

Synthesis, characterization of polytridecamethylene 2,6-naphthalamide as semiaromatic polyamide containing naphthalene-ring

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Abstract. A novel engineering plastic polytridecamethylene 2,6-naphthalamide (PA13N) was prepared via a reaction of 2,6-naphthalene dicarboxylic acid and 1,13-tridecanediamine through a three-step procedure. The structure of synthesized PA13N was characterized by elemental analysis, Fourier transform infrared (FT-IR) spectroscopy and proton nuclear magnetic resonance (¹H-NMR). The thermal behaviors were determined by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA). The solubility, water-absorbing capacity, and mechanical properties of PA13N have also been investigated. Melting temperature (T_m), glass transition temperature (T_g) and decomposition temperature (T_d) of PA13N are 288, 129 and 492°C, respectively. The results show that the heat resistance and mechanical properties of PA13N are near to those of polynonamethylene terephthalamide (PA9T), and PA13N is a promising heat-resistant and processable engineering plastic.

Keywords: mechanical properties, thermal properties, polyamides, synthesis, polycondensation

1. Introduction

Aromatic polyamides and semiaromatic polyamides have been widely used in many industrial and commercial applications, especially in surface-mount technology and automobile industries, by virtue of their excellent characteristics such as good thermal stability, chemical resistance, low creep and high modulus [1–3]. The commonly mentioned aromatic and semiaromatic polyamides [4–15] cannot be processed by melt methods due to their high melting temperature and relatively lower decomposition temperatures [16–18]. Therefore, several approaches have been made through synthetic modification by the incorporation of flexible linkages [19, 20], bulky pendant groups [21] and non-coplanar biphenylene moieties [22] into the polymer back-

bones. Polynonamethylene terephthalamide (PA9T) inherits the merits of the heat resistance of aromatic polyamides and the processability of aliphatic polyamides [23]. However, the high cost of PA9T limited its applications.

In order to increase the processability and decrease the cost of semiaromatic polyamides, long flexible aliphatic chains are usually introduced into their backbones [24–26]. It has been reported that diacids with long molecular chains can be prepared from petroleum fermentation process using light wax as raw material [27], and the long chain diamines can be prepared from the corresponding long chain diacids by cyanation and amination process [28]. The cost of obtained long chain diacids and diamines was reduced accordingly.

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It was noticeable that naphthalene-ring can be also introduced into the molecular chain of polyamides and high thermal stability was retained, as expected. However, the semiaromatic polyamides containing naphthalene-ring presented relatively low molecular weight and unsatisfactory performance which would not meet the requirements for commercialization [29–33]. Therefore, it is of great significance to synthesize novel, low-cost, high-performance and processable semiaromatic polyamides containing naphthalene-ring.

In this work, the polytridecamethylene 2,6-naphthalamide (PA13N) was successfully synthesized by the polycondensation reaction of 2,6-naphthalenedicarboxylic acid and 1,13-tridecanediamine in water. PA13N was investigated by Fourier transform infrared (FT-IR) spectroscopy, proton nuclear magnetic resonance ($^1\text{H-NMR}$), differential scanning calorimetry (DSC), thermo-gravimetric analysis (TGA) and dynamic mechanical analysis (DMA). Intrinsic viscosity, water-absorbing capacity and mechanical properties of PA13N were also studied.

2. Experimental

2.1. Materials

2,6-naphthalenediacarboxylic acid was purchased from Mitsubishi Gas Chemical Company, Inc (MGC, Japan). 1,13-tridecanediamine was provided commercially by Zibo Guangtong Chemical Limited Company (China), and purified by vacuum distillation prior to use.

