

Synthesis and Characterization of Polyamides X 18

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ABSTRACT: Step heating melt polycondensation was adopted in the preparation of polyamides based on 1,16-octadecane diacid and α,ω -(CH₂)_{2n} diamines ($n = 1-6$). The structure was confirmed by various spectroscopic techniques (IR, Raman, ¹H-NMR, and ¹³C-NMR). High molecular masses were obtained only in the presence of an excess of diamine and when the diamine possessed low volatility. The molecular masses were between $(0.94 \text{ and } 2.1) \times 10^4$ Da for all polyamides under consideration. An excellent correlation between size exclusion chromatography and ¹H-NMR data was demonstrated in the measurement of the degree of

polymerization. The melting temperatures of the polyamides decreased from polyamide 12 18 to polyamide 2 18 as the amide density along the molecular chain declined. No significant variation was observed in the glass-transition and decomposition temperatures of the polyamides that were obtained. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 1565–1571, 2005

Key words: polyamide; NMR; size exclusion chromatography; synthesis; characterization

INTRODUCTION

As significant industrial materials, polyamides are widely used because of their excellent comprehensive performance. For instance, almost all polyamides present relatively high strength, good toughness, and abrasion resistance. Their peculiar crystal structure, which is controlled by the interchain hydrogen bonds between amide groups, provides polyamides with attractive physical properties. Hydrogen bonds play an important role not only in determining the crystal structure but also in the overall performance of polyamides. Therefore, those polyamides with long or short alkyl segments have attracted much attention in recent years.¹⁻⁵ Long alkyl segment aliphatic polyamide has a relative low hydrogen bond concentration and thus a low melting point. It also shows prominent impact properties, a lower dielectric constant, and lower water affinity compared with other polyamides containing short alkyl segments.⁶⁻⁸

A series of polyamides based on 1,16-octadecane diacid are synthesized by a melt polycondensation procedure. The length of the diamine chain varies

from 2 to 12 CH₂ moieties. Moreover, the resulting polymers are studied systematically by IR and Raman spectroscopy, ¹H- and ¹³C-NMR, size exclusion chromatography (SEC), thermogravimetric analysis (TGA), and dynamic mechanical analysis (DMA).

EXPERIMENTAL

Materials

1,16-Octadecane diacid (TCI), 1,12-diaminododecane (Aldrich), 1,10-diaminododecane (Aldrich), 1,8-diaminooctane (Aldrich), 1,6-diaminohexane (Aldrich), 1,4-diaminobutane (Fluka), and ethylenediamine (Aldrich) were used as received.

Syntheses

All syntheses were performed by the melt polycondensation procedure starting from corresponding salts. Preparation of polyamide 12 18 is reported as an example. Table I shows the polymerization conditions for each polymer. 1,16-Octadecane diacid (2.0 mmol) was dissolved in absolute alcohol (5 mL) at 50°C and a solution of 1,12-diaminododecane (2.1 mmol) in absolute alcohol (3 mL) was added slowly under vigorous stirring. The mixture was stirred for 30 min at 50°C and then cooled to room temperature. The salt was repeatedly washed with absolute alcohol and filtered before drying in a vacuum oven. The salt was obtained as a white powder with a yield of 92%. Subsequently, the salt was put into a glass tube with a

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TABLE I
Polymerization Conditions and Yields of Polyamides

Polyamide	T_1 (°C)	T_2 (°C)	T_3 (°C)	Excess of diamine (mol %)	Yield (%)
12 18	170	180	190	0	89
10 18	170	180	195	0	88
8 18	175	190	200	0.5	86
6 18	185	200	210	0.5	83
4 18	190	215	230	1	83
2 18	190	215	240	1	87

slight excess of diamine (<1%) in order to compensate any possible loss. After fitting the glass tube into an autoclave, the autoclave was evacuated and flushed three times with nitrogen. The condensation polymerization started under a constant nitrogen pressure of 10 atm as the temperature was rapidly increased to 170°C (T_1). After being kept for 2 h at 170°C, the autoclave was heated to 180°C (T_2) and kept for 2 h under this condition. The pressure was decreased to 5 atm and the autoclave temperature was raised to 190°C (T_3). The last step continued for 2 h at 0.01 atm. Finally, the autoclave was cooled to room temperature. The resulting product was an ivory-white polymer.

