Synthesis of Polyundecamethylene 2,6-Naphthalamide as Semiaromatic Polyamide-Containing Naphthalene ring

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ABSTRACT: A novel engineering plastic polyundeca-methylene 2,6-naphthalamide (PA11N) was prepared via a reaction of 2,6-naphthalene dicarboxylic acid and 1,11-undecanediamine through a three-step procedure. The structure of synthesized PA11N was characterized by elemental analysis, Fourier transform infrared spectroscopy, and proton nuclear magnetic resonance (^{1}H-NMR). The thermal behaviors were determined by differential scanning calorimetry, thermogravimetric analysis, and dynamic mechanical analysis. The solubility, water-absorbing capacity, and mechanical properties of PA11N have also been investigated. Melting temperature (T_m), glass transition temperature (T_g), and decomposition temperature (T_d) of PA11N are 294, 139, and 493°C, respectively. The results show that the heat resistance and mechanical properties of PA11N are near to those of polynonamethylene terephthalamide, and PA11N is a promising heat-resistant and processable engineering plastic. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 1094–1099, 2010

Key words: polyamides; synthesis; polycondensation; thermal properties; mechanical properties

INTRODUCTION

Aromatic polyamides and semiaromatic polyamides play an important role in many industrial and commercial applications, especially in surface-mount technology and automobile industries, by virtue of their good thermal stability, chemical resistance, low creep, and high modulus.[1–4] The commonly mentioned aromatic and semiaromatic polyamides are poly(*p*-phenylene terephthalamide) (PPTA),[5,6] poly(*m*-phenylene isophthalamide) (PMIA),[7–9] polyhexamethylene terephthalamide (PA6T),[10–12] polynonamethylene terephthalamide (PA9T),[13,14] and poly(*m*-xylylene adipamide) (MXD6).[15]

However, PPTA, PMIA, and PA6T can not be processed by melting method because of their high-melting temperature and relatively lower decomposition temperatures caused by their high-crystallinity, high-stiffness of the polymer backbone.[16–19] The relatively lower glass transition temperature (T_g, 75°C) and lower melting temperature (T_m, 243°C) of MXD6 limited its applications in heat-resistant materials.[20] Therefore, PA9T has been the most commercially used semiaromatic polyamide in electric and automobile industries, which inherits the merits of the heat resistance of aromatic polyamides and the processing ability of aliphatic polyamides.[21,22] However, as one kind of primary polymeric monomer of PA9T, nonanediamine is prepared by a complex procedure, which resulted in the high-cost of PA9T.

For increasing processing ability and decreasing the cost of semiaromatic polyamides, long flexible aliphatic chains are usually introduced into their backbones,[23–26] which cause a decrease in the crystallinity and therefore improves the processability. It has been reported that diacids with long aliphatic chains can be prepared from petroleum fermentation process using light wax as raw materials.[27–30] The long chain diamines were prepared from the corresponding long chain diacids by cyanation and amination process.[31] The cost of obtained long chain diamines was reduced accordingly.

It was noticeable that naphthalene ring can be also introduced into the molecular chain of polyamides and high-thermal stability was retained expectably. However, the polyamides containing naphthalene ring presented relatively low-molecular weight and unsatisfactory performance, which would not meet the requirements for commercialization.[32,33] Therefore, it is of great significance to synthesize novel, low-cost, high-performance, and processability semiaromatic polyamides containing naphthalene ring.

