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Synthesis and characterization of novel even–odd nylons based on undecanedioic acid

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Abstract

A series of novel even–odd nylons were synthesized through step-heating melting-polycondensation of undecanedioic acid with various diamines. The synthesized polyamides were characterized comprehensively by means of elements analysis, intrinsic viscosity, Fourier transform infrared (FTIR) spectroscopy, nuclear magnetic resonance (NMR), Raman spectra, thermogravimetry analysis (TGA) and differential scanning analysis (DSC). The obtained products except nylons 4 11 and 2 11 have intrinsic average molecular weights ranging from 1.3×10^4 to 2.5×10^4. Nylons 4 11 and 2 11 have intrinsic average molecular weights of 8400 and 7200, respectively. The melting temperatures of this series of even–odd nylons decrease with declining the concentration of hydrogen bonds. Furthermore, the dynamic mechanical analysis (DMA) was performed for nylons 12 11, 10 11, 8 11 and 6 11. The glass transition temperatures of nylons 12 11, 10 11, 8 11 and 6 11 are in the range of 40.1–45.7 °C.

Keywords: Even–odd nylons; Undecanedioic acid; Melting-polycondensation

1. Introduction

The polyamides family can be subdivided to six categories, i.e. even–even, odd–odd, even–odd, odd–even, even and odd polyamides [1–7], according to their composition. The six types of polyamides have their corresponding hydrogen bond structures, respectively, which exert a tremendous influence on their properties [8,9]. On the other hand, the concentration of the hydrogen bonds in polyamides also strongly effects their properties [7]. In even–even, even and odd polyamides, the –NH- and –CO-groups can fully form hydrogen bonds between molecular chains and the interaction between –NH- and –CO-groups is saturated. Alternatively, considering the extended conformation of the molecular chain, in even–odd polyamides only one part of –NH- and –CO-groups constitute hydrogen bonds and the other part of –NH- and –CO-groups remain free. Fig. 1 shows the structure of hydrogen bonds of polyamide 6 11, in which a half of –NH- and –CO-groups form hydrogen bonds whatever the hydrogen-bonded molecular chains array parallely or antiparallely. However, Kinoshita reported a different conformation for even–odd nylons in which all the hydrogen bonds can be established [10]. Therefore, even–odd nylons have a different crystal structure from even–even nylons, resulting in some different properties from even–even nylons. Even–even, even and odd polyamides, such as polyamides 66, 1012, 6, 11, were widely studied and used in industry in the past decades [11–13,8]. To our knowledge, only a few even–odd polyamides, such as nylons 69 and 65, have been investigated [3,14]. In order to explore the relationship between the properties of polyamides and the structure of hydrogen bonds, it seems necessary to comprehensively study the novel even–odd polyamides.

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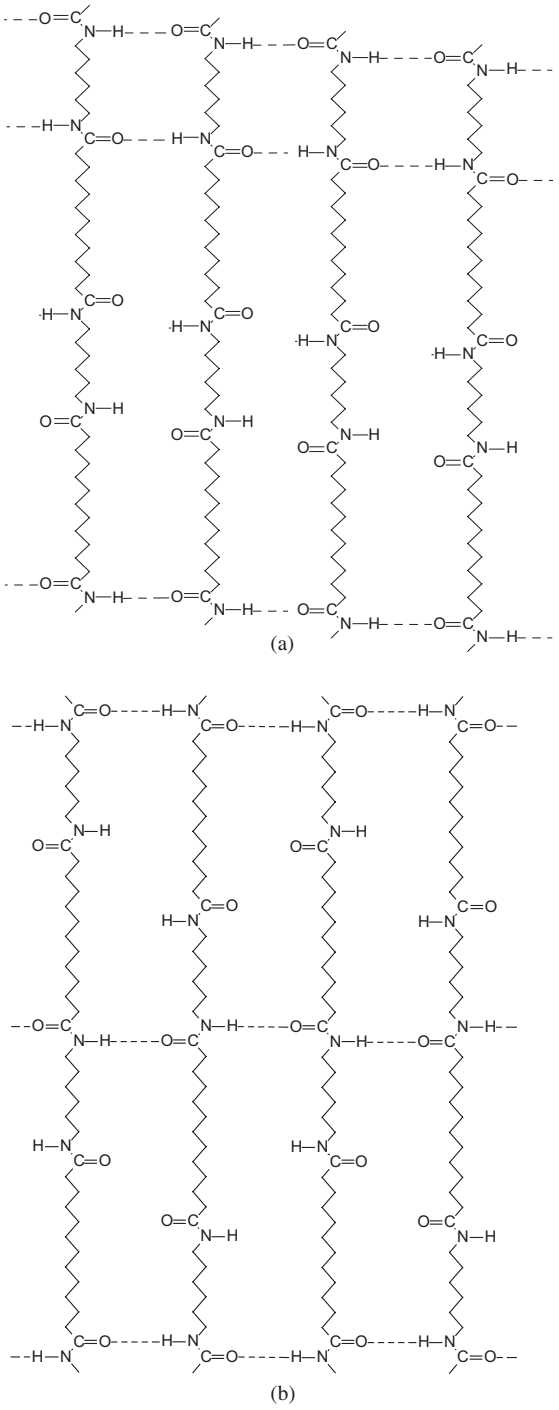

