Synthesis and Thermal Decomposition of Poly(dodecamethylene terephthalamide)

Minying Liu, Kaifeng Li, Shaohui Yang, Peng Fu, Yudong Wang, Qingxiang Zhao

School of Materials Science and Engineering, Zhengzhou University, Zhengzhou 450052, People's Republic of China

ABSTRACT: A kind of semiaromatic polyamide, poly(dodecamethylene terephthalamide) (PA12T) was synthesized via a polycondensation reaction of terephthalic acid and 1,12-dodecanediamine. The structure of prepared PA12T was characterized by Fourier transform infrared spectroscopy, proton nuclear magnetic resonance (^{1}H-NMR), and elemental analysis. The mechanical properties of PA12T were also studied. The thermal behavior of PA12T was determined by differential scanning calorimetry, thermogravimetric analysis, and dynamic mechanical analysis. Pyrolysis products and thermal decomposition mechanism of PA12T were analyzed by pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS). Melting temperature (T_m), glass transition temperature (T_g), and decomposition temperature (T_d) of PA12T are 310°C, 144°C, and 429°C, respectively. The Py-GC/MS results showed that the pyrolysis products were mainly composed of 32 kinds of compounds, such as benzonitrile, 1,4-benzenedicarbonitrile, *N*-methylbenzamide, *N*-hexylbenzamide, and aromatic compounds. The major pyrolysis mechanisms were β-CH hydrogen transfer process, main-chain random scission, and hydrolytic decomposition. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 3369–3376, 2011

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

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.[1,2] The commonly mentioned aromatic and semiaromatic polyamides cannot be processed by melting method, because their decomposition temperatures are usually lower than melting temperatures,[3,4] such as PA6T. To improve their processing performance, several approaches have been made through synthetic modification by incorporation of flexible linkages,[5] bulky pendant groups,[6] and noncoplanar biphenylene moieties[7] into molecular chains of semiaromatic polyamides. Introducing long flexible aliphatic chains into the backbone of semiaromatic polyamides is a commonly used method.[8–10] Polynonamethylene terephthalamide (PA9T), which has relative longer molecular chain length than PA6T, keeps the merits of the heat resistance of aromatic polyamides and the processing ability of aliphatic polyamides.[11] However, the high price of nonanediamine resulted in high cost of PA9T, which limited its applications. Therefore, it is of great significance to synthesize novel and low-cost semiaromatic polyamides with high performance and good processability.

It has been reported that diamines with long molecular chains can be prepared from a petroleum fermentation process using light wax as raw material.[12] The cost of obtaining long-chain diamines was reduced accordingly. In this work, poly(dodecamethylene terephthalamide) (PA12T) was prepared using 1,12-dodecanediamine [NH$_2$—(CH$_2$)$_{12}$—NH$_2$] obtained by petroleum fermentation process, which has relatively lower price compared to PA9T. Comparing with PA6T, PA9T, or PA10T, which has comparable molecular weight, PA12T has longer molecular chain, fewer numbers of amide groups, and more numbers of methylene, which brings on lower water absorption, better dimensional stability, better processing performance, and higher impact resistance.

Polymers or copolymers based on PA12T have been reported earlier.[13–18] However, most of these references did not describe the synthesis of PA12T, and mechanical properties and thermal performance were not reported hitherto. In this work, PA12T was synthesized by polycondensation reaction of terephthalic acid and 1,12-dodecanediamine in water. The structure of PA12T was investigated by Fourier transform infrared (FTIR) spectroscopy, proton nuclear magnetic resonance (^{1}H-NMR), and elemental

analysis. The thermal property was studied by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and dynamic mechanical analysis (DMA). The thermal decomposition process was analyzed by pyrolysis-gas chromatography/ mass spectrometry (Py-GC/MS). The solubility, intrinsic viscosity, water-absorbing capacity, and mechanical property of PA12T were also studied.

EXPERIMENTAL

Materials

Terephthalic acid was purchased from Luoyang Petrochemical Engineering Corp. (China), and 1,12-dodecanediamine was provided commercially by Zibo Guangtong Chemical Co. (China) and purified by vacuum distillation before use.

Synthesis of PA12T

PA12T was prepared from the reaction of terephthalic acid and 1,12-dodecanediamine through a three-step procedure: salt formation, prepolymerization, and solid-state polymerization (SSP; Fig. 1).

Terephthalic acid (332 g and 2.0 mol) was dissolved in distilled water (1000 mL) at 80°C. Then, the solution was added slowly into 500 mL of distilled water mixture of 1,12-dodecanediamine (400 g and 2.0 mol) with vigorous stirring and then stirred for 2 h at 80°C. Finally, a slight excess of 1,12-dodecanediamine (2 g and 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 1,12-dodecanediamine-terephthalic acid salt (PA12T salt) was precipitated from the solution.