Spectroscopic characterization

IR measurements were carried out on a Bruker Equinox-55 Fourier transform IR spectrometer, and Raman spectra were run on a FRA 106/S Raman spectrometer. A Varian Mercuryplus-400 or a Bruker Avance 400

was used for ^1H - and ^{13}C -NMR spectra in trifluoroacetic acid solution.

Molecular mass determination

SEC analyses were performed in anhydrous CH_2Cl_2 at 20°C after N-trifluoroacetylation.⁹ A set of five Styragel columns was used (two HR 4, two HR 3, and one HR 5). Column calibration was performed with polystyrene standards. The linear polyamide calibration curve was calculated according to the universal calibration principle.^{10,11}

Thermal and mechanical properties

The thermal properties were recorded on a Perkin-Elmer Pyris-1 differential scanning calorimetry (DSC) calorimeter, and the temperature was calibrated with indium at a heating rate of 20 K/min. TGA was performed on a Perkin-Elmer TGA7 thermobalance under a nitrogen atmosphere at a heating rate at 20 K/min.

The dynamic mechanical properties were measured on a TA 2980 dynamic mechanical analyzer.

RESULTS AND DISCUSSION

Syntheses of polyamides 12 18, 10 18, 8 18, 6 18,¹² 4 18, and 2 18

It is well known that the polycondensation reaction of A-A/B-B monomers must be performed on a well-balanced system in order to have high molecular masses. This requirement is generally obtained when

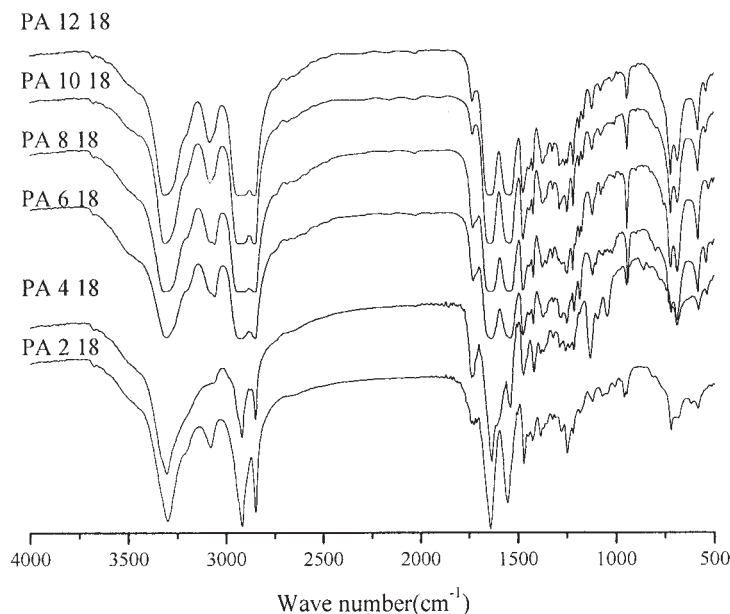


Figure 1 IR spectra of the resulting products.

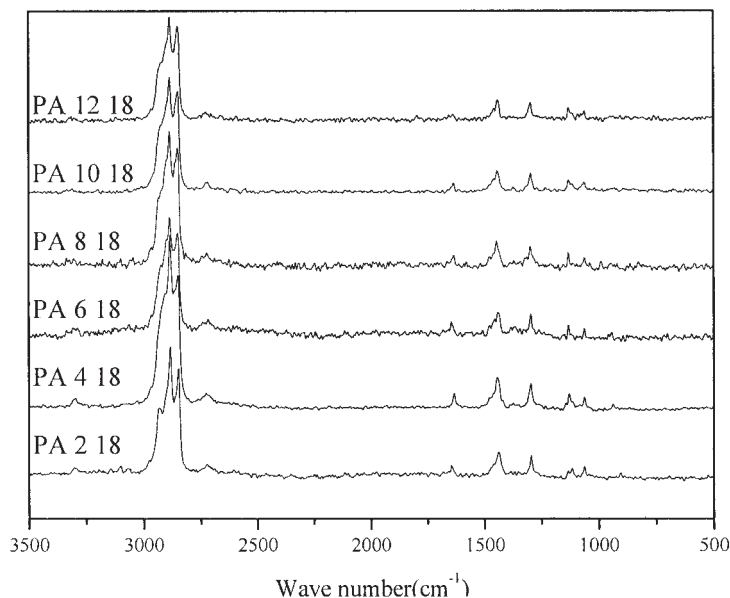


Figure 2 Raman spectra of the polyamides.