Fig. 1. The structure of hydrogen bonds in polyamide 6 11. (a) Hydrogen-bonded molecule chains array parallely, (b) hydrogen-bonded molecule chains array antiparallely.

In this paper, a series of novel even–odd polyamides based on undecanedioic acid, including polyamides 12 11, 10 11, 8 11, 6 11, 4 11 and 2 11, were successfully synthesized via step-heating melting-polycondensation. Fig. 2 illustrates the computer-generated space filling structures of polyamide 12 11 repeat units under consideration. The study on the crystal structure of the even–odd polyamides will be reported next time.

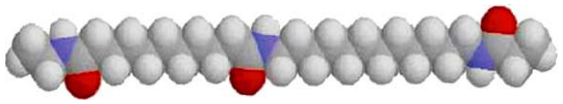

Fig. 2. Computer-generated space filling structure of nylon 12 11. Color code: hydrogen, white; carbon, grey; nitrogen, blue; oxygen, red. (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.)

2. Experimental

2.1. Materials

Undecanedioic acid (ACROS ORGANICS), 1,12-diaminododecane (Aldrich), 1,10-diaminodecane (Aldrich), 1,8-diaminooctane (Aldrich), 1,6-diaminohexane (Aldrich), 1,4-diaminobutane (Aldrich) and ethylenediamine (Aldrich) were used as received.

2.2. Synthesis

Undecanedioic acid was dissolved in absolute alcohol at 40 °C. The solution was added slowly into absolute alcohol solution of the corresponding diamine with vigorously stirring. The white diamine-diacid salt was precipitated immediately. The mixture was continued to stir for 30 min at 40 °C and cooled to room temperature. Then the salt was filtered with Buchner funnel and washed with absolute alcohol repeatedly before it was dried in a vacuum desiccator overnight. Finally, the salt was obtained as white powder.

The obtained salt was filled into a tailor-made glass tube and a slightly excess of the corresponding diamine was added to compensate its volatilization during the polymerization. The glass tube was fitting into the autoclave and the autoclave was evacuated and flushed with nitrogen for three times. Subsequently, the autoclave was heated to T_1 with the nitrogen pressure of 10 atm when the polycondensation reaction started. After 2 h under this condition, the reaction temperature was increased to T_2 and was kept for another 2 h with the nitrogen pressure decreasing to 5 atm. The last-step polymerization was carried out at T_3 after the autoclave was evacuated to 40 Pascal. Two hours later, the autoclave temperature was cooled to room temperature and the reaction was stopped. Finally, the ivory-white product was obtained. Table 1 shows the reaction temperature and yield of the polyamides under study.

