Synthesis and Characterization of Novel Odd–Even Nylons Based on Eicosanedioic Acid

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ABSTRACT: A series of novel odd–even nylons based on eicosanedioic acid, including nylons 11/20, 9/20, 7/20, 5/20, and 3/20, were prepared through step-heating melting polycondensation with various diamines, and the products were comprehensively characterized. The results of FTIR, Raman spectra, NMR, and elemental analysis confirmed that the synthesized polyamides had the expected chemical structures. The viscosity-average molecular weights of the obtained polyamides were in the range of 6.0×10^3–1.4×10^4. The melting points of the nylons, determined by differential scanning calorimetry, changed from 167 to 194°C. Thermogravimetric analysis gave the decomposition temperatures of the obtained nylons at about 460°C, except for nylon 3/20. Furthermore, dynamic mechanical analysis (DMA) was applied to nylons 11/20, 9/20, 7/20, and 5/20. The glass-transition temperatures, measured by DMA, ranged from 29 to 52°C. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 2066–2071, 2004

Key words: polyamides; synthesis; polycondensation; differential scanning calorimetry (DSC); odd–even nylons

INTRODUCTION

Polyamides, or nylons, have been widely used in industry as engineering materials because of their excellent properties, such as high modulus, eminent toughness, abrasion resistance, and good temperature stability, since polyamide 6/6 was first synthesized in 1934. Over the years, they have been studied widely and comprehensively in various scientific investigations.[1–5] In recent years, many even–even nylons with long alkane segments have been synthesized and their properties have also been investigated.[6–8] As the length of the alkane segment in nylons increases, the concentration of hydrogen bonds in nylons gradually decreases, and thus these nylons exhibit desirable properties such as low melting temperature, low density, poor water affinity, and ease of processing. These polyamides are expected to perform with properties analoguous to those of polyethylene as the density of H-bonds declines. Some researchers used them as "compatibilizers" in preparation of blends of commercial nylons and polyolefins.[9–11] Like even–even nylons mentioned above, odd–even polyamides with long alkane segments also have low density of H-bonds and are also characterized by these attractive properties. Therefore, they constitute another kind of compatibilizer for this purpose. On the other hand, odd–even nylons have crystalline structures different from those of even–even nylons because of the odd methylene units in their diamine segments. Some odd–even nylons, such as nylons 56, 5/10, and 92, have been investigated in the past decades.[12–14] However, the odd–even polyamides with long alkane segments have never been synthesized before. Consequently, it is essential to prepare some novel odd–even nylons with long methylene segments and study their properties and crystalline structures.

In this work, the novel odd–even nylons, including nylons 11/20, 9/20, 7/20, 5/20, and 3/20, were synthesized by step-heating melting polycondensation. All the prepared polyamides are based on eicosanedioic acid, which introduces long methylene segments into the molecular chain between every two –CO– groups. Nylons 9/20 and 11/20 have very low melting temperatures at 170 and 167°C, respectively, which are close to the melting temperatures of polyethylene and polypropylene. Therefore, these nylons are the ideal candidates for use as compatibilizer of the blend of commercial nylons and polyolefins.

EXPERIMENTAL

Materials

Eicosanedioic acid [Tokyo Chemical Industry (TCI), Tokyo, Japan], 1,11-diaminoundecane (TCI), 1,9-dia-

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TABLE I
Polymerization Temperatures and Yields of the Nylons[a]

Nylon	T_1 (°C)	T_2 (°C)	T_3 (°C)	Yield (%)
Nylon 11/20	150	170	190	86
Nylon 9/20	155	175	195	84
Nylon 7/20	160	180	200	81
Nylon 5/20	170	190	210	80
Nylon 3/20	170	190	210	76

[a] T_1, the first-step polymerization; T_2, the second-step polymerization; T_3, the last-step polymerization.

minononane (Acros Organics, Morris Plains, NJ), 1,7-diaminoheptane (Acros Organics), 1,5-diaminopentane (Acros Organics), and 1,3-diaminopropane (Acros Organics) were used as received.

