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Preparation and characterization of a series of polyamides with long alkylene segments: Nylons 12 20, 10 20, 8 20, 6 20, 4 20 and 2 20

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Summary

A series of nylons with long alkylene segments between amide groups were newly prepared by step-heating melt-polycondensation of 1,18-octadecanedicarboxylic acid with various diamines. The prepared polyamides were characterized carefully. The results show that many properties of the prepared nylons change regularly with the length of methylene segments in diamines. In addition, nylon 2 20 has a relatively low molecular weight and much different melting and thermal decomposition behaviors in comparison with other nylons.

Introduction

Nylons are an important family of industrial materials, valued for their prominent properties such as relatively high strength, good toughness, abrasion resistance and good processability. Those attractive physical properties of nylons originate from the strong interchain hydrogen bonds formed between neighboring amide groups, and greatly depend on the length of alkylene sequences in chains, which determines the concentration of hydrogen bonds. As significant members of nylon family, long alkylene segment aliphatic polyamides which have low hydrogen bonds concentration, have attracted much attention in recent years [1-5], due to their special properties including lower densities, lower melting points, lower dielectric constant and poorer water affinity than those of other nylons containing short alkylene segments. Furthermore, sometimes the long alkylene segment nylons that have appropriate CH_2/amide ratio can be used as "compatibilizers" to bridge the gap between polyamides and polyolefins [6]. Therefore, the relationship between the CH_2/amide ratio and the properties of long alkylene segment nylons deserves to be investigated carefully.

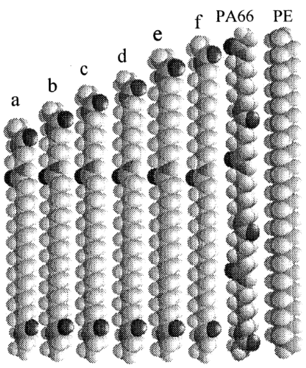

Figure 1. Structure of the nylons a:2 20, b: 20, c:6 20, d:8 20, e:10 20, f:12 20, PA66 an PE. Color code: hydrogen, white; carbon mid-gray; nitrogen, gray; oxygen, dark.

This paper reports the preparation of a series of nylons with long alkylene segments, including nylons 12 20, 10 20, 8 20, 6 20, 4 20 and 2 20. All these nylons are based on 1,18-octadecanedicarboxylic acid that introduces an 18-methylene segment into the molecular chain between every two —CO— groups. Figure 1 illustrates the structure of PA 66, PE and the nylons prepared in this paper. This reveals that the structures of the prepared nylons are intermediate between common polyamides and polyethylene and incline to perform like polyethylene more and more with the increase of methylene segments in diamine units. It implies that some of the prepared nylons might have potential applications as compatibilizers for blends of polyamides and polyolefins.

In this study, the resulting products were carefully characterized by infrared (IR) and Raman spectra, elementary analysis, ^{1}H and ^{13}C nuclear magnetic resonance (NMR), intrinsic viscosity, differential scanning calorimetry (DSC), thermogravimetry analysis (TGA) and dynamic mechanical thermal analysis (DMTA). The crystallization behaviors of these nylons will be reported elsewhere.

Experimental

Materials

1,18-Octadecanedicarboxylic acid (Tokyo Kasei Kogyo), 1,12-dodecanediamine (Aldrich), 1,10-decanediamine (Aldrich), 1,8-octanediamine (Aldrich), 1,6-hexanediamine (Aldrich), 1,4-butanediamine (Fluka) and ethylenediamine (Aldrich) were used as received.

Polymer Synthesis

Synthesis of nylon 12 20:

1,18-Octadecanedicarboxylic acid (1.53 g, 0.005 mol) was dissolved in absolute alcohol (20 ml) at 65 °C, then a solution of 1,12-dodecanediamine (1.01 g, 0.00505mol) in absolute alcohol (10 ml) was slowly added under vigorous stirring. Immediately, the dodecanediamine-eicosanedioic acid salt precipitated. The mixture was stirred for 30 minutes at 50 °C and then was cooled to the room temperature. After filtration the salt was washed repeatedly with absolute alcohol and dried in a vacuum oven at 30 °C, 0.5 atm. Finally, the salt was obtained as white powder (2.29 g, 94%).