Table 1
Polymerization temperature and yields of the polyamides

Nylons	*T_1 (°C)	T_2 (°C)	T_3 (°C)	Yield (%)
Nylon 12 11	170	190	210	90
Nylon 10 11	180	195	215	88
Nylon 8 11	190	205	220	87
Nylon 6 11	195	210	225	86
Nylon 4 11	200	220	240	80
Nylon 2 11	210	240	270	76

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

2.3. Characterization

The obtained products were characterized comprehensively by several methods including FTIR, Raman spectra, ^{1}H NMR, ^{13}C NMR, element analysis, intrinsic viscosity, differential scanning analysis (DSC) and thermogravimetry analysis (TGA). Furthermore, DMA was applied for polyamides 12 11, 10 11, 8 11 and 6 11.

IR measurement was carried out on a Perkin-Elmer Paragon 1000 PC Fourier infrared (FTIR) spectrometer at frequencies from 500 to 4000 cm^{-1} with a resolution of 0.5 cm^{-1}. Raman spectra were collected on a Bruker Equinox-55 Raman spectrometer. ^{1}H NMR spectra were obtained from a Varian Mercury Plus spectrometer at 400.155 MHz while ^{13}C NMR spectra were measured at 100.626 MHz with trifluoroacetic acid used as solvents. Element analysis was resulted from a Perkin–Elmer 2400 II CHN/O analyzer at 975 °C under nitrogen condition. Intrinsic viscosity in dichloroacetic acid was determined in an Ubbelodhe viscometer at 25 ± 0.1 °C. The DSC curves were recorded on a Perkin–Elmer Pyris-1 differential scanning calorimeter calibrated the temperature with indium at the rate of 10 °C min^{-1}. TGA was performed on a Perkin-Elmer TGA-7 thermobalance with heating rate at 20 °C min^{-1} and nitrogen was used as the purge gas. DMA was measured on a RSI Orchestrator at a strain percent of 0.01% and a frequency of 1 Hz.

3. Results and discussion

3.1. Synthesis of nylons 12 11, 10 11, 8 11, 6 11, 4 11 and 2 11

A series of novel even–odd nylons based on undecanedioic acid were synthesized through step-heating melting-polycondensation. In order to assure the accurate equivalent ratio of undecanedioic acid and the corresponding diamine, the salt of the diacid and the diamine was needed to prepare before melting-polycondensation. After the salt was dried enough in a desiccator, it was filled into a glass-round stoppered tube and an excess of the corresponding diamine was added to compensate the loss. The high pressure was applied in the early stage of polycondensation to minimize the loss of diamine. Step-heating method was adopted in the process to make the reaction feasible and reduce the evaporation of diamine as well. In the last step the reaction system was evacuated to remove the water generated during the polycondensation and make the molecular weight of the polyamides higher. Finally, the expected polyamides were prepared.

3.2. Intrinsic viscosity and M_η

The intrinsic viscosities of the synthesized polyamides are listed in Table 2. The viscosity average molecular weight is derived from Mark–Houwink equation [15]:

$$[\eta] = 0.005 + 3.52 \times 10^{-3}\ M^{0.551}$$

It is well known that the Mark–Houwink equation is deduced for nylon 66. Here, the molecular weight of the synthesized even–odd polyamides derived from this equation has deviation. However, for a series of even–odd nylons, the relative molecular weight can be compared using it. The obtained products except polyamides 4 11 and 2 11 have high viscosity average molecular weights above 1.3×10^4. Polyamides 4 11 and 2 11 have relatively low molecular weights of 8400 and 7200. It is the different volatility of various diamines that make such a remarkable difference in the molecular weight of the prepared polyamides. Therefore, through the method described above, it was somewhat difficult to obtain a high molecular weight polyamide from the diamine with short methylene segment, such as ethylenediamine and 1,4-diaminobutane.