Synthesis

Nylons $x/20$ (x = 3, 5, 7, 9, 11) were synthesized by means of salt-forming and melting polycondensation as follows: eicosanedioic acid was dissolved in absolute alcohol and was added slowly to an absolute alcohol solution of the corresponding diamine with vigorous stirring. A white salt was precipitated after the solution was stirred for 30 min. Before it was dried in a vacuum desiccator overnight, the salt was filtered with a Buchner funnel (Indigo Instruments, Waterloo, Ontario, Canada) and washed repeatedly with absolute alcohol. Finally, the salt was obtained as a white powder.

The obtained salt was charged to a tailor-made glass tube and a slight excess of the corresponding diamine was added to compensate for the volatilization during the polymerization. The glass tube was fitted into the autoclave. The autoclave was then evacuated and flushed three times with nitrogen. Subsequently, the autoclave was heated to the melting temperature, in a nitrogen environment, at which point the polycondensation reaction started. After 4 h under this condition, the autoclave was evacuated to 40 Pa for further polycondensation. Two hours later, the autoclave was cooled to room temperature and the reaction was stopped. Finally, an ivory-white product was obtained.

Characterization

The obtained polymers were characterized comprehensively by FTIR, Raman spectra, ^{1}H-NMR, ^{13}C-NMR, elemental analysis, intrinsic viscosity, DSC, and TGA. Furthermore, DMA was applied for investigation of nylons 11/20, 9/20, 7/20, and 5/20. Nylon 3/20 was too fragile to be measured by DMA. IR measurement was carried out on a Perkin–Elmer Paragon 1000 PC FTIR spectrometer (Perkin Elmer Cetus Instruments, Norwalk, CT) with a resolution of 0.5 cm^{-1}. Raman spectra were collected on an Equinox-55 Raman spectrometer (Bruker Instruments, Darmstadt, Germany). ^{1}H-NMR spectra were obtained from a Varian Mercury Plus spectrometer (Varian Associates, Palo Alto, CA) at 400.155 MHz, whereas ^{13}C-NMR spectra were measured at 100.626 MHz with trifluoroacetic acid used as solvents. Elemental analysis was determined by use of a Perkin–Elmer 2400II CHN/O analyzer at 975°C under nitrogen condition. Intrinsic viscosity in dichloroacetic acid was determined in a Ubbelohde viscometer (Cannon–Ubbelohde, State College, PA) at 25 ± 0.1°C. The DSC curves were recorded on a Perkin–Elmer Pyris-1 differential scanning calorimeter, calibrating the temperature with indium. Thermogravimetric analysis was performed on a Perkin–Elmer TGA-7 thermobalance, at a heating rate at 20°C min^{-1}, and nitrogen was used as the purge gas. Dynamic mechanical analysis was measured using RSI Orchestrator software (Rheometric Scientific, Piscataway, NJ) at a strain percent of 0.01% and a frequency of 1 Hz.

RESULTS AND DISCUSSION

Synthesis of nylons 11/20, 9/20, 7/20, 5/20, and 3/20

The step-heating melting polycondensation was applied to prepare the novel odd–even nylons based on eicosanedioic acid. To ensure the precise equivalent ratio of eicosanedioic acid and the corresponding diamine, it is necessary to form the salt of eicosanedioic acid and the corresponding diamine in advance of melting polycondensation. The step-heating method was adopted in the process to reduce the evaporation of the diamine and to ensure the feasibility of the reaction. In the last step, the reaction autoclave was evacuated to remove the water generated during the reaction process and to ensure a high molecular weight of the synthesized polyamide. In addition, although 10% diaminopropane was added to the glass tube to compensate for the loss of diaminopropane, it was impossible to prepare nylon 3/20 with high molecular weight by melting polycondensation. The reaction conditions are listed in Table I.

TABLE II
Intrinsic Viscosity and Viscosity-Average Molecular Weights of the Prepared Polyamides (M_η)

Nylon	[η] (dL/g)	M_η
Nylon 11/20	0.67	1.4×10^4
Nylon 9/20	0.59	1.1×10^4
Nylon 7/20	0.57	1.0×10^4
Nylon 5/20	0.56	9.7×10^3
Nylon 3/20	0.43	6.0×10^3