the corresponding salt is prepared. Thus, polyamides were synthesized by step heating polycondensation based on 1,16-octadecane diacid and various diamines previous formed from the corresponding salts. In order to reduce any possible loss resulting from volatilization of diamine, a slight excess of diamine was added and, at the early stages of the condensation polymerization, high pressure nitrogen was applied. As the polycondensation proceeded, the temperature was increased step by step and exceeded the melting point of the reactants throughout the polymerization process (Table I). Subsequently, the pressure of the system was reduced and a vacuum was applied to remove the water that was produced. The yields reported in the table refer to the weight of the obtained polymer and are not related to the molecular masses of the materials.

IR and Raman spectra

Figure 1 provides the IR spectra of the resulting products. As expected, all present the characteristic bands of amide and methylene groups. For example, they give absorption at 3308 (NH vibration), 3070 (NH vibration), 1648 (amide I, C=O stretch), 1548 (amide II, C—N stretch plus CO—N—H bend), 949 (amide IV, C—CO stretch), 724 (CH₂ rocking), 686 (amide V, N—H out of plane bend), and 586 cm⁻¹ (amide VI, C=O out of plane bend). These absorption bands in the IR spectra are consistent with those reported for other even-even nylons.¹²⁻¹⁴

The Raman spectra of the polyamides are shown in Figure 2. The characteristic bands are located in the same regions as in the IR spectra. However, the intensities of the peaks are not so strong, except for the

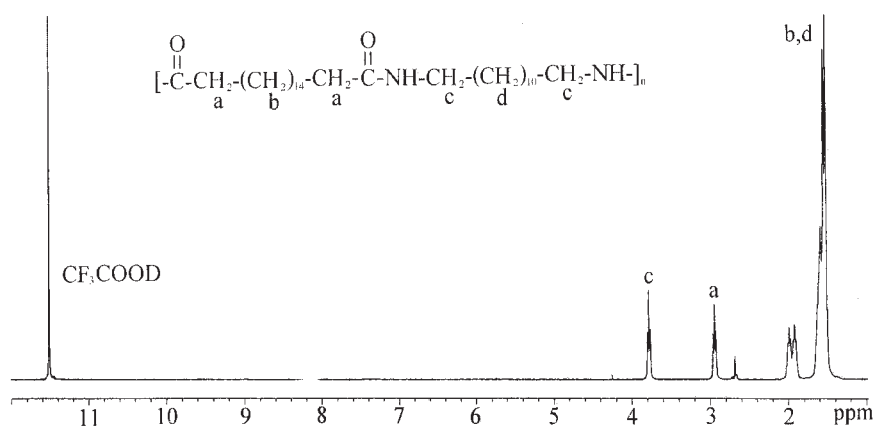


Figure 3 ¹H-NMR spectra of polyamide 12 18.

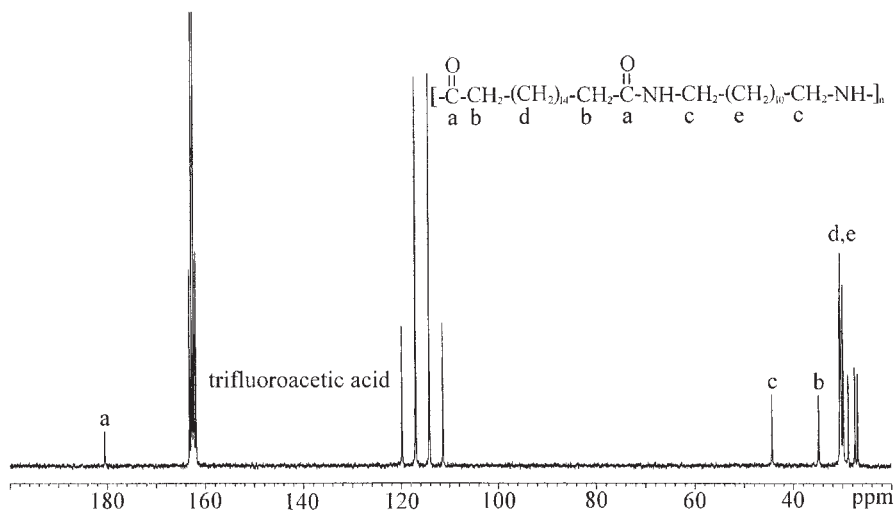


Figure 4 ^{13}C -NMR spectra of polyamide 12 18.