After filtering over a Buchner funnel and drying in a vacuum desiccator for 8 h, the white salt of PA12T (553 g) and water (110 mL) was added into an autoclave for polymerization. The autoclave was filled with carbon dioxide and then heated to 220°C while increasing the pressure to 3.2 MPa with stirring. After 2 h, the pressure of autoclave was gradually decreased to normal pressure in 2 h by deflating, and the reaction temperature was increased to 230°C. After reaction for another 1.5 h, the ivory-white PA12T powders with diameter of 0.1–3 mm were obtained (503 g).

The obtained PA12T powders were dried at 80°C in a vacuum oven for 12 h and then added into a stainless steel kettle for SSP process, and the SSP process was carried out at 280°C for 15 h under a vacuum of 10 Pa. Finally, the kettle was cooled to room temperature, and white granular PA12T products were obtained (478 g).

Characterization of PA12T

FTIR, ^{1}H-NMR, and elemental analysis were used to confirm the structure of PA12T. The thermal behaviors were determined by DSC, TGA, and DMA. Thermal decomposition mechanisms of PA12T were analyzed by Py-GC/MS. The solubility, intrinsic viscosity, inherent viscosity, water-absorbing capacity, and mechanical property of PA12T were also studied.

Intrinsic viscosity and inherent viscosity of PA12T dissolved in concentrated sulfuric acid were determined in an Ubbelohde viscometer at 25°C $\pm$ 0.1°C. The water absorbing of PA12T was measured according to GB/T1034 (China standard).

FTIR measurement was carried out on a NICOLET 460 spectrometer. ^{1}H-NMR spectra were 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 with a heating rate of 10°C min^{-1} in a nitrogen stream. DMA was carried out on a NETZSCH DMA-242 apparatus operating in the bending mode at 1 Hz and a heating rate 3°C min^{-1} from −170 to 200°C.

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

The samples of PA12T were pyrolyzed with a set point of 700°C per 5 s using a Chemical Data Systems Pyroprobe 2000. Pyrolyses were carried out in helium using a coil probe. The sample weights used ranged from 0.1 to 1 mg, and no changes in pyrolysis product distribution were observed. Analysis was performed using an Agilent GC/MS(6890A/ 5973) system with a DB-FFAP (nitroterephthalic acid modified polyethylene glycol) capillary columns from J and W Company (60 μm × 250 μm × 0.25
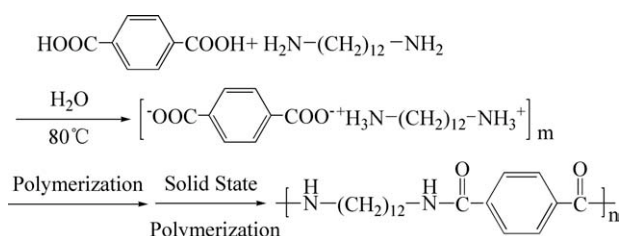
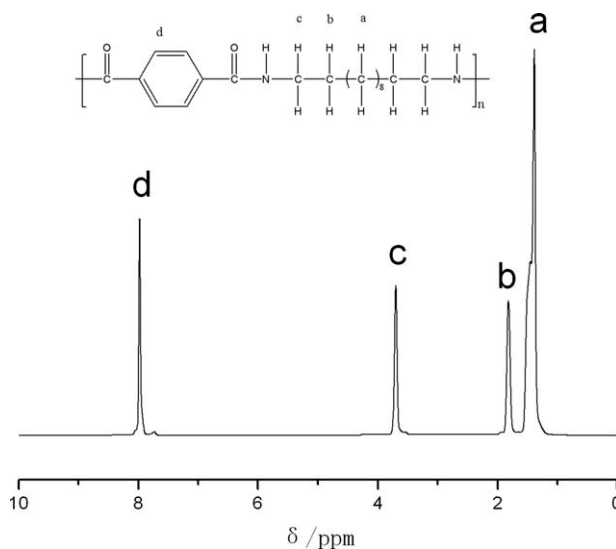**Figure 1** The synthetic route of PA12T.
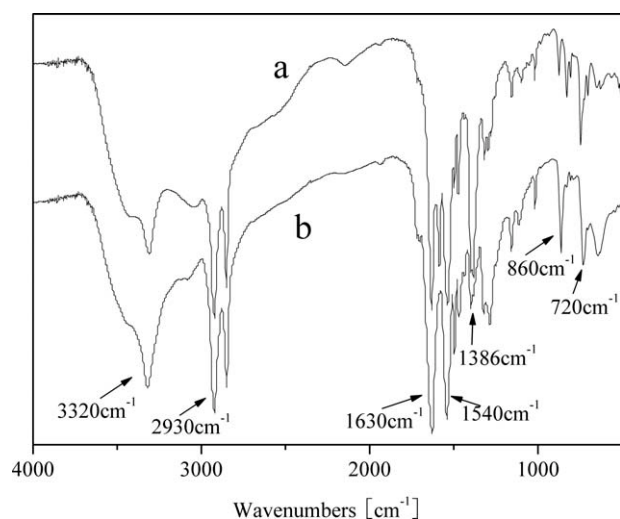
Figure 2 FTIR spectra of PA12T prepared by (a) polymerization and (b) SSP.