3.3. Infrared spectra

Infrared spectra of the polyamides are shown in Fig. 3. All the characteristic absorption bands of amide groups and methylene segments of polyamides display: 3290 cm^{-1} (Amide A), 3080 cm^{-1} (Amide B), 1640 cm^{-1} (Amide I, C=O stretch), 1540 cm^{-1} (Amide II, C–N stretch and CO–N–H bend), 940 cm^{-1} (Amide IV, C–CO stretch), 721 cm^{-1} (CH_2 wag), 690 cm^{-1} (Amide

Table 2
Intrinsic viscosity [η] and viscosity average molecular weights (M_η) of the prepared polyamides

Nylons	[η] (dl/g)	M_η
Nylon 12 11	0.94	2.5×10^4
Nylon 10 11	0.91	2.4×10^4
Nylon 8 11	0.77	1.7×10^4
Nylon 6 11	0.66	1.3×10^4
Nylon 4 11	0.51	8.4×10^3
Nylon 2 11	0.47	7.2×10^3

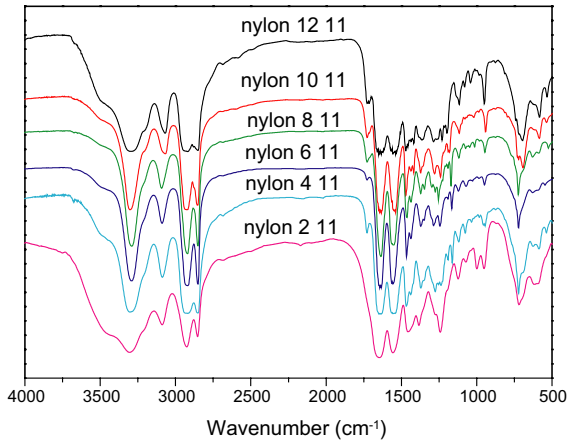

Fig. 3. Infrared spectra of the obtained products.

V,N–H out of plane bend) and 580 cm^{-1} (Amide VI, C═O out of plane bend). It is noticed that a weak absorption peak appears at 1680 cm^{-1}. Huczkowski pointed out that oligoamides decomposited from polyamide 66 would appear a absorption bands at 1680 cm^{-1} [16]. The weak absorption peak at 1680 cm^{-1} indicates that there is a small account of oligoamides in the prepared even–odd nylons.

3.4. Raman spectra

Fig. 4 displays the Raman spectra of the polyamides. Compared to the characteristic bands of the polyamides in infrared spectra, the corresponding absorption bands of amide groups in Raman spectra locate in the same region but present relatively weak intensity. In addition, the intensities of the CH_2 absorption bands at 2900 and 1440 cm^{-1} increase with the methylene segment length between amide groups.

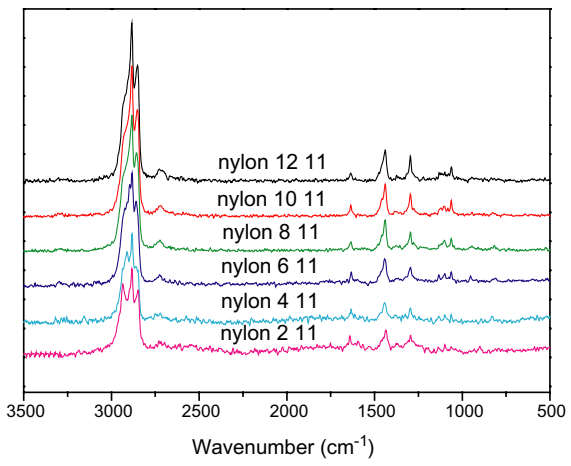

Fig. 4. Raman spectra of the resulting products.

3.5. NMR analysis

Figs. 5 and 6 present ^1H and ^{13}C NMR spectra of the prepared polyamides in trifluoroacetic acid, respectively. The chemical shift at 3.1 ppm in ^1H NMR originates from the protons next to the NH group while that at 2.2 ppm comes from the protons adjacent to the CO group. The peak at 11.6 ppm is assigned to solvent. The weak peak at about 8.0 ppm stems from the proton in the NH group. It is the interaction of hydrogen bonds between the NH group and the solvent molecule that makes the peak shift downfield. The rest of peaks belong to the other protons in the aliphatic chains.

