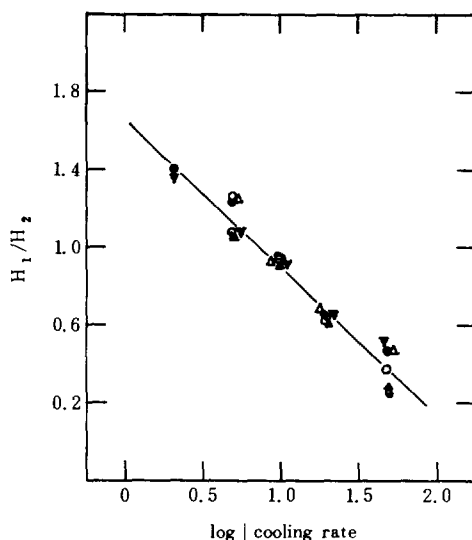


Fig. 11. The plot of the melting peak height ratio ( $H_1/H_2$ ) of copolyamide 6/6.6 against  $\log | \text{cooling rate} |$ .

Table 2. Changes in Melting Temperature as a Function of Comonomer Composition and Cooling Rate

Sample code	Comonomer comp. (mol%)	$T_{m1}$ and $T_{m2}$ at various cooling rates				
		-2	-5	-10	-20	-50
6.A	4.4	207/	205/207	201/208	199/208	194/208
6.B	8.2	203/	200/205	199/205	196/205	193/205
6.C	17.5	186/	184/188	182/188	180/188	178/188
6.D	26.7	180/	177/182	176/182	174/182	171/182
6.E	33.3	171/174	169/174	168/174	165/174	163/174
P.A	2.0	207/	205/207	203/207	200/208	195/208
P.B	4.1	199/	196/	194/199	191/200	188/200
P.C	7.6	183/	180/184	177/184	172/184	169/184
P.D	13.5	170/176	167/176	165/176	162/176	159/176
P.E	19.6	151/173	147/172	145/169	143/167	142/165

crystallize and will have larger and more perfect crystal than one obtained from fast cooling rate. Since slow cooling rate and high crystallization temperature have similar effects on crystallization, the same interpretations can be applied to the crystallization under dynamic conditions.

#### 4. Conclusions

Two series of copolyamides are found to form random copolymers. In copolyamide 6/6.6, which shows reduced depression in  $T_m$  than expected from Flory's equation, it is concluded that some amounts of 6.6 units are incorporated in the crystalline lattice, but it is not apparent in 6/PXD.6.  $T_{m0}$ , the lowest melting peak temperature in isothermally crystallized sample, is due to the melting of small and unstable crystal formed during annealing.  $T_{m1}$  increases as crystallization temperature increases or cooling rate decreases, but  $T_{m2}$  is independent of the crystallization conditions. From these phenomena it is concluded that the origin of the double melting in copolyamide 6/6.6 and 6/PXD.6 is the melting of melt crystallized crystal and subsequent recrystallization followed by remelting.

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