Figure 3 ^{1}H-NMR spectra of PA12T.

μm). The oven temperature program was as follows: 40°C, initial time 5 min, heating rate 3°C min^{-1}, then temperature 200°C holding 10 min, and final temperature 230°C for 20 min. Helium was used as the carrier gas. Mass spectra were acquired by a Nist98 Mass Spectra Library data system operating under HP Chemistry Station G1034. The mass spectrometer was scanned, repetitively, from m/z 500 to m/z 20 at a scan rate of 0.7 s/decade, and the ionizing conditions were 70 eV.

RESULTS AND DISCUSSION

Synthesis of PA12T

PA12T was prepared from the reaction of terephthalic acid and 1,12-dodecanediamine through a three-step procedure: salt formation, polymerization, and SSP. To assure an accurate equivalent ratio of 1,12-dodecanediamine to terephthalic acid, PA12T salt was prepared first. Then, an slight excess 1,12-dodecanediamine was added into the salt solution to compensate reaction system for the loss during the polymerization reaction. It is noticeable that the solvent for salt formation reaction is water, which is cheaper and environmental friendly compared with ethanol, usually used in preparing other common polyamides.[19] To obtain high vapor pressure, water was added to reduce volatilization of diamine during the polymerization. The powdered product was convenient for discharging from the bottom of autoclave and benefit for removing water during the stage of SSP reaction. To avoid side reaction and improve the molecular weight of the polyamide, high vacuum was maintained during the SSP reaction. The products obtained from polymerization and SSP proc-

esses have been boiled in Soxhlet apparatus and extracted with ethanol for 8 h before used. The intrinsic viscosity and inherent viscosity of prepared PA12T are 1.76 and about 1.68 dLg^{-1}, respectively.

FTIR spectrum of PA12T is shown in Figure 2. All the characteristic peaks of amide groups and methylene segments of polyamide are listed as follows: 3320 cm^{-1} (hydrogen-bonded and N—H stretching vibration), 2930 cm^{-1} (N—H in-plane bending vibration and CH$_2$ stretching vibration), 1630 cm^{-1} (amide I, C=O stretching vibration), 1540 cm^{-1} (amide II, C—N stretching, and CO—N—H bending vibration), 1386 cm^{-1}(amide III, C—N stretching, and C—H in-of-plane bending vibration), 1285 cm^{-1} (amide IV, C—CO stretching vibration), 720 cm^{-1} (CH$_2$ wagging), 640 cm^{-1} (amide V, N—H out-of-plane bending vibration), and 860 cm^{-1} (CH of phenylene vibration).

Figure 3 presents the ^{1}H-NMR spectrum of PA12T in deuterated TFA. The chemical shift in the range at 8.0 ppm (4H) is attributed to the aromatic protons (position d). The chemical shift at 3.7 ppm (4H) originates from the two methylene group protons neighboring —NH— (position c) while that at 1.8 ppm (4H) comes from two other methylene group protons jumping —NH— (position b). The peak at 1.5 ppm (16H) belongs to the other methylene group protons of the aliphatic chains (position a). The results of FTIR and ^{1}H-NMR analysis indicate that the desired product is synthesized.

The elemental analysis data of PA12T are listed in Table I. The calculated components are presented for comparison. The resulting value of elemental analysis was the average of five parallel experiments. The hydrogen content of PA12T is higher than the theoretical value owing to the absorption of water. The

TABLE I
Elemental Analysis Data of PA12T

Sample	Carbon (%)		Hydrogen (%)		Nitrogen (%)		Oxygen (%)	
	Calc.	Meas.	Calc.	Meas.	Calc.	Meas.	Calc.	Meas.
PA12T	72.7	72.7	9.10	9.15	8.49	8.48	9.70	10.10

other measurement results are in agreement with the theoretical values.

The water absorbing of PA12T was measured according to GB/T1034 (China standard), and the result is 0.13. The low water absorption, close to PA9T (0.17),[20] is conductive to maintain dimensional and mechanical stability of products.

The solubilities (sample 100 mg, solvent 10 mL) of PA12T were tested in different organic solvents. PA12T can easily dissolve in acidity solvents such as concentrated sulfuric acid and TFA at room temperature, while it is insoluble in dimethylsulphoxide, N,N'-dimethylformamide, 1-methyl-2-pyrrolidenone, dimethylacetamide, m-cresol, tetrahydrofuran, pyridine, tetrachloroethane, chlorobenzene, methanol, toluene, chloroform, phenol, and formic acid. The results show that PA12T exhibits well chemical solvent resistance.