A custom ground-glass stoppered tube was filled with dodecanediamine-eicosanedioic acid salt (2.0 g, 0.0041 mol), and a slight excess of 1,12-dodecanediamine (0.08 g, 0.4 mmol) was added to compensate the possible loss during polymerization. The glass tube was tight fitted into an autoclave, and then the autoclave was evacuated and flushed with nitrogen for three times. Subsequently, under a constant nitrogen pressure of 10 atm, the reaction was started along with the autoclave temperature quickly increased to 160 °C, the first-step temperature (T_1). After being kept for 1 h at 160 °C, the autoclave was heated to 180 °C, the second-step temperature (T_2), and was kept for 1.5 h under this condition. Then, the nitrogen pressure was decreased to 5 atm and the autoclave temperature was increased to 190 °C, the last-step temperature (T_3). After being kept for 2 h in this step, the autoclave was vacuumized to 0.01 atm and the reaction was continued for another 2 h. Finally, the autoclave was cooled to room temperature and the condensation polymerization was completed. The product was obtained as an ivory-white plastic (1.72 g, 89%).

Other nylons were prepared by way of a similar procedure with various polymerization temperatures because the melting temperatures of the resulting nylons are different from one another. Table 1 shows the three step temperatures for preparation of nylons and yield of the resulting polymers in our studies.

Table 1. Polymerization temperatures and yields of prepared nylons (°C)

Nylons	*T_1	T_2	T_3	Yield
Nylon 12 20	160	180	190	89%
Nylon 10 20	170	185	200	90%
Nylon 8 20	185	195	205	87%
Nylon 6 20	190	210	220	90%
Nylon 4 20	190	220	230	86%
Nylon 2 20	200	230	240	84%

*T_1: the first-step temperature; T_2: the second-step temperature; T_3: the last-step temperature.

Characterizations and Measurement Instruments

The resulting polymers were carefully characterized by means of intrinsic viscosity, IR and Raman spectra, ^1H and ^{13}C NMR, elementary analysis, DSC, TGA and DMTA. IR and Raman spectra were collected on a Bruker Equinox-55 FT-IR and Raman spectrometer. ^1H and ^{13}C NMR spectra of nylons 2 20 and 6 20 were obtained on a Bruker DRX500 NMR spectrometer at 500MHz, while the NMR spectra of the other four nylons were obtained on a GEMINI-2000 NMR spectrometer at 300MHz, with trifluoroacetic acid being used as solvents. The intrinsic viscosity was determined in dichloroacetic acid in an Ubbelohde viscometer at 25 °C. The thermal properties were recorded on a Perkin-Elmer Pyris-1 differential scanning calorimeter calibrated the temperature with indium, and TGA was carried out on a Perkin-Elmer TGA7 thermobalance at heating rate of 20℃/min. The data of DMTA of nylons 12 20, 10 20, 8 20, 6 20 and 4, 20 were measured on a RSI Orchestrator at a strain percent of 0.01% and a frequency of 10Hz, while the prepared nylon 2 20 was too fragile to undergo the measurement.

Results and discussion

Preparation of nylons 12 20, 10 20, 8 20, 6 20, 4 20 and 2 20

The main focus of this paper is preparation of a series of long alkylene segments nylons based on the long alkylene segment diacid, 1,18-octadecanedicarboxylic acid. The step-heating melt-polycondensation was adopted to synthesize the nylons for their low melt temperatures [5,6]. The salt of diamine and diacid was prepared in advance in order to assure the accurate equivalent ratio of the raw materials. In the reaction system a slight excess diamine was added to compensate the possible loss caused by evaporation under high reaction temperature. Then the condensation polymerization was carried out through three steps. Firstly, polycondensation of the salt with a tiny excess diamine was started under nitrogen, and the reaction temperature was increased to the melting point of the salt. Then the polymerization was kept for 1 h to insure the complete reaction of monomers. Secondly, the temperature was raised about 10~20 °C for further polycondensation. Finally, the polymerization was going on under vacuum and the reaction temperature was kept at 20 °C above the melting point of the related polyamide in order to remove the by-product, water, and get high molecular weight polymers.