^{13}C NMR spectra further approve the resulting products with expected chemical structure. The chemical shifts at 42.7 and 33.1 ppm are due to the carbons next to the NH and CO groups, respectively. The peak at 179.0 ppm results from carbonyl groups. The peaks below 30 ppm are assigned to the rest carbons of alkane segment. The peaks between 100 and 170 ppm are attributed to the solvent. Table 3 summarizes the shifts of the peaks of the prepared polyamides. There are no other peaks in the spectra, which excludes the branching and other unanticipated chemical structure in the synthesized nylons.

3.6. Element analysis

The measured contents of carbon, hydrogen, nitrogen and oxygen of the prepared polyamides are listed in Table 4. The calculated values are presented for comparison. Due to the easy absorption of water in polyamides, the oxygen contents of polyamides are higher than the theoretical values. The results demonstrate that the measured results are in agreement with the theoretical values.

3.7. Thermogravimetry analysis

The decomposition temperatures obtained from Fig. 7 are listed in Table 4. The polyamides under study have the high decomposition temperatures at about 460 °C except that nylon 2 11 decomposes at 440 °C. It is the low molecular weight of polyamide 2 11 that leads to the relatively low decomposition temperature.

3.8. Differential scanning calorimetry

The DSC thermograms of the synthesized polyamides are shown in Fig. 8. In order to reduce the effect of previous treatment of the prepared nylons, the samples were firstly heated until melt at the rate of 10 °C min^{-1} and then cooled to room temperature at the same rate. At last, the samples were heated until melt at the rate of 10 °C min^{-1}. The DSC curves shown in Fig. 8 are the second heating process. The melting tempera-

