Synthesis and Crystallization Behavior of Nylon 12,14. I. Preparation and Melting Behavior

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ABSTRACT: A long-alkane-segment semicrystalline polyamide based on 1,12-diaminododecane and 1,12-dodecanedicarboxylic acid was synthesized and characterized. The polymer was prepared by melt polycondensation. The molecular weight of the material ranged from 20,000 to 40,000 g/mol, depending on the polymerization conditions. The resulting product was characterized by means of elemental analysis, infrared spectrometry, ^{1}H- and ^{13}C-NMR, intrinsic viscosity, differential scanning calorimetry (DSC), thermogravimetric analysis, dynamic mechanical analysis, and wide-angle X-ray diffraction (WAXD). Some mechanical properties were measured. In addition, the thermal behavior of nylon 12,14 was systematically investigated with DSC and variable-temperature WAXD. Double endotherms were observed during the melting of the polymer, which might have originated from the melt and recrystallization processes of nylon 12,14 on heating. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 1581–1589, 2003

Key words: melt; polycondensation; nylon

INTRODUCTION

Since the synthesis of nylon 6,6 by Carothers in 1934,[1,2] many nylons have been developed, a number of which have been commercialized during the past 50 years. They have widely been used in many applications (e.g., fibers, engineering plastics, and coatings) because of their unique properties.[3] Almost all nylons are semicrystalline polymers, and they usually exhibit good toughness and strength, high modulus, excellent resistance to abrasion, and relatively high temperature resistance. This attractive matrix of properties originates from the strong hydrogen bonds of amide groups.[4] Therefore, the properties of nylons vary with the concentration of amide groups in the macromolecular chains.

In recent years, many attempts have been made to explore new nylons, especially synthesized short- and long-alkane-segment nylons. The chemical structure and amide content of short-alkane-segment nylons (e.g., nylon 2,4 and nylon 2,2) are close to those of silk fibroin.[5] Therefore, some studies have been made to synthesize these nylons for a better understanding of the performance–structure relationship in silk fibroin.[6] However, few practical applications can be found because of their very high melting temperatures (T_m's).

However, long-alkane-segment polyamides (greater than dodecane) have also attracted much attention because of their special properties and application fields. Long-alkane-segment nylons have high CH_2/amide ratios. Therefore, they have more advantages than other nylons, including lower T_m's, lower densities, lower dielectric constants, and water affinity. They can also bridge the gap between polyamides and polyethylene in terms of structures and properties.[7]

In this article, the first part of a series, we report a new long-alkane-segment polyamide, nylon 12,14, synthesized by melt polycondensation based on 1,12-diaminododecane and 1,12-dodecanedicarboxylic acid. The product was systematically characterized by infrared (IR) spectrometry, ^{1}H- and ^{13}C-NMR, wide-angle X-ray diffraction (WAXD), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and dynamic mechanical analysis (DMA). The thermal behavior of nylon 12,14 was also investigated. The second part of this series is dedicated to the crystallization, crystal structure, and crystalline transition of nylon 12,14 and will be published elsewhere.

EXPERIMENTAL

Polymer synthesis

1,12-Dodecanedicarboxylic acid (5.16 g, 0.02 mol) was dissolved in absolute ethanol (50 mL) at 50°C, and a solution of 1,12-diaminododecane (4.20 g, 0.021 mol) in absolute ethanol (30 mL) was added under vigorous stirring. The dodecanediamine/dodecanedicarboxylic acid salt immediately precipitated. The mixture was stirred for another 30 min at 50°C and allowed to cool to room temperature, and a white product was col-

lected by filtration. The salt was recrystallized from a mixture of ethanol (130 mL) and water (40 mL) and was obtained as a white powder (8.12 g, 87%; mp = 170.4°C).

A glass tube was charged with dodecanediamine/dodecanedicarboxylic acid salt (6.84 g, 0.015 mol), and a slight excess of 1,12-diaminododecane (0.03 g, 0.15 mmol) was added. The glass tube was snugly fitted into an autoclave. After the autoclave had been evacuated and flushed with nitrogen and after this cycle had been repeated three times, a nitrogen pressure of 10 atm was applied. The reaction was subsequently started by the autoclave temperature being quickly raised to 180°C. After the autoclave was kept for 2 h at 180°C, the temperature was increased to 190°C; after 1.5 h under these conditions, the pressure was decreased (5 atm), and the autoclave was kept for 2 h. In the last step, a vacuum (<0.1 atm) was established, the temperature was increased to 195°C, and the reaction was continued for another 2 h. The autoclave was then cooled to room temperature. The resulting nylon 12,14 was obtained as a white solid (5.68 g, 83%) and was pulverized in a freezing mill.

