

# Environment-Friendly Synthesis of Long Chain Semiaromatic Polyamides with High Heat Resistance

Wenzhi Wang, Xianwen Wang, Ruixue Li, Baoyu Liu, Ergang Wang, Yonghua Zhang

College of Material Science and Engineering, South China University of Technology, Guangzhou 510640, People's Republic of China

Received 24 September 2008; accepted 4 May 2009

DOI 10.1002/app.30774

Published online 30 June 2009 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Long chain semiaromatic polyamides have been synthesized by the reactions of terephthalic acid with long chain aliphatic diamines, and characterized by infrared spectrum, nuclear magnetic resonance and elemental analysis. The thermal behaviors were studied by differential scanning calorimetry analysis and thermogravimetric analysis. The resultant polyamides have intrinsic viscosity ranging from 1.75 to 1.93 dLg<sup>-1</sup>. The solubility, dynamic mechanical and mechanical properties of the polyamides have also been investigated. The mechanical properties and heat resistance of long chain semiaromatic

polyamides were compared with those of PA9T. PA10T has the advantages of low cost and preparation from environmental friendly solvents and possesses the similar mechanical properties and heat resistance compared to PA9T. The long chain semiaromatic polyamides are a class of promising, heat-resisting and processability engineering plastics. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 2036–2042, 2009

**Key words:** semiaromatic polyamides; polycondensation; characterization; engineering plastics

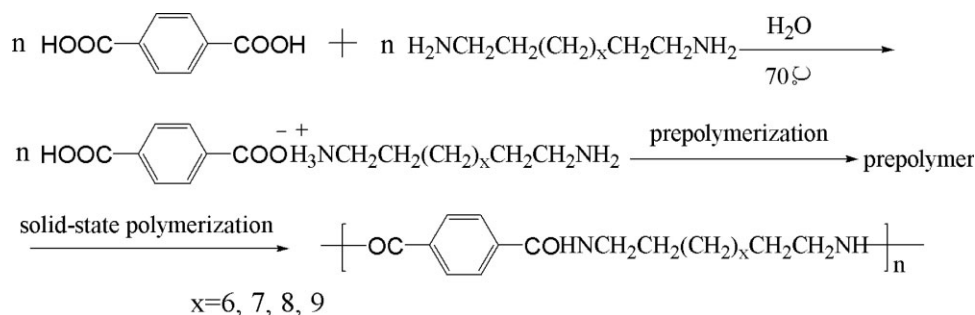
## INTRODUCTION

Aliphatic polyamides such as poly( $\epsilon$ -caprolactam) (nylon6) and poly(hexamethylene adipamide) (nylon66), are a class of engineering thermoplastics, which play key roles in industrial and commercial applications<sup>1</sup> because of their high tensile strength, excellent chemical resistance, fine abrasion and easily processing characteristics. However, these aliphatic polyamides also have some disadvantages such as high moisture absorption, poor dimensional stability and thermal properties. The application of them are limited to those involving exposure to temperatures which remain below 100°C for their low glass transition temperature ( $T_g$ ) of  $\sim 50^\circ\text{C}$ . For improving the heat resistance and strength of polyamides, aromatic rings were incorporated into their backbone.<sup>2–11</sup> According to these strategies, lots of aromatic and semiaromatic polyamides are commercial available, such as poly(*p*-phenylene terephthalamide) (PPTA),<sup>12</sup> poly(*m*-phenyleneisophthalamide) (PMIA),<sup>13</sup> poly(hexamethyleneterephthalamide) (PA6T),<sup>14,15</sup> poly(hexamethyleneisophthal-amide) (PA6I),<sup>16,17</sup> poly(nonamethylenetere-phthalamide) (PA9T).<sup>18,19</sup> Aromatic polyamides, PPTA and PMIA have been noted for their high thermal stability, chemical resistance, high strength, and high modulus as fibers. However, it is

impossible to produce them by melting process due to their high glass transition and melting temperatures originated from the strong interchain forces and inherent macromolecular rigidity. The semiaromatic polyamide, which contained aliphatic chain, can modify their processability of them. Nevertheless, PA6T contained six-methylene is difficult to produce by melting process owing to the excessive high  $T_m$ . Increasing the number of methylene to nine yields PA9T, which exhibits good processability due to the long flexible aliphatic linkage. Thus, PA9T inherits the merits of the heat-durability of aromatic polyamides and the processing ability of aliphatic polyamides, resulting in their wide application in the electric/electronic and automobile industries. However, nonanediamine, the monomer material of PA9T was prepared by complex procedures, resulting in the high price of PA9T, which limits their applications in extensive industrial fields. Therefore, it is of great significance to synthesize novel, low-cost, high-performance and processability semiaromatic polyamide.