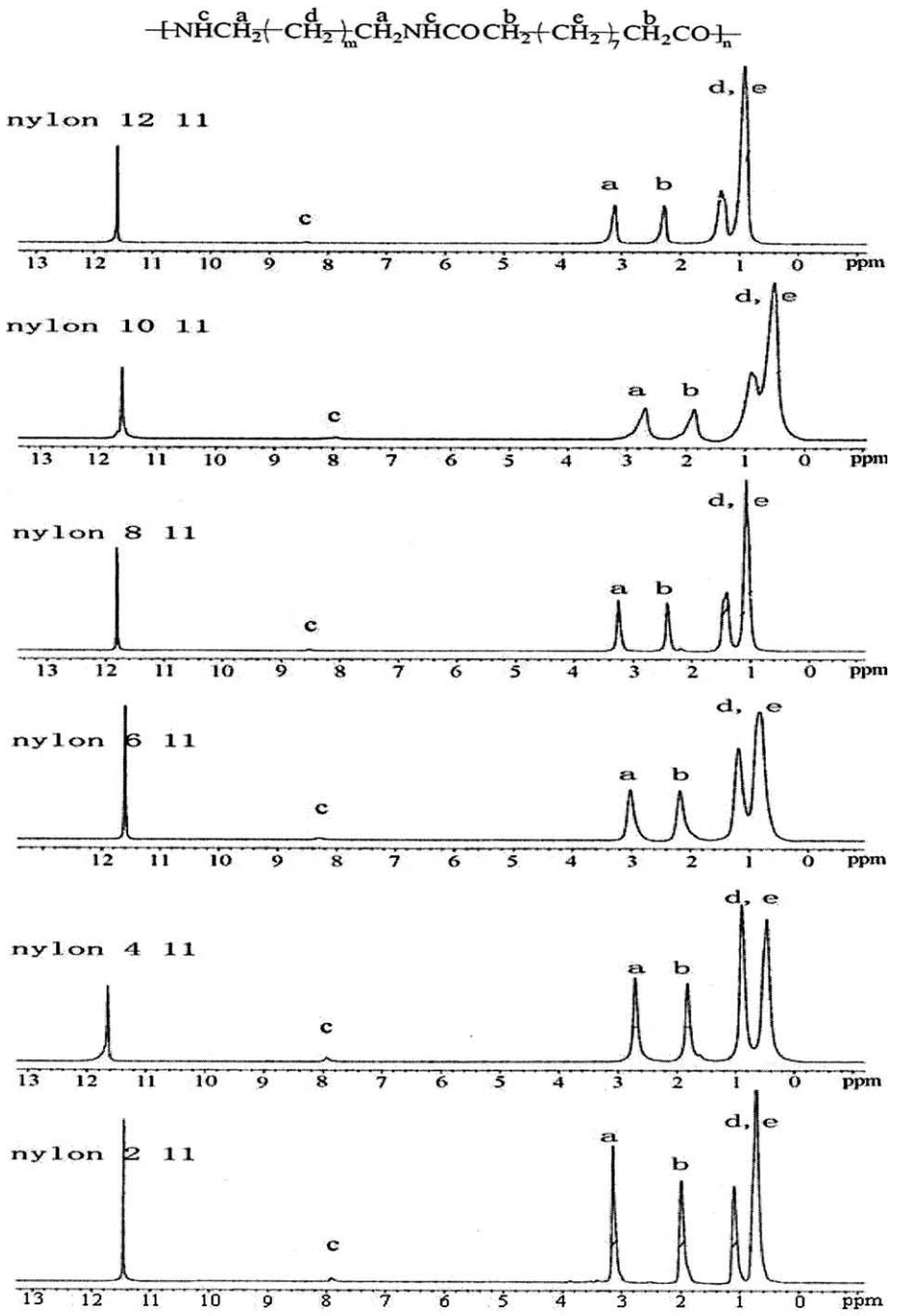

Fig. 5. ^{1}H NMR spectra of the prepared polyamides.

tures of the polyamides increase with decreasing the methylene segment length between the amide groups. In the series of the prepared polyamides, nylon 12 11 has the lowest melting temperature at 181 °C and nylon 2 11 has the highest melting temperature at 268 °C. It is the different concentration of hydrogen bonds in the polyamides that makes so much difference in melting temperatures of the obtained polyamides. Furthermore, all the polyamides exhibit the double-melting endotherm, which is a common phenomenon in even–even polyamides [12]. For some polyamides, there are obvious exothermic perks shown in Fig. 8. Li reported that

