

Synthesis and Characterization of Nylons Based on Hexadecane Diacid

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ABSTRACT: A series of nylons with long alkane segments between amide groups were synthesized by using hexadecane diacid and various diamines, and the resulting polyamides were characterized comprehensively. It was shown that the molecular weights of nylons 6 16, 8 16, 10 16, and 12 16 in our studies exceed 1.1×10^4 , whereas nylons 2 16 and 4 16 have relatively low molecular weights. In addition, the

melting temperatures, the decomposition temperatures, and the glass transition temperatures of the nylons obtained were measured. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 2462–2467, 2003

Key words: nylon; polymerization; FT-IR; NMR; thermal properties

INTRODUCTION

Aliphatic polyamide, or nylon, is a significant member of polymer material family. Because nylon 6 6 was firstly synthesized in 1934, many nylons have been commercialized owing to their excellent comprehensive performances. Almost all nylons exhibit a relatively high modulus, eminent toughness, and strength, as well as good temperature resistance and abrasion resistance. It is the unique crystal structure originated from the hydrogen bonds formed by —NH— and —CO— groups between adjacent molecular chains that provides nylon's higher melting temperature compared with some other kinds of semicrystalline polymers, such as polyethylene. It was supposed that nylons tend to perform more like polyethylene when the density of amide groups (—NHCO—) along the polymeric chains becomes very low. Because the syntheses of short^{1–4} and long alkane segment nylons^{5–9} have attracted much attention in recent years, a better understanding of the relationship between the concentration of amide groups and the properties of nylons is expected to be presented.

In this article, a series of nylons, including nylons 2 16,¹⁰ 4 16, 6 16,¹¹ 8 16, 10 16, and 12 16, were synthesized on the basis of a long alkane diacid, 1,14-hexadecane diacid. In addition, the resulting polyamides were characterized by infrared (IR) spectrum, nuclear magnetic resonance (NMR), elementary analysis, in-

trinsic viscosity, thermal analysis, and dynamic mechanical analysis (DMA).

EXPERIMENTAL

Materials

1,14-Hexadecane diacid (Acros Organics, Belgium), 1,12-diaminododecane (Aldrich, USA), 1,10-diaminododecane (Aldrich), 1,8-diaminooctane (Aldrich), 1,6-diaminohexane (Aldrich), 1,4-diaminobutane (Fluka, USA), and ethylene diamine (Aldrich) were used as received.

Syntheses

Nylon 12 16 was synthesized by the melt polycondensation method as follows. 1,14-Hexadecane diacid was dissolved in absolute alcohol at 50°C and was slowly added to a solution of 1,12-diaminododecane in absolute alcohol under vigorous stirring. Subsequently, the diaminododecane–hexadecane diacid salt was formed. Before cooling to room temperature, the mixture was stirred for 30 more minutes at 50°C. The salt was dried in a vacuum desiccator after being filtered and repeatedly washed with absolute alcohol. Then the salt was put into a tailor-made glass tube and a slight excess of diaminododecane (about 1%) was added to compensate any possible loss. After fitting the glass tube into an autoclave, the autoclave was evacuated and flushed with nitrogen three times. A nitrogen pressure of 10 atm was applied and then the temperature was rapidly increased to 170°C (T_1). In this way, the condensation polymerization started. After being kept for 2 h in this condition, the autoclave was heated to 180°C (T_2). Another 2 h was needed before the pressure was decreased to 5 atm. Then, the

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TABLE I
Polymerization Temperatures of Nylons (°C)

	T_1	T_2	T_3
Nylon 2 16	185	210	240
Nylon 4 16	180	205	230
Nylon 6 16	180	200	220
Nylon 8 16	180	195	210
Nylon 10 16	175	190	200
Nylon 12 16	170	180	190

autoclave was evacuated, and the temperature was raised to 190°C (T_3). The last step continued for 2 h. Finally, the autoclave was cooled and the resulting polymer was obtained.

Other nylons were prepared by using a similar process where the polymerization temperatures varied from each other. Table I shows the temperatures for synthesizing nylons in our studies.

Characterizations and measurement instruments

The resulting products were generally characterized by several methods, such as IR spectrum, ^1H - and ^{13}C -NMR, elementary analysis, intrinsic viscosity, and thermal analysis. Furthermore, DMA was also measured for nylons 6 16, 8 16, 10 16, and 12 16.

