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Semiaromatic polyamides containing ether and different number of methylene (2~10) units: Synthesis and Properties

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Abstract: A series of semiaromatic difluorobenzamide monomers were synthesized by the reaction of diamine and 4-fluorobenzoic chloride with facile interfacial method. They were conducted to react with 1,1-bis(4-hydroxyphenyl)-1-phenylethane (BHPPE) to prepare semiaromatic polyamides containing ether units by the method of nucleophilic polycondensation. They had excellent thermal properties with glass transition temperatures (Tg) of 134.4-195.6 ^{o}C and initial degradation temperatures (T$_d$) of 405-443 ^{o}C. The activation energies of degradation were in range of

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180.1-275.9 KJ/mol. The resultant polymers can be dissolved in strong polar solvents and supply a tough film with tensile strength of 89-105 MPa. Also we found that the complex viscosities of these semiaromatic polyamides were range from 77-688 Pa·s at 290 °C. They had appropriate complex viscosities for melt processing. And they had much wider processing windows than that of traditional semiaromatic polyamides such as poly(hexamethylene terephthalamide) (PA6T). Interestingly, a part of the resultant polymers were found to be natural self-retardant.

Keywords: polyamides, retardancy, rheology

Introduction

Nylons (such as PA6 or PA66) are a kind of engineering thermoplastics that widely applicated in modern industrial and commercial applications in the last three decades. They can be easily processed by melt processing to form different kinds of structural parts, polymer films and polymer fibers [1-3]. With increasingly stringent requirements, applications of aliphatic polyamide are limited in some fields because of their poor dimensional stability and thermal properties, especially in surface mount technology (SMT) and the shells of automobile engines. To improve the thermal properties of polyamides, fabrication of polyamides compounds [4] or incorporating aromatic rings act as an efficient approach [5-9]. The aromatic polyamides such as poly(p-phenylene terephthalamide) (PPTA) [10] and poly(m-phenyleneisophthalamide) (PMIA) [11] have been commercially accepted in

industry for their excellent balance of mechanical and thermal properties. Despite

their outstanding properties, they also have limited applications because they can only

be processed by special methods (they do not melt below their decomposition

temperatures) [12, 13]. The high melting temperatures of aromatic polyamides are

attributed to high density of aromatic rings and strong inter-chain forces, mainly

hydrogen bonding, that enhance effective molecular packing [14]. Then, semiaromatic

polyamides were developed rapidly in the last 20 years. The semiaromatic polyamides

have been noted for their high thermal stability and chemical resistance. However,

only several semiaromatic polyamides are commercially available. These include

copolymers of PA6T [15], poly(nonamethylene terephthalamide) (PA9T) [16-19] and

the product of Dupont, Evonik, Mitsui, and Solvay and so on. Usually, if the melting

point of a semiaromatic polyamide is higher than 340 ^{o}C, it is thought to be not

suitable for thermal processing [20]. Thus the melt processing is impractical for these

semiaromatic polyamides with short aliphatic diamines (2-7 CH_2's) because of their

melt temperatures surpass thermal decomposition temperature, such as PA4T (T_m =

430 ^{o}C, T_d = 350 ^{o}C) and PA6T (T_m = 370 ^{o}C, T_d = 350 ^{o}C). Therefore, several

synthetic approaches have been developed such as incorporating naphthalene rings

(T_m=320 ^{o}C, T_d=495 ^{o}C) [21], benzylidene structure (T_m = 290 ^{o}C) [22], bulky

pendant groups ($T_g \approx$ 270 ^{o}C, $T_d \approx$ 500 ^{o}C) [14], noncoplanar biphenylene moieties

($T_g \approx$ 300 ^{o}C, $T_{d-10\%} \approx$ 510 ^{o}C) [23], azo groups [24, 25], sulfone units [26],

triazole units [27], thioether units [28] and long-chain diamines ($T_m \approx$ 290 ^{o}C, $T_d \approx$ 490

