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SYNTHESIS OF SEMIAROMATIC POLYAMIDES BASED ON DECANEDIAMINE

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Abstract Long chain semiaromatic polyamides were synthesized by the reactions of decanediamine with various aromatic diacids and characterized by Fourier transform infrared spectroscopy (FT-IR) and nuclear magnetic resonance (^{1}H-NMR). The thermal behaviors were determined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The solubility, dynamic mechanical, physical and mechanical properties of the polyamides have also been investigated. The resultant polyamides have intrinsic viscosity ranging from 1.7 dL/g to 2.1 dL/g. Their melting temperatures range from 305°C to 343°C, and the glass transition temperatures fall in the range of 125–130°C. The tensile strength of the polyamides is above 100 MPa.

Keywords: Semiaromatic; Polyamide; Decanediamine.

INTRODUCTION

Aliphatic polyamides such as poly(ε-caprolactam) (nylon 6) and poly(hexamethylene adipamide) (nylon 66), are a series of engineering thermoplastics which play important roles in many industrial and commercial applications[1], However, their poor mechanical and thermal properties impose limitations on successful applications in some industrial and other fields, such as automobile industry and surface mount technology (SMT). In order to improve their heat resistance and mechanical strength, aromatic rings have been incorporated into the molecular chains[2–5]. And lots of available aromatic and semiaromatic polyamides have been prepared, such as poly(*p*-phenylene terephthalamide) (PPTA)[6], poly(hexamethyleneterephthalamide) (PA6T)[7] and poly(nonamethylenetere-phthalamide) (PA9T)[8]. Morgan and Kwolek have synthesized a series of semiaromatic polyamides based on *p*-phenylenediamine and *m*-phenylenediamine[9]. Jackson have studied the properties of poly(hexamethylene isophthalamide) (PA6I) and poly(dodecamethylene terephthalamide) (PA12T)[10]. These aromatic and semiaromatic polyamides have been noted about the high thermal stability, chemical resistance, high strength and high modulus as fibers. However, it is impossible to produce them by melting processing due to their high glass transition and melting temperatures except for PA9T, PA6I and PA12T. The long chain diamines can be prepared by successive cyanation and amination of the corresponding long chain diacids, which can be facilely obtained from light wax. The low cost preparation of the long chain diamines obviously reduces the price of the resulting polyamides, compared with the commercialized PA9T. Meanwhile, long chain diamines give long chain semiaromatic polyamides more chain flexibility and low water absorption. Therefore, synthesis of novel long chain, high-performance and machinable semiaromatic polyamides is an attractive work.

We have synthesized a series of semiaromatic polyamides based on terephthalic acid and long chain diamines[11]. In this contribution, we present here a series of semiaromatic polyamides of poly(decanediamine terephthalic amides) (PA10T), poly(decanediamine biphenyldicarboxylic amides) (PA10B), poly(decanediamine

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dicarboxydiphenyl ether amides) (PA10O) and poly(decanediamine dicarboxydiphenyl sulphone amides) (PA10S), which have been synthesized by condensation polymerization of 1,10-decanediamine and terephthalic acid, 4,4'-biphenyldicarboxylic acid, 4,4'-dicarboxydiphenyl ether and 4,4'-dicarboxydiphenyl sulphone in water. Compared to ethanol which was used in preparing other common polyamides, water is cheaper, safer and environmental friendly. The resultant polyamides were investigated by Fourier transform infrared spectroscopy (FT-IR), nuclear magnetic resonance (^{1}H-NMR), thermal analysis, physical and mechanical properties and dynamic mechanical analysis (DMA).

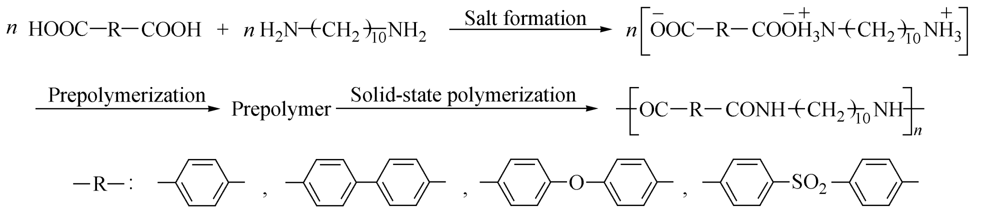
EXPERIMENTAL

Materials

Terephthalic acid, 4,4'-biphenyldicarboxylic acid, 4,4'-dicarboxydiphenyl ether and 4,4'-dicarboxydiphenyl sulphone were purchased from Beijing Yanshan Lithification Chemical Co. Ltd (China), and 1,10-decanediamine was provided commercially by Zibo Guangtong Chemical Co. Ltd (China). 1,10-Decanediamine was vacuum distilled, and aromatic diacids were recrystallized before use.