In this contribution, we have synthesized a series of novel semiaromatic polyamides: poly(decamethyleneterephthalamide) (PA10T), poly(undecamethyleneterephthalamide) (PA11T), poly(dodecamethyleneterephthalamide) (PA12T) and poly(tridecamethyleneterephthalamide) (PA13T) by the reactions of terephthalic acid with 1,10-decanediamine, 1,11-undecanediamine, 1,12-dodecanediamine, and 1,13-tridecanediamine, respectively. The long chain diamines

Correspondence to: W. Wang (wwwzscut@gmail.com).



Scheme 1 Synthesis of the polyamides.

are prepared from the corresponding long chain diacids by cyanating and aminating subsequently, which can be facily obtained from light wax. The low cost preparation of the long chain diamines obviously reduces the price of the resulting polyamides PA10T, PA11T, PA12T, and PA13T, compared to the commercialized PA9T. The influence of the different number of methylene ranging from 10 to 13 on thermal and mechanical properties was studied. The resultant polyamides were investigated by infrared spectrum (FTIR), nuclear magnetic resonance ( $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$ ). The thermal analysis, mechanical property, water-absorbing capacity, and dynamic mechanical analysis (DMA) of the resultant polyamides were studied.

## EXPERIMENTAL

### Materials

Terephthalic acid was purchased from Beijing Yan-shan Lithification Chemical Co. (China) and 1,10-decanediamine, 1,11-undecanediamine, 1,12-dodecanediamine, 1,13-tridecanediamine were provided commercially by Zibo Guangtong Chemical Co. (China). Diamines were purified by vacuum distillation before use.

### Synthesis

PA10T was synthesized as follows (Scheme 1). 1,10-decanediamine (258 g, 1.5 mol) was dissolved in distilled water (1000 mL) at  $70^\circ\text{C}$ . 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  $85\text{--}95^\circ\text{C}$ . The white 1,10-decanediamine-terephthalic acid salt (PA10T salt) precipitated from the solution was filtered over a Buchner funnel and then repeatedly washed with distilled water. After drying in a vacuum desiccator for 12 h, the salt was obtained as a white powder (476.6 g, 94%).

PA10T salt (476.6 g) was added into an autoclave and distilled water (400 g) was added to reduce volatilization of diamine during the polymerization. The autoclave was filled with carbon dioxide at

room temperature and then heated to  $220^\circ\text{C}$ , meanwhile the pressure up 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  $240^\circ\text{C}$ . After reaction for another 2 h, the prepolymer of PA10T was obtained (433.6 g, 91%).

The prepolymer of PA10T was added into a solid-state polymerization kettle. Then, the kettle was evacuated to 10 Pa and the reaction temperature was increased to  $250^\circ\text{C}$ . After 24 h, the kettle was cooled to room temperature and the high molecular weight of PA10T was obtained (412 g, 95%).

PA11T, PA12T, and PA13T were prepared by the similar procedures with 1,11-undecanediamine, 1,12-dodecanediamine, and 1,13-tridecanediamine instead of 1,10-decanediamine, respectively.

### Characterization

The polyamides were characterized by FTIR,  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$ , elemental analysis, intrinsic viscosity, differential scanning calorimetry (DSC), DMA and TGA. The mechanical properties were investigated at different temperatures by the universal testing machine.

The intrinsic viscosities of the polyamides dissolved in concentrated sulfuric acid were determined in an Ubbelohde viscometer at  $25^\circ\text{C} \pm 0.1^\circ\text{C}$ . The FTIR spectra were prepared by melting pressed-disc technique on a NICOLET 460 spectrometer.  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra were recorded with a Bruker DPX-400 (400 MHz), using deuterated trifluoroacetic acid as solvents and tetramethylsilane as an internal reference. Elemental analyses were performed on a Perkin-Elmer 2400 CHNS/O elemental analyzer at  $975^\circ\text{C}$  under nitrogen atmosphere.

