Melt-Polymerized Aliphatic-Aromatic Copolyamides. I. Melting Points of Nylon 66 Copolymerized with Aromatic Diamines and Terephthalic Acid

K. KUDO, T. SUGUIE, and M. HIRAMI*

Research and Development Center, Unitika Ltd., 23 Kozakura, Uji, Kyoto 611, Japan

SYNOPSIS

Measurements of melting points were made for melt-polymerized aliphatic-aromatic copolyamides; (i) N66PT, (ii) N66CT, and (iii) N66ST, i.e., nylon 66 [poly(hexamethylene adipamide)] copolymerized with three kinds of aromatic diamines, p-phenylenediamine (P), bis(p-aminophenyl) methane (C), and bis(p-aminophenyl) sulfone (S), and terephthalic acid (T). As the mole fraction of copolymerized component n_1, increases in the case of (ii) or (iii), the melting point decreases uniformly according to the relationship of Flory. In the case of (i), the melting point first decreases and then begins to increase after passing a minimum at $n_1 \simeq 0.2$. A preliminary WAXD (wide-angle X-ray diffraction) study on N66PT crystals shows that the basal plane of the crystal lattice shifts from that of nylon 66 toward hexagonal packing with the increase of n_1. It was suggested that the formation of mixed crystals for a series of N66PT will be attributed to their melting point behavior.

INTRODUCTION

We have undertaken a series of investigations to synthesize copolyamides of aliphatic and aromatic units by melt-polymerization and to examine their structures and properties. In this article, we describe the synthesis, measurements of their melting points, and a preliminary WAXD (wide-angle X-ray diffraction) study for three kinds of copolyamides (which shall be designated as N66PT, N66CT and N66ST), i.e., nylon 66 [poly(hexamethylene adipamide)] copolymerized with three kinds of aromatic diamines, namely p-phenylenediamine (P), bis(p-aminophenyl) methane (C), and bis(p-aminophenyl) sulfone (S), and terephthalic acid (T). These copolyamides correspond to copolymeric hybrids of nylon 66 and aromatic polyamides; for example, N66PT corresponds to the copolymeric hybrid of nylon 66 and PPTA [poly(p-phenylene terephthalamide)].

For synthesized samples of these copolyamides, measurements of melting points were made and the results were analyzed by the Flory's theory[1,2] which predicts the relationship of the melting point depression of copolymers depending on the content of copolymerized units. Among three series of the copolyamides, only N66PT reveals a novel trend in the melting point depression deviating markedly from the Flory relationship.

A preliminary WAXD study was made and the possibility of forming some mixed crystals was suggested for a series of N66PT copolyamides. The mechanism which causes the melting point behavior of N66PT was discussed in terms of the findings from the WAXD study.

EXPERIMENTAL

Samples of copolyamides were prepared by melt-polycondensation of the given ratio of mixtures of hexamethylene adipate to equimolar mixtures of X (X = P, C, or S) and T. With an autoclave, polymerization was performed by heating under pressure in the first stage (3 h), under pressure release in

Table I Values of Molecular Weight and Melting Point for Synthesized Copolyamides

	Copolymerized Component mol %	Intrinsic Viscosity $[\eta]$	Molecular Weight M_n	Melting Point T_m °C
N66PT	10	1.25	18,600	252
	20	1.11	16,000	249
	25	0.93	12,500	260
	30	0.64	7,560	271
N66CT	10	0.67	7,990	257
	20	1.19	17,400	247
	30	1.70	28,300	226
N66ST	10	0.46	4,870	250
	20	0.38	3,790	242
	30	0.28	2,440	206
N66 (Control)	—	1.33	20,400	267

the second stage (1 h) and under vacuum in the third stage (5 h) during the course of polycondensation similar to the process for the synthesis of nylon 66.[3]

All samples synthesized were slightly yellowish in color. The appearance of samples of N66CT and N66ST became transparent with an increase in the copolymerized components. Particularly, samples of N66CT seemed to be rubbery and those of N66ST to be glassy. Samples of N66PT were tough and crystalline (not transparent) and this appearance remained almost unchanged irrespective of composition.