Synthesis

PA10T, PA10S, PA10O and PA10B were synthesized *via* a three-step procedure of salt formation, prepolymerization and solid-state polymerization, as shown in the Scheme 1.



Scheme 1 Synthesis route of the polyamides

Preparation of PA10T Salt

1,10-Decanediamine (258 g, 1.5 mol) was dissolved in distilled water (1000 mL) at 70°C. Then the solution was added slowly into 500 mL distilled water mixture of terephthalic acid (249.2 g, 1.5 mol) with vigorous stirring and then stirred for 120 min at 85–90°C. Finally, the white 1,10-decanediamine-terephthalic acid salt (PA10T salt) solution was cooled to 20°C, PA10T salt was precipitated from the solution and filtered over a Buchner funnel, then repeatedly washed with distilled water. After drying in a vacuum desiccator for 12 h, the salt was obtained as white powder (476.6 g, 94 %). The T_m of salts of PA10B, PA10O, PA10S and PA10T was 278°C, 272°C, 269°C and 266°C, respectively.

Preparation of Prepolymer of PA10T

PA10T salt (476.6 g) was added into an autoclave, and distilled water (400 g) was added to reduce volatilization of diamine during polymerization. The autoclave was filled with carbon dioxide at room temperature, then heated to 220°C and raised the pressure to 2.5 MPa. After 2 h, the pressure of the autoclave was gradually decreased to atmospheric pressure in 2 h by deflating, and the reaction temperature of the autoclave was increased to 240°C. After reaction for another 2 h, the prepolymer of PA10T was obtained (433.6 g, 91%). The T_m of the prepolymers of PA10B, PA10O, PA10S and PA10T was 328°C, 309°C, 308°C and 301°C, respectively, and the intrinsic viscosity values of the prepolymers of PA10B, PA10O, PA10S and PA10T were 0.9, 1.1, 1.0 and 1.3 dL/g, respectively.

Preparation of PA10T

The prepolymer of PA10T was added to a solid-state polymerization kettle. The kettle was evacuated to 10 Pa, and the reaction temperature was increased to 250°C. After 24 h, the kettle was cooled to room temperature, and the PA10T with high molecular weight was obtained (412 g, 95%). The intrinsic viscosity of PA10T, dissolved in concentrated sulfuric acid, was determined in an Ubbelohde viscometer at (25 ± 0.1)°C. The intrinsic viscosity value was 2.1 dL/g.

PA10S, PA10O and PA10B have been prepared by the similar procedures only using 4,4'-biphenyldicarboxylic acid, 4,4'-dicarboxydiphenyl ether and 4,4'-dicarboxydiphenyl sulphone instead of terephthalic acid, respectively. The intrinsic viscosity values of PA10S, PA10O and PA10B were 1.7, 1.9 and 1.8 dL/g, respectively.

Characterization

Intrinsic viscosity

The intrinsic viscosities of the polyamides were determined in concentrated sulphuric acid with an Ubbelohde viscometer at (25 ± 0.1)°C.

FT-IR

FT-IR spectra were recorded on a Nicolet Avatar 370 DTGS spectrometer. The disc samples were prepared by melt pressing.

^{1}H-NMR

^{1}H-NMR spectra were recorded with a Bruker 400 MHz nuclear magnetic resonance spectrometer and CF_3COOD was used as solvent.

Thermal analysis

DSC was carried out in a nitrogen stream using a NETSCH 204 calorimeter with a heating rate of 10 K min^{-1}, and TGA was performed in a nitrogen stream using a NETZSCH TG 209 calorimeter with a heating rate of 10 K min^{-1}.

Mechanical properties

Mechanical properties were investigated by a universal testing machine (CMT5104) according to ASTM D638, ASTM D790 and ASTM D4508-06.