Thermal analysis (DSC-TG) was carried out in a nitrogen stream using a NETSCH 204 calorimeter with a heating rate of  $10^\circ\text{C min}^{-1}$ . DMA was performed on a NETZSCH DMA-242 apparatus operating in tensile mode at a frequency of 2 Hz in the temperature ranged from  $-160^\circ\text{C}$  to  $160^\circ\text{C}$  with a heating rate of  $3^\circ\text{C min}^{-1}$ . Mechanical properties

were investigated by a universal testing machine (CMT5104) equipped with a temperature controlled oven at 23, 50, 100, and 150°C.

## RESULTS AND DISCUSSION

### Synthesis of PA10T, PA11T, PA12T, and PA13T

A series of novel high molecular weights semiaromatic polyamides were synthesized by the reactions of terephthalic acid with 1,10-decanediamine, 1,11-undecanediamine, 1,12-dodecanediamine, and 1,13-tridecanediamine, respectively. For improving the molecular weights of the polyamides, polyamide salts were prepared beforehand so as to maintain 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. At the stages of the prepolymerization, high vapor pressure was applied to reduce the diamine loss. In the step of solid-state polycondensation, high vacuum was maintained, which is benefit for avoiding side reaction and improving the molecular weights of the polyamides. The molecular weights of the polyamides were characterized by intrinsic viscosities, which are listed in Table 2.

### Infrared spectra

FTIR spectra of the PA10T, PA11T, PA12T, and PA13T are shown in Figure 1. All the characteristic absorptions of amide groups and methylene segments of polyamide are listed as following: 3290/3293/3305/3297  $\text{cm}^{-1}$  (hydrogen-bonded and N—H stretching vibration), 2913/2915/2919/2912  $\text{cm}^{-1}$  (N—H in-plane bending vibration), 1623/1630/1624/1629  $\text{cm}^{-1}$  (amide I, C=O stretching vibration), 1538/1540/1538/1541  $\text{cm}^{-1}$  (amide II, C—N stretching and CO—N—H

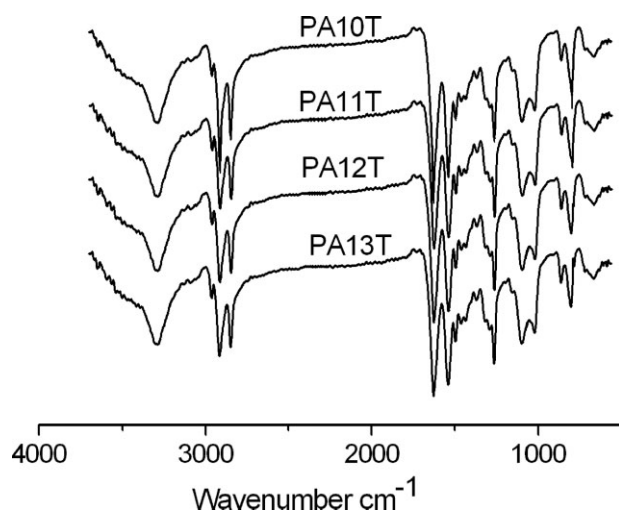


Figure 1 FTIR spectra of the obtained polyamides.

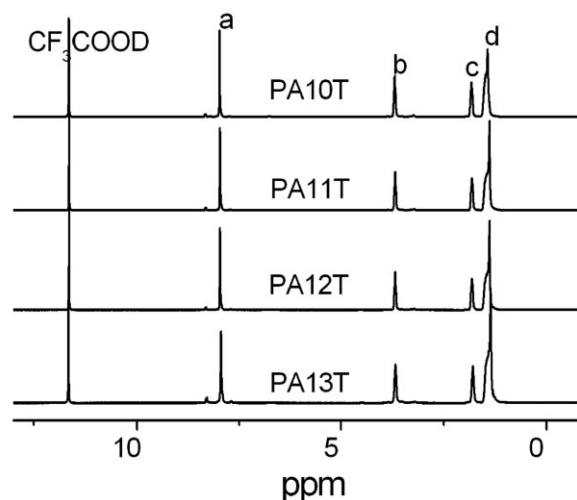
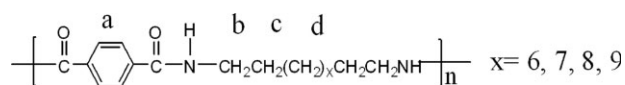


Figure 2  $^1\text{H-NMR}$  spectra of the obtained polyamides.

bending vibration), 1020/1013/1020/1021  $\text{cm}^{-1}$  (amide IV, C—CO stretching vibration), 804/797/797/812  $\text{cm}^{-1}$  ( $\text{CH}_2$  wagging), 650/658/650/673  $\text{cm}^{-1}$  (amide V, N—H out-of-plane bending vibration) and 866/866/859/868  $\text{cm}^{-1}$  (CH of phenylene vibration).