The samples were dissolved in 96% sulfuric acid at polymer concentrations C of 0.2, 0.4, 0.6 and 0.8 g/100 cc. and relative viscosities η_{rel} of the solutions were measured with an Ubbelohde-type viscometer at 25°C. Intrinsic viscosity $[\eta]$ of each sample was determined by extrapolating the plot of $(\eta_{rel} - 1)/C$ versus C to infinite dilution $(C \rightarrow O)$, and the apparent molecular weight M_n (number average) was estimated from $[\eta]$ by applying the relationship of Ogata derived for nylon 66.[4]

$$\log M_n = 4.14 + 1.35 \log[\eta] \qquad (1)$$

The values obtained for $[\eta]$ and M_n are shown in Table I.

Measurements of the melting point T_m (°K) were made by the following procedure with the use of a Perkin-Elmer DSC-2/TAD. The value of melting point was read from the position of endothermic peak in the thermogram.[5] In advance of the principal measurement, the apparent melting point T'_m (°K) had been obtained with a high rate of heating, i.e. 80°K/min. Let T''_m (°K) be defined as $T''_m = T'_m$

− 10. With the aid of the attached program the equipment was set to heat at 10°K/min, from room temperature to T''_m, to stay at T''_m for 5 hours and then to heat at 2.5°K/min from T''_m. Thus the value of T_m was read from the thermogram. Obtained values of T_m are also shown in Table I.

WAXD photographs were taken for all synthesized samples. Cu-K$_\alpha$ radiation was used. For a series of N66PT, diffraction curves were obtained with the use of microphotometer. The spacings corresponding to (100) and [(010), (110)] of nylon 66 crystals[6] were calculated from two maxima of the diffraction curves.

RESULTS AND DISCUSSION

During melt-polycondensation, the tendency to obtain a high molecular weight of polymer decreases by introducing copolymerized units. The initial rate of this tendency is in order as N66PT > N66CT > N66ST, if we compare the values of $[\eta]$ in Table I for the samples at $n_1 = 0.10$, where n_1 is the mole fraction of copolymerized component. An exceptional behavior was found in the case of N66CT, namely $[\eta]$ increases with the increase of n_1. This behavior may be attributed to the occurrence of the low degree of gelation, corresponding to the rubbery appearance of the samples. For the elucidation of this behavior, further characterization studies on N66CT are proceeding in our laboratory, but we will not enter into this problem here.

Let us examine the melting point behavior of three kinds of copolyamides. As can be seen in Figure 1, in the case of N66CT or N66ST, the melting point decreases uniformly with the increase of n_1, while
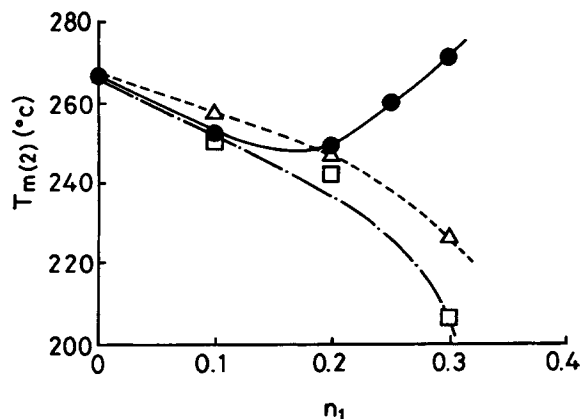
Figure 1 Plot of melting point $T_{m(2)}$ as a function of the mole fraction of copolymerized units n_1 for: (●) N66PT; (□) N66CT; (△) N66ST.

in the case of N66PT, the melting point first decreases and then begins to increase after passing a minimum at $n_1 \simeq 0.2$.

Provided the conditions as shown below are satisfied, the melting point of nylon 66 copolymers $T_{m(2)}$ can be described by the Flory relationship;[1,2]

$$1/T_{m(2)} - 1/T^0_{m(2)}$$

$$= -(R/\Delta h_{u(2)})\ln(1 - n_1) \quad (2)$$

where R is the gas constant, $T^0_{m(2)}$ is the melting point of nylon 66 homopolymer and $\Delta h_{u(2)}$ is the heat of fusion per structural unit of nylon 66 crystals.