The intrinsic viscosity and M_η of the prepared nylons are summarized in Table 2. The viscosity average molecular weights of the nylons were deduced according to Mark-Howink equation [7]:

$$[\eta]=0.005+3.52\times10^{-3}M^{0.551}$$

Table 2. Intrinsic viscosity and viscosity-average molecular weights of the prepared nylons

	Nylon 2 20	Nylon 4 20	Nylon 6 20	Nylon 8 20	Nylon 10 20	Nylon 12 20
[η] (dl/g)	0.55	0.67	0.73	0.78	0.83	0.92
M_η	0.93×10^4	1.3×10^4	1.6×10^4	1.8×10^4	2.0×10^4	2.4×10^4

Infrared and Raman spectra

Infrared spectra of the products are shown in Figure 2. All resulting polymers can be quickly identified as nylons [8-10] by the characteristic absorption bands of amide groups and methylene groups: 3310 cm^{-1} (hydrogen-bonded N-H stretch), 3080 cm^{-1} (overtone of N-H in plane bending), 1640 cm^{-1} (Amide I, C=O stretch), 1540 cm^{-1} (Amide II, C-N stretch + CO-N-H bend), 940 cm^{-1} (Amide IV, C-CO stretch), 721 cm^{-1} (CH_2 wag), 690 cm^{-1} (Amide V, N-H out-of-plane bend) and 580 cm^{-1} (Amide VI, C=O out-of-plane bend).

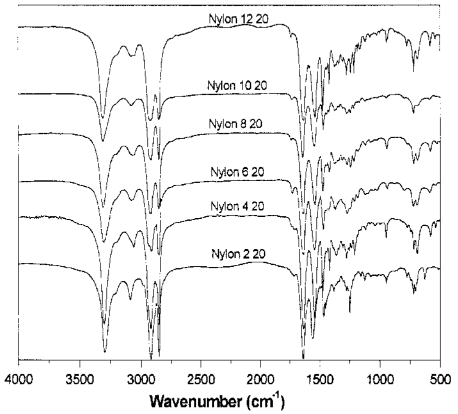

Figure 2. Infrared spectra of the prepared nylons

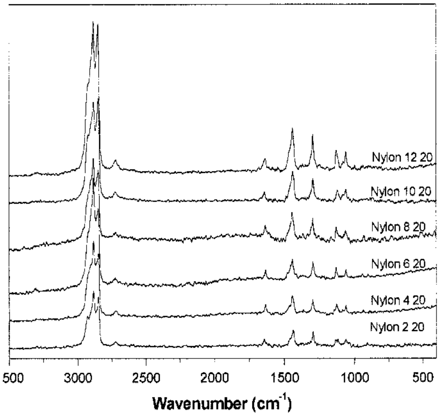

Figure 3. Raman spectra of the prepared nylons

Raman spectra of the nylons are displayed in Figure 3. The characteristic bands of amide group in Raman spectra locate in the same regions as in IR spectra but are relatively weak, while the C-H stretch bands between 2800 and 3010 cm^{-1} are very strong and the intensities of those bands obviously increase with the alkylene sequence length. In addition, some researchers [11-13] suggest that the ratio of the appropriate band intensities might plot linearly against the number of CH_2 groups. Figure 4 gives a plot that displays the relation between the number of methylene in diamine and the intensity ratio of the band 1440 cm^{-1} (corresponding to CH_2 bending) to 1640 cm^{-1} (Amide I).