In this work, the polyundecamethylene 2,6-naphthalamide (PA11N) was successfully synthesized by the polycondensation reaction of 2,6-naphthalene dicarboxylic acid and 1,11-undecanediamine in water. PA11N was investigated by Fourier transform infrared (FTIR) spectroscopy, proton nuclear magnetic
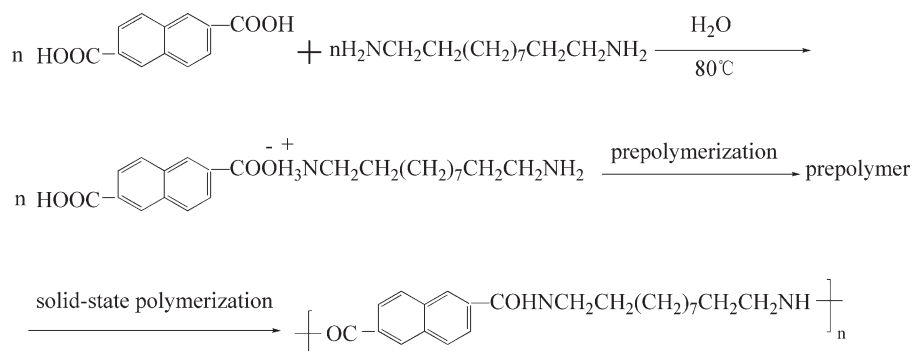
Figure 1 The synthetic route of PA11N.

resonance (^{1}H-NMR), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and dynamic mechanical analysis (DMA). Intrinsic viscosity, water-absorbing capacity and mechanical property of PA11N were also studied.

EXPERIMENTAL

Materials

2,6-naphthalene diacrboxylic acid was purchased from Mitsubishi Gas Chemical Company (MGC, Japan). 1,11-undecanediamine was provided commercially by Zibo Guangtong Chemical (China), and purified by vacuum distillation before use.

Synthesis

PA11N was synthesized through a three-step procedure (Fig. 1). 1,11-undecanediamine (372 g, 2 mol) was dissolved in 1000 mL of distilled water at 80°C. Then the solution was added slowly into 500 mL of distilled water mixture of 2,6-naphthalene diacrbox-

ylic acid (432 g, 2 mol) with vigorous stirring and then stirred for 2 h at 80°C. Finally, a slight excess of 1,11-undecanediamine (2 g, 0.01 mol) was added into the solution with continuous stirring for 1 h at 80°C. The pH value of the solution was adjusted to 7.2. The white 1,11-undecanediamine-2,6-naphthalene diacrboxylic acid salt (PA11N salt) precipitated from the solution.

After filtering over a Buchner funnel and drying in a vacuum desiccator for 12 h, the white salt of PA11N (751 g, 93%) and distilled water (800 mL) were added into an autoclave. The autoclave was filled with carbon dioxide and then heated to 245°C while increasing the pressure to 2.5 MPa. After 2 h, the pressure of the autoclave was gradually decreased to normal pressure in 2 h by deflating and the reaction temperature of the autoclave was increased to 260°C. After reaction for another 1.5 h, the ivory-white prepolymer of PA11N was obtained (706 g, 94%).

The prepolymer of PA11N was ground into particles with diameter of 0.1 ~ 2 mm and dried at 90°C in a vacuum oven for 4 h. Then, the prepolymer of PA11N was added into a solid-state polymerization
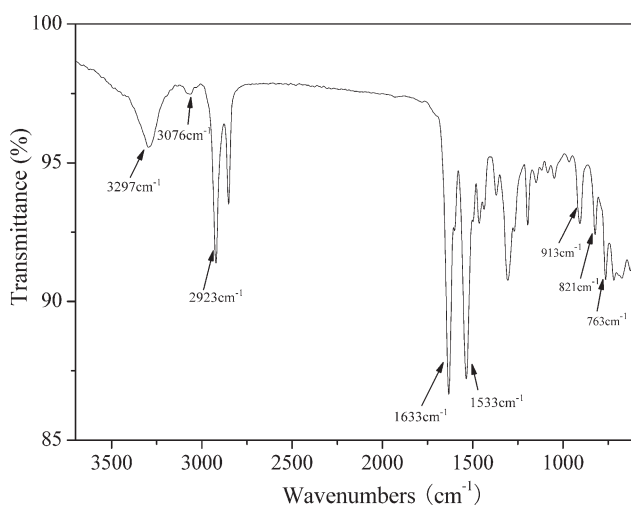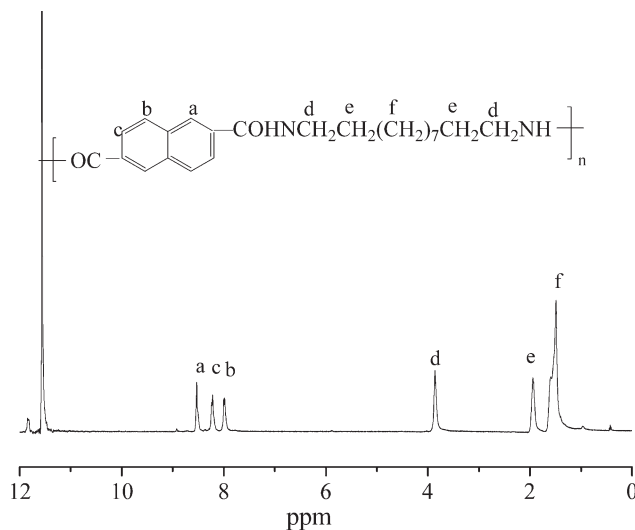