The conditions assumed as the basis for the derivation of Eq. (2) are:

I. Copolymerized units are distributed in a random fashion along the molecular chain.

II. Copolymerized units are excluded from nylon 66 crystals. In other words, mixed crystals of nylon 66 with the copolymerized components cannot be formed in the present system.

The reciprocal $1/T_{m(2)}$ derived from Eq. (2), is plotted against $-\ln(1 - n_1)$ is shown in Figure 2. The initial slope of the plot should be inversely proportional to the heat of fusion for nylon 66 crystals, $\Delta h_{u(2)}$. The heat of fusion $\Delta h_{u(2)}$ thus obtained was 4,000, 6,100 and 3,400 cal/mole for N66PT, N66CT, and N66ST, respectively; these figures are less than the reported value of 10,300 cal/mole as $\Delta h_{u(2)}$ of nylon 66 crystals obtained by the calorimetric method.[7,8] A discrepancy of this type was early indicated by Flory,[9,10] namely the heats of fusion estimated from the dependence of $T_{m(2)}$ on copolymer composition are appreciably smaller than those obtained by other methods.

The linearity of plot for the reprocical $1/T_{m(2)}$ of N66PT against $\ln(1 - n_1)$ does not hold except for the region where n_1 is small. This means that the mechanism supporting the melting point depression in terms of the Flory relationship does not necessarily work in the case of N66PT copolymers.

Next we describe our preliminary WAXD study on three kinds of nylon 66 copolymers in comparison with that of nylon 66 as a reference. WAXD photographs for N66CT and N66ST show that the diffraction pattern corresponding to that of nylon 66 crystals appears in a weakened and diffused manner, and this feature is promoted with the increase of the copolymerized components CT and ST. In the case of N66PT, the sharp diffraction pattern remains and is similar to that of nylon 66, without a new diffraction pattern, although the two principal peaks corresponding to the spacings of (100) and [(010), (110)] planes of crystal lattice of nylon 66 become nearer as n_1, the mole fraction of copolymerized units of the component PT, increases. As an example, we present WAXD photographs for N66 and N66PT at $n_1 = 0.25$ in Figure 3.

The plot of the spacing for two principal diffraction peaks of N66PT crystals against n_1 is shown in Figure 4. With the increase of n_1, the values of the two spacings become nearer and coincide with one at $n_1 \simeq 0.2$. This indicates that the basal plane of the lattice of N66PT crystals shifts from that of nylon 66 crystals toward hexagonal packing, i.e., in the direction of increasing the degree of symmetry. The cause of this tendency may be some contribu-
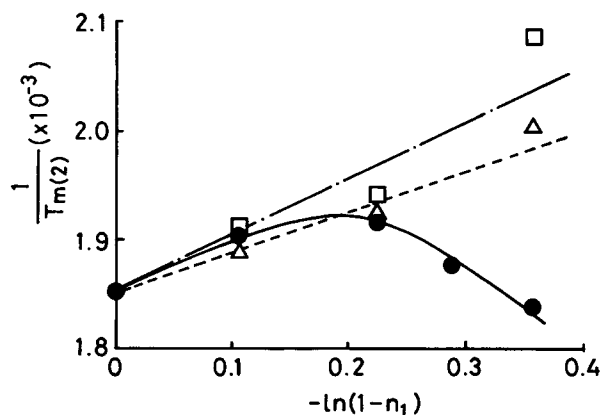

Figure 2 The reciprocal melting point $1/T_{m(2)}$ plotted against $-\ln(1 - n_1)$ for: (●) N66PT; (□) N66CT; (△) N66ST.

tions from the copolymerized units in N66PT molecules.

There are three possibilities, namely:

1. The copolymerized units are incorporated thoroughly in the crystal lattice of nylon 66.
2. The copolymerized units are incorporated partly in the crystal lattice of nylon 66.
3. The copolymerized units influence the nylon 66 crystal lattice of nylon 66 from outside the lattice without being incorporated.