Polymer characterization

The resulting nylon 12,14 was characterized by the intrinsic viscosity, IR, ^{1}H- and ^{13}C-NMR, TGA, DMA, and WAXD. The sample used in the characterization except for the intrinsic viscosity showed an intrinsic viscosity of 1.22 dL/g. The IR spectrum was determined on a PerkinElmer Paragon 1000 PC Fourier transform infrared spectrometer. Trifluoroacetic acid was used as a solvent for the NMR measurements. ^{1}H-NMR spectra were obtained in deuterated trifluoroacetic acid with a Bruker Avance 500 spectrometer (Germany) operated at 500 MHz. ^{13}C-NMR spectra were recorded with the same instrument operated at about 125 MHz. The intrinsic viscosity was determined in dichloroacetic acid in an Ubbelohde viscometer at 25°C. TGA was performed on a PerkinElmer TGA7 thermobalance at a heating rate of 20°C/min. DMA was performed on a Rheometric Scientific dynamic mechanical thermal analyzer in the tensile mode. A frequency of 1 Hz and a temperature scan rate of 3°C/min were used. The value of the peak in the curve of the loss tangent versus the temperature was recorded as the glass-transition temperature (T_g). The WAXD measurements were conducted with a Rigaku III Dmax 2500 diffractometer (Japan) with Cu radiation (35 kV, 25 mA).

Mechanical properties

Polymer film samples with a thickness of 0.4 mm were used for mechanical tensile testing on an Instron 4464. The water absorption of the material was measured according to ASTM D 574. The specific gravity was determined according to ASTM D 792.

Melting behavior

A sample film approximately 0.2 mm thick was obtained with a hot mold at 5.0 MPa and 200°C for several minutes and then quenched to room temperature. The specimens for DSC measurements were subjected to various prescribed thermal treatments described in more detail in the Results and Discussion section. A PerkinElmer Pyris-1 differential scanning calorimeter, with the temperature calibrated with indium, was used to record the thermal behavior of nylon 12,14. A relatively small sample weight (3–5 mg) was used to minimize the effect for low thermal conductivities of the polymers.

RESULTS AND DISCUSSION

Synthesis and characterization of the polymer

Synthesis of the polymer

Nylon 12,14 was synthesized by the standard melt polycondensation of 1,12-diaminododecane and 1,12-dodecanedicarboxylic acid. To prepare high molecular weight polymers, we first produced the dodecanediamine salt of 1,12-dodecanecarboxylic diacid and thoroughly purified the salt by recrystallization from a mixture of ethanol and water. Subsequently, the salt was polymerized in an autoclave; this allowed for the careful control of the pressure and temperature during the reaction. The routine application of a high pressure (nitrogen) prevented the evaporation of the diamine during the early stage of the polycondensation. Also, a small excess of diamine was added to the salt to compensate for any losses. Finally, reducing the pressure of the reaction system further removed water from the system and ensured a high degree of polymerization. Figure 1 gives the relationship between the pressure of the autoclave in the last step of polymerization and the intrinsic viscosity of the resulting products. The intrinsic viscosity increased dramatically with the vacuum degree increasing in a certain vacuum range, but further increases of the vacuum degree did not increase the molecular weight any more.

Elemental analysis

The contents of the carbon, hydrogen, nitrogen, and oxygen were measured by elemental analysis. The measured data agreed well with the theoretical values of nylon 12,14.

ELEM. ANAL. Calcd. for $C_{26}H_{50}N_2O_2$: C, 73.93%; H, 11.78%; N, 6.60%; O, 7.69%. Found: C, 73.93%; H, 11.84%; N, 6.63%; O, 7.58%.

Intrinsic viscosity

The intrinsic viscosity of the product in dichloroacetic acid was measured at 25°C. The molecular weights
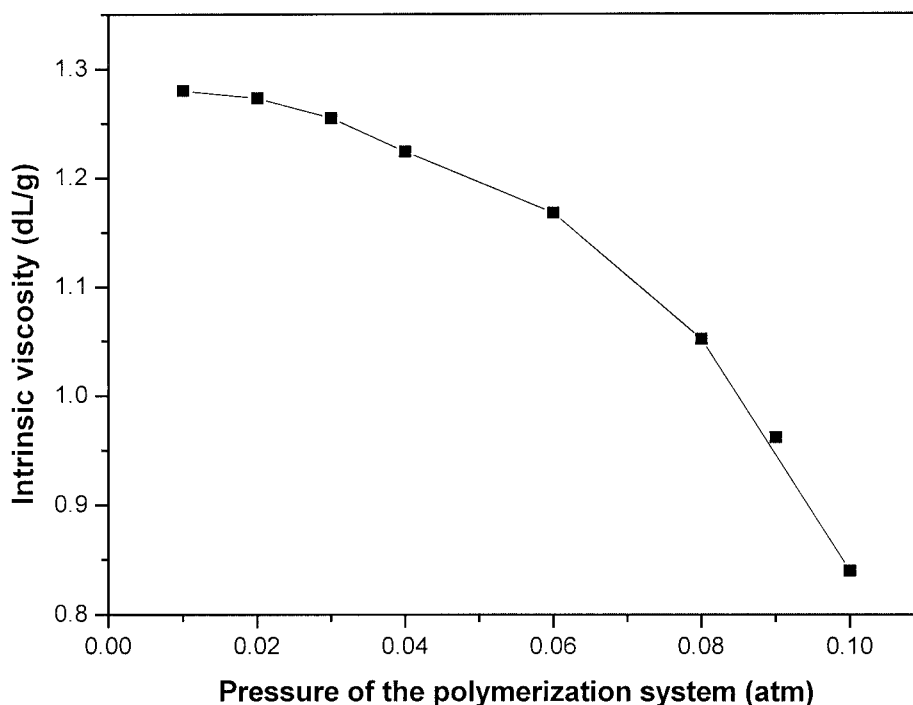
Figure 1 Effect of vacuum on the intrinsic viscosity of the polymer (the other polymerization conditions are described in the Experimental section).