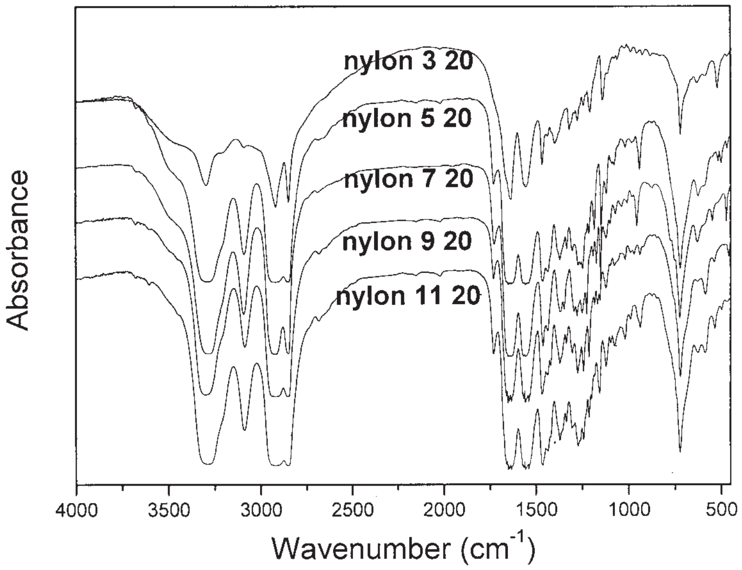

Figure 1 Infrared spectra of the obtained polyamides.

Intrinsic viscosity and M_η

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

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

The parameters of the Mark–Houwink equation are deduced for nylon 66. The molecular weights of the prepared odd–even nylons were derived from this equation, although it does not influence our comparison of the relative molecular weights of the prepared polyamides. The viscosity-average molecular weights of the prepared nylons are in the range of 6.0×10^3–1.4×10^4. Polyamide 3/20 has a low viscosity-average molecular weight of 6.0×10^3. It is difficult to obtain high molecular weight nylons based on diaminopropane because of its high evaporation through the method discussed above.

Infrared spectra

Figure 1 shows the infrared spectra of the obtained polyamides. The characteristic absorption bands of amide groups and methylene segments of odd–even

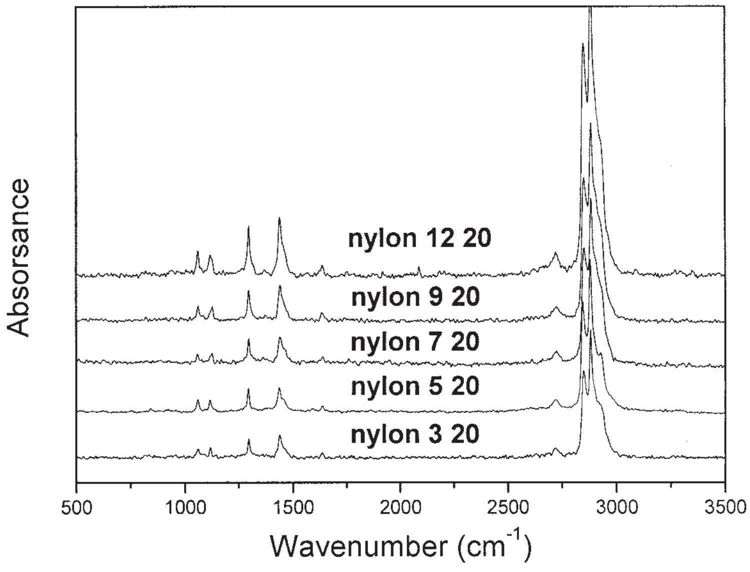

Figure 2 Raman spectra of the resulting products.

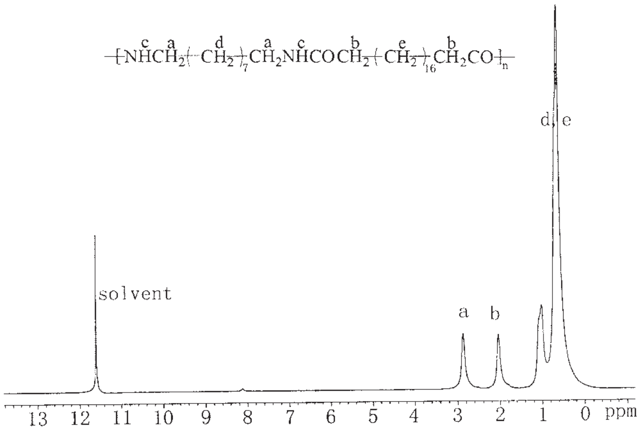

Figure 3 ^{1}H-NMR spectrum of nylon 9/20.

polyamides, and their assignments, are as follows: 3290 cm^{-1} (H-bonded N—H stretch vibration), 3080 cm^{-1} (N—H in-plane bending), 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 II, N—H out-of-plane bend), and 580 cm^{-1} (Amide IV, C═O out-of-plane bend).