### $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ analysis

Figure 2 presents the  $^1\text{H-NMR}$  spectra of the resultant polyamides in deuterated trifluoroacetic acid. The chemical shifts in the range at 7.7–8.3 ppm (4H) are attributed to the aromatic protons (position *a*). The chemical shifts at 3.7 ppm (4H) originate from the protons at the position *b*, and that at 1.8 ppm (4H) come from the protons at the position *c*. The peaks at 1.4 ppm belong to the other protons of the aliphatic chains (position *d*). The peaks at 11.6 ppm are attributed to trifluoroacetic acid.

The  $^{13}\text{C-NMR}$  spectra of the polyamides (Figure 3) show that the peaks at 171.4 ppm correspond to the carbon atoms of  $-\text{C}^*\text{ONH}-$ . The chemical shifts at 134.8 ppm and 127.9 ppm come from the carbon atoms of benzene. The chemical shifts at 42.1 ppm come from the carbon atoms of  $-\text{CONHC}^*\text{H}_2-$ . The peaks at 110.2–118.1 and 161.7 ppm are attributed to trifluoroacetic acid. The rest bands are owing to the aliphatic carbon atoms of  $-\text{C}^*\text{H}_2-$ .

The Chemical Shifts of the  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra of the resultant polyamides agree well with the theoretical values of the title compounds.

### Elemental analysis

Table 1 presents the measured and calculated percentages of carbon, hydrogen, nitrogen and oxygen of the