2.2. Synthesis

PA13N was synthesized through a three-step procedure (Figure 1). 1,13-tridecanediamine (321 g, 1.5 mol) was dissolved in distilled water (1000 ml) at 90°C. Then the solution was added slowly into 500 ml of distilled water mixture of 2,6-naphthalene diacarboxylic acid (324 g, 1.5 mol) with vigor-

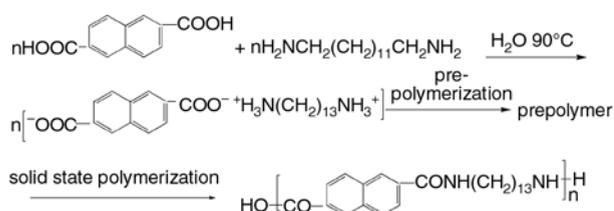


Figure 1. The synthetic route of PA13N

ous stirring and then stirred for 2 h at 90°C. Finally a slight excess of 1,13-tridecanediamine (2 g, 0.01 mol) was added into the solution with continuous stirring for 1 h at 90°C. The pH value of the solution was adjusted to 7.2. The white 1,13-tridecanediamine-2,6-naphthalene diacarboxylic acid salt (PA13N salt) precipitated from the solution.

After filtering over a Buchner funnel and drying in a vacuum desiccator for 12 h, the white salt of PA13N (608.2 g) and distilled water (500 ml) were added into an autoclave. The autoclave was filled with carbon dioxide and then heated to 210°C while increasing the pressure to 2.1 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 230°C. After reaction for another 1.5 h, the ivory-white prepolymer of PA13N was obtained (559.5 g).

The prepolymer of PA13N 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 PA13N was added into a solid-state polymerization kettle, the reaction was carried out at 230°C for 15 h with a vacuum of 10 Pa. Finally, the kettle was cooled to room temperature and straw yellow polymer of PA13N was obtained (539.9 g).

2.3. Characterizations

FT-IR, $^1\text{H-NMR}$ and elemental analysis were used to confirm the structure of PA13N. The thermal behaviors were determined by DSC, TGA and DMA. The solubility, intrinsic viscosity, water-absorbing capacity and mechanical properties of PA13N were also studied.

The intrinsic viscosity of PA13N dissolved in concentrated sulfuric acid was determined in an Ubbelohde viscometer at 25±0.1°C. The water-absorbing capacity of PA13N was measured according to GB/T1034 (Chinese standard).

The FT-IR 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 PA13N in KBr pellet (200 mg) was 1%. $^1\text{H-NMR}$ spectra was recorded with a Bruker DPX-400 (400 MHz), using deuterated trifluoroacetic acid as solvent and tetramethylsilane (TMS) 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 PA13N (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 PA13N (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 to 170°C at 1 Hz. The sample geometry was 60 mm×12 mm×3.0 mm. The clamp configuration was 3-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 (Chinese standard). Tensile strength and elongation at break were measured according to GB/T 1040 (Chinese standard). Bending strength was measured according to GB/T 9341 (Chinese standard). All tests were carried out at room temperature (23°C). The resulting value of each sample was the average of five specimens.

3. Results and discussion

3.1. Synthesis of PA13N

PA13N was prepared from the reaction of 2,6-naphthalene dicarboxylic acid and 1,13-tridecane-diamine through a three-step procedure: salt formation, prepolymerization and solid-state polymerization. In order to assure an accurate equivalent ratio of 1,13-tridecane-diamine to 2,6-naphthalene dicarboxylic acid, PA13N salt was prepared firstly. Then a slight excess of 1,13-tridecane-diamine 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 [34]. In order 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. In order to avoid side reaction and to improve the molecular weight of the polyamide, the high vacuum was maintained during the solid-state polymerization reaction. The molecular weight of the PA13N was characterized by intrinsic viscosity. The intrinsic viscosity of PA13N is 1.91 dl·g⁻¹.

3.2. Fourier transform infrared spectra

FT-IR spectrum of the PA13N is shown in Figure 2. All the characteristic peaks of amide groups and methylene segments of polyamide are listed as follows: 1630 cm⁻¹ (amide I, C=O stretching vibration), 1535 cm⁻¹ (amide II, C–N stretching and CO–N–H bending vibration), 2921 cm⁻¹ (N–H in-plane bending vibration and CH₂ vibration), 3291 cm⁻¹ (hydrogen-bonded and N–H stretching vibration), 3074 cm⁻¹ (N–H in-plane bending), 910 cm⁻¹ (amide IV, C–CO stretching vibration), 820 cm⁻¹ (CH₂ wagging), 766 cm⁻¹ (C–H of naphthalene ring vibration).