Figure 2 FTIR spectra of PA11N.

Figure 3 ^{1}H-NMR spectra of PA11N.

TABLE I
Elemental Analysis Data of PA11N

Sample	Carbon (%)		Hydrogen (%)		Nitrogen (%)		Oxygen (%)	
	Calculated	Measured	Calculated	Measured	Calculated	Measured	Calculated	Measured
PA11N	75.4	75.4	8.20	8.24	7.65	7.64	8.75	8.72

kettle, the reaction was carried out at 240°C for 15 h with a vacuum of 10 Pa. Finally, the kettle was cooled to room temperature, and straw yellow polymer of PA11N was obtained (685 g, 97%).

Characterization

FTIR, ^{1}H-NMR, and elemental analysis were used to confirm the structure of PA11N. PA11N was also characterized by intrinsic viscosity, DSC, TGA, DMA, and mechanical properties.

The intrinsic viscosity of PA11N dissolved in concentrated sulfuric acid (sample 125 mg, solvent 25 mL) was determined in an Ubbelohde viscometer at 25 ± 0.1°C. The water-absorbing of PA11N was measured according to GB/T 1034 (China standard).[34]

The FTIR measurement was carried out on a NICOLET 460 spectrometer (KBr pellet) in the range of 4000–400 cm^{-1} with the resolution of 4 cm^{-1}. The concentration of PA11N in KBr pellet (200 mg) was 1%. ^{1}H-NMR spectra was recorded with a Bruker DPX-400 (400 MHz), using deuterated trifluoroacetic acid (TFA) as solvents and tetramethylsilane as an internal reference. Elemental analysis was performed on a Perkin-Elmer 2400 CHNS/O elemental analyzer at 975°C under nitrogen.

Thermal analysis (DSC and TGA) was recorded on a NETSCH 204 calorimeter, using dry nitrogen flow as atmosphere with a flowing rate of 70 mL min^{-1}. The conditions for the thermal analysis were summarized as follows: for DSC, the sample of PA11N (about 2 mg) was sealed in aluminum pan, then heated from 50 to 350°C at a heating rate of 10°C min^{-1}; for TGA, the sample of PA11N (about 2 mg) was put in platinum open pan with a heating rate of 10°C min^{-1} from 50 to 550°C. DMA was carried out on a NETZSCH DMA-242 apparatus with a heating rate of 3°C min^{-1} from –170°C to 170°C at 1Hz. The sample geometry was 60 mm × 12 mm × 3.0 mm. The clamp configuration was three-point bending, and the stress on the sample was 2 N. The static atmosphere was used in the DMA test.

All samples for mechanical tests were prepared by injection molding. The izod impact strength was measured according to GB/T 1843 (China standard).[35] Tensile strength and elongation at break were measured according to GB/T 1040 (China standard).[35] Bending strength was measured according to GB/T 9341 (China standard).[35] All tests were carried out at room temperature (23°C). The resulting value of each sample was the average of five specimens.