Thermal properties of PA12T

For heat-resistant material, melting point, crystallization temperature, thermal degradation temperature and glass transition temperature are all very important parameters. To study the thermal behavior of PA12T, DSC, TGA, and DMA were carried out. Figure 4 depicts the DSC curves of PA12T. Curve A is the second heating DSC curve, while B is a cooling DSC curve. The heating rate is 10°C min^{-1}, and the test temperature is 50 to 330°C. PA12T 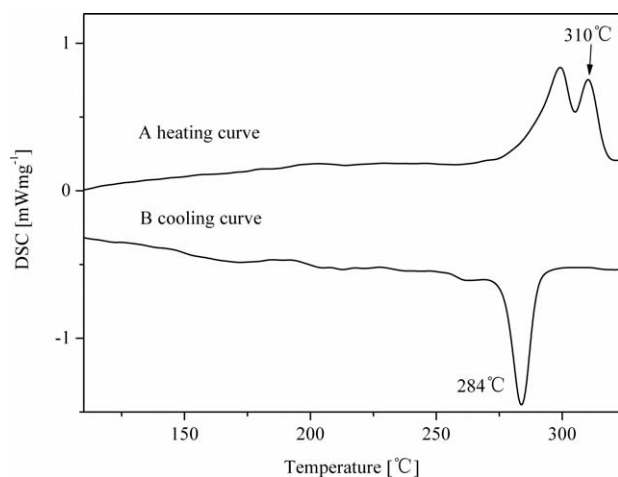exhibit double-melting endotherms, which is a common phenomenon observed in semicrystalline polymers.[21,22] The melting temperature (T_m) of PA12T is 310°C based on curve A, and the crystallization temperature (T_c) of PA12T is 284°C based on curve B.

TGA curves of PA12T are shown in Figure 5. The TG curve of PA12T shows a one-stage weight loss process in nitrogen. The decomposition temperature (T_d) of PA12T is $\sim$ 429°C, and the termination temperature of thermal degradation is about 477°C. The maximum degradation temperature (T_{max}) of PA12T is 464°C.

The T_m of PA12T is far below T_d of PA12T. Therefore, the melt processing ability of PA12T is excellent. In addition, the T_d of PA12T is higher than that of aliphatic polyamides.[23] The results show that the thermal stability of PA12T has been improved by inserting benzene linkage into the polymeric backbone.

DMA was also used to characterize the thermal property of PA12T (Fig. 6). Three obvious transition peaks can be observed and are defined as α, β, and γ relaxation, respectively. The glass transition temperature (T_g) of the PA12T is 144°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) is all below 80°C. The results show that T_g of PA12T is higher than aliphatic polyamides. As expected, the heat resistance of PA12T was improved by the introduction of benzene ring. The β relaxation reflects the mobility of carbonyl group of amorphous region, and the γ relaxation reflects the comoving of amido
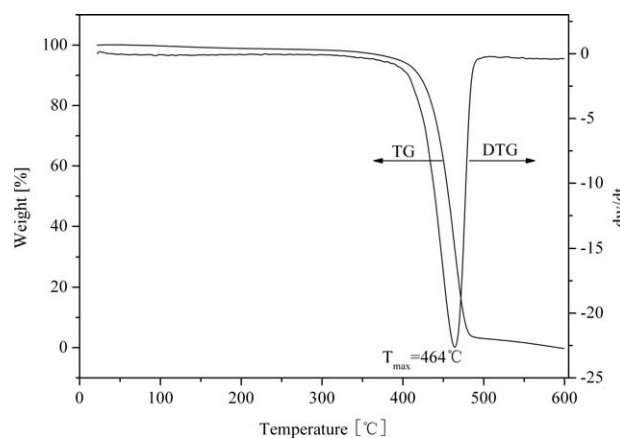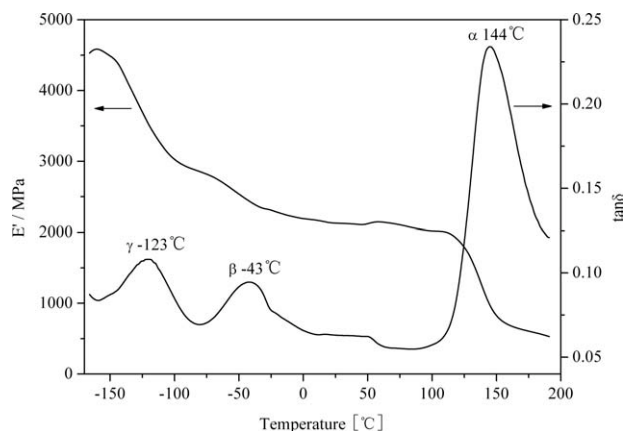

Figure 4 DSC curves of PA12T.

Figure 5 TGA curves of PA12T.