The second possibility (2) seems to be the most plausible from the following reasons. In the case of (1), the crystal structure of nylon 66 could be remarkably changed so as to give a different diffraction pattern as a mixed crystal. Such a change was not recognized in the WAXD pattern. In the case of (3), it is difficult to explain the melting point behavior of N66PT, which deviates markedly from the Flory relationship. So let the remaining case of (2) be assigned to Assumption III, which should be applied to the copolyamide of N66PT instead of Assumption II.

In N66PT molecules, four kinds of copolymerized units are involved, i.e. hexamethylene adipamide [66], hexamethylene terephtalate [6T], p-phenylene adipamide [P6], and p-phenylene terephtalamide [PT] units, where the square bracket shows the pair of diamine and dicarboxylic acid used to form the respective amide unit. Under the Assumption I described before, these four kinds of linkage units are distributed randomly along the molecular chain. In addition to [66] units, it seems that [6T] units could be incorporated in N66PT crystals, judging from the existence of mixed crystals of nylon 66 and nylon 6T [poly(hexamethylene terephthalamide)][11] composed of [66] and [6T] units, where the for-
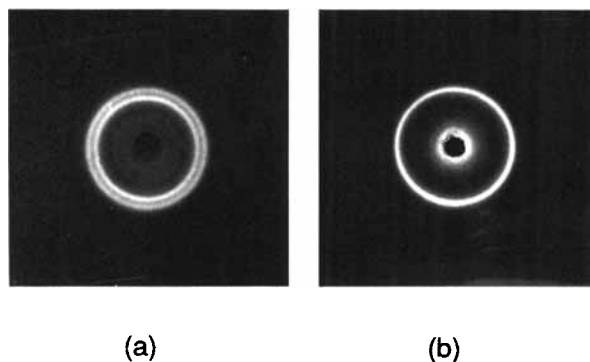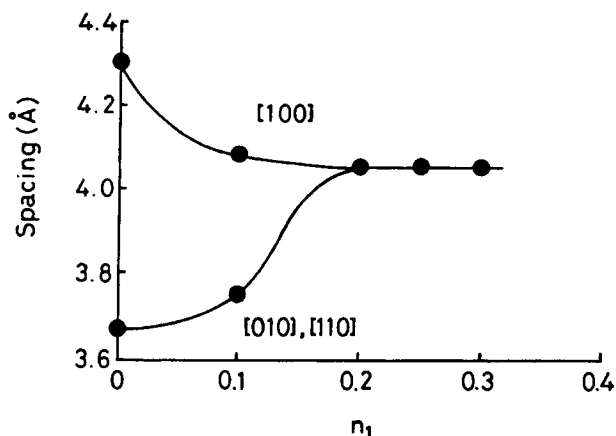

Figure 4 Plot of the spacing against n_1 for two principal diffraction peaks of N66PT crystals.

mation of mixed crystals is thought to be due to the similarity in identity period of their units along the fiber axis.

Finally we will comment on the potential of applications of N66PT from the technological viewpoint. Aliphatic-aromatic polyamides which are more thermally stable than aliphatic-aliphatic polyamides have been widely examined.[12] A typical example is nylon 6T, which possesses a variety of desirable properties.[13] However, the commercial application of nylon 6T has been prevented since solution-fabrication is needed due to its high melting point (370°C).

In the case of N66PT, for example, by choosing an appropriate content of copolymerized units, a product of N66PT whose melting point ranges from 280°C to 300°C, can be prepared as a melt-processable copolyamide by melt-polymerization. The product of such N66PT is expected to have attractive properties, namely to have highly crystalline features like nylon 66 but to be more thermally stable than nylon 66.

There remain several problems to be solved for N66PT including the evidence which supports the Assumption I and III. Further studies on the structure and properties of N66PT are in progress in our laboratory and the results will be reported in the forthcoming papers. It is to be noted that a part of our rheological study on N66PT has already been presented elsewhere.[14]

(a)   (b)

Figure 3 WAXD photographs for (a) N66 and (b) N66PT at $n_1 = 0.25$.

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