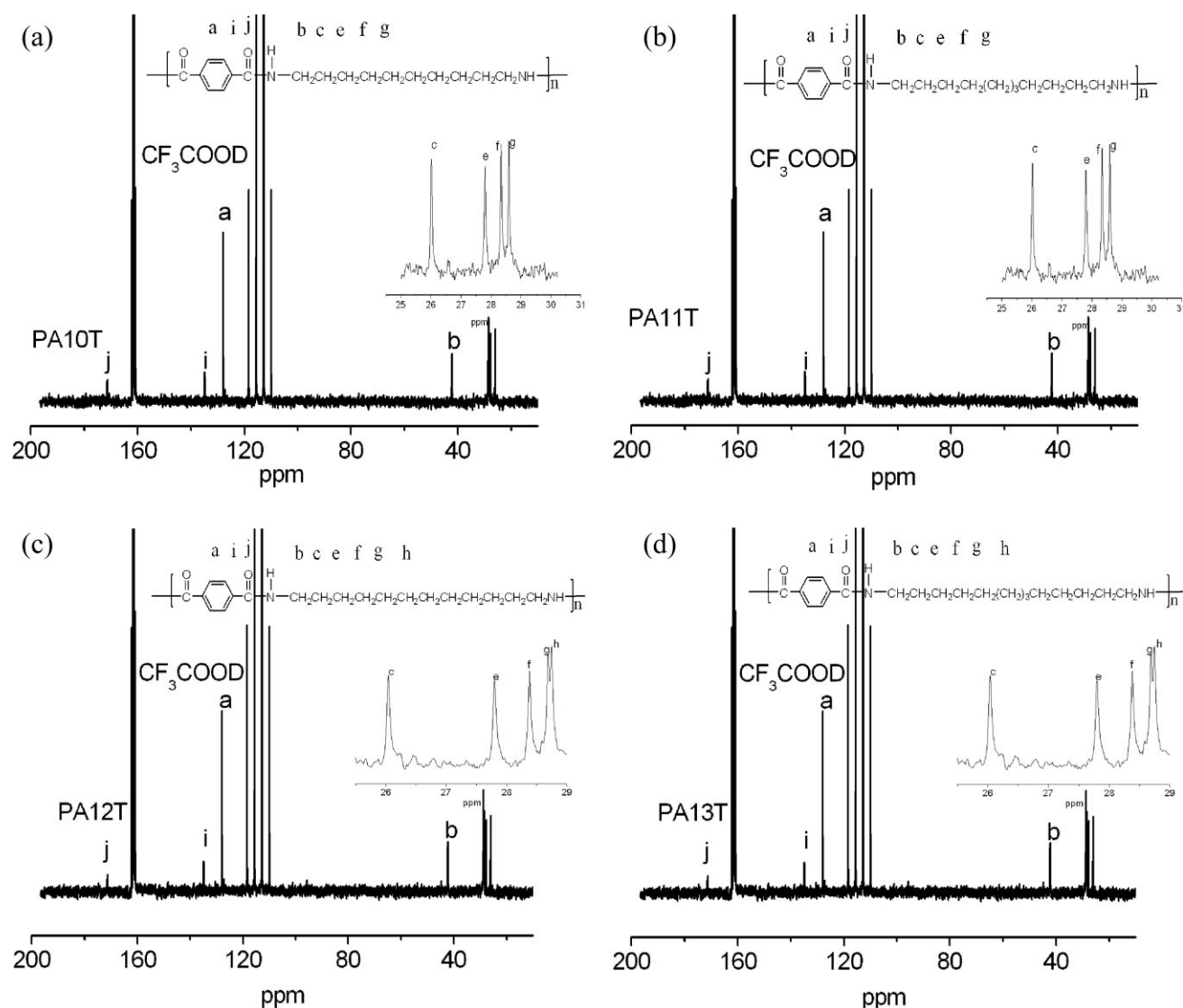


Figure 3  $^{13}\text{C}$ -NMR spectra of the obtained polyamides (a) PA10T, (b) PA11T, (c) PA12T, (d) PA13T.

polyamides. The result suggests that the measured values are comparable to the theoretical ones.

#### Water-absorbing of the obtained polyamides

The water-absorbing of the resultant polyamides were measured according to ASTM D570 Standard, and the results are listed in Table 2. It can be seen that the water-absorbing of the resultant polyamides decrease slowly with increasing the amount of meth-

ylene of polymer backbone, and all of them are slightly lower than that of PA9T. The low water absorption is conducive to maintain dimensional and mechanical stability of products.

#### Thermal behaviors

Figure 4 depicts the DSC curves of the polyamides. PA10T and PA11T exhibit double-melting endotherms, which is a common phenomenon observed

TABLE I  
Elemental Analysis Data of the Obtained Polyamides

Sample	Carbon (%)		Hydrogen (%)		Nitrogen (%)		Oxygen (%)	
	Calc.	Meas.	Calc.	Meas.	Calc.	Meas.	Calc.	Meas.
PA10T	64.67	64.65	7.78	7.73	8.38	8.35	19.16	19.18
PA11T	65.51	65.34	8.05	8.01	8.05	8.04	18.39	18.41
PA12T	66.29	66.26	8.29	8.27	7.73	7.69	17.68	17.73
PA13T	67.02	66.98	8.51	8.44	7.45	7.37	17.02	17.08

**TABLE II**  
The Intrinsic Viscosity, Thermal Data, and Water-Absorbing Capacity of the Obtained Polyamides

Samples	$[\eta]$ (dL g <sup>-1</sup> )	$T_m$ (°C)	$T_c$ (°C)	$T_d$ (°C)	$T_g$ (°C)	Water-absorbing capacity (%)
PA10T	1.75	313	276	491	132.6	0.15
PA11T	1.89	300	263	490	123.4	0.13
PA12T	1.76	294	254	489	118.5	0.12
PA13T	1.93	285	238	487	111.4	0.10

in semicrystalline polymers.<sup>20–22</sup> Additionally, the melting temperatures ( $T_m$ ) and the crystalline temperatures ( $T_c$ ) of the polyamides decrease with increasing the amount of methylene of polymeric backbone. PA13T has the lowest melting point and crystallizing point among the series of the resultant polyamides, with the  $T_m$  of 284°C and  $T_c$  of 239°C, respectively.

TG curves of the resultant polyamides are shown in Figure 5. All the polyamides begin decomposition at about 426°C, with the framework collapses temperatures ( $T_d$ ) at about 490°C, which are higher than those of nylon 66.<sup>23</sup> The result suggests that the thermal stability of the polyamides has been improved by insetting phenylated linkage into the polymeric backbone. The thermal data of the polyamides in this work are listed in Table 2.