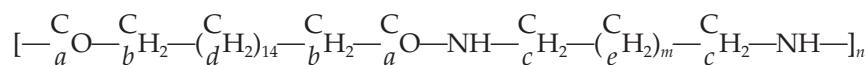
C—H stretch at 2800 and 3010 cm^{-1} . The Raman spectra are also in accordance with the data reported in previous articles.^{15,16}

NMR spectra

Examples of the ^1H - and ^{13}C -NMR spectra of the products are given in Figures 3 and 4, respectively. Chemical shifts in the ^1H spectra are assigned as follows: the peaks at about 3.8 and 2.9 ppm are due to the methylene protons adjacent to —NH— and —CO— groups, respectively. The other peaks originate from the inner protons of the aliphatic chains. In the spectra of polyamides 2 18 and 4 18, peaks at higher field with respect to methylene adjacent to the carbonyl group are observed; these peaks corre-

spond to the methylenes in the β position with respect to the terminal COOH groups. From the relative areas the average degree of polymerization (DP_n) can be evaluated. As an example, for polyamide 4 18, a DP_n value of 12.5 is measured. This result is in excellent agreement with the value obtained from SEC analysis.

The ^{13}C -NMR spectra confirm the expected structure: the absorption at 182 ppm comes from the carbon atom of the amide group, whereas the peaks at 44 and 36 ppm correspond to the methylene signals at 3.8 and 2.9 ppm in the ^1H -NMR spectra. The other absorption peaks stem from the inner methylene groups. In the NMR spectra, no signal related to branched structure was detected. Table II reports the chemical shift data for the polyamides in the study.



SEC measurements

Two examples of SEC curves of N-trifluoroacetylated polyamides are presented in Figure 5. All polymers are completely soluble in the elution solvent. Table III

TABLE II
Chemical Shifts in ^{13}C -NMR for Polyamides (ppm)

Polyamide	a	c	b	d,e
12 18	180.4	44.3	34.8	30.5–26.9
10 18	183.3	47.0	37.6	33.2–29.6
8 18	180.5	44.1	34.8	30.4–26.8
6 18	180.8	43.9	34.9	30.5–26.9
4 18	181.0	42.7	34.9	30.3–25.8
2 18	181.0	40.7	35.0	29.8–26.0

displays the molecular weights of the polyamides in reference to linear nylon 6. High molecular weight polymers are obtained for polyamides 12 18, 10 18, 8 18, and 6 18, as shown in Table III. On the contrary, polyamides 4 18 and 2 18 have considerably low molecular weights under the similar synthetic condition. Such a remarkable difference comes from the different volatilities of the diamines involved in the synthesis. The numerical results in Table III require further comment. The column set was calibrated with polystyrene standards and the polystyrene calibration was transformed in linear nylon 6 according to the universal calibration concept. This transformation was tested for nylon 6 and it is also reliable for nylon 6/6. The α parameter of the Mark–Houwink relation is near 0.7 for N-trifluoroacetylated polyamide 6 in CH_2Cl_2 at