were estimated with the Mark–Houwink–Sakurada[8] equation for nylon 6,6:

$$[\eta] = 0.005 + 35.2 \times 10^{-5} M^{0.551} \qquad (1)$$

The measured intrinsic viscosities of the product ranged from 0.84 to 1.26 dL/g, depending on the reaction conditions, such as the pressure of the autoclave, the reaction temperature, and the reaction time. The molecular weight of the product estimated with eq. (1) was 2.0×10^4 to 4.0×10^4.

IR spectrum

The IR spectrum of the product showed characteristic amide and methylene absorption bands at 3308 (N—H stretching), 3089 (overtone of N—H in plane bending), 2943 (C—H stretching), 1639 (amide I), 1538 (amide II), 1277 (amide III), 938 (amide IV), and 690 cm^{-1} (amide V), and this is consistent with some commercial nylons. It should be noted that the intensity of the peak at 2943 cm^{-1} was much stronger than that for ordinary nylons because of the longer methylene segments between adjacent amide groups along the chains.

^{1}H- and ^{13}C-NMR

The ^{1}H- and ^{13}C-NMR spectra of the product are given in Figure 2(a,b), respectively. For the ^{1}H spectrum, the absorption at 3.65 came from the protons adjacent to —NH— groups, and the absorption at 2.81 originated from the protons adjacent to —CO— groups. In addition, the small peak close to the 2.81 ppm signal is indicative of terminal carboxylic groups. The molecular weight of the sample was calculated to be about 18,000 from the NMR spectra. All additional absorption peaks corresponded to other protons in the aliphatic chains. These chemical shifts of the intense signals fully agreed with the anticipated chemical composition. The ^{13}C spectrum absorption at 182.8 was due to the carbon atoms at —C*ONH—. The two peaks at 45.4 and 35.86 corresponded to the carbon atoms on —CONH—C*H$_2$— and —C*H$_2$—CONH—, respectively. The other absorptions at 31.407, 31.332, 31.189, 30.915, 30.859, 29.841, 28.509, and 27.941 all belonged to aliphatic carbon atoms (—CH$_2$—).[3] The chemical-shift assignments are listed in Table I. Both ^{1}H- and ^{13}C-NMR confirmed that the resulting product was nylon 12,14. Furthermore, no sign of branching or irregularities was detected in its NMR spectrum.