Raman spectra

The Raman spectra of the polyamides are shown in Figure 2. The strong absorption bands at 2900 and 1440 cm^{-1} are attributed to the CH$_2$ segments of the prepared nylons, and their intensities increase with the methylene segment length between amide groups. On the other hand, the absorption bands of the CO groups at 1640 cm^{-1} are very weak and their intensities remain unchanged.

NMR analysis

Figures 3 and 4 show the ^{1}H- and ^{13}C-NMR spectra of polyamide 9/20 in trifluoroacetic acid, respectively. In the ^{1}H-NMR spectrum, the chemical shift at 2.9 ppm originates from the protons next to the NH group, whereas that at 2.1 ppm arises from the protons adjacent to the CO group. The peak at 11.6 ppm is attributed to the solvent. The peaks below 1.2 ppm are assigned to the other protons in the aliphatic chains. In addition, the weak peak at about 8.0 ppm is attributed to the proton in the NH group. The interaction of hydrogen bonds between the NH group and the solvent molecule causes the peak to shift downfield.

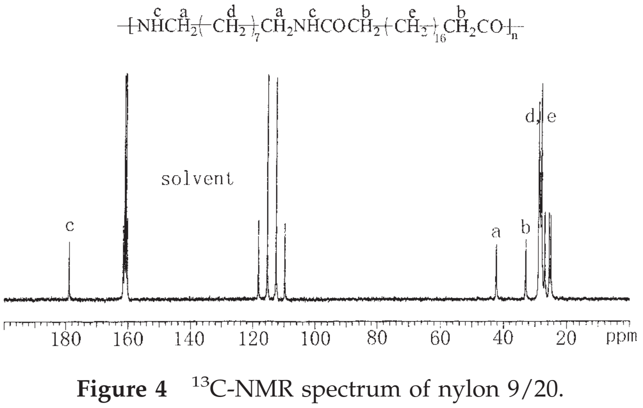

Figure 4 ^{13}C-NMR spectrum of nylon 9/20.

TABLE III
Characteristic NMR Bands of the Prepared Nylons (Chemical Shift in ppm)

Nylon[a]	c	a		b		d, e	
		^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C
Nylon 11/20	179	2.9	43	2.1	33	<1.2	<30
Nylon 9/20	179	2.9	42	2.0	33	<1.1	<29
Nylon 7/20	179	2.9	42	2.1	33	<1.1	<29
Nylon 5/20	179	2.9	42	2.1	33	<1.1	<29
Nylon 3/20	180	3.2	41	2.3	33	<1.7	<29

[a] Triflorouacetic acid as solvent.

a: α-methylene adjacent to nitrogen; b: α-methylene adjacent to carbonyl; c: carbonyl; d,e: other methylene units.

The ^{13}C-NMR spectrum of nylon 9/20 provides further evidence of its chemical structure. The chemical shifts at 42.7 and 33.1 ppm are attributed to the carbons next to the NH and CO groups, respectively. The peak at 179.0 ppm results from the carbonyl groups. The peaks below 29 ppm are assigned to the remaining carbons of the alkane segments in polyamide. The peaks between 100 and 170 ppm are attributed to the solvent. There are no other peaks in the spectrum, which excludes the branching and other unanticipated chemical structure in the synthesized nylons. The data of NMR of other nylons prepared in this work are listed in Table III.

Elemental analysis

Table IV presents the measured and calculated contents of carbon, hydrogen, nitrogen, and oxygen of the prepared polyamides. It was found that the oxygen contents of polyamides are higher than the theoretical values because polyamides have good water affinity and thus easily absorb the water in air. The results demonstrate that the measured results are in accordance with the theoretical values.