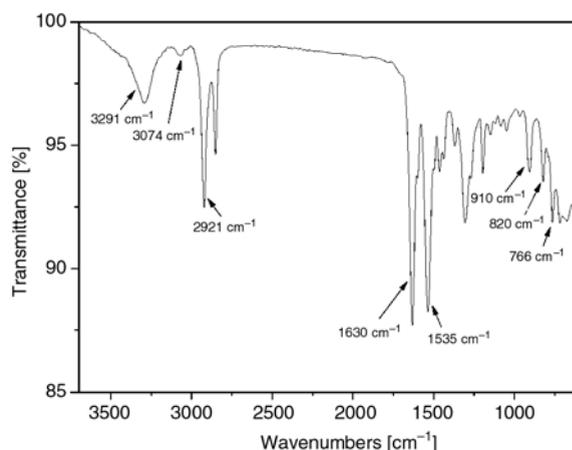


Figure 2. FT-IR spectra of PA13N

3.3. Proton nuclear magnetic resonance

Figure 3 presents the ¹H-NMR spectrum of PA13N in deuterated trifluoroacetic acid. The chemical shifts at 8.46 ppm (2H), 7.95 ppm (2H) and 8.16 ppm (2H) are attributed to the naphthalene ring protons (*a*, *b* and *c*). The chemical shift at 3.83 ppm (4H) originates from the protons at the position *d* while that at 1.88 ppm (4H) comes from the protons at the position *e*. The peak at 1.42 ppm

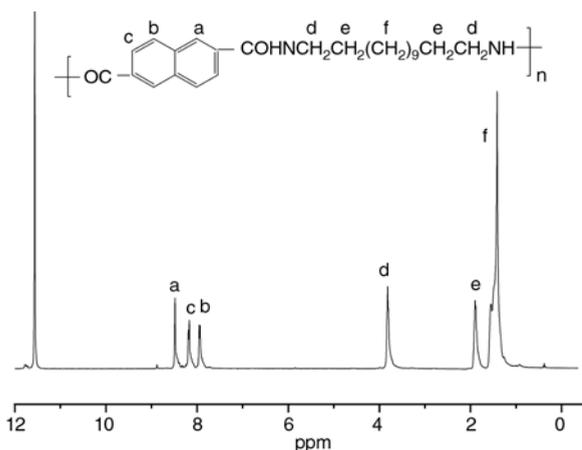


Figure 3. $^1\text{H-NMR}$ spectra of PA13N

(18H) belongs to the other protons of the aliphatic chains (*f*). The peak at 11.6 ppm was assigned to trifluoroacetic acid.

3.4. Elemental analysis

The elemental analysis data of PA13N are listed in Table 1. The calculated components are presented for comparison. The hydrogen content of PA13N is higher than the theoretical value owing to the absorption of water. The other measurement results are in agreement with the theoretical values.

3.5. Water absorption

The water-absorbing capacity of PA13N was measured according to GB/T1034 (Chinese standard), and the result is 0.07. The water-absorbing capacity of polydodecamethylene 2,6-naphthalamide (PA12N) was measured according to the same standard, and the result is 0.10. The low water absorption, close to PA9T (0.17), polydecamethylene 2,6-naphthalamide (PA10N) (0.14), polyundecamethylene 2,6-naphthalamide (PA11N) (0.12) and PA12N [35–37], is conducive to maintain dimensional and mechanical stability of products.

3.6. Solubility

The solubilities (sample 100 mg, solvent 10 ml) of PA13N were tested in different organic solvents. PA13N can easily dissolve in acidic solvents such

as concentrated sulfuric acid and trifluoroacetic acid (TFA) at room temperature, while it is insoluble in dimethylsulphoxide (DMSO), *N,N*-dimethylformamide (DMF), 1-methyl-2-pyrrolidinone (NMP), dimethylacetamide (DMAc), *m*-cresol, tetrahydrofuran (THF), tetrachloroethane, chlorobenzene, pyridine, methanol, toluene, chloroform, phenol and formic acid.