IR measurement was carried out on a Perkin-Elmer Paragon 1000PC Fourier transform infrared spectrometer. ^1H -NMR spectra were obtained on a Bruker DRX500 spectrometer at 500 MHz, while ^{13}C -NMR spectra were obtained on a Gemini-2000 spectrometer at 300 MHz, with trifluoroacetic acid being used as solvents. The intrinsic viscosity was determined in dichloroacetic acid in an Ubbelohde viscometer at $25 \pm 0.1^\circ\text{C}$. The thermal properties were recorded on a Perkin-Elmer Pyris-1 differential scanning calorimeter (DSC) and the temperature was calibrated with indium; thermogravimetry analysis (TGA) was performed on a Perkin-Elmer TGA7 thermobalance with a heating rate at $20^\circ\text{C}/\text{min}$. For nylons 6 16, 8 16, 10 16, and 12 16, dynamic mechanical properties were measured by using an RSI Orchestrator at a strain percent of 0.01% and a frequency of 1 Hz.

RESULTS AND DISCUSSION

Syntheses of nylons 2 16, 4 16, 6 16, 8 16, 10 16, and 12 16

A series of nylons was synthesized by conventional melt polycondensation on the basis of a long alkane carboxylic diacid, 1,14-hexadecane diacid. To assure the accurate equivalent ratio between the diacid and the diamine, it was preferable to form salt before polymerization. At the early stages of the condensation polymerization, high nitrogen pressure was applied to reduce the possible losses resulting from evaporation of diamine. In addition, a slight excess

diamine was added to compensate any loss. To remove water generated during reaction, the system's pressure was reduced in the last step. In this way, the resulting product with the expected polymerization degree was obtained successfully.

Infrared spectra

Infrared spectra of the products are shown in Figure 1. It can be observed that all nylons under consideration display the characteristic absorption bands of amide groups and methylene groups at about 3306 cm^{-1} (NH vibration), 3082 cm^{-1} (NH vibration), 1640 cm^{-1} (amide I), 1539 cm^{-1} (amide II), 940 cm^{-1} (amide IV), and 721 cm^{-1} (CH_2 rocking). The spectra are similar to those of other commercial nylons, such as nylon 6 6 and nylon 6 10.¹²

NMR analysis

Figure 2 gives ^1H -NMR spectra of the products. The peaks of chemical shift are assigned as follows: the absorption at about 3.6 and 2.7 originate from the protons adjacent to NH group and the protons adjacent to the CO group, respectively. The remaining peaks stem from other protons on the aliphatic chains. Studies of the absorptions in ^{13}C -NMR spectra (Fig. 3) show that the peak at 182 corresponds to the carbon atoms of $-\text{C}^*\text{ONH}-$. The absorption at about 44 and 36 comes from the carbon atoms adjacent to amide group (i.e., $-\text{CONHC}^*\text{H}_2-$ and $-\text{C}^*\text{H}_2\text{CONH}-$, respectively). All other bands are owing to the aliphatic carbon atoms of $-\text{CH}_2-$. These results are completely agreeable to the anticipated chemical structure. In addition, the NMR spectra illustrate that there is no branching structure in the resulting polymers.

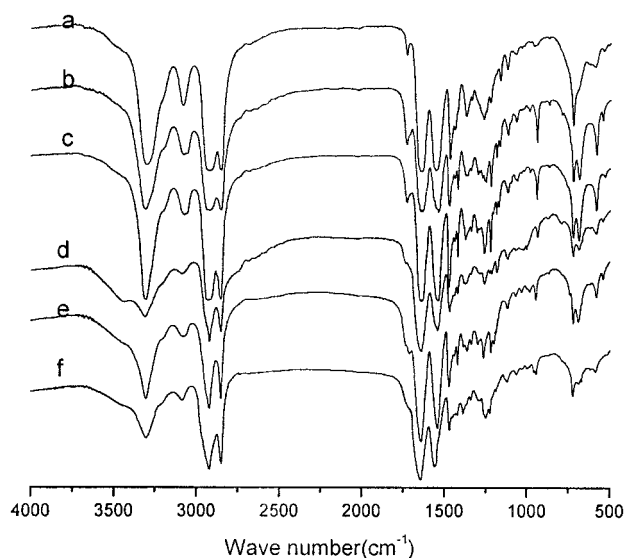


Figure 1 Infrared spectra of the products. (a) 12 16; (b) 10 16; (c) 8 16; (d) 6 16; (e) 4 16; (f) =16.