RESULTS AND DISCUSSION

Synthesis of PA11N

PA11N was prepared from the reaction of 2,6-naphthalene dicarboxylic acid and 1,11-undecanediamine through a three-step procedure: salt formation, prepolymerization, and solid-state polymerization. To assure an accurate equivalent ratio of 1,11-undecanediamine to 2,6-naphthalene dicarboxylic acid,
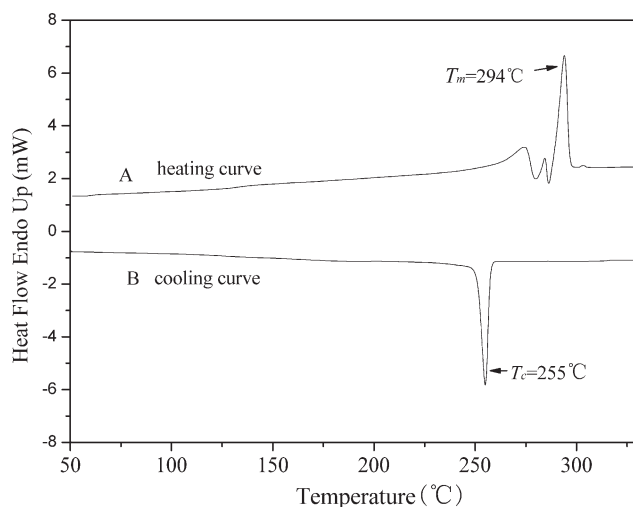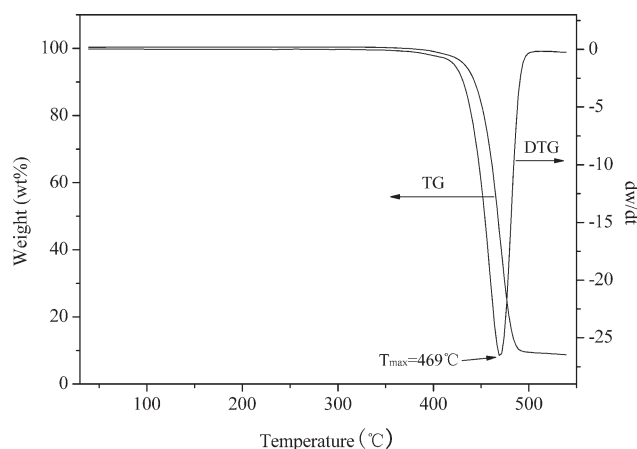

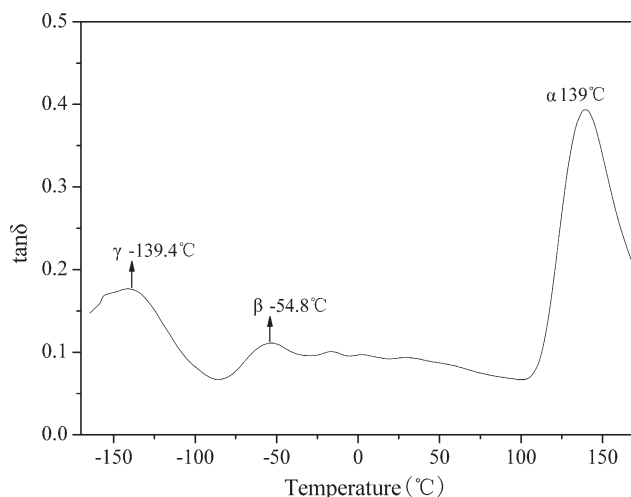**Figure 4** DSC curves of PA11N.

Figure 5 TGA curves of PA11N.

Figure 6 The tan delta curve of PA11N (1 Hz).

Figure 7 The storage modulus and loss modulus curves of PA11N (1 Hz).