Figure 6 DMA curve versus temperature of PA12T (1 Hz).

and methenes. The thermal data of PA12T in this work are listed in Table II.

Mechanical properties of PA12T

All dry and standard samples of PA12T for mechanical tests were prepared by injection molding in an injection-molding machine. Table III summarized the mechanical properties of PA12T, and, to comparison, the data of PA9T were also listed in Table III. Based on Table III, it can be observed that the tensile strength, breaking elongation, and Izod impact strength of PA12T are higher than those of PA9T at room temperature.[24]

Flash Py-GC/MS analysis

It is important to have excellent thermal stability for the heat-resistance engineering plastic. To investigate the thermal stability and flame resistant of PA12T systematically, the thermal decomposition process of PA12T was studied. Pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) is well established as a method for the analysis of the thermal decomposition of polymers.[25–29] The investigation of Py-GC/MS can provide unique information on the primary processes of the thermal decomposition of polymers and also important structural information, such as structural identification of homopolymers, differentiation of isomeric structures, and copolymer composition.

A typical pyrogram of PA12T (total ion chromatogram of the pyrolysates) obtained by flash pyrolysis at 700°C was shown in Figure 7. The pyrolysates were identified by mass spectra and confirmed by comparing their retention times.[30–32] The results of identification, the molecular weight, and relative intensity of pyrolysis products were reported in Table IV. The relative intensity is a ratio of integral shadow area among them. The weight of each sample used in the analysis is 0.1, 0.2, 0.5, and 1 mg. Four parallel experiments were carried out for each sample with different sample weight, and no changes in relative intensity of pyrolysis product were observed. The resulting value was the average of four parallel experiments.

The inferred thermal decomposition processes

The bond strength of C—N is 305 kJ mol^{-1}, which is less than the value of 346 kJ mol^{-1} for a C—C bond,[33] and so many evidences suggested that the primary polyamide chain scission occurs either at the peptide C—N or at adjacent bonds.[34] Homolytic scission, hydrolysis, intramolecular C—H transfer, and cis-elimination (a particular case of C—H transfer) are all suggested as possible primary chain-scission mechanisms.[34] Benzene rings are stabilized in the process of pyrolysis of PA12T, the cleavage of C—N amide bond, and the homolytic scission of C_{phenyl}—C_{amido} bond were the primary pyrolysis pathways. According to the pyrolysis products, the possible pyrolysis pathways are illustrated in Figures 8–11 (Marked as route A, B, C, and D, respectively). The four possible routes happen randomly at the same time.

Route A indicated that PA12T was decomposed via a β-CH hydrogen transfer process with the formation of amide and olefin end-groups.[35] The products containing amide end-groups could further undergo thermal decompositions and produce compounds with nitrile end-group, such as 1,4-benzenedicarbonitrile. The olefins and dienes could further pyrolysis to short-chain olefins and dienes.

Route B showed homolytic cleavage occurred at one side of the C_{phenyl}—C_{amido} bonds, which form benzamide and alkylamide radicals. Then, benzamide radical reacted with hydrogen radical, alkyl radical, and eliminating water. Finally, benzonitrile and 4-alkyl-benzonitrile were obtained. Alkyl amides

TABLE II
The Viscosity, Thermal Data, and Water-Absorbing Capacity of PA12T Compared to PA9T

Sample	[η] (dL g^{-1})	$\frac{\ln \eta_r}{C}$ (dL g^{-1})	T_m (°C)	T_c (°C)	T_d (°C)	T_g (°C)	Water-absorbing capacity (%)
PA12T	1.76	1.68	310	284	429	144	0.13
PA9T[20]	–	–	308	–	–	125	0.17

TABLE III
**The Mechanical Property of PA12T Compared to PA9T**

Samples	Tensile strength (MPa)	Breaking elongation (%)	Bending strength (MPa)	Bending modulus (GPa)	Izod impact strength (kJ m^{-2})
PA12T	95	22	94	2.1	5.4
PA9T[24]	92	20	120	2.6	4.9
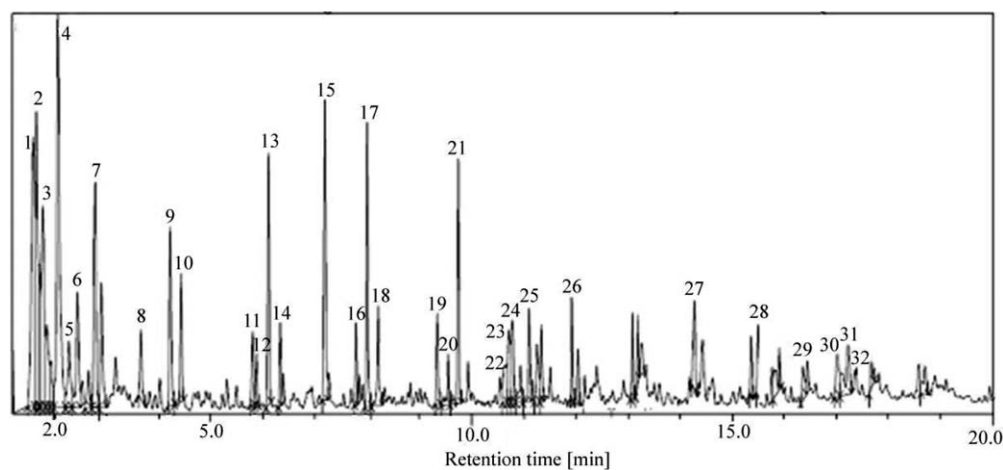
Figure 7 Py-GC/MS chromatogram of PA12T at 700°C.