Dynamic mechanical analysis

DMA was performed on a NETZSCH DMA-242 apparatus operating in tensile mode at a frequency of 2 Hz in the temperature range from –160°C to 160°C with a heating rate of 3 K/min.

RESULTS AND DISCUSSION

Synthesis of the Polyamides

The semiaromatic polyamides with high molecular weight have been synthesized by using 1,10-decanediamine with various aromatic diacids in water. In order to improve the molecular weight of the polyamide, the polyamide salts were prepared beforehand so as to obtain the accurately equal reaction ratio of the diacid and the diamine. It is worth noting that the solvent for the salt forming reaction is water, which is cheaper and environmental friendly compared with ethanol used in preparing other common polyamides. In the step of solid-state polycondensation, high vacuum was maintained, which was beneficial for improving the molecular weigh of the polyamides.

FT-IR Analysis

FT-IR spectra of the polyamides are shown in Fig. 1. All the characteristic peaks of amide groups and methylene segments of polyamide are listed as follows: 3329 cm^{-1} (hydrogen-bonded and N—H stretching vibration), 2920 cm^{-1} (N—H in-plane bending vibration), 1632 cm^{-1} (amide I, C=O stretching vibration), 1542 cm^{-1} (amide II, C—N stretching and CO—N—H bending vibration), 1010 cm^{-1} (amide IV, C—CO stretching vibration), 820 cm^{-1} (CH_2 wagging), 655 cm^{-1} (amide V, N—H out-of-plane bending vibration) and 856 cm^{-1} (CH of phenylene vibration).

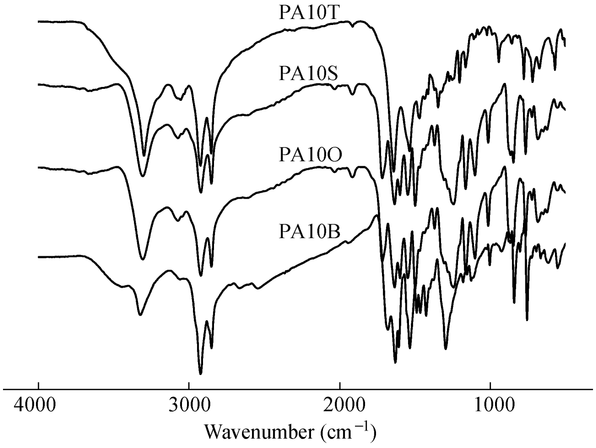
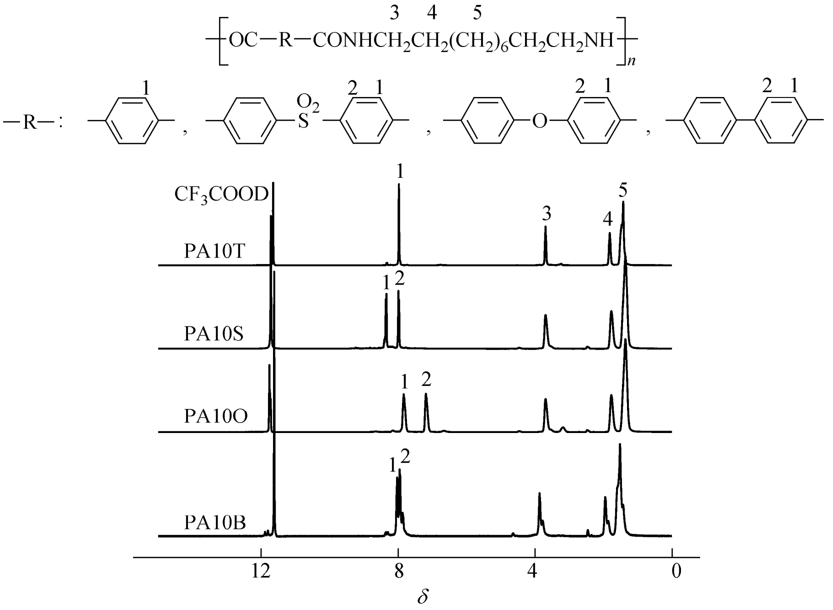