Thermogravimetic analysis

Figure 5 gives the thermogravimetric analysis spectra of the synthesized polyamides, whose obtained decomposition temperatures are listed in Table IV. The polyamides under study, except nylon 3/20, have high decomposition temperatures above 460°C. Nylon 3/20 starts to decompose at 433°C. The low molecular

TABLE IV
Elemental Analysis Data for the Resulting Polymers (%)

Nylon	Carbon		Hydrogen		Nitrogen		Oxygen	
	Calcd	Measured	Calcd	Measured	Calcd	Measured	Calcd	Measured
Nylon 11/20	75.55	75.14	12.27	12.07	5.68	5.63	6.49	7.16
Nylon 9/20	74.94	74.74	12.14	12.08	6.03	5.96	6.88	7.22
Nylon 7/20	74.26	74.13	12.00	11.61	6.41	6.28	7.33	7.98
Nylon 5/20	73.48	73.30	11.84	11.55	6.85	6.84	7.83	8.31
Nylon 3/20	72.58	72.25	11.65	11.36	7.36	7.16	8.41	8.90

weight of polyamide 3/20 is responsible for the relatively low decomposition temperature. The instability of diaminopropane is also the reason for the reduced decomposition of nylon 3/20.

Differential scanning calorimetry

The DSC curves of the prepared nylons are shown in Figure 6. In the series of odd–even nylons, nylon 11/20 has the lowest melting temperature (at 167°C) and nylon 5/20 has the highest melting temperature (at 194°C). The melting points of polyamides 11/20, 9/20, 7/20, and 5/20 increase with decreasing methylene-segment length between the amide groups. Although nylon 3/20 has the highest density of H-bonds in this series of nylons, its melting temperature is lower than the melting temperature of nylon 5/20. This can be understood because nylon 3/20 has a low molecular weight ($\sim 6.0 \times 10^3$). The melting temperatures of nylon 9/20 and 11/20 are below 170°C and close to the melting points of polyethylene and polypropylene, which make them ideal candidates for use as compatibilizer of the blend of commercial nylons and polyolefins. Furthermore, polyamides 5/20 and 3/20 exhibit double-melting endotherms, which is a common phenomenon in even–even polyamides.[7,8]

Dynamic mechanical analysis

Polyamides 11/20, 9/20, 7/20, and 5/20 were subjected to dynamic mechanical analysis (DMA). Nylon 3/20 is too fragile to be measured by DMA because of its low molecular weight. The results are presented in Figure 7. Two obvious transition behaviors at about 40 and −70°C may be observed in Figure 7(B) and are defined as α- and β-relaxation, respectively. As known, the α-relaxation responds to the glass-transition temperature, whereas the β-relaxation reflects the mobility of hydrogen-bonded amide groups.[16,17] The glass-transition temperatures of the measured polyamides increase, from 29 to 52°C, with the increment of the density of H-bonds in nylons. Table V summarizes the glass-transition temperatures, the melting temperatures, and the decomposition temperatures of the synthesized polyamides. From Figure 7(A), it may be observed that the storage moduli of the prepared nylons are very high. Low melting temperatures and high moduli are two excellent properties for the synthesized odd–even polyamides.

CONCLUSIONS

A series of novel odd–even polyamides based on eicosanedioic acid, including nylons 11/20, 9/20, 7/20, 5/20, and 3/20, were synthesized through step-heating melting polycondensation. Elemental analysis, FTIR, NMR, and Raman spectra confirmed the chemical structure of the prepared nylons, whose viscosity-average molecular weights ranged from 6.0×10^3 to 1.4×10^4. Nylon 3/20 has a low molecular weight ($\sim 6.0 \times 10^3$) because of the high evaporation of diamin-

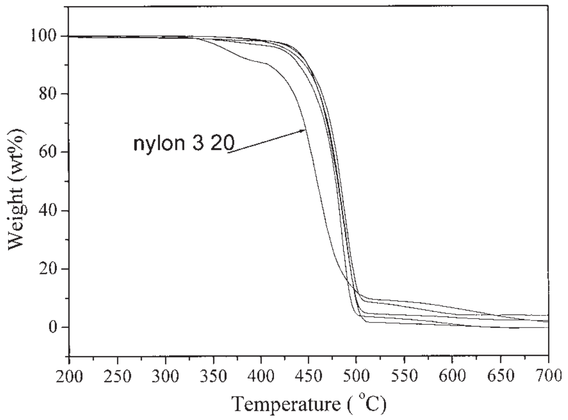

Figure 5 TGA plots of the prepared polyamides.