^{o}C) [29] [such as PA9T (T_m = 305 ^{o}C, $T_{d-5\%}$ = 464 ^{o}C), PA-10T (T_m = 315 ^{o}C, $T_{d-5\%}$ =

472 ^{o}C) [30], PA-12T (T_m = 295 ^{o}C, T_d = 429 ^{o}C) [31], PA-18T (T_m = 245 ^{o}C) and so on] into the polymer backbones. It is known that the ether linkage is a flexible bond. It can be incorporated into the polymer backbone to improve the resin's processability, such as poly(arylene ether amide) [2] and poly(arylene ether ether sulfone) [32]. They all have excellent processability, mechanical, thermal and antioxidant properties. Therefore, here, we expected to incorporate the ether (-O-) and different number of methylene units into the main chain of semiaromatic polyamides to improve their properties. In this study, five kinds of semiaromatic difluorobenzamide monomers which contained 2-10 CH_2's group were prepared by the reaction of 4-FBC with different diamine (ethylenediamine, 1,6-hexanediamine, 1,4-butanediamine, 1,8-octanediamine, and 1,10-decanediamine). Then they were conducted to react with BHPPE by nucleophilic polycondensation to prepare semiaromatic polyamides (Usually, the polyamides were prepared by the reaction of dicarboxylic acid (dicarboxylic chloride) and diamine with electrophilic substitution). The effects of chemical structure on thermal performances, mechanical properties, processability, flame retardant property and thermal degradation kinetics of the resultant semiaromatic polyamides were investigated in detail.

Experimental

Materials

4-Fluorobenzoic choride (4-FBC) (99.5%, Lanning Chemical Company Limited), BHPPE was prepared according to the method reported earlier by our group [33],

sodium hydroxide (NaOH) (AR, SiChuan ChengDu ChangLian Chemical Reagent Company), N-methyl-2-pyrrolidone (NMP) (JiangSu NanJing JinLong Chemical Industry Company), ethylenediamine, 1,4-butanediamine, 1,6-hexanediamine, 1,8-octanediamine, 1,10-decanediamine and other reagents were obtained commercially.
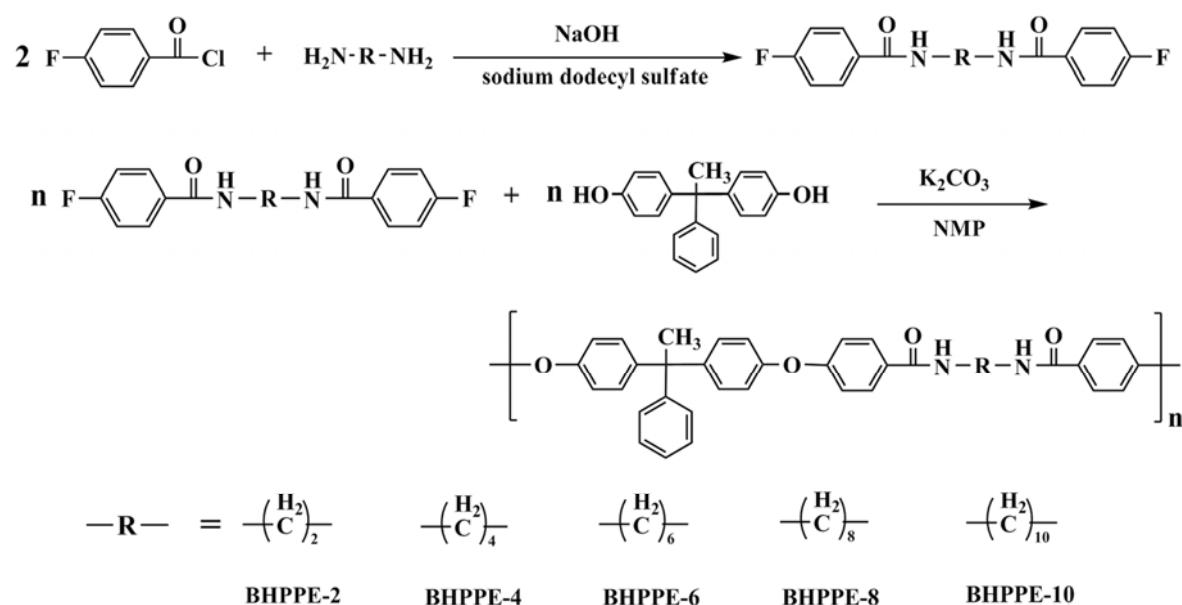
1, 2-N,N'-bis(4-fluorobenzamide) ethane (BFBE) (Scheme 1)