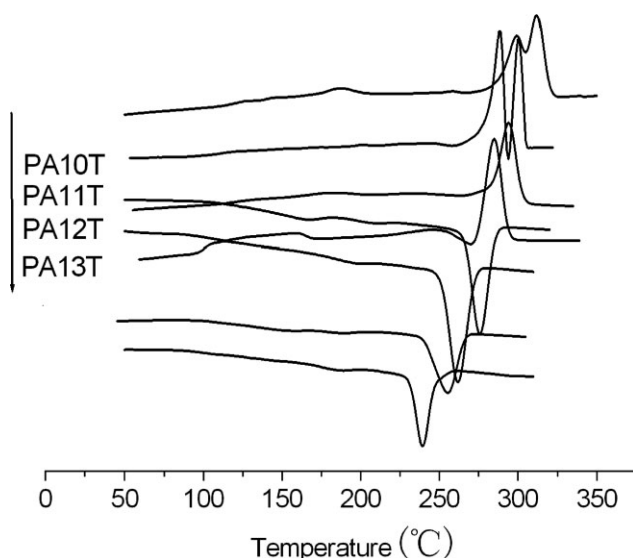
### The solubility of the resultant polyamides

The solubility of the resultant polyamides was tested with different organic solvents which are shown in Table 3. The sample (100 mg) of the polyamides was added into test tube (10 mL) containing appropriate solvent, and the solubility was observed. The resultant polyamides can easily dissolve in acidity solvents such as concentrated sulfuric acid and tri-

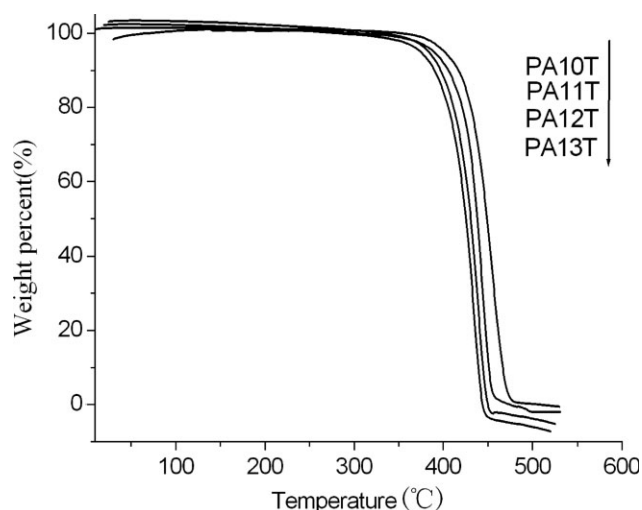
fluoroacetic acid (TFA) at room temperature, while they are insoluble in dimethylsulphoxide, *N,N'*-dimethylformamide (DMF), 1-methyl-2-pyrrolidone (NMP), dimethylacetamide (DMAc), *m*-cresol, tetrahydrofuran (THF), and chloroform. The result shows that the resultant polyamides exhibit well chemical solvents resistance.

### Dynamic mechanical analysis

DMA was used to characterize the resultant polyamides, and the curves are shown in Figure 6. Three obvious transition behaviors can be observed, and are defined as  $\alpha$ ,  $\beta$ , and  $\gamma$  relaxation, respectively. It is well known that the  $T_g$  of polyamide can be determined by  $\alpha$  relaxation, since it is usually related to the segment movements in the noncrystalline area.<sup>24</sup> The  $\beta$  relaxation reflects the mobility of carbonyl group of amorphous region, and the  $\gamma$  relaxation reflects the comoving of amido and methene. It is noted that the  $\gamma$  relaxation also reflects the resultant polyamides exhibit fine low-temperature mechanical properties. The temperatures of  $\alpha$  relaxation of the polyamides are 132.6, 123.4, 118.5, and 111.4°C; the temperatures of  $\beta$  relaxation are -38.9, -43.1, -51.2, and -58.2°C, and the temperatures of  $\beta$  relaxation are -121.5, -125.3, -131.8, and -135.2°C. The  $\alpha$ ,  $\beta$ , and  $\gamma$  relaxation temperatures decrease with increasing the amount of methylene of polymeric backbone.