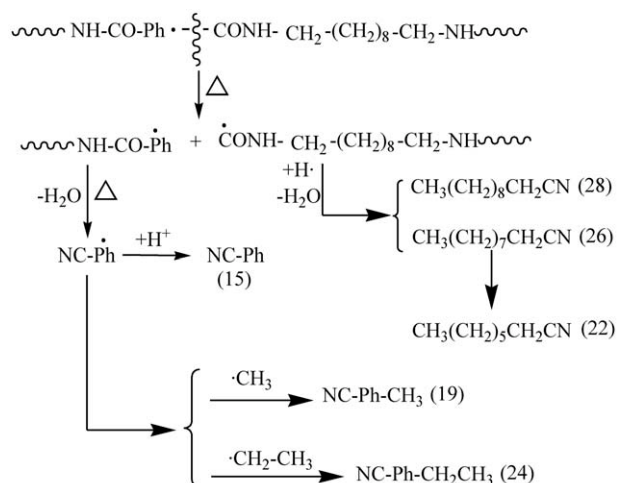**TABLE IV**
Analysis Results of PA12T by Py-GC/MS

No.	Tentative compounds	Molecular weight	Retention time/min	Formula	Relative intensity
1	Carbon oxide	44	1.59	CO_2	4.05
2	1,3-Butadiene	54	1.65	C_4H_6	3.35
3	1-Pentene	70	1.78	C_5H_{10}	3.83
4	1-Hexene	84	2.07	C_6H_{12}	3.99
5	Benzene	78	2.44	C_6H_6	3.62
6	1-Heptene	98	2.78	C_7H_{14}	3.04
7	Heptane	100	2.90	C_7H_{16}	3.14
8	Toluene	92	3.66	C_7H_8	2.77
9	1-Octene	112	4.22	C_8H_{16}	2.62
10	Ocetane	114	4.43	C_8H_{18}	2.21
11	Styrene	104	5.80	C_8H_8	2.89
12	1,8-Nonadiene	124	5.88	C_9H_{16}	2.02
13	1-Nonene	126	6.11	C_9H_{18}	2.09
14	Nonane	156	6.33	C_9H_{20}	1.98
15	Benzonitrile	103	7.18	C_7H_5N	2.45
16	1,9-Decadiene	138	7.78	$C_{10}H_{18}$	1.79
17	1-Decene	140	8.00	$C_{10}H_{20}$	2.01
18	Decane	142	8.21	$C_{10}H_{22}$	2.48
19	p-Methylbenzonitrile	117	9.34	C_8H_7N	2.17
20	1,11-Dodecadiene	166	9.55	$C_{12}H_{22}$	2.41
21	1-Dodecene	168	9.74	$C_{12}H_{24}$	2.00
22	n-Pentylbenzene	148	10.63	$C_{11}H_{16}$	5.46
23	Octanenitrile	125	10.71	$C_8H_{15}N$	4.05
24	p-Ethylbenzonitrile	131	10.94	C_9H_9N	3.10
25	1,4-Benzenedicarbonitrile	128	11.25	$C_8H_4N_2$	3.41
26	Decanenitrile	153	11.98	$C_{10}H_{19}N$	3.01
27	N-Methylbenzamide	135	14.25	C_8H_9NO	2.74
28	Undecanenitrile	167	15.56	$C_{11}H_{21}N$	2.20
29	N-Ethylbenzamide	149	16.38	$C_9H_{11}NO$	1.45
30	N-Propylbenzamide	163	17.06	$C_{10}H_{13}NO$	1.32
31	N-Butylbenzamide	177	17.39	$C_{11}H_{15}NO$	1.61
32	N-Hexylbenzamide	205	17.66	$C_{13}H_{19}NO$	1.24
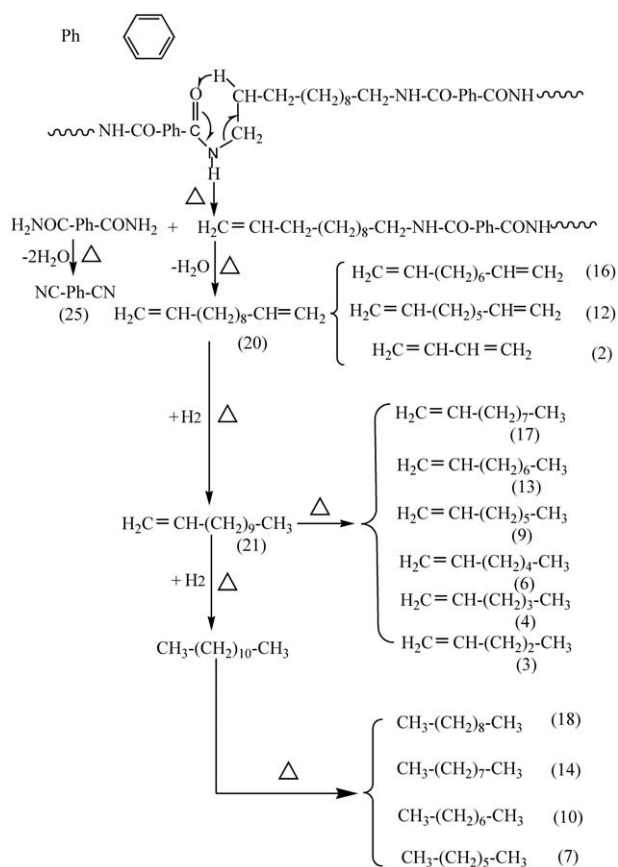
Figure 8 Thermal decomposition mechanism A of PA12T.