BFBE was prepared according to the following procedure: 4-FBC (320 g, 2.02 mol) and dichloromethane (2000 ml) were added into a 5000 ml three-necked flask equipped with mechanical stirrer and thermometer. Then the mixture of ethylenediamine (60 g, 1 mol) and NaOH (80 g, 2 mol) (dissolved in 1000 ml deionized water) and sodium dodecyl sulfate (3 g, 0.01 mol) was added into the flask dropwise within 2 h. The mixture was vigorous stirred at 5-10 $^{\circ}$C for about 6 h. After that the reaction mixture was evaporated under 50 $^{\circ}$C to recover the solvent dichloromethane. Then the crude product was washed with hot deionized water, then the mixture was filtered, and the above steps were repeated three times. Next, the wet filter cake was recrystallized from ethanol to afford needle-like crystals. The purified product was then vacuum-dried at 80 $^{\circ}$C for more than 12 h to yield colourless crystals BFBE.

Yield: 263.6 g, 86.7%.

Elemental analysis (%): Found: C, 62.93 (63.15); H, 4.60 (4.64); N, 9.31(9.21) (data in brackets are calculated). Melt point: 234-236.4 $^{\circ}$C. FT-IR (KBr, cm^{-1}): 3302 (N-H),

1633 (-CO-), 3053 (C-H aromatic ring), 2944, 2883 (-CH$_2$-), 1604, 1559, 1506 (C=C

aromatic ring), 854 (para substituent of the aromatic ring). NMR [400 MHz,

deuterated dimethyl sulfoxide (DMSO-d6)/tetramethylsilane (TMS), ppm]:

3.422-3.473 (m, 4H, H1), 7.266-7.325 (m, 4H, H2), 7.888-7.931 (m, 4H, H3), 8.627

(s, 2H, H4); 39.67 (C1), 115.23 (C2), 129.83 (C3), 130.98 (C4), 162.54 (C5) and

165.41 (C6). The other monomers were prepared with similar method as that of

BFBE.

Scheme 1 Synthesis routes of semiaromatic difluorobenzamide monomers and

polymers.

1, 4-N,N'-bis(4-fluorobenzamide) butane (BFBB): Yield: 283.2 g, 85.3%.

Elemental analysis (%): Found: C, 65.33 (65.05); H, 5.41 (5.46); N, 8.48 (8.43) (data

in brackets are calculated). Melt point: 228.4-231.8 °C. FT-IR (KBr, cm^{-1}): 3314

(N-H), 1630 (-CO-), 3036 (C-H aromatic ring), 2948, 2876 (-CH$_2$-), 1605, 1540, 1504

(C=C aromatic ring), 850 (para substituent of the aromatic ring). NMR [400 MHz,

deuterated dimethyl sulfoxide (DMSO-d6)/tetramethylsilane (TMS), ppm]: 1.558 (s, 4H, H1), 3.272-3.330 (d, 4H, H2), 7.261-7.306 (m, 4H, H3), 7.886-7.922 (m, 4H, H4), 8.492 (s, 2H, H5); 26.65 (C1), 39.66 (C2), 115.17 (C3), 129.74 (C4), 131.07 (C5), 162.49 (C6) and 165.02 (C7).