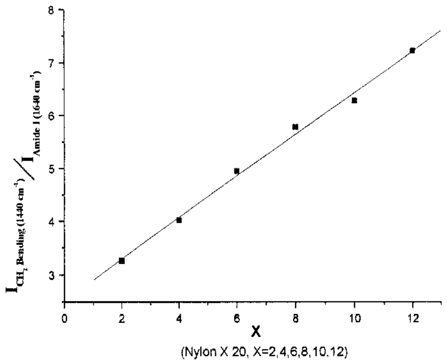

Figure 4. Plot of the ratio of the relative Raman intensity of band 1440 to 1640 vs the number of CH_2 groups in diamine.

NMR analysis

Figures 5 and 6 show ^1H and ^{13}C NMR spectra of the products, respectively. The signals in the figures indicate that the resulting polymers are completely consistent with the anticipated chemical composition and there is no branching or any unexpected structure in the nylons prepared. The signals of chemical shifts at about 3.4 ppm in ^1H NMR and 45 ppm in ^{13}C NMR originate from the protons adjacent to NH group, and the signals at about 2.5 ppm in ^1H and 36 ppm in ^{13}C correspond to the protons adjacent to CO group. The signals around 182 ppm in ^{13}C spectra come from the carbon atoms of –*CONH–. All other signals are corresponding to the aliphatic carbon atoms on the methylene segments [14-17]. Table 3 lists some characteristic peaks of the prepared nylons.

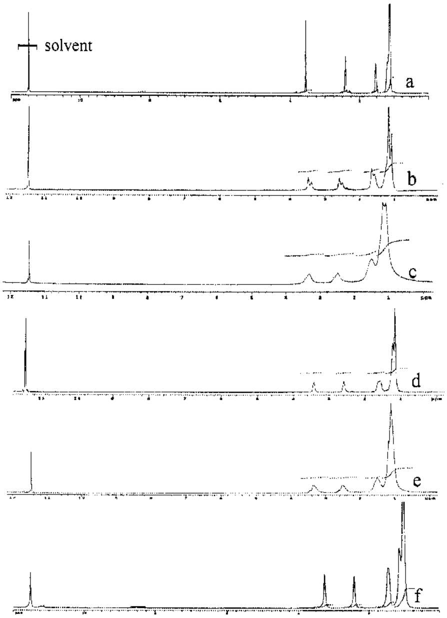

Figure 5. ^1H NMR spectra of the prepared nylons a: nylon 2 20. b: nylon 4 20. c: nylon 6 20. d: nylon 8 20. e: nylon 10 20. f: nylon 12 20.

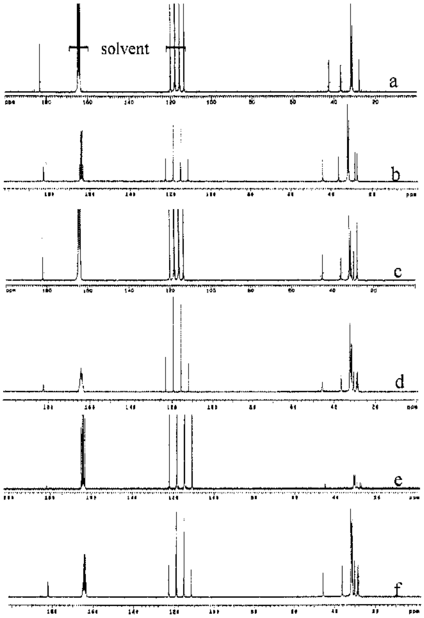

Figure 6. ^{13}C NMR spectra of the prepare nylons. a: nylon 2 20. b: nylon 4 20. c: nylon 6 20. d: nylon 8 20. e: nylon 10 20. f: nylon 12 20.

Table 3. Characteristic NMR bands of the prepared nylons (chemical shift in ppm)

$-NH-\overset{a}{CH_2}-\overset{c}{CH_2}-\overset{def}{(CH_2)_n}-$ $\quad$ $-CO-\overset{b}{CH_2}-\overset{c}{CH_2}-\overset{def}{(CH_2)_{14}}-$