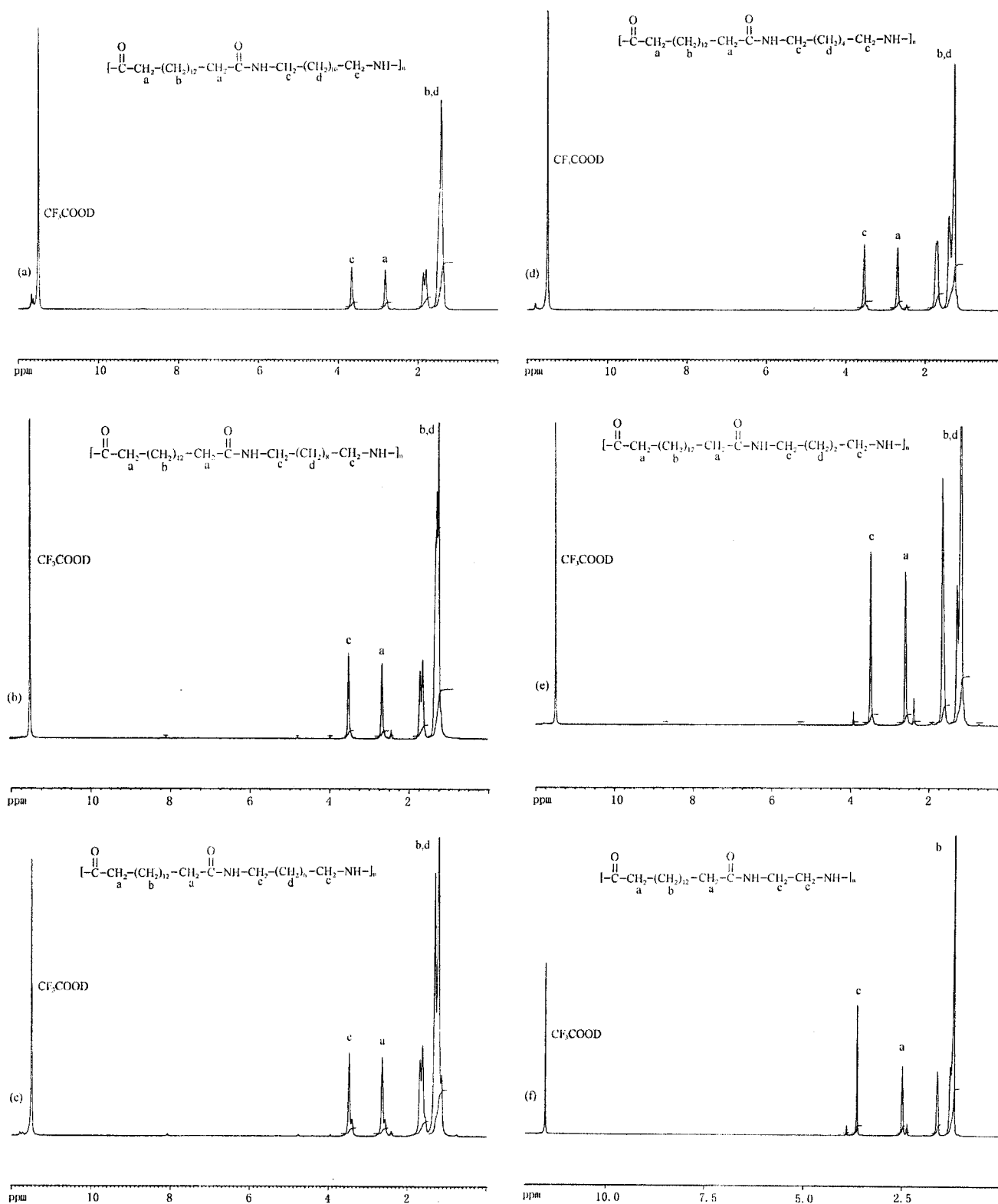


Figure 2 $^1\text{H-NMR}$ spectra of the resulting polyamides: (a) 12 16; (b) 10 16; (c) 8 16; (d) 6 16; (e) 4 16; (f) 2 16.

Elementary analysis

The contents of carbon, hydrogen, nitrogen, and oxygen of the synthetic nylons are listed in Table II. The

theoretical compositions are also presented for comparison. The results demonstrate that the experimental data are in full agreement with the theoretical values.