1, 6-N,N'-bis(4-fluorobenzamide) hexane (BFBH): Yield: 320.0 g, 88.9%. Elemental analysis (%): Found: C, 66.39 (66.65); H, 6.17 (6.15); N, 7.89 (7.77) (data in brackets are calculated). Melt point: 197.8-200 °C. FT-IR (KBr, cm^{-1}): 3317 (N-H), 1630 (-CO-), 3033 (C-H aromatic ring), 2937, 2868 (-CH$_2$-), 1606, 1541, 1504 (C=C aromatic ring), 850 (para substituent of the aromatic ring). ^{1}H-NMR [400 MHz, deuterated dimethyl sulfoxide (DMSO-d6)/tetramethylsilane (TMS), ppm]: 1.333 (s, 4H, H1), 1.504-1.536 (t, 4H, H2), 3.217-3.266 (d, 4H, H3), 7.258-7.302 (m, 4H, H4), 7.880-7.915 (m, 4H, H5), 8.463 (s, 2H, H6); 26.20 (C1), 29.05 (C2), 39.67 (C3), 115.17 (C4), 129.73 (C5), 131.11 (C6), 162.47 (C7) and 164.97 (C8).

1, 8-N,N'-bis(4-fluorobenzamide) octane (BFBO) : Yield: 327.1 g, 84.3%. Elemental analysis (%): Found: C, 68.35 (68.02); H, 6.73 (6.75); N, 7.34 (7.21) (data in brackets are calculated). Melt point: 174-176.8 °C. FT-IR (KBr, cm^{-1}): 3318 (N-H), 1631 (-CO-), 3064 (C-H aromatic ring), 2935, 2855 (-CH$_2$-), 1606, 1541, 1505 (C=C aromatic ring), 849 (para substituent of the aromatic ring). ^{1}H-NMR [400 MHz, deuterated dimethyl sulfoxide (DMSO-d6)/tetramethylsilane (TMS), ppm]: 1.97 (s, 8H, H1-H2), 1.510 (s, 4H, H3), 3.212-3.260 (m, 4H, H4), 7.259-7.303 (m, 4H, H5), 7.885-7.919 (m, 4H, H6), 8.457 (s, 2H, H7); 26.44 (C1), 28.72 (C2), 29.04 (C3),

39.68 (C4), 115.18 (C5), 129.72 (C6), 131.13 (C7), 162.46 (C8) and 164.93 (C9).

1, 10-N,N'-bis(4-fluorobenzamide) decane (BFBD): Yield: 338.2 g, 81.3%. Elemental analysis (%): Found: C, 69.39 (69.21); H, 7.24 (7.26); N, 6.96 (6.73) (data in brackets are calculated). Melt point: 170-172.4 °C. FT-IR (KBr, cm^{-1}): 3321 (N-H), 1631 (-CO-), 3068 (C-H aromatic ring), 2923, 2852 (-CH$_2$-), 1606, 1538, 1504 (C=C aromatic ring), 849 (para substituent of the aromatic ring). ^{1}H-NMR [400 MHz, deuterated dimethyl sulfoxide (DMSO-d6)/tetramethylsilane (TMS), ppm]: 1.269 (s, 12H, H1-H3), 1.483-1.516 (t, 4H, H4), 3.202-3.252 (m, 4H, H5), 7.257-7.301 (m, 4H, H6), 7.878-7.913 (m, 4H, H7), 8.448 (s, 2H, H8); 26.44 (C1), 28.73 (C2), 28.92 (C3), 29.92 (C4), 39.68 (C5), 115.20 (C6), 129.73 (C7), 130.87 (C8), 162.18 (C9) and 164.83 (C10).