Fig. 1 FT-IR spectra of the polyamides

^{1}H-NMR Analysis

Figure 2 presents the ^{1}H-NMR spectra of the polyamides in deuterated trifluoroacetic acid. The chemical shifts in the range at δ = 7.2–8.4 can be attributed to the aromatic protons (position 1, 2). The chemical shifts at δ = 3.6–3.7 (4H) may be originated from the protons at the position 3, and those at δ = 1.7–1.9 (4H) should come from the protons at the position 4. The peak at δ = 1.3–1.5 (12H) belongs to the other protons of the aliphatic chains (position 5). The peak at δ = 11.6 could be attributed to trifluoroacetic acid. The chemical shifts of the ^{1}H-NMR and FT-IR spectra of the polyamides agree well with the theoretical values of the title compounds.



$$\left[\mathrm{OC{-}R{-}CONH\overset{3}{C}H_2\overset{4}{C}H_2(\overset{5}{C}H_2)_6CH_2CH_2NH}\right]_n$$

Fig. 2 ^{1}H-NMR spectra of the polyamides

Thermal Behavior

Figure 3 depicts the DSC curves of the polyamides. PA10O and PA10T exhibit a double-melting endotherm, which is a common phenomenon observed in semicrystalline polymers. The phenomenon must likely have been caused by recrystallization[12, 13]. The melting temperatures (T_m) of the polyamides gradually increase with increasing the rigid character of the polymeric backbone by enhancing the aromaticity. T_m of PA10T, PA10S, PA10O and PA10B are 305°C, 312°C, 317°C and 343°C. PA10B is difficult to be used by melting processing due to its high T_m.

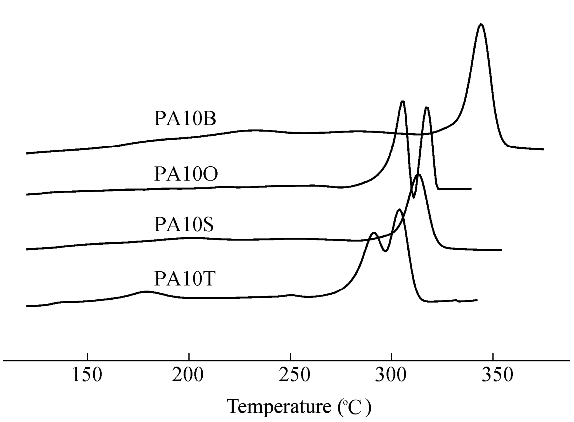


Fig. 3 DSC curves of the polyamides

TGA curves of the polyamides are shown in Fig. 4. All the polyamides start to decompose at about 445°C, with the main weight loss occurring at temperatures of about 482°C (= T_d), which are higher than those of aliphatic polyamides, for example, nylon 66[14]. The results suggest that the thermal stability of the polyamides has been improved by insetting phenylated linkages into the polymeric backbone.

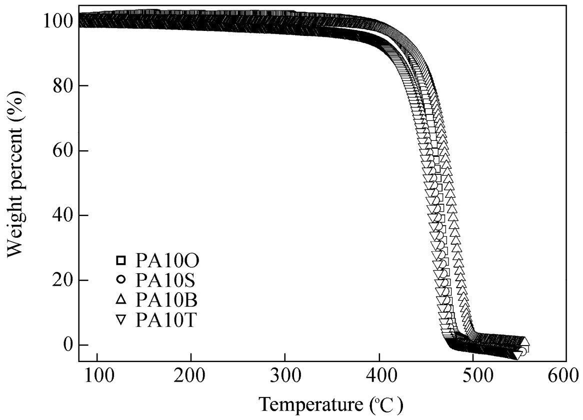


Fig. 4 TGA curves of the polyamides

Dynamic Mechanical Analysis

DMA was used to characterize the polyamides except for PA10B, and the curves are shown in Fig. 5. Three obvious transition behaviors can be observed, and are defined as α, β and γ relaxations, respectively. It is well known that the glass transition temperature (T_g) of polyamide can be determined by α relaxation, since it is usually related to the segment movements in the noncrystalline area[15]. The β relaxation reflects the mobility of carbonyl groups of amorphous region, and the γ relaxation reflects the co-moving of amido and methenes. The γ relaxation also reflects the resultant polyamides exhibit fine low-temperature mechanical properties. The temperatures of α relaxation of PA10T, PA10S and PA10B are about at 125.3°C, 128.6°C and 130.1°C, and the temperatures of β relaxation are about at −44.3°C, −42.5°C and −40.8°C, and the temperatures of γ relaxation are about at −126.9°C, −122.6°C and −120.6°C. The γ relaxations in low temperature area indicate that the polymers have excellent low temperature toughness.