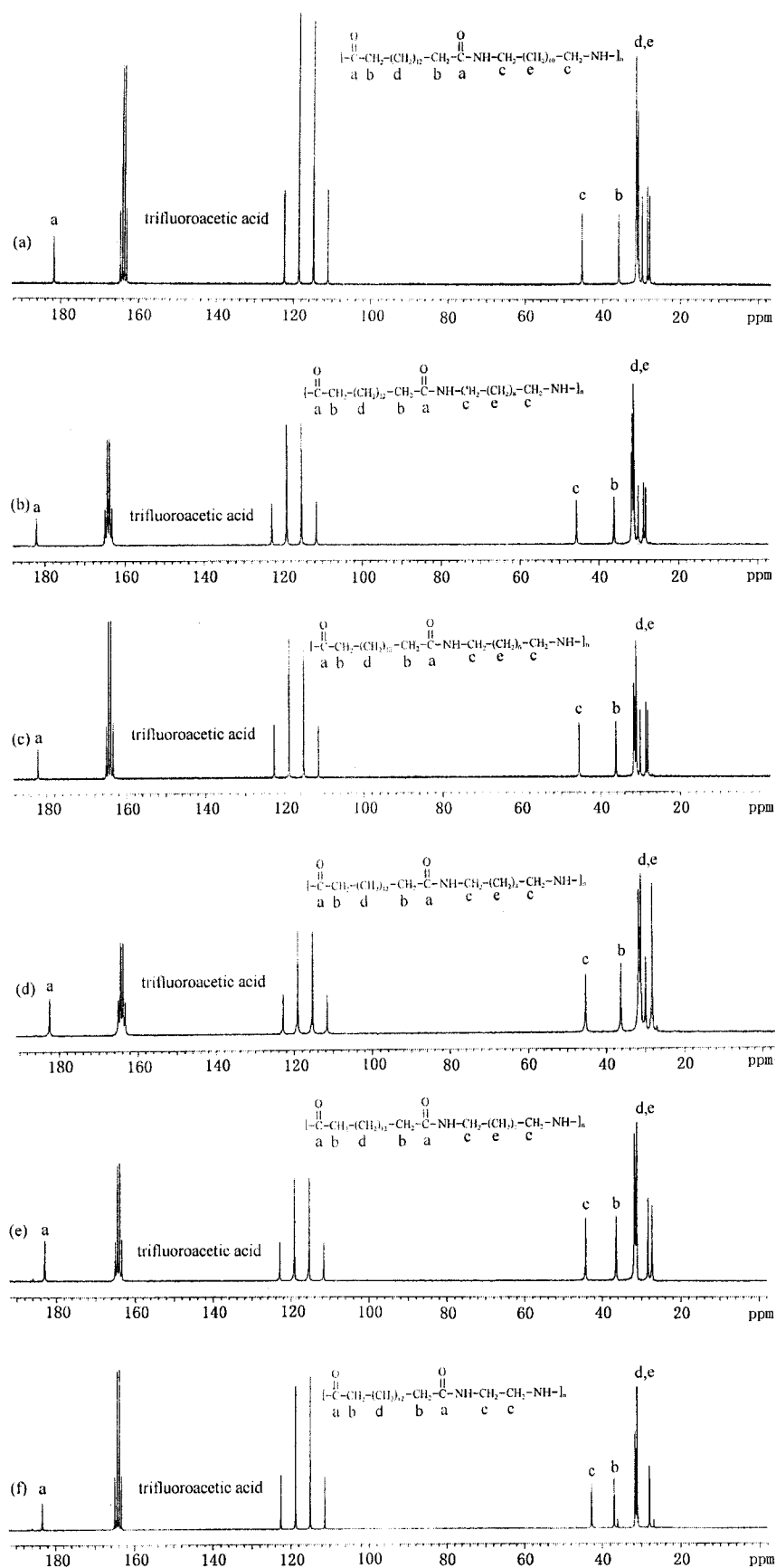


Figure 3 ^{13}C -NMR spectra of the resulting polyamides: (a) 12 16; (b) 10 16; (c) 8 16; (d) 6 16; (e) 4 16; (f) 2 16.