Polymer Synthesis (as shown in Scheme 1)

A typical polymerization was performed as shown in **Scheme 1**. NMP (150 ml), toluene (20 ml), BHPPE (29.0 g, 0.1 mol), potassium carbonate (27.6 g, 0.2 mol) and BFBE (30.4 g, 0.1 mol) were added into a 500 mL three-necked flask equipped with "Dean Stark" trap, mechanical stirrer and thermometer. The flask was heated to 160 °C and maintained for about 2 h; during this period, 26.7 mL of liquid was removed. Then the reaction flask was heated to 200 °C and maintained for another 8 h. After that the reaction solution was poured into water with stirring to precipitate white fibrous polymers. The collected polymer was washed with water and ethanol, pulverized to a powder, washed with water and ethanol again, and dried in a vacuum oven at 100 °C for 12 h to give BHPPE-2. (Yield: 51.4 g, 92.8%).

BHPPE-4, BHPPE-6, BHPPE-8 and BHPPE-10 were prepared with a similar procedure as that of BHPPE-2. The yields were as following: BHPPE-4, 53.1 g (91.3%); BHPPE-6, 57.2 g (93.8%); BHPPE-8, 59.0 g (92.6%); BHPPE-10, 61.0 g (91.6%).

Characterization

The intrinsic viscosities of BHPPE-(2-10) were obtained at 30 ±0.1 $^{\circ}$C with 0.500 g of polymer dissolved in 100 mL of NMP, using a Cannon-Ubbelodhe viscometer. The values were obtained by the one-point method (or Solomon-Ciuta equation):

$$\eta_{\text{int}} = \frac{\sqrt{2(\eta_{sp} - \ln\eta_r)}}{C}$$

Where $\eta_r = \eta/\eta_0$, $\eta_{sp} = \eta/\eta_0 - 1$.

The number-average molecular weights (M_n) and weight-average molecular weight (M_w) were obtained via GPC performed with a Waters 1515 performance liquid chromatography pump, a Waters 2414 differential refractometer (Waters Co., Milford, MA) and a combination of Styragel HT-3 and HT-4 columns (Waters Co., Milford, MA), the effective molecular weight ranges of which were 500-30000 and 5000-800000, respectively. N, N-dimethyl formamide (DMF) was used as an eluent at a flow rate of 1.0 ml/min at 35 $^{\circ}$C. Polystyrene standards were used for calibration.

The samples of monomers were measured with an elemental analyzer (EURO EA-3000). The melting point of monomers was measured with micro melting point apparatus (XRC-1). FT-IR spectroscopic measurements were performed on a Nexus670 FT-IR instrument. H nuclear magnetic resonance (NMR) spectra were

obtained on a Bruker-400 NMR spectrometer in deuterated dimethyl sulfoxide. Differential scanning calorimetry (DSC) was performed on a Netzsch DSC 200 PC thermal analysis instrument. The heating rate for DSC measurements was 10 ^{o}C/min. Thermogravimetric analysis (TGA) was performed on a TGA Q500 V6.4 Build 193 thermal analysis instrument with a heating rate of 5-40 ^{o}C/min under nitrogen atmosphere. The polymer powder was processed into the sheet shape by a hydraulic press (YJAC, Chengdu Hangfa Group, China) at 290 ^{o}C with a pressure of 8 MPa for 10 min. Then the sheets were cut into specific shapes for the different tests. The water absorption of the samples was measured according to standard GB/T1034. An Instron Corporation 4302 instrument was used to study the stress-strain behavior of the samples. Dielectric constants were measured on a TH2819A in a frequency region of 0.1 KHz-100 KHz at 25 °C. Dynamic mechanical analysis (DMA) was performed on a TA-Q800 apparatus operating in tensile mode at a frequency of 1 Hz from 40 to 250 ^{o}C with a heating rate of 5 ^{o}C/min. A Parallel plates rheometer (Bohlin Gemini 200, Britain) was fitted with 2.5 cm diameter stainless steel parallel plates. Temperature, frequency and time sweep tests were performed under nitrogen atmosphere. Quantitative information for the melt flow of the samples could be obtained by recording the complex viscosities versus temperature, time and shear frequency during processing. The UL-94 vertical test was performed according to the testing procedure of FMVSS 302/ZSO 3975 with a test specimen bar of 127 mm in length, 12.7 mm in width and about 1.27 mm in thickness. In the test, the polymer specimen was subjected to two 10 s ignitions. After the first ignition, the flame was removed