Polymer*	Carbonyl	a		b		c		def	
		^1H	^{13}C	^1H	^{13}C	^1H	^{13}C	^1H	^{13}C
Nylon 2 20	183.1	3.70	42.4	2.32	36.7	1.53	31.6	<1.21	<31.5
Nylon 4 20	182.8	3.48	44.2	2.59	36.4	1.67	31.8	<1.30	<31.5
Nylon 6 20	181.9	3.30	44.8	2.42	35.7	1.46	31.4	<1.25	<30.5
Nylon 8 20	182.3	3.32	45.6	2.49	36.4	1.52	32.1	<1.34	<30.9
Nylon 10 20	181.8	3.44	45.3	2.61	35.8	1.59	31.5	<1.32	<31.1
Nylon 12 20	182.2	3.35	45.7	2.50	36.2	1.51	31.9	<1.32	<31.5

*solvent: trifluoroacetic acid

Elementary analysis

The calculated and measured values of contents of carbon, hydrogen, nitrogen and oxygen of the prepared nylons are listed in Table 4. The results display that the measured data are in full agreement with the theoretical values.

Table 4. Elemental analysis data for the prepared nylons (%)

Polymer	Carbon		Hydrogen		Nitrogen		Oxygen	
	Calc.	Meas.	Calc.	Meas.	Calc.	Meas.	Calc.	Meas.
Nylon 2 20	72.13	72.54	11.47	10.95	7.66	7.84	8.74	8.67
Nylon 4 20	73.10	72.83	11.67	11.25	7.11	7.17	8.12	8.73
Nylon 6 20	73.93	73.56	11.85	12.17	6.64	6.76	7.58	7.52
Nylon 8 20	74.67	74.21	12.00	12.14	6.22	6.41	7.11	7.24
Nylon 10 20	75.31	74.94	12.13	12.23	5.87	6.08	6.69	6.74
Nylon 12 20	75.89	75.95	12.25	12.34	5.54	5.73	6.32	5.98

Thermal analysis

Differential scanning calorimetry

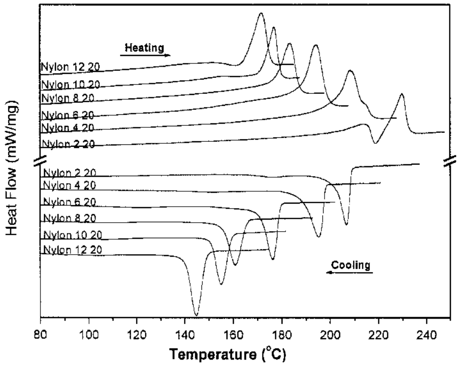

Figure 7. DSC thermograms of the prepared nylons

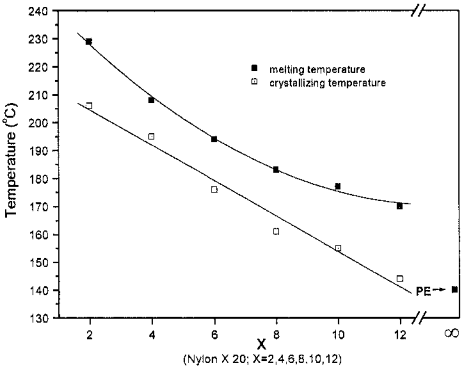

Figure 8. Melting and crystallizing temperatures of polyamide series nylon X 20 (X=2,4,6,8,10,12)

Figure 7 gives DSC thermograms of the prepared nylons. The melting and crystallizing points of the prepared nylons decrease with the increase of CH_2 units in chains. As expected, nylon 12 20 has the lowest melting temperature among the series, which is as low as 170 °C. The curves in Figure 8 reveal that the crystallizing points are nearly linear against the number of CH_2 groups in diamine; however, the decline of the melting points is nonlinear with the length of alkylene sequence in diamine owing to the slow-down of the decrease of the hydrogen-bond density. Additionally, the DSC curve for nylon 2 20 in Figure 7 clearly exhibits a double-melting endotherm, which is a common phenomenon in nylon family and many other semi-crystalline polymers [18,19]. We believe this multi-melting behavior of nylon 2 20 is due to its relative lower degree of crystalline perfection.