TABLE II
Elementary Analysis Data of the Resulting Polymers (%)

	Measurement values				Calculation values			
	C	H	N	O	C	H	N	O
Nylon 2 16	69.31	11.40	8.91	10.38	69.63	11.04	9.02	10.31
Nylon 4 16	70.82	11.51	8.16	9.51	70.96	11.32	8.28	9.45
Nylon 6 16	71.93	11.71	7.56	8.80	72.08	11.55	7.64	8.73
Nylon 8 16	72.88	11.95	6.95	8.22	73.04	11.75	7.10	8.11
Nylon 10 16	73.61	12.07	6.58	7.74	73.88	11.92	6.63	7.57
Nylon 12 16	74.33	12.26	6.12	7.29	74.61	12.08	6.22	7.10

Intrinsic viscosity and M_n

The intrinsic viscosity of nylons in our works is collated in Table III. The viscosity average molecular weights of the synthetic nylons are deduced according to the Mark-Houwink equation¹³:

$$[\eta] = 0.5 + 0.352M^{0.551} \quad (1)$$

It is found that the molecular weights of nylons 6 16, 8 16, 10 16, and 12 16 in our studies are between 1.1×10^4 and 2.0×10^4 , whereas the other two nylons in the series have relatively low molecular weights (i.e., less than 8000). Such a remarkable difference may result from the different volatility of the diamines used in preparation. Although all nylons were synthesized under similar conditions, it was somewhat difficult to obtain a high molecular weight sample from the diamine with short methylene segments, such as ethylene diamine and 1,4-diaminobutane.

Thermal properties

Figure 4 gives DSC curves of the synthetic nylons. It is seen that several samples exhibit double-melting endotherms, which is a common phenomenon observed in semicrystalline polymers.^{14,15} Additionally, the melting temperatures (T_m) of the synthetic nylons decrease with declining the density of hydrogen bonds. Consequently, nylon 12 16 has the lowest melting point among the series, which is as low as 170°C.

TGA profiles are shown in Figure 5. All polyamides under consideration except nylon 2 16 start to decompose at about 350°C, and the decomposition tempera-

tures (T_d) are 470°C. The values are very close to those of nylon 6 6¹⁶ and nylon 4 14.¹ The stability of nylons 2 16 and 4 16 is not as good as the others because of the relatively low molecular weights.

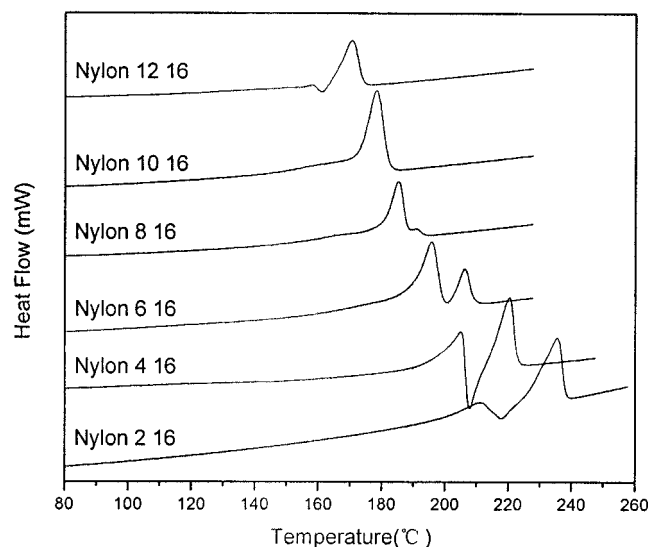


Figure 4 DSC curves of the synthetic nylons.