and the time for the polymer to self-extinguish (t_1) was recorded. Cotton ignition was noted when polymer dripping occurred during the test. After cooling, the second ignition was performed on the same sample and the self-extinguishing time (t_2) and dripping characteristics were recorded. The flame test was performed on five specimens. If the average t_1 plus t_2 is less than 10 s without any dripping, the polymer is considered to be a V-0 material. If t_1 plus t_2 is in the range of 10-30 s without any dripping, the polymer is considered to be a V-1 material [34]. The LOI was determined with an Atlas Limiting Oxygen Index Chamber. The solubility of the polymers in various solvents was tested at room temperature and the boiling points of the solvents.

Results and Discussion

Synthesis of semiaromatic difluorobenzamide monomers (BFBE, BFBB, BFBH, BFBO, BFBD)

The synthesis route of monomers is shown in **Scheme 1**. The monomers were prepared with a facile interfacial reaction through one-step procedure. The reaction temperature in this procedure can not exceed $30\,^{\circ}\text{C}$, or the reaction was difficult to control and the side effect maybe occurred, in that case the resultant product was difficult to purify and the yield was low.

Chemical Structure of monomers

The FT-IR spectra of monomers **(Supplementary data Figure 1)** showed the

characteristic absorptions of -CONH- near 3300 and 1630 cm^{-1}. The characteristic absorption of benzene rings (C-H) was observed near 3050 cm^{-1}. The aliphatic chain (-CH$_2$-) was observed near 2970 and 2850-2880 cm^{-1}. The absorptions near 1340 cm^{-1} and 850 cm^{-1} were attributed to the vibration of C-F and para-substituted benzene rings. The ^{1}H-NMR and ^{13}C-NMR spectra of monomers (BFBE) (**Supplementary data Figure 2 and Figure 3**) showed two groups of peaks ranged from 7.2 to 8.0 ppm. That attributed to the two proton signals of benzene ring. The aliphatic chain proton signals were ranged from 1.2-3.5 ppm. The signals near 8.5 ppm were assigned to amide units. Six groups of peaks C1-C6 were 39.67, 115.23, 129.83, 130.98, 162.54 and 165.41**.** Combining the FT-IR and elemental analysis results suggests that the monomers were synthesized as depicted in **Scheme 1**.

Synthesis of BHPPE-(2-10)

The polycondensation reaction was carried out by nucleophilic substitution polymerization using potassium carbonate as catalyst. The reaction temperature was in the range of 160-200 $^{\circ}$C. The purpose of first step was mainly to form bisphenol salt and dehydrate water (with the azeotropic role of toluene). That was beneficial for getting polymers with large molecular weight. The molecular weights of the polymers were measured by intrinsic viscosity and GPC. As shown in **Table 1**, the η_{int} values of BHPPE-(2-10) ranged from 0.71 to 1.01 dL/g, the M_n and M_w values were in the range of $6.0*10^4$-$10.5*10^4$ and $1.26*10^5$-$2.02*10^5$, respectively. This suggests that the resultant polyamides had more than 100 repeated units. The polydispersity indices

(PDIs) of polymers were in the range of 1.8-2.3.