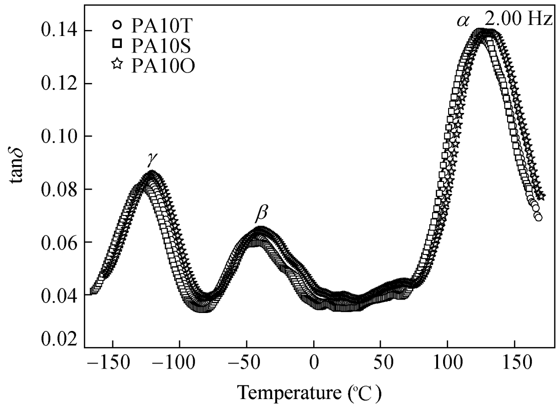


Fig. 5 DMA curves of the polyamides

Water Absorption and Mechanical Properties

Dry and standard samples of the polyamides except for PA10B were prepared by injection-moulding, and their mechanical properties and water absorptions were measured. From Table 1 we can see that the tensile strength and bending modulus of the polyamides are almost the same as those of PA9T and higher than those of PA12T at room temperature[10, 16], and their water absorption is lower than that of PA9T. The low water absorption is conducive to maintain dimensional and mechanical stability of the products.

Table 1. The physical and mechanical properties of PA10T, PA10S, PA10O, PA9T and PA12T

Item	PA10T	PA10O	PA10S	PA9T	PA12T
Density ($g\cdot cm^{-3}$)	1.13	1.14	1.17	1.14	–
Water absorption (%)	0.14	0.13	0.12	0.17	–
Tensile strength (MPa)	100.8	106.9	108.1	92	71.5
Breaking elongation (%)	33	28	31	20	30–50
Bending modulus (GPa)	2.3	2.9	3.2	2.6	2.5
Impact strength ($kJ\cdot m^{-2}$)	5.6	4.4	3.9	–	–

The Solubility of the Resultant Polyamides

The solubility of the polyamides tested with different organic solvents is shown in Table 2. The polyamides can easily dissolve in acidic solvents such as concentrated sulfuric acid and trifluoroacetic acid (TFA) at room temperature, while they are insoluble in dimethylsulphoxide (DMSO), *N*,*N*'-dimethylformamide (DMF), 1-methyl-2-pyrrolidenone (NMP), dimethylacetamide (DMAc), *m*-cresol, tetrahydrofuran (THF), chloroform and other organic solvents. The results show that the polyamides exhibit excellent chemical solvent resistance.

Table 2. The solubility of the polyamides

	PA10T	PA10S	PA10O	PA10B
DMF	–	–	–	–
NMP	–	–	–	–
DMAc	–	–	–	–
DMSO	–	–	–	–
Sulfuric acid	+	+	+	+
m-Cresol	+–	+–	+–	–
Pyridine	–	–	–	–
Chloroform	–	–	–	–
Tetrachloroethane	–	–	–	–
Chlorobenzene	–	–	–	–
Toluene	–	–	–	–
Methanol	–	–	–	–
TFA	+	+	+	+

"+" Soluble at room temperature; "+–" Partially soluble at room temperature; "–" Not soluble at room temperature

CONCLUSIONS

A series of novel semiaromatic polyamides with high molecular weights including PA10T, PA10S, PA10O and PA10B have been synthesized by using 1,10-decanediamine with various aromatic diacids, and characterized by FT-IR and ^{1}H-NMR spectra. The thermal, mechanical properties and dynamic mechanical properties were investigated. Polyamides PA10T, PA10S and PA10O display good mechanical properties and heat resistance, which are very close to those of PA9T. It's worth noting that the polyamides could be prepared from convenient raw materials using the environmental friendly solvent (water). Compared with PA9T, the low water absorption and good flexibility of the polyamides demonstrate that they could be promising engineering plastics with excellent heat resistance and processibility.

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