PA11N salt was prepared firstly. Then an slight excess 1,11-undecanediamine was added into the salt solution to compensate reaction system for the loss during the prepolymerization reaction. It is noticeable that the solvent for the salt formation reaction is water, which is cheaper and environmental friendly compared with ethanol, usually used in preparing other common polyamides.[36] To obtain high vapor pressure, the distilled water was added to reduce volatilization of diamine during the prepolymerization. The prepolymer was ground into small particles, which are convenient for removing water. To avoid side reaction and improve the molecular weight of the polyamide, the high-vacuum was maintained during the solid-state polymerization reaction. The molecular weight of the PA11N was characterized by intrinsic viscosity. The intrinsic viscosity of PA11N is 181 mL g^{-1}.

FTIR spectrum of the PA11N is shown in Figure 2. All the characteristic peaks of amide groups and methylene segments of polyamide are listed as follows: 1633 cm^{-1} (amide I, C=O stretching vibration), 1533 cm^{-1} (amide II, C—N stretching and CO—N—H bending vibration), 2923 cm^{-1} (N—H in-plane bending vibration and CH$_2$ vibration), 3297 cm^{-1} (hydrogen-bonded and N—H stretching vibration), 3076 cm^{-1} (N—H in-plane bending), 913 cm^{-1} (amide IV, C—CO stretching vibration), 821 cm^{-1} (CH$_2$ wagging), 763 cm^{-1} (C—H of naphthalene ring vibration).

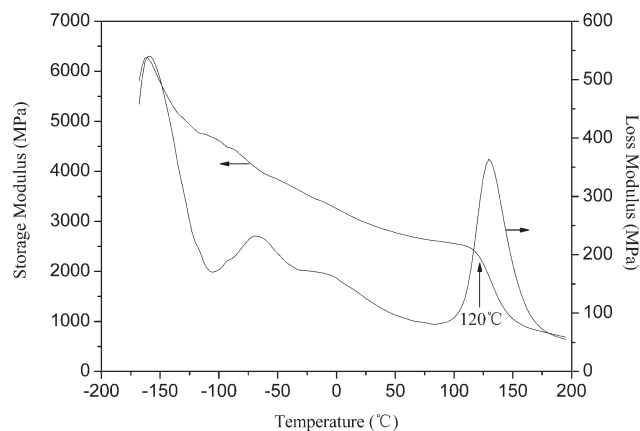Figure 3 presents the ^{1}H-NMR spectrum of PA11N in deuterated TFA. The chemical shifts at 8.53 ppm (2H), 7.98 ppm (2H) and 8.22 ppm (2H) are attributed to the naphthalene ring protons (a, b, and c). The chemical shift at 3.87 ppm (4H) originates from the protons at the position d while that at 1.94 ppm (4H) comes from the protons at the position e. The peak at 1.48 ppm (14H) belongs to the other protons of the aliphatic chains (f). The peak at 11.55 ppm was assigned to TFA.

The elemental analysis data of PA11N are listed in Table I. The calculated components are presented for comparison. The hydrogen content of PA11N is higher than the theoretical value owing to the absorption of water. The other measurement results are in agreement with the theoretical values.

The water-absorbing of PA11N was measured according to GB/T1034 (China standard), and the result is 0.12. The low water absorption, close to PA9T (0.17),[37] is conducive to maintain dimensional and mechanical stability of products.

The solubilities (sample 100 mg, solvent 10 mL) of PA11N were tested in different organic solvents. PA11N can easily dissolve in acidity solvents, such as concentrated sulfuric acid and TFA at room temperature, whereas it is insoluble in dimethylsulphoxide, N,N′-dimethylformamide, 1-methyl-2-pyrrolidenone, dimethylacetamide, m-cresol, tetrahydrofuran, tetrachloroethane, chlorobenzene, pyridine, methanol, toluene, chloroform, phenol, and formic acid.

Thermal and mechanical properties of PA11N

The thermal property of PA11N was evaluated by DSC, TGA, and DMA techniques.