Table 1 Intrinsic viscosity (η_{int}) and molecular weights of polymers (BHPPE-(2-10))

Polymers	η_{int} (dL/g)	M_n (g/mol)	M_w (g/mol)	PDI (Mw/Mn)
BHPPE-2	0.71	6.0×10^4	1.26×10^5	2.10
BHPPE-4	0.84	7.9×10^4	1.56×10^5	1.97
BHPPE-6	0.95	9.4×10^4	1.72×10^5	1.83
BHPPE-8	1.01	1.05×10^5	2.02×10^5	1.92
BHPPE-10	0.89	8.6×10^4	1.99×10^5	2.31

Chemical Chain Structure of BHPPE-(2-10)

The chemical structure of the resultant polymers was characterized by FT-IR and
^{1}H-NMR. The FT-IR spectra (**Figure 1**) of polymers exhibited the characteristic ether
stretching near 1100 cm^{-1}. The absorptions near 3320, 1640 cm^{-1} were attributed to the
amide group. Comparing with the spectra of monomers, the characteristic absorption
around 1340 cm^{-1} (C-F) had disappeared. **Figure 2** shows the ^{1}H-NMR spectra of
BHPPE-(2-10). The signals of protons on bezene ring are ranged from 6.6 to 8.0 ppm.
The chemical shifts were so close that could not distinguish the proton peaks. The
signals near 2.12 and 8.5 ppm were assigned to -CH$_3$ and amide unit. From **Figure 2**
we found that the proton signals shifted to high field with increase of carbon numbers
of the diamine used in the reaction. That may be caused by the shielding effects of
methylene unit. Combined with the FT-IR results, it suggested that the polymerization
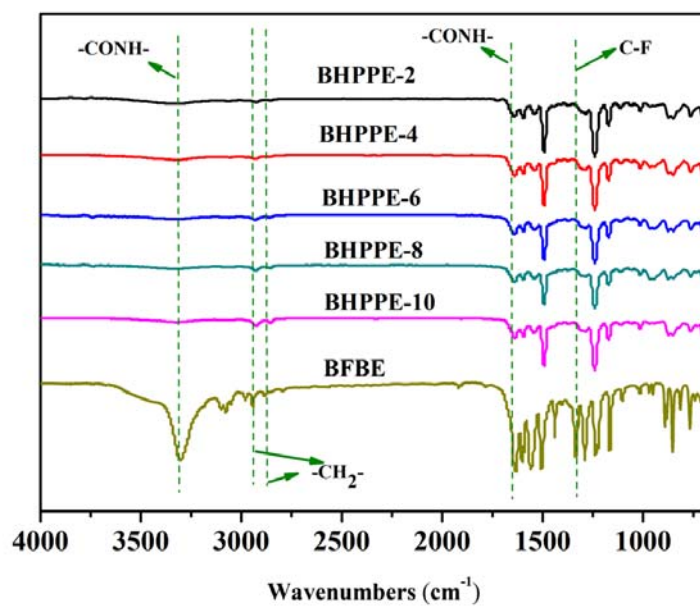proceeded as described in **Scheme 1**.