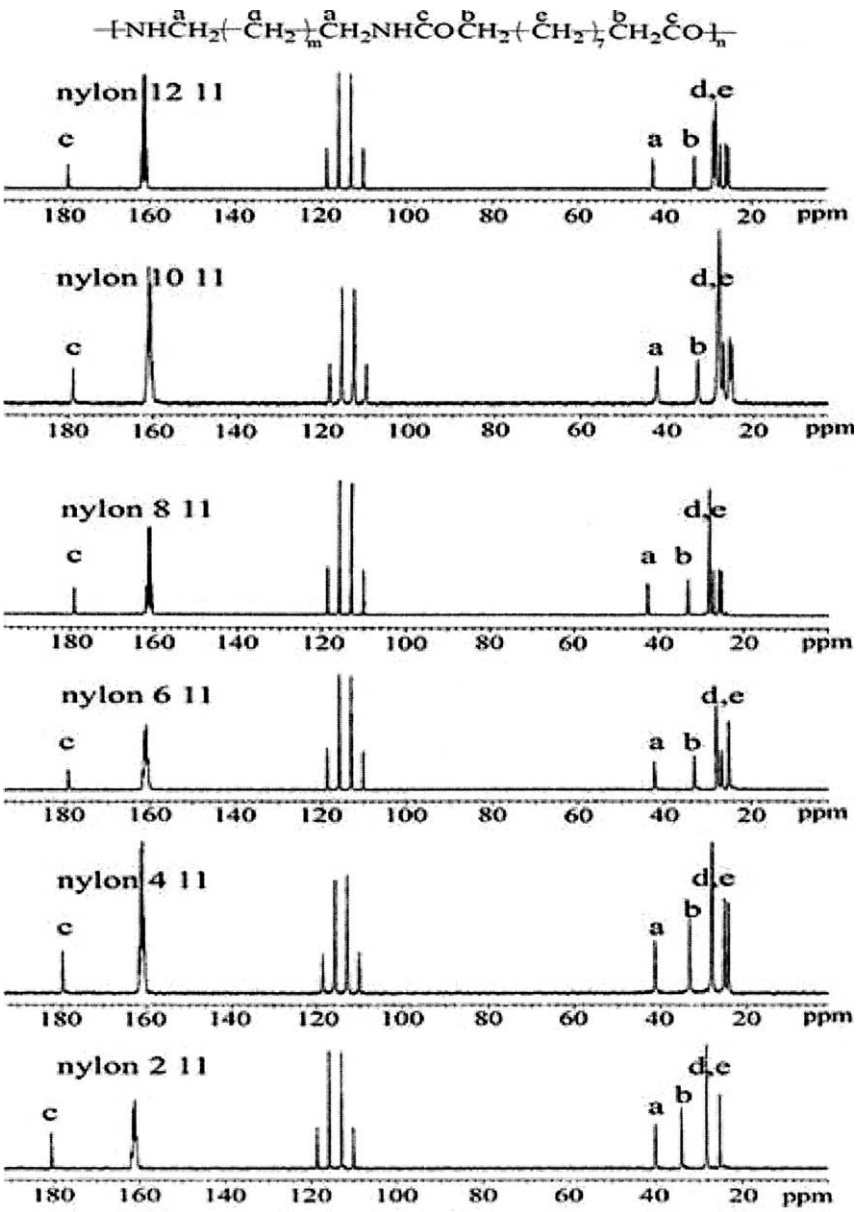

Fig. 6. ^{13}C NMR spectra of the synthesized polyamides.

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

Nylons	c	a		b		d,e	
		^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C
Nylon 12 11	179.0	3.11	42.7	2.27	33.2	<1.30	<28.7
Nylon 10 11	179.1	3.16	42.5	2.22	33.1	<1.25	<28.2
Nylon 8 11	179.1	3.22	42.6	2.21	33.1	<1.26	<28.1
Nylon 6 11	179.2	3.26	42.3	2.17	33.1	<1.19	<28.0
Nylon 4 11	179.3	3.29	41.9	2.22	33.2	<1.26	<28.0
Nylon 2 11	180.3	3.15	40.0	2.21	33.4	<1.19	<28.1

Table 4
Elemental analysis data for the resulting polyamides

Nylons	Carbon (%)		Hydrogen (%)		Nitrogen (%)		Oxygen (%)	
	Calc.	Meas.	Calc.	Meas.	Calc.	Meas.	Calc.	Meas.
Nylon 12 11	72.58	72.20	11.65	11.94	7.36	7.16	8.41	8.70
Nylon 10 11	71.54	71.45	11.44	11.41	7.95	7.86	9.07	9.28
Nylon 8 11	70.32	70.17	11.18	11.23	8.64	8.59	9.86	10.01
Nylon 6 11	68.88	68.76	10.88	10.75	9.45	9.36	10.79	11.13
Nylon 4 11	67.13	67.02	10.51	10.50	10.44	10.38	11.92	12.10
Nylon 2 11	64.96	64.79	10.06	10.09	11.66	11.42	13.32	13.70

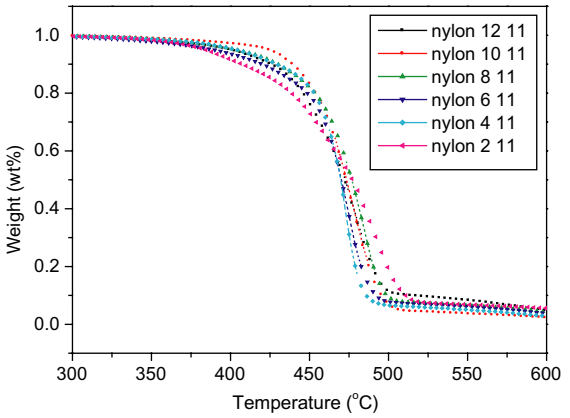

Fig. 7. TGA plots of the prepared polyamides.