TABLE II
The Intrinsic Viscosity, Thermal Data and Water-Absorbing Capacity of PA11N

Sample	[η] (mL g^{-1})	T_m (°C)	T_c (°C)	T_d (°C)	T_g (°C)	Water-absorbing capacity (%)
PA11N	181	294	255	455	139	0.12

TABLE III
The Mechanical Properties of PA11N Compared with PA9T

Samples	Tensile strength (MPa)	Tensile modulus (GPa)	Breaking elongation (%)	Bending strength (MPa)	Bending modulus (GPa)	Izod impact strength (kJ m^{-2})
PA11N	89	1.8	54	76	1.8	5.3
PA9T	92	—	20	120	2.6	4.9

Figure 4 depicts the DSC curves of PA11N. Curve A is the second heating DSC curve, whereas B is cooling curve with a heating rate of 10°C min^{-1} from 50°C to 340°C. The melting temperature (T_m) of PA11N is 294°C based on curve A, and the crystallization temperature (T_c) of PA11N is 255°C based on curve B.

TGA curves of PA11N are shown in Figure 5. The curve A of PA11N shows a one-stage weight loss process in nitrogen. The onset of decomposition temperature (T_d) of PA11N is approximately 493°C; and the termination temperature of thermal degradation is about 500°C. The maximum degradation temperature (T_{max}) of PA11N is 469°C.

The T_m of PA11N, close to that of PA9T (308°C),[38] is far below T_d of PA11N. Therefore, the melt processing ability of PA11N is excellent. In addition, the T_d of PA11N is higher than that of aliphatic polyamides.[39,40] The results show that the thermal stability of PA11N has been improved by inserting naphthalene linkage into the polymeric backbone.

DMA was also used to characterize the thermal property of PA11N (Figs. 6 and 7). As shown in Figure 6, three obvious transition behaviors can be observed, and are defined as α, β, and γ relaxation, respectively. The glass transition temperature (T_g) of the PA11N is 139°C according to α relaxation. T_g of aliphatic polyamides, such as poly(ε-caprolactam) (nylon6) (T_g = 60°C) and poly(hexamethylene adipamide) (nylon66) (T_g = 50°C) are all below 90°C. The results show that T_g of PA11N is higher than aliphatic polyamides. As expected, the heat resistance of PA11N was improved by the introduction of naphthalene ring. The β relaxation reflects the mobility of carbonyl group of amorphous region, and the γ relaxation reflects the comoving of amido and methenes. Figure 7 displays the storage modulus and loss modulus curves of PA11N and illustrate the viscoelastic behavior of the PA11N. As shown in Figure 7, the PA11N has high-storage moduli beyond 2 × 10^3 MPa below 120°C. When the temperature increased above 120°C, the storage modulus begins to decrease precipitously. The thermal data of PA11N in this work are listed in Table II.

All dry and standard samples of PA11N for mechanical tests were prepared by injection molding in an injection-molding machine. Based on Table III, it can be observed that the tensile strength of PA11N

is almost as same as that of PA9T at room temperature.[38,41]

CONCLUSIONS

PA11N with high-molecular weight was prepared from the reaction of 2,6-naphthalene dicarboxylic acid and 1,11-undecanediamine. The characterization of FTIR, ^{1}H-NMR spectroscopy and elemental analysis confirmed that the obtained product has the expected chemical structure and composition. T_m, T_g, and T_d of PA11N are 294, 139, and 493°C, respectively. The intrinsic viscosity of PA11N is 181 mL g^{-1}. The results show that PA11N has better thermal stability than aliphatic polyamides. The low water absorption, close to that of PA9T, is conducive to maintain dimensional and mechanical stability of products for surface-mount technology. Compared with PA9T, the low-cost and good performance of PA11N demonstrate it could be a promising, heat-resisting and well processable engineering plastic, and it can be a candidate nylon for the industrial production.

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