**Figure 4** DSC curves of the obtained polyamides.



**Figure 5** TG curves of the obtained polyamides.

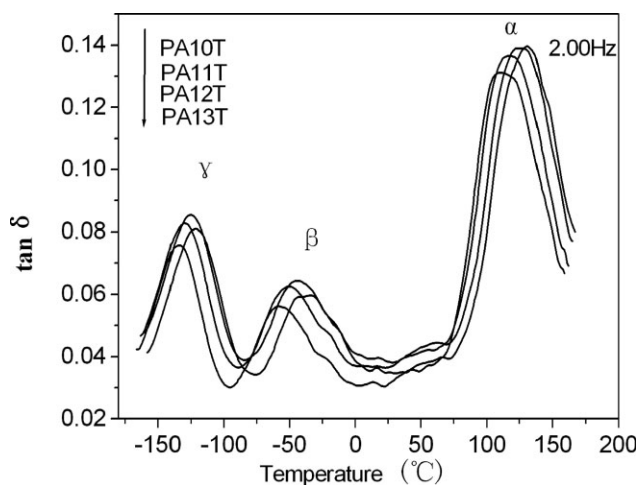
**TABLE III**  
The Solubility of the Obtained Polyamides

	PA10T	PA11T	PA12T	PA13T
DMF	-	-	-	-
NMP	-	-	-	-
DMAc	-	-	-	-
DMSO	-	-	-	-
Sulfuric acid	+	+	+	+
m-Cresol	±	±	±	±
Pyridine	-	-	-	-
Chloroform	-	-	-	-
Tetrachloroethane	-	-	-	-
Chlorobenzene	-	-	-	-
Toluene	-	-	-	-
Methanol	-	-	-	-
TFA	+	+	+	+

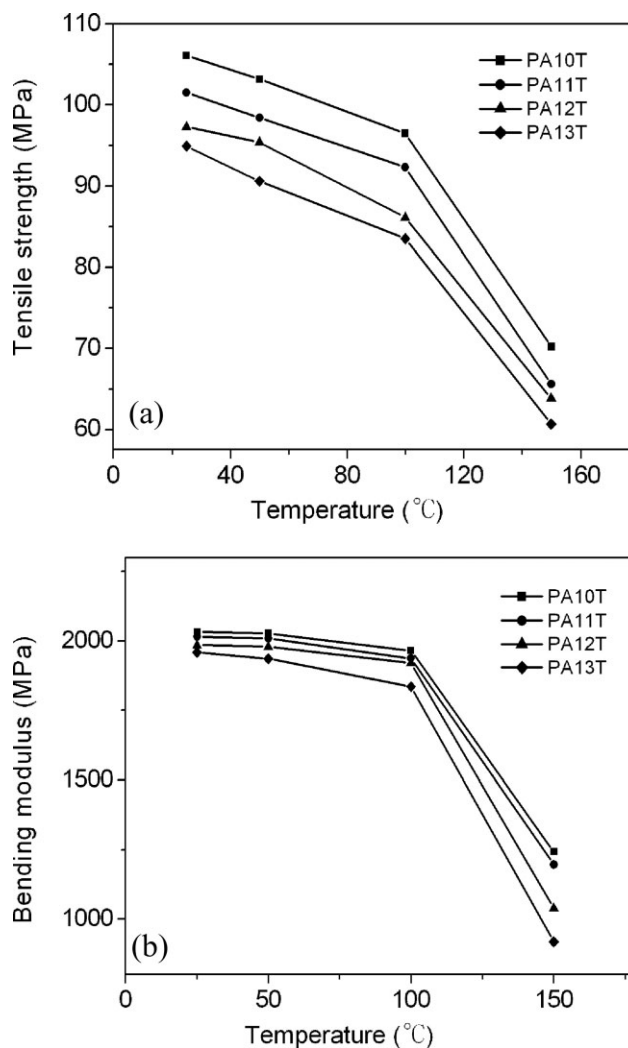
“+” indicating soluble at room temperature, “±” indicating partially soluble at room temperature, and “-” indicating insoluble.

### Mechanical properties

Dry and standard specimens of the polyamides by injection moulding were prepared, and their mechanical properties were measured according to ASTM D638 Standard and ASTM D790. The tensile strength (above 95 MPa) and bending strength (above 1952 MPa) of the resultant polyamides are almost equal to that of PA9T at room temperature, as shown in Figure 7.<sup>25</sup> With the measurement temperature increasing from 25 to 100°C, its strength decrease slowly. Above 100°C, the tensile strength decrease quickly. This phenomenon is similar to that of PA9T because the molecular chain is easy to move above the glass transition temperature, which is in accordance with the result of DMA of the obtained polyamides.