Thermogravimetry analysis

TGA plots are displayed in Figure 9. All samples except nylon 2 20 start to decompose at about 435 °C, and the decomposition temperatures are around 460 °C, which are similar to those of other even-even nylons [5,20]. However, due to its relatively low molecular weight, nylon 2 20 is not so stable as the others, which starts to decompose at about 360 °C.

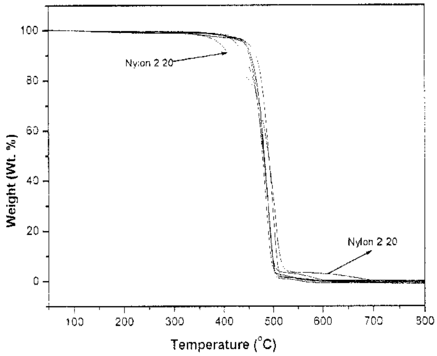

Figure 9. TGA plots of the prepared nylon series.

Dynamic mechanical thermal analysis

The DMTA curves for the prepared nylons except nylon 2 20 are displayed in Figure 10. Figure 10A reveals that the modulus of the nylons under consideration decline with increasing alkylene sequence length. Similar to many nylons, the prepared nylons exhibit two transition behaviors at about 45 and -60 °C, which are defined as α and β relaxation of nylons (see in Figure 10B). The glass transition temperature of a nylon can be acquired by α relaxation as the latter corresponds to the segment movements in non-crystalline regions [21,22]. In Figure 10B, the glass transition temperatures slightly decline with the increase of CH_2 groups. Table 5 gives the glass transition, melting and decomposition temperatures of the prepared nylons.

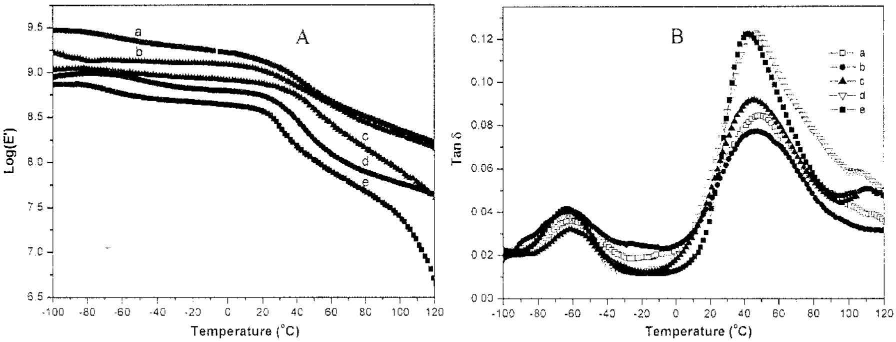

Figure 10. DMTA plots of the prepared nylons. a: nylon 4 20. b: nylon 6 20. c: nylon 8 20. d: nylon 10 20. e: nylon 12 20.

Table 5. The glass transition temperature (T_g), melting temperature (T_m) and decomposition temperature (T_d) of the prepared nylons. (°C)

	Nylon 2 20	Nylon 4 20	Nylon 6 20	Nylon 8 20	Nylon 10 20	Nylon 12 20
T_g	-	49.3	48.0	46.7	45.9	42.6
T_m	230.0	208.9	194.5	183.8	177.2	170.4
T_d	459.0	455.1	464.8	456.8	453.4	457.4

Conclusion

A series of long alkylene segments nylons 12 20, 10 20, 8 20, 6 20, 4 20 and 2 20 were synthesized by step-heating melt-polycondensation. The measurement of IR, Raman, NMR and elementary analysis confirm that the products have the anticipated chemical composition and structure. The intrinsic viscosity of the prepared nylons demonstrates that the resulting polymers in our studies, except for nylon 2 20, have the molecular weights beyond 1.3×10^4. The thermal analyses, including DSC, TGA and DMTA give the melting temperatures, the decomposition temperatures and the glass transition temperatures of the prepared nylons. The experimental data show that T_m and T_g decline with increasing CH_2 number in diamine. Furthermore, although T_d has not significant difference among the prepared nylons, the beginning temperature of decomposition of nylon 2 20 is much lower than that of others.

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