Thermal properties

Double melting peaks were found for the sample in the heating thermograms of DSC, a very common observation in thermal studies of nylons, which we will investigate carefully in the next part of this series. The high T_m was about 179.5°C. The value, not surprisingly, was lower than T_m reported for nylon 12,12 (181°C)[9] and higher than that of polyethylene (130°C).
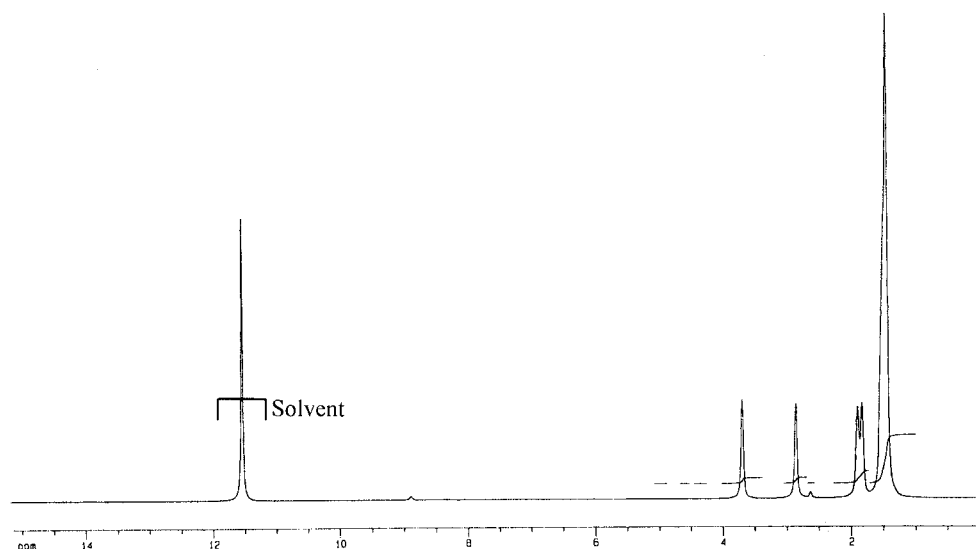
(a)
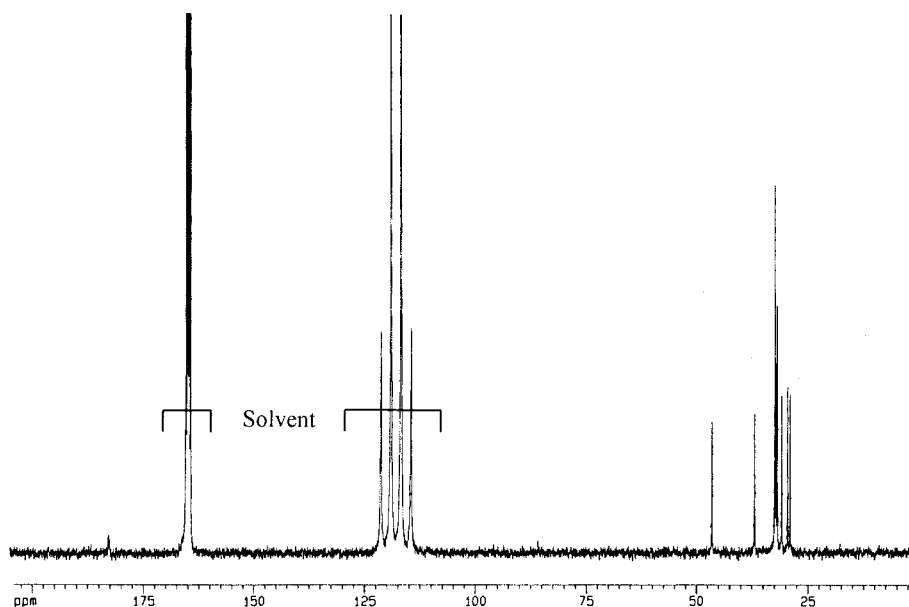
(b)

Figure 2 (a) ^{1}H-NMR and (b) ^{13}C-NMR spectra of the polymer.

TGA for nylon 12,14 showed that the initial decomposition temperature was about 420°C and that the maximum decomposition temperature was 470°C, similar to that for nylon 6,6.[10] Two well-defined transition peaks could be observed in the loss tangent curve of

DMA in the measurement range. The two transition peaks were assigned as α and β transitions. The α relaxation was due to the motion of long segments in the amorphous portions of the polymer, which corresponded to the glass transition. Therefore, T_g of nylon

TABLE I
Chemical-Shift Regions for Nylon 12,14

a	b	c	d	e	f	g	h
—NH—CH$_2$—CH$_2$—CH$_2$—CH$_2$					—CO—CH$_2$—CH$_2$—CH$_2$—		
Chemical shifts (in ppm)							
^{1}H							
3.65	1.79	1.4	1.4		2.81	1.86	1.41
^{13}C							
45.4	28	30	31	183	35.9	30.9	31.4

12,14 could be determined to be 48°C. The β relaxation was attributed to the relaxation of smaller segments.

WAXD

WAXD of nylon 12,14 showed two prominent reflections (Fig. 3) at room temperature, indicating a significant degree of crystallinity in this material. The WAXD patterns were quite similar to those of many even–even nylons; this means that the crystal structure of nylon 12,14 at room temperature could be α or β forms.[9,11,12] The two peaks at $2\theta = 20°$ and $2\theta = 24°$ corresponded to two spacings at 0.44 and 0.37 nm, respectively, which represented the projected interchain distance within a hydrogen-bonded sheet and the intersheet distance, respectively. A detailed analysis of the crystal structure of the polymer will be published elsewhere.

Physical properties

Melt-pressed polyamide films were prepared, and the mechanical properties were tested by standard tensile tests; Young's modulus and the elongation were also obtained. The specific gravity, water absorption, and T_m were also determined according to the ASTM method. The results are listed in Table II. The physical properties of nylon 6,6, nylon 10,10, and polyethylene are also attached for comparison. As expected, the tensile strength, modulus, density, water absorption, and T_m decreased with decreasing amide concentration, but the elongation increased accordingly.