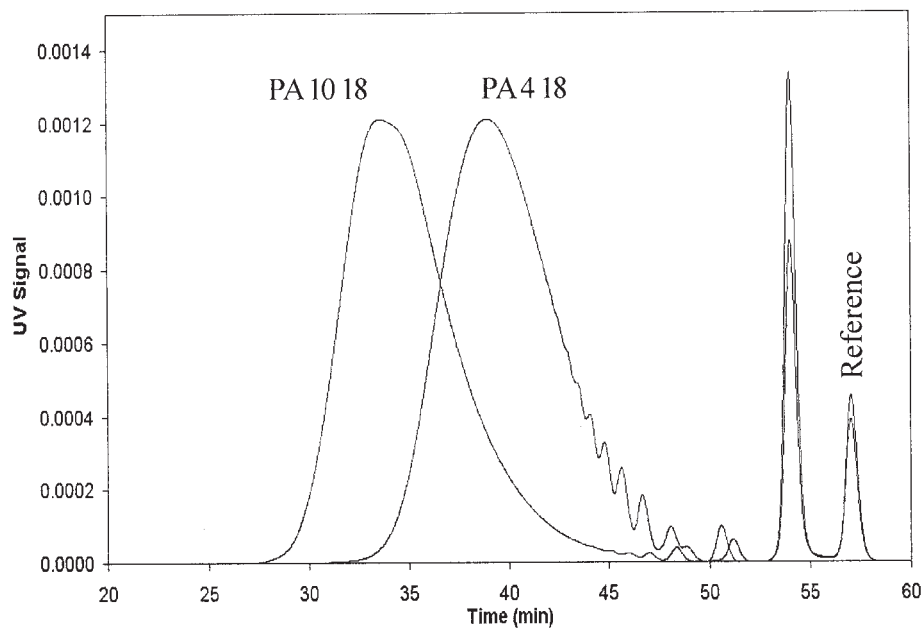


Figure 5 SEC curves of N-trifluoroacetylated polyamides 12 18 and 4 18.

TABLE III
Molecular Weights of Resulting Polyamides

Polyamide	M_n^a	M_w^a	M_z^a	M_w/M_n	M_z/M_w	DP_n^b
12 18	21065	43065	71343	2.04	1.66	44.1
10 18	19159	41347	72285	2.16	1.75	42.6
8 18	9389	19650	33185	2.09	1.69	22.2
6 18	10283	19377	29087	1.88	1.50	26.1
4 18	5063	9982	15313	1.97	1.53	13.8
2 18	1394	4090	6286	2.93	1.54	4.1

^a Evaluated as a linear nylon 6 equivalent.

^b Calculated considering the correct repeating unit mass.

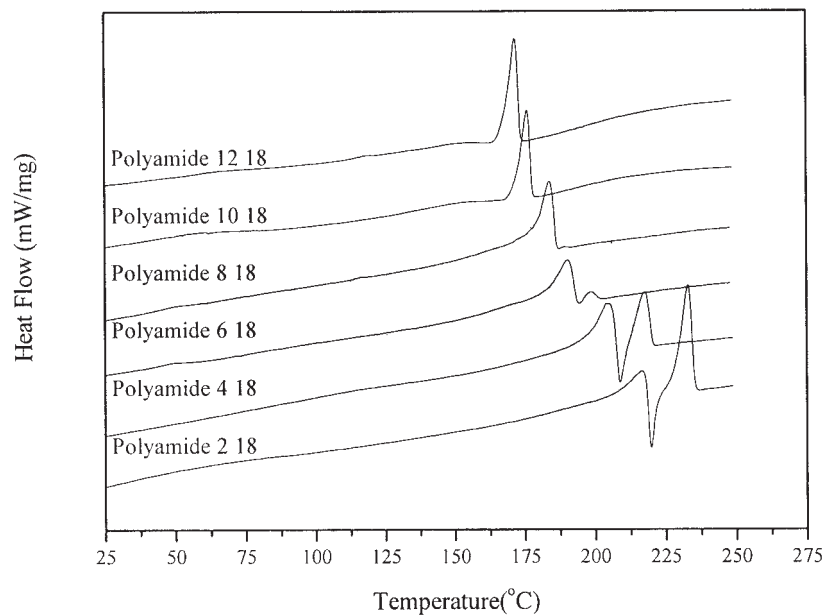


Figure 6 DSC patterns of the synthetic polyamides.

TABLE IV
Melting, Glass-Transition, and Decomposition
Temperatures of Synthetic Polyamides

Polyamide	T_g by DMA (°C)	T_m (°C)	T_d (°C)
12 18	43	172	457
10 18	46	176	459
8 18	36	184	462
6 18	47	199	457
4 18	—	218	452
2 18	—	233	427

room temperature. Accordingly, we compared the estimated SEC DP_n value with the corresponding data from the $^1\text{H-NMR}$ run in quantitative conditions by accounting for the different molecular weights of repeating units. In the case of polyamide 4 18, a DP_n value of 13.5 was obtained from SEC; this value is in excellent agreement with the value of 12.5 from the $^1\text{H-NMR}$ spectrum. An equivalent estimation of the DP_n for all polymers was done accordingly (Table III).