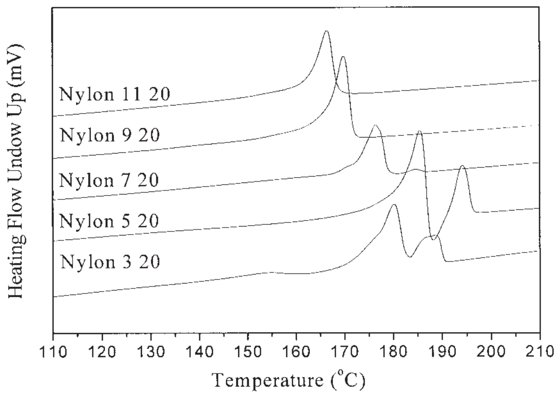

Figure 6 DSC thermograms of the synthetic nylons.

TABLE V
Glass-Transition Temperature (T_g), Melting Point (T_m), and Decomposition Temperature (T_d) of the Prepared Polyamides

Nylon	T_g (°C)	T_m (°C)	T_d (°C)
Nylon 11/20	29	167	465
Nylon 9/20	42	170	466
Nylon 7/20	46	176	461
Nylon 5/20	52	194	461
Nylon 3/20	—	189	433

opropane, which leads to the low melting temperature and decomposition temperature. The melting temperatures of polyamides 11/20, 9/20, 7/20, and 5/20 increased, from 167 to 194°C, concomitantly with the increment of the methylene segment length between two amide groups. TGA provided the decomposition temperatures of the obtained nylons and DMA was used to measure their glass-transition temperatures and moduli. Nylons 11/20 and 9/20 have low melting temperatures (<170°C) and high storage moduli (>2.0 × 10^4), which make them ideal candidates for use as compatibilizer of the blend of polyolefins and commercial nylons. Other excellent properties, such as poor water affinity and ease of processing, are also attributed to the low concentration of hydrogen bonds of the novel odd–even nylons, which warrant some important applications in industry.

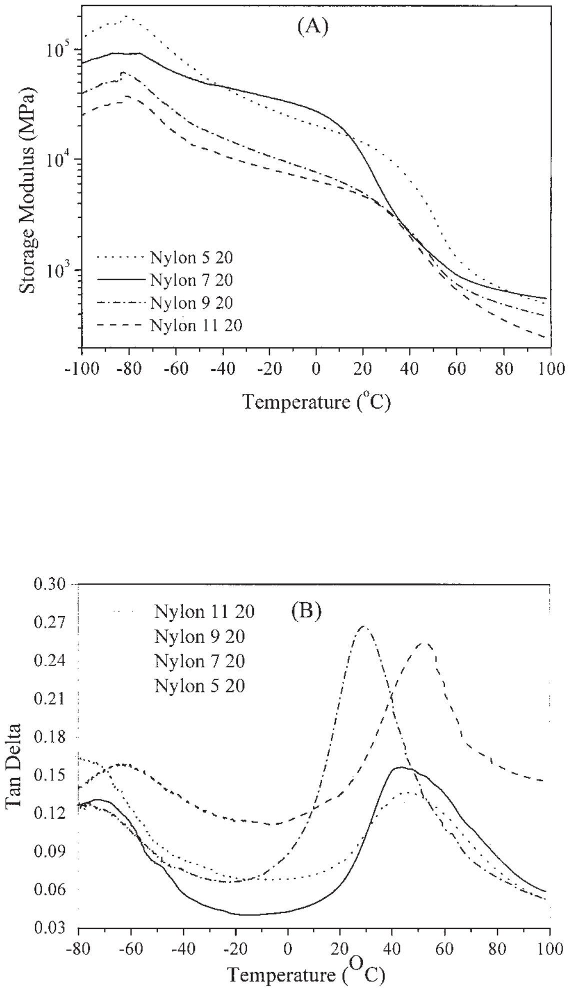

Figure 7 DMA curves of the finished nylons.

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