Melting behavior of the polymer

Many nylons display multiple melting behaviors during heating. The interpretation of the melting behaviors varies from different crystal structures[13,14] or lamellar thicknesses[15,16] to simultaneous melting and recrystallization.[17,18] Figure 4 shows a set of DSC heating thermograms that were collected at a heating rate of 10°C/min for nylon 12,14 isothermally crystallized at a specified temperature. The DSC endotherms exhibited double melting peaks in addition to a small peak at a lower temperature. The double endotherms were distinguishable at the crystallization temperature (T_c) below 165°C. Moreover, the low melting peak increased in size and moved to a higher temperature with increasing T_c. However, the high melting peak became smaller as T_c increased, and the position was preserved, regardless of the change in the isothermal crystallization temperature. The double melting be-
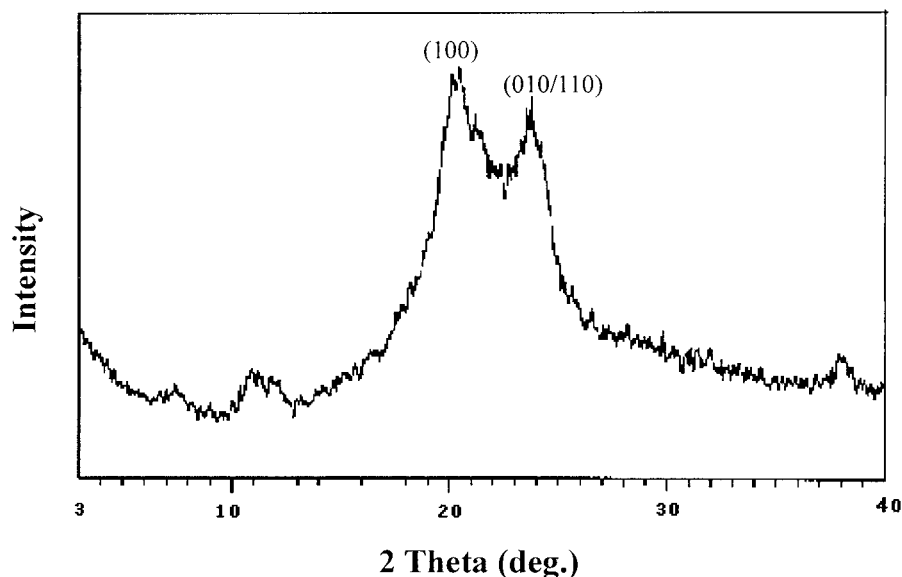

Figure 3 WAXD pattern of nylon 12,14 at room temperature.

TABLE II
Some Basic Properties of Nylon 12,14 as Compared with Nylon 6,6, Nylon 10,10, and Polyethylene

Polymer	Tensile strength (MPa)	Modulus (MPa)	Elongation (%)	Density (g/cm^3)	Water absorption (%)	T_n (°C)
Nylon 6,6[a]	81	2400	60	1.15	1.2	252
Nylon 10,10[a]	54	1904	150	1.06	0.42	203
Nylon 12,14	42	1700	300	1.02	0.12	179
Polyethylene[a]	30	1300	420	0.95	0.04	130

[a] See ref. 22.

havior of nylon 12,14 could be attributed to the recrystallization on heating. The low melting peak resulted from melting of the material crystallized at the isothermal crystallization temperature, and the high melting peak was caused by melting of the recrystallized material. With an increasing isothermal crystallization temperature, the crystals thickened and became more perfect; therefore, T_m increased. However, the original crystals melted and then recrystallized during the heating of the sample, and the recrystallized material showed an almost constant T_m, regardless of the isothermal crystallization temperature. Another interesting melting characteristic of nylon 12,14, which could be observed directly from its melting endotherms, was a small peak at a temperature close to T_c (ca. $T_c + 4$°C). The phenomenon was considered to be the annealing effect at T_c. That is, in addition to the major lamellae, crystals developed during isothermal crystallization; a small fraction of the polymer was packed into minor

crystal aggregates of smaller lamellar thickness, which in DSC curves led to the observed phenomenon of the minor melting peak located further below the main melting peaks.

The equilibrium melting temperature (T_m^o) of nylon 12,14 was determined with the Hoffmann–Weeks equation,[19] with the extrapolation of the plot of T_m versus T_c to $T_m = T_c$. The variation of the observed T_m with T_c is shown in Figure 5. In the explored range of T_c, T_m of nylon 12,14 increased almost linearly with T_c. T_m^o was found to be 187°C by extrapolation, lower than that of nylon 10,12 (206°C).[20]