Figure 9 Thermal decomposition mechanism B of PA12T.
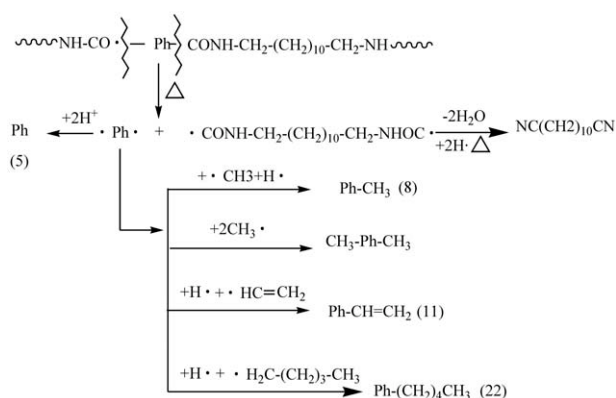
Figure 10 Thermal decomposition mechanism C of PA12T.

radical, and ethene radical and then formatted aromatic compounds. Alkyldiamide further underwent decompositions with the formation of alkyl dinitrile.

Route D presented the amide bond led to hydrolysis in the presence of water, which formed $-NH_2$ and $-COOH$ end-groups,[36] $-COOH$ end-groups were further degraded to form CO_2.

Alkenes and diolefines are easy to take part in homolytic radical scission of $C-C$ bonds at high temperature to form smaller fragments. These fragments might react with benzene and benzonitrile-free radical, so that alkenes and diolefines were not detected in the pyrolysis products.

were further degraded to form compounds of alkyl nitriles.

Route C presented the bonds cleavage occurred at the two sides of $C_{phenyl}-C_{amido}$ bonds forming compounds containing benzene and alkylamide radicals. Benzene radical reacted with hydrogen radical, alkyl

CONCLUSIONS

The PA12T with high viscosity was successfully synthesized via a polycondensation reaction of terephthalic acid and 1,12-dodecanediamine in water. FTIR and NMR spectra confirmed the chemical structure of PA12T. The T_m, T_c, T_d, and T_g were determined by DSC, TGA, and DMA, respectively. The tensile strength, breaking elongation, and Izod impact strength of PA12T are higher than those of PA9T at
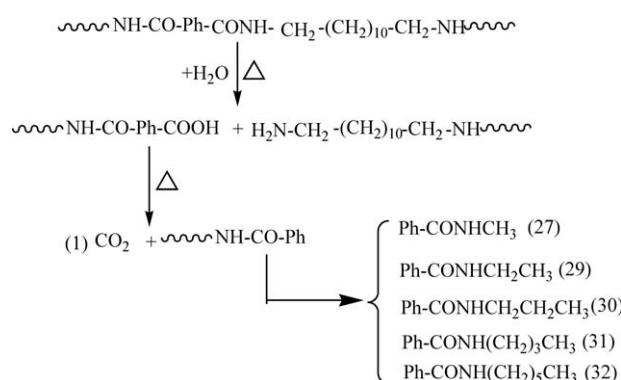
Figure 11 Thermal decomposition mechanism D of PA12T.

room temperature. The results of Py-GC/MS showed that the major pyrolysis products were benzonitrile, alkylbenzonitrile, 1,4-benzenedicarbonitrile, alkyl nitriles, aromatic compounds, and a series of *N*-alkyl-benzamide. The major pyrolysis mechanism included β-CH hydrogen transfer process, main-chain random scission, and hydrolytic decomposition. The pyrolysis products and pyrolysis mechanism further confirmed that PA12T is synthesized.