3.7. Thermal behaviors

Figure 4 depicts the DSC curves of PA13N. Curve A is the second heating DSC curve with a heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$ from 50 to 320°C , while B is the cooling curve with a cooling rate of $10^\circ\text{C}\cdot\text{min}^{-1}$ from 320 to 50°C . The melting temperature (T_m) of PA13N is 288°C based on curve A, and the crystallization temperature (T_c) of PA13N is 251°C based on curve B. PA13N exhibits double-melting endotherms, which is a common phenomenon observed in semicrystalline polymers [38–40].

TGA curves of PA13N are shown in Figure 5. The curve A of PA13N shows a one-stage weight loss process in nitrogen. The decomposition temperature (T_d) is approximately 492°C , and the termination temperature of thermal degradation is about 500°C . The maximum degradation temperature (T_{max}) of PA13N is 474°C .

The T_m of PA13N is far below T_d of PA13N. Therefore, the melt processability of PA13N is excellent. In addition, the T_d of PA13N is higher than that of

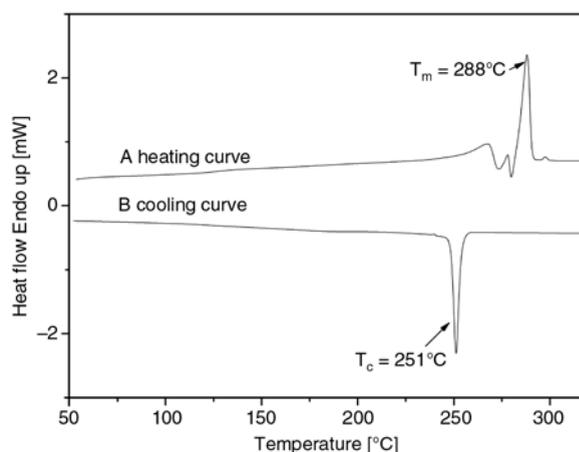


Figure 4. DSC curves of PA13N

Table 1. Elemental analysis data of PA13N

Sample	Carbon [%]		Hydrogen [%]		Nitrogen [%]		Oxygen [%]	
	Calculated	Measured	Calculated	Measured	Calculated	Measured	Calculated	Measured
PA11N	76.1	76.0	8.62	8.69	7.10	7.04	8.18	8.27

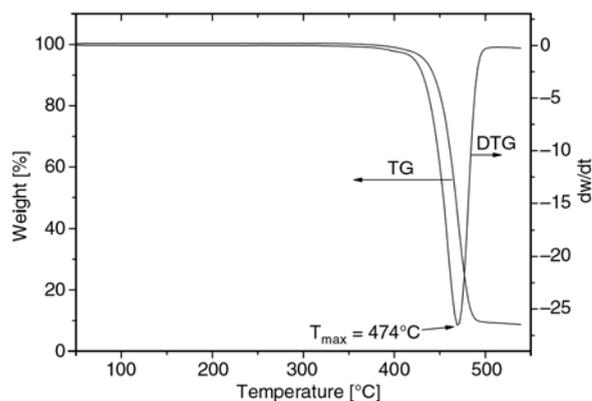


Figure 5. TGA curves of PA13N

aliphatic polyamides [41, 42]. The results show that the thermal stability of PA13N has been improved by inserting naphthalene linkage into the polymeric backbone.

DMA was also used to characterize the thermal property of PA13N (Figure 6 and Figure 7). As shown in Figure 6, three obvious transition behaviors can be observed, and are defined as α , β and γ

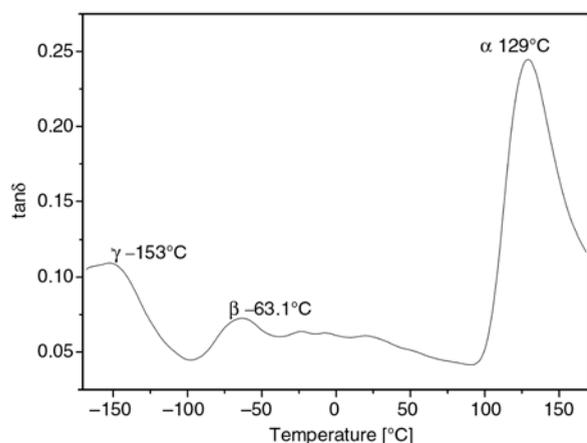


Figure 6. The tan delta curve of PA13N (1 Hz)