**Figure 6** DMA curves versus temperature of the obtained polyamides.



**Figure 7** Mechanical properties versus temperature of the obtained polyamides (a) Tensile strength; (b) bending modulus.

### CONCLUSION

A series of novel high molecular weights semi-aromatic polyamides PA10T, PA11T, PA12T, and PA13T have been synthesized by the reactions of the terephthalic acid with long chain diamines, respectively. The resultant polyamides were investigated by infrared spectrum (FTIR), nuclear magnetic resonance (<sup>1</sup>H-NMR and <sup>13</sup>C-NMR), thermal analysis, mechanical property, and DMA. The polyamides exhibit well processability, high melting temperature, low water-absorbing capacity, and excellent mechanical property, and are promising high performance engineering plastics.

### References

- Sergei, V. L.; Edward, D. W.; Menachem, L. *Polym Int* 1999, 48, 532.

2. Kudo, K.; Suguie, T.; Hiram, M. *J Appl Polym Sci* 1992, 44, 1625.
3. Liu, Y.; Donovan, J. A. *Polymer* 1995, 36, 4797.
4. Zhang, G. Z.; Yoshida, H.; Kawai, T. *Thermochim Acta* 2004, 416, 79.
5. Khanna, Y. P.; Murthy, N. S.; Kuhn, W. P.; Day, E. D. *Polym Eng Sci* 1999, 39, 2222.
6. Brisson, J.; Breault, B. *Macromolecules* 1991, 24, 495.
7. Persyn, O.; Miri, V.; Lefebvre, J. M.; Ferreiro, V.; Brink, T.; Stroeks, A. *J Polym Sci Part B: Polym Phys* 2006, 44, 1690.
8. Shibayama, M.; Uenoyama, K.; Oura, J. I.; Nomura, S.; Iwamoto, T. *Polymer* 1995, 36, 4811.
9. Endo, M.; Morishima, Y.; Yano, S.; Tadano, K.; Murata, Y.; Tsunashima, K. *J Appl Polym Sci* 2006, 101, 3971.
10. Ellis, T. S. *Macromolecules* 1990, 23, 1494.
11. Hiroshi, A.; James, L.W.; John, F. F. *J Appl Polym Sci* 1979, 23, 2293.
12. Rao, Y.; Waddon, A. J.; Farris, R. J. *Polymer* 2001, 42, 5937.
13. Juan, J. F.; Jose, G.; Campa, D. L.; Angel, E. L.; Javier, D. A. *J Appl Polym Sci Part A: Polym Chem* 2005, 43, 5300.
14. Alberto, B.; Domennico, G.; Mario, G.; Pietro, M.; Giorgio, M. *Macromoleculen* 1986, 19, 2693.
15. Kudo, K.; Suguie, J.; Hiram, M. *J Appl Polym Sci* 1992, 44, 1625.
16. Siciliano, A.; Severgnini, D.; Seves, A.; Pedrelli, T.; Vicini, L. *J Appl Polym Sci* 1996, 60, 1757.
17. Eersels, K. L.; Groeninckx, G. *Polymer* 1996, 37, 983.
18. Ahmed, J. U.; Ohkoshi, Y.; Gotoh, Y. *J Polym Sci Part B: Polym Phys* 2003, 41, 2878.
19. Ahmed, J. U.; Ohkoshi, Y.; Gotoh, Y. *J Polym Sci Part B: Polym Phys* 2004, 42, 433.
20. Li, Y. J.; Zhu, X. Y.; Tian, G. H.; Yan, D.; Zhou, E. L. *Polym Int* 2001, 50, 677.
21. Ramesh, C.; Keller, A.; Eltink, S. J. *Polymer* 1994, 35, 5300.
22. Hvharl, F. J.; Plan, J. D. *J Appl Polym Sci* 1967, 11, 1449.
23. Levchik, S. V. *Polym Int* 1999, 48, 532.
24. Li, W. H.; Yan, D. Y. *J Appl Polym Sci* 2003, 88, 2462.
25. Ma, J. M.; Song, S. W.; Guo, J. *Mod Plast Process Appl* 2003, 15, 41.