References

1. Persyn, O.; Miri, V.; Lefebvre, J. M.; Ferreiro, V.; Brink, T.; Stroeks, A. J Polym Sci Part B: Polym Phys 2006, 44, 1690.
2. Endo, M.; Morishima, Y.; Yano, S.; Tadano, K.; Murata, Y.; Tsunashima, K. J Appl Polym Sci 2006, 101, 3971.
3. Ferreiro, J. J.; de la Campa, J. G.; Lozano, A. E.; deAbajo, J. J Polym Sci Part A: Polym Chem 2005, 43, 5300.
4. Rao, Y.; Waddon, A. J.; Farris, R. J. Polymer 2001, 42, 5937.
5. Liaw, D. J.; Liaw, B. Y.; Tseng, J. M. J Polym Sci Part A: Polym Chem 1999, 37, 2629.
6. Liaw, D. J.; Hsu, P. N.; Chen, W. H.; Lin, S. L. Macromolecules 2002, 35, 4669.
7. Liaw, D. J.; Chang, F. C.; Leung, M. K.; Chou, M. Y.; Muellen, K. Macromolecules 2005, 38, 4024.
8. Wang, W. Z.; Wang, X. W.; Li, R. X.; Liu, B. Y.; Wang, E. G.; Zhang, Y. H. J Appl Polym Sci 2009, 6, 2036.
9. Yang, S. H.; Fu, P.; Liu, M. Y.; Wang, Y. D.; Li, Z. P.; Zhao, Q. X. Expr Polym Lett 2010, 4, 346.
10. Yang, S.; Fu, P.; Liu, M.; Wang, Y.; Zhao, Q. J Appl Polym Sci 2010, 118, 1094.
11. Ahmed, J. U.; Ohkoshi, Y.; Gotoh, Y. J Polym Sci Part B: Polym Phys 2004, 42, 433.
12. Jiang, T.; Liu, M.; Fu, P.; Wang, Y.; Fang, Y.; Zhao, Q. Polym Eng Sci 2009, 49, 1366.
13. Papenfuss, D. S.; Hartman, M. S.; Kraimer, A. L.; Wuest, S. E. U.S. Pat. 7,862,869 (2011).
14. Shinohara, K.; Kurokawa, T.; Arai, H. U.S. Pat. 7,728,071 (2011).
15. Grah, M. D. U.S. Pat. 7,678,841 (2010).
16. Wolf, J. R.; Zix, T. B. U.S. Pat. 7,673,564 (2010).
17. Shinohara, K. U.S. Pat. 7,659,230 (2010).
18. Ng, H. U.S. Pat. 6,355,769 (2002).
19. Cui, X. W.; Li, W. H.; Yan, D. Y. Polym Int 2004, 53, 1729.
20. Zou, S. Mod Plast 2000, 12, 62.
21. Li, Y. J.; Zhu, X. Y.; Tian, G. H.; Yan, D. Y.; Zhou, E. Polym Int 2001, 50, 677.
22. Ramesh, C.; Keller, A.; Eltink, S. J. Polym 1994, 35, 5300.
23. Wang, Y. D.; Liu, M. Y.; Zhao, Q. X. Polym Mater Sci Eng 1999, 15, 78.
24. Ma, J. M.; Song, S. W.; Guo, J. Mod Plast 2003, 15, 41.
25. Zhang, Y.; Cheng, K. L.; Xu, J. R. Thermochim Acta 2005, 425, 137.
26. Pramoda, K. P.; Chung, T. S.; Liu, S. L.; Oikawa, H.; Yamaguchi, A. Polym Degrad Stab 2000, 67, 365.
27. Perng, L. H. Polym Degrad Stab 2000, 69, 323.
28. Herrera, M.; Matuschek, G.; Kettrup, A. Thermochim Acta 2000, 361, 69.
29. Leichtnam, L. N.; Schwartz, D.; Gadiou, R. J Anal Appl Pyrolysis 2000, 55, 255.
30. Czégény, Z.; Blazsó, M. J Anal Appl Pyrolysis 2001, 58, 95.
31. Herrera, M.; Matuschek, G.; Kettrup, A. Chemosphere 2001, 42, 601.
32. Linda, J. B.; Michael, T. K.; Barry, D. D.; Stephen, M. A. J Appl Polym Sci 1995, 56, 803.
33. Cottrell, T. L. Butter-worths: London, 1958.
34. Sergei, V. L.; Edward, D. W.; Menachem, L. Polym Int 1999, 48, 532.
35. Ballistreri, A.; Garozzo, D.; Maravigna, P. J Polym Sci Part A: Polym Chem 1987, 25, 1049.
36. Khanna, Y. P.; Pearce, E. M.; Smith, J. S. J Polym Sci Part A: Polym Chem 1981, 19, 2817.