Thermal and mechanical analysis

DSC measurements were carried out from -10 to 250°C for all polymers (Fig. 6). The melting temperatures (T_m) are reported in Table IV. As expected, the T_m values of the polyamides are related to the concentration of amide groups and decrease from polyamide 2 18 to polyamide 12 18. Double-melting phenomena were present in several polyamides, which were devoted to the melting and recrystallizing of crystalline phases.^{17,18} In the present case, two thermal peaks

were clearly observed in polymers with short chain diamines. In the heating process, a part of thin lamellae began melting. Then, the thick parts remained unmelted and became the cores. Finally, the melted polyamide recrystallized around them. This led to the clear exothermic peaks in the DSC curves.

TGA patterns are shown in Figure 7 for the polyamides in our study. The thermal decomposition temperatures (T_d) are presented in Table IV. Except for polyamide 2 18, all polyamides began to decompose at about 340°C and the T_d values were around 450°C . The poorer stability of polyamide 2 18 can be related to low molecular mass and to the intrinsic low stability of the ethylenediamine unit.

DMA

The dynamic mechanical properties were measured. No peculiar behavior was observed in the DMA curves. Corresponding T_g values are reported in Table IV because the T_g corresponds to the movement of segments in the polymer chains.

CONCLUSION

Polyamides 12 18, 10 18, 8 18, 6 18, 4 18, and 2 18 were synthesized using a step heating melt polycondensation procedure. The chemical structure of the resulting polymers was confirmed by spectroscopic methods. High molecular masses were obtained only in the presence of an excess of diamine and when the diamine possessed low volatility. The number-average molecular weights of polyamides 12 18, 10 18, 8 18,

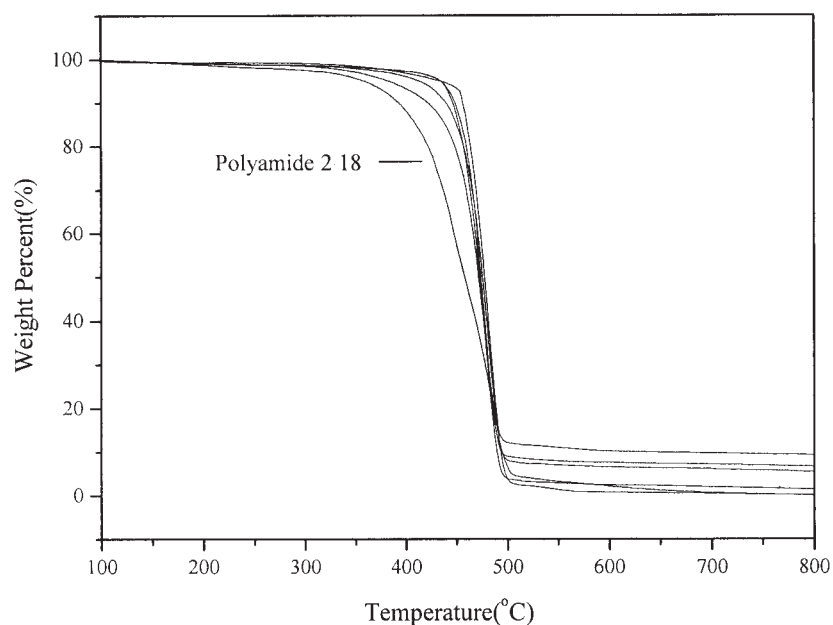


Figure 7 TGA profiles of the synthetic polyamides.

and 6 18 were between $(0.94 \text{ and } 2.1) \times 10^4$ Da. An excellent correlation between SEC and $^1\text{H-NMR}$ data was demonstrated in the measurement of the degree of polymerization. The T_m of the polyamides decreased with a decline in the amide density along the molecular chains. Moreover, no significant variation was observed in the T_g and T_d for polyamides under consideration.

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