The extrapolation of T_m versus T_c (Fig. 5) showed that T_m of the lower endothermic peak lay on a straight line along with those obtained when only one melting peak was observed. The high-temperature melting peaks of the samples with various T_c's were approximately at the same position and were independent of T_c. This behavior suggests that a recrystallization process probably oc-
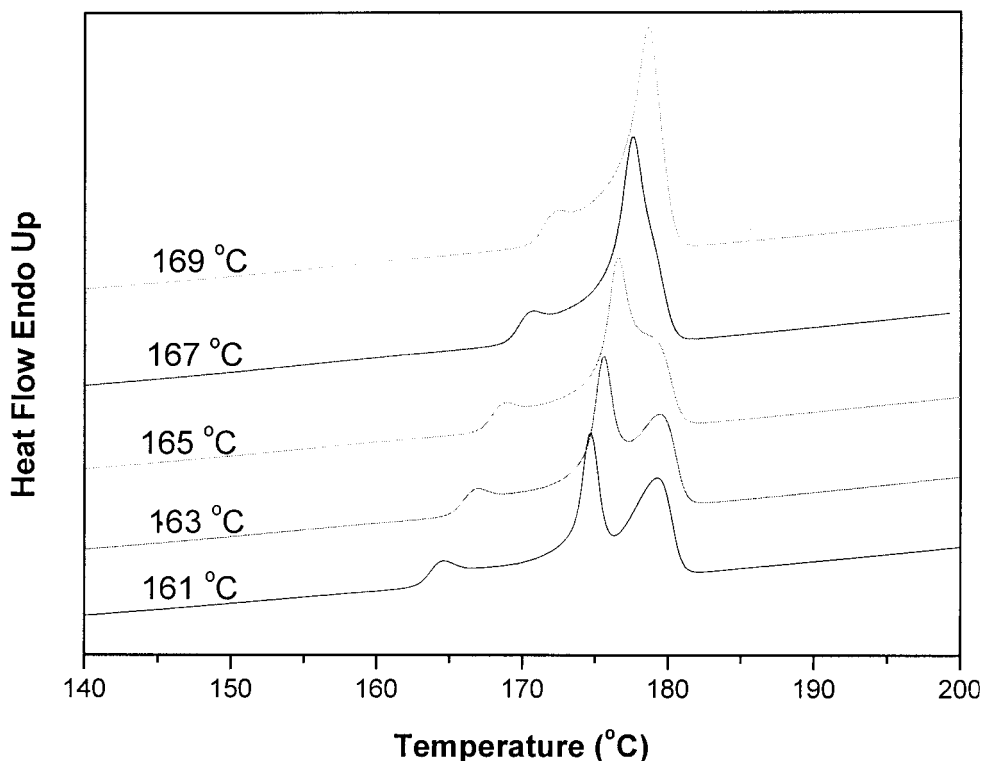

Figure 4 DSC thermograms of nylon 12,14 isothermally crystallized at a specified temperature at a heating rate of 10°C/min.
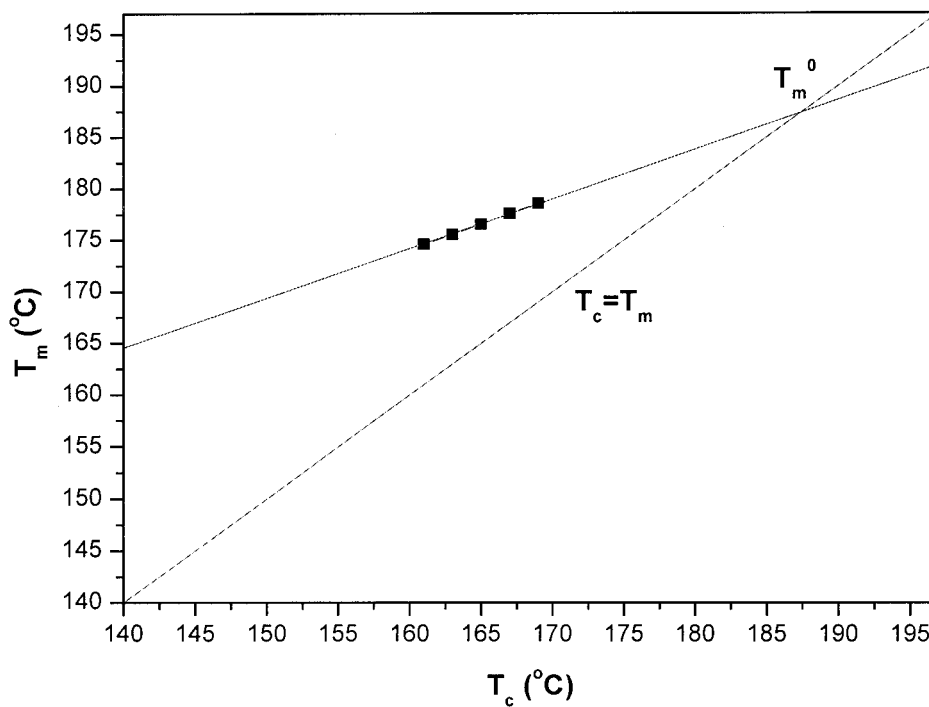
Figure 5 T_m as a function of T_c for nylon 12,14.

curred.[21] Accordingly, the sample melted at a temperature dependent on the crystallization conditions, recrystallized from the melt, and finally melted.