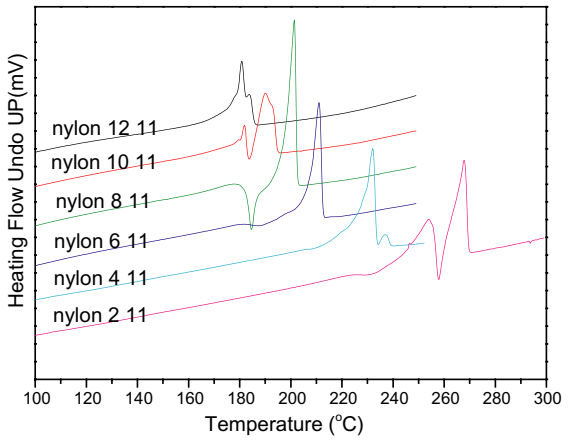

Fig. 8. DSC thermograms of the synthetic polyamides.

nylons appear in the multiple melting behaviors in the melt-crystallized samples [17]. In the heating process of the polyamide sample, a part of thin lamellas begin melting. Then the thick parts retain unmelted and become the cores. At last, the melted polyamide recrystallizes around them. This leads to the clear exothermic peaks in the DSC curves.

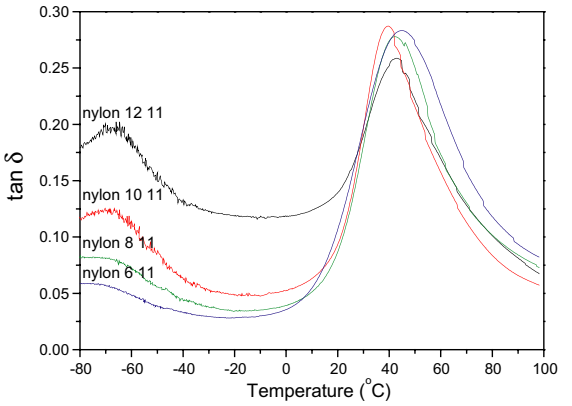

Fig. 9. DMA curves of the synthetic polyamides.

3.9. Dynamic mechanical analysis

Fig. 9 presents the dynamic mechanical analysis (DMA) curves of polyamides 12 11, 10 11, 8 11 and 6 11 and gives the tan δ of those under study. Polyamides 4 11 and 2 11 are too fragile to be measured in DMA due to their low molecular weights. In Fig. 9, two obvious transition behaviors at about 40 and −70 °C are defined as α and β relaxation, respectively. As known, the α relaxation is responding to the glass transition temperature while the β relaxation reflects the mobility of hydrogen-bonded amide groups [18–20]. The glass transition temperatures of the prepared polyamides range from 40.1 to 45.7 °C. Table 5 summarizes the glass

Table 5
T_g[a], T_m[b] and T_d[c] of the prepared polyamides

Nylons	T_g (°C)	T_m (°C)	T_d (°C)
Nylon 12 11	42.8	181	458
Nylon 10 11	40.1	190	452
Nylon 8 11	42.1	201	458
Nylon 6 11	45.7	212	454
Nylon 4 11	–	232	457
Nylon 2 11	–	268	440

[a] The glass transition temperature.
[b] The melting temperature.
[c] The decomposition temperature.

transition temperatures, the melting temperatures and the decomposition temperatures of the synthesized polyamides.

4. Conclusion

In the work, a series of novel even–odd polyamides 12 11, 10 11, 8 11, 6 11, 4 11 and 2 11 were synthesized by step-heating melting-polycondesation. The characterization of FTIR, Raman, NMR and element analysis confirms the obtained products have the expected chemical structure and composition. The viscosity average molecular weights of the synthesized polyamides arrange from 7200 to 25,000. Polyamides 4 11 and 2 11 have low viscosity average molecular weights due to the high volatility of diaminobutane and ethylenediamine. The thermal analyses, including TGA, DSC and DMA, give the decomposition temperatures, the melting temperatures and the glass transition temperatures of the even–odd polyamides. Polyamides 4 11 and 2 11 cannot be performed DMA because of their lower molecular weights. The melting temperatures of the even–odd polyamides increase with declining the length of the methylene units between the amide groups. The polyamides present the decomposition temperatures at about 460 °C except polyamide 2 11. It is the different density of hydrogen bonds in polyamides that makes them present different melting temperatures.

Acknowledgements

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