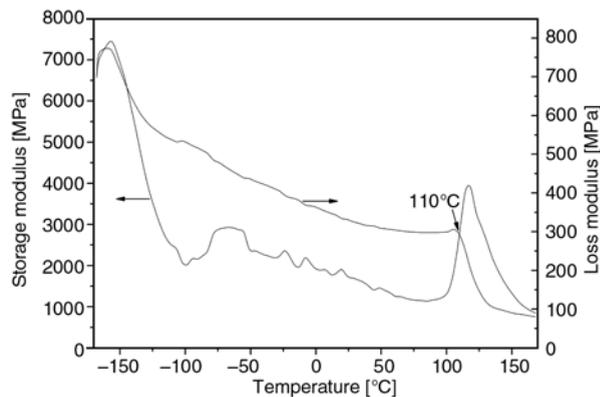


Figure 7. The storage modulus and loss modulus curves of PA13N (1 Hz)

relaxation, respectively. The glass transition temperature (T_g) of the PA13N is 129°C according to α relaxation. T_g of aliphatic polyamides such as poly(ϵ -caprolactam) (nylon6) ($T_g = 60^\circ\text{C}$) and poly(hexamethylene adipamide) (nylon66) ($T_g = 50^\circ\text{C}$) are all below 90°C. The results show that T_g of PA13N is higher than aliphatic polyamides. As expected, the heat-resistance of PA13N 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 simultaneous movement of amido and methane groups. Figure 7 displays the storage modulus and loss modulus curves of PA13N and illustrate the viscoelastic behavior of the PA13N. As shown in Figure 7, the PA13N has high storage moduli beyond $2 \cdot 10^3$ MPa below 110°C. When the temperature increased above 110°C, the storage modulus begins to decrease precipitously. The thermal data of PA13N in this work are listed in Table 2.

Table 2. The Intrinsic viscosity, thermal data and water-absorbing capacity of of PA10N, PA11N, PA12N and PA13N

Sample	$[\eta]$ [dl·g ⁻¹]	Tm [°C]	Tc [°C]	Td [°C]	Tg [°C]	Water-absorbing capacity [%]
PA13N	1.91	288	251	492	129	0.07
PA12N	1.84	299	273	498	120	0.10
PA11N	1.81	294	255	455	139	0.12
PA10N	1.85	320	297	495	144	0.14

Table 3. The mechanical properties of PA13N compared with PA10N, PA11N, PA12N and PA9T

Samples	Tensile strength [MPa]	Tensile modulus [GPa]	Breaking elongation [%]	Bending strength [MPa]	Bending modulus [GPa]	Izod impact strength [kJ·m ⁻²]
PA13N	90	1.7	56	80	1.9	5.1
PA12N	88	1.7	29	53	1.5	5.3
PA11N	89	1.8	54	76	1.8	5.3
PA10N	94	1.7	40	92	1.9	5.2
PA9T	92	–	20	120	2.6	4.9

3.8. Mechanical properties

All dry and standard samples of PA13N for mechanical tests were prepared by injection molding in an injection-molding machine. Based on Table 3, it can be observed that the tensile strength of PA13N is almost as same as that of PA9T [43], PA10N [36], PA11N [37] and PA12N [44] at room temperature.

4. Conclusions

PA13N with high molecular weight was prepared from the reaction of 2,6-naphthalene dicarboxylic acid and 1,13-tridecanediamine. The characterization of FT-IR, ¹H-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 PA13N are 288, 129 and 492°C, respectively. The intrinsic viscosity of PA13N is 1.91 dl·g⁻¹. The results show that PA13N has better thermal stability than aliphatic polyamides. The low water absorption, close to 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 PA13N 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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