Nylon can crystallize into different crystal structures, including α, β, and γ forms. Every crystal form may have a different T_m. Therefore, the multiple melt-
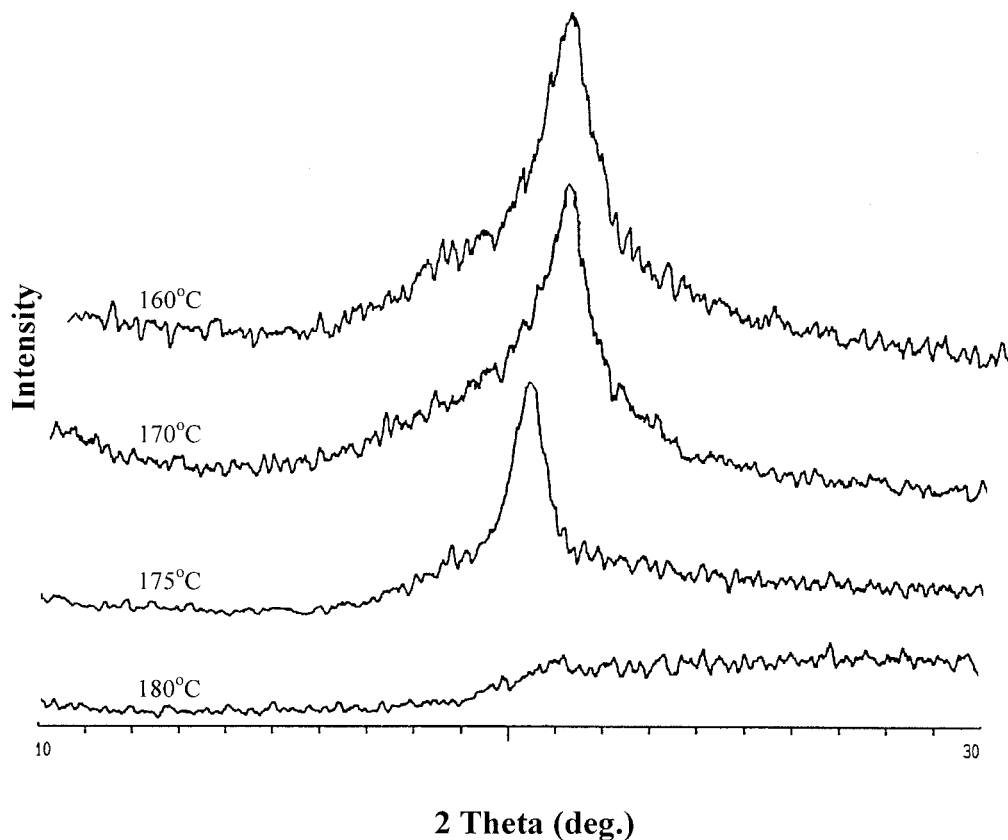

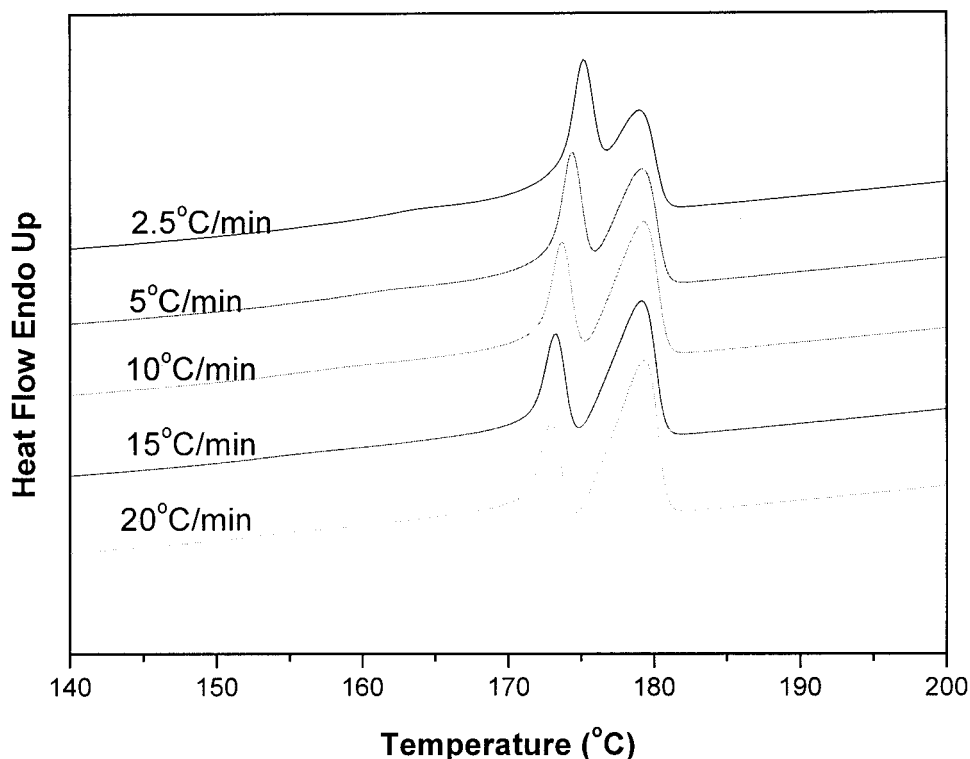**Figure 6** WAXD patterns of nylon 12,14 at 160, 170, 175, and 180°C.