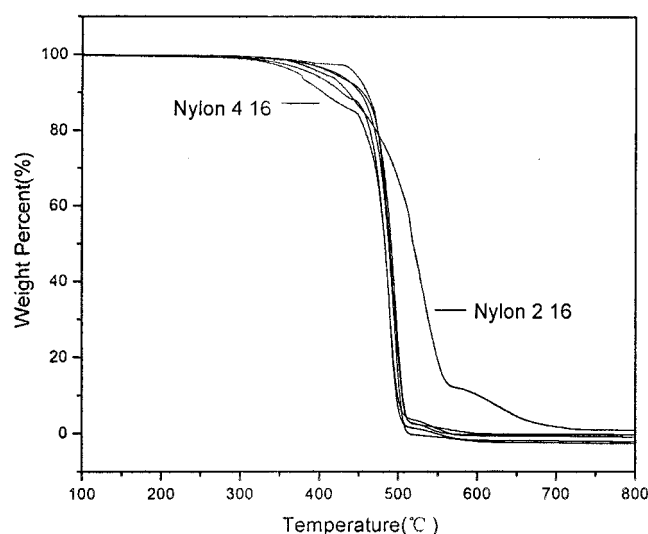


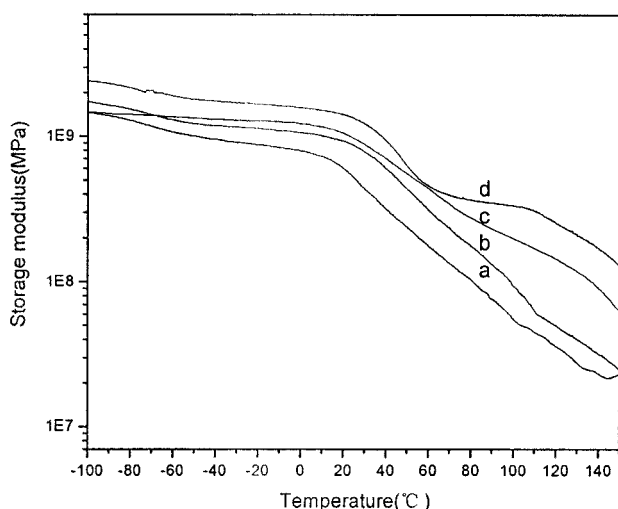
Figure 5 TGA profiles of the synthetic nylons.

TABLE III
Viscosity and Molecular Weights
of the Synthetic Nylons

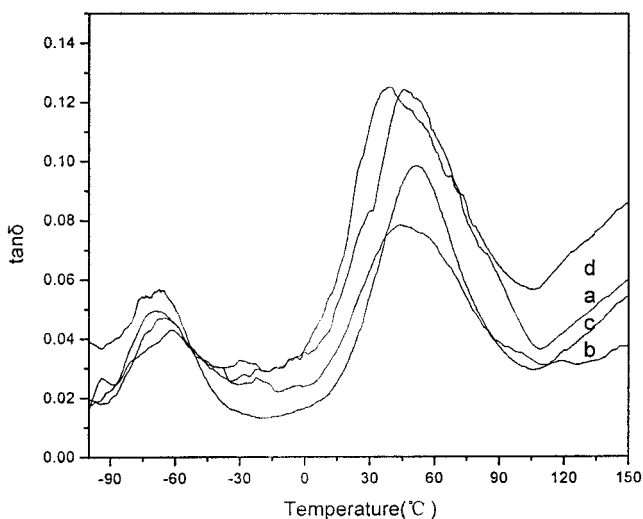
	$[\eta]$ (ml/g)	M_n
Nylon 2 16	41	5.5×10^3
Nylon 4 16	47	7.1×10^3
Nylon 6 16	59	1.1×10^4
Nylon 8 16	60	1.1×10^4
Nylon 10 16	72	1.5×10^4
Nylon 12 16	84	2.0×10^4

Dynamic mechanical analysis

Figure 6 gives the dynamic mechanical analysis curves for nylons 6 16, 8 16, 10 16, and 12 16 of our studies. Two apparent transitions occurred at about -60 and 50°C , which correspond to the α - and β -relaxation, respectively. The glass transition temperature (T_g) for nylons can be determined by the α -relaxation because it is usually related to the segment movements in the noncrystalline area. There is no significant difference in T_g between different samples in our studies. Table IV shows the T_g 's, T_m 's, and T_d 's of the synthetic nylons.



(a)



(b)

Figure 6 DMA patterns of the nylons (a) 12 16, (b) 10 16, (c) 8 16, (d) 6 16.

TABLE IV
 T_g 's, T_m 's, and T_d 's of the Nylons ($^\circ\text{C}$)

	T_g	T_m	T_d
Nylon 2 16	—	235	436
Nylon 4 16	—	218	462
Nylon 6 16	40	206	470
Nylon 8 16	52	185	466
Nylon 10 16	45	178	464
Nylon 12 16	46	170	467

CONCLUSION

Nylons 2 16, 4 16, 6 16, 8 16, 10 16, and 12 16 were synthesized on the basis of a long alkane diacid, hexadecane diacid. The synthetic polymers were confirmed to have the anticipated chemical structure by the measurement of IR, NMR, and elementary analysis. The molecular weights of nylons 6 16, 8 16, 10 16, and 12 16 in our works are beyond 1.1×10^4 ; however, the molecular weights of nylons 2 16 and 4 16 are 5.5×10^3 and 7.1×10^3 , respectively. The thermal analysis and the dynamic mechanical analysis give the melting temperatures, the decomposition temperatures, and the glass transition temperatures of the synthetic nylons. The results in our studies demonstrate that T_m decreases with the falling of amide density along the molecular chains. Furthermore, T_g and T_d do not show such a significant variation as T_m .

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