Figure 7 DSC thermograms of nylon 12,14 nonisothermally crystallized at a specified cooling rate at a heating rate of 10°C/min.

ing behavior of nylons may be caused by the crystalline transitions with the heating of the samples; that is, different melting peaks correspond to the melting of different crystal structures. However, no crystallization transition was observed in the melting range for nylon 12,14 (Fig. 6). X-ray diffractions were recorded at 160, 170, 175, and 180°C, even though the sample showed the γ form because the measuring temperatures were all higher than the Brill transition of nylon 12,14 (the melt-crystallized nylon 12,14 showed a Brill transition at about 90°C; a detailed analysis of the behavior of crystalline transitions will be published elsewhere); the diffraction patterns were the same in terms of diffraction peaks. This indicates that only one crystal structure existed in nylon 12,14 during the melting process. Therefore, the possibility that the multiple endotherms resulted from different crystalline forms could be excluded. Moreover, the diffraction angle varied between 170 and 175°C, and this might have been due to the normal thermal expansion.

The DSC melting thermograms performed after nonisothermal crystallization at different cooling rates are presented in Figure 7. The peak temperature of the low-temperature endotherm increased with a decreasing cooling rate during nonisothermal crystallization because more perfect crystals formed at a lower cooling rate. When the nonisothermally crystallized sample was heated, a recrystallization and melt process took place. Therefore, the positions of higher T_m's were the same, being independent of the cooling rate.

To study the effects of the heating rate on the observed melting behavior, we heated samples of nylon 12,14 nonisothermally crystallized at a cooling rate of 10°C/min at various rates ranging from 2.5 to 30°C/min (Fig. 8). With an increasing heating rate, the two T_m peaks moved toward each other, and the lower T_m peak became larger. In fact, the observed multiple melting endotherms are thought to be the net illustrative effect of three thermal processes: the melting of the original imperfect crystals, the recrystallization of some or all of this material, and the melting of the recrystallized material. With an increasing heating rate, the contribution of the recrystallization process was more and more restricted, and the sample passed through the annealing temperature region so quickly that there was not enough time for the original material to recrystallize. Consequently, the extent of recrystallization decreased, and the recrystallized material melted at lower and lower temperatures.

CONCLUSIONS

A new long-alkane-segment polyamide, nylon 12,14, was synthesized by melt polycondensation. Some physical properties of the polymer were measured; it showed a much lower T_m, lower density, lower water absorption, and higher elongation than nylon 6,6. T_g was found to be 49°C according to DMA. The melting behavior of the nylon under different conditions was carefully investigated by DSC. The double melting
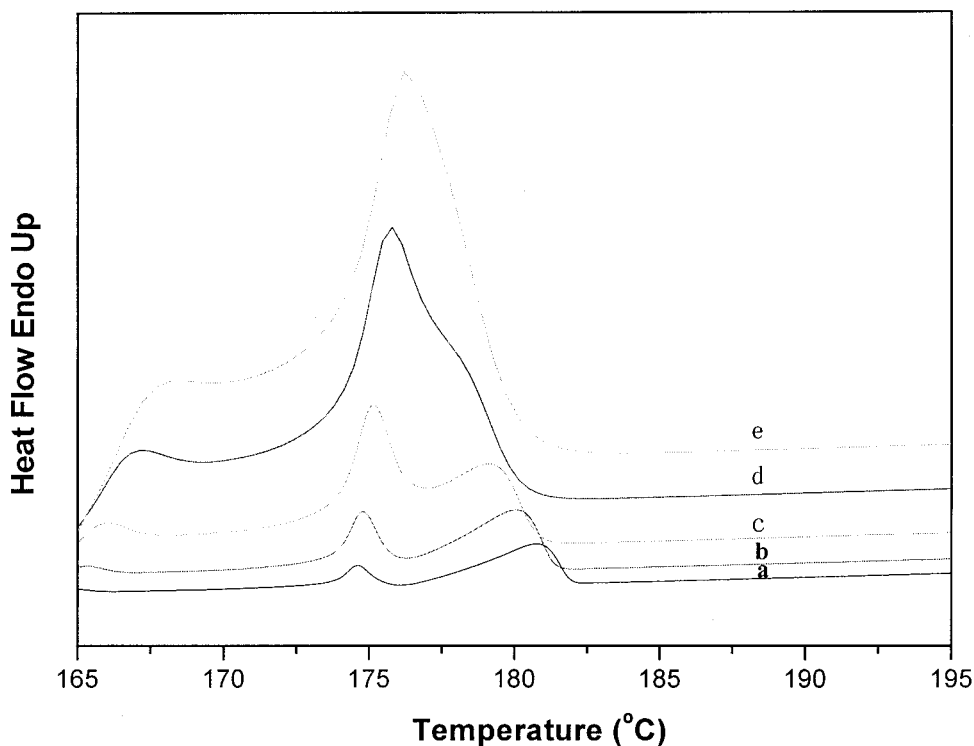
Figure 8 Effect of the heating rate on the melting behavior of nylon 12,14: (a) 2.5, (b) 5, (c) 10, (d) 20, and (e) 30°C/min.

behavior of nylon 12,14 originated from the melt and recrystallization mechanism. T_m^o was determined to be 187°C.

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