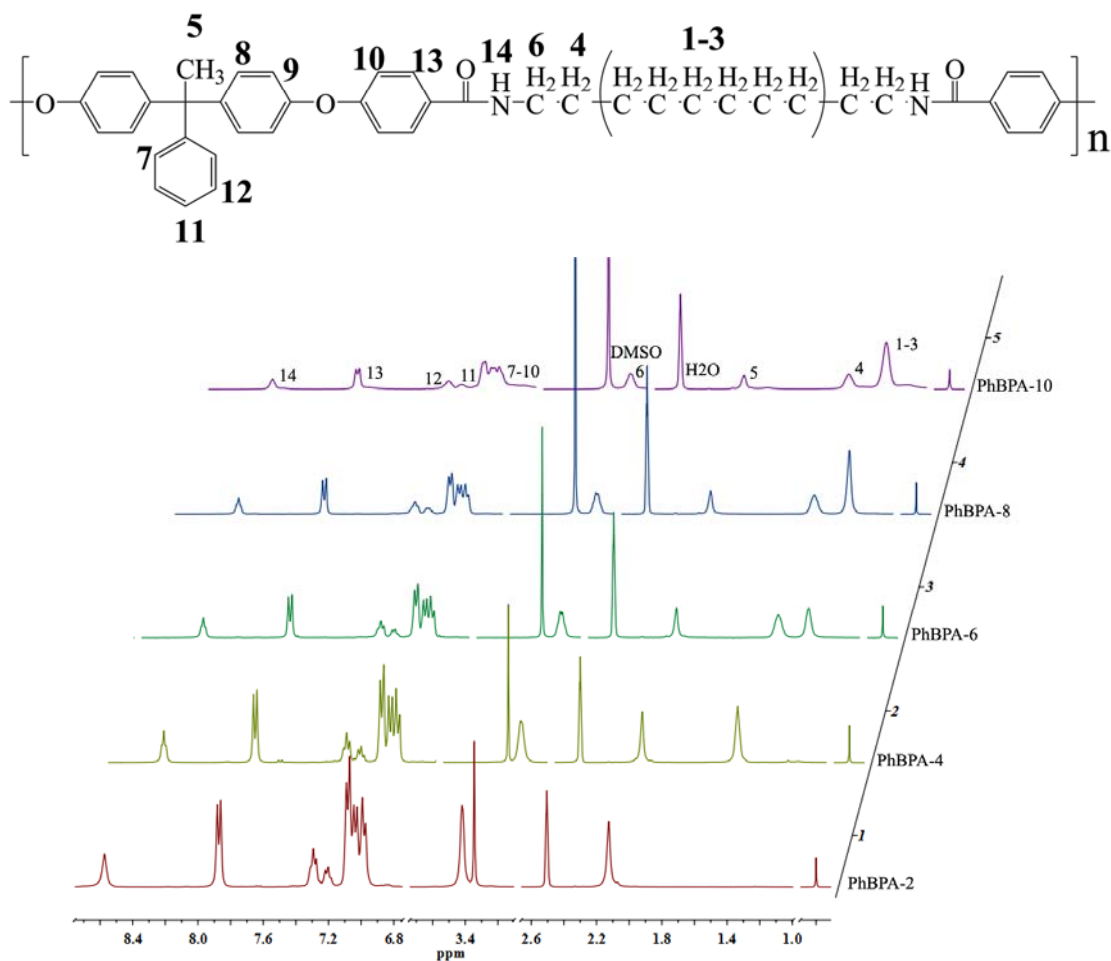**Figure 1** The FT-IR spectra of BFBE and polymers (BHPPE-(2-10)).

Figure 2 The ^{1}H-NMR spectra of polymers (BHPPE-(2-10)).

Tensile Properties

The average tensile strength values of BHPPE-(2-10) are summarized in **Table 2**. As

Table 2 Thermal and mechanical properties of BHPPE-(2-10) and PA9T

Polymers	T_g (°C)	$T_{5\%}$ (°C)	Char Yield (%)	Tensile strength (MPa)	Young's Modulus (GPa)	Elongation at break (%)	Storage Modulus at 125 °C (GPa)	Glass Transition Temperature [a] (°C)
BHPPE-2	195.6	405	28.3	97	2.1	14.4	1.9	210.8
BHPPE-4	170.4	417	7.5	103	1.9	16.7	1.6	186.1
BHPPE-6	156.5	441	4.1	105	1.8	19.8	1.6	171.3
BHPPE-8	145.6	442	2.3	94	1.5	18.7	1.7	159.5
BHPPE-10	134.4	443	0.9	89	1.1	23.2	1.4	150.6
PA9T	115	464	-	86	2.7	4.2	-	-

[a] detected by dynamic mechanical analysis (DMA).

shown in **Table 2**, the average tensile strengths of BHPPE-(2-10) were 89-105 MPa.

The elongation at break was in the range of 13.2-18.7%. It suggests that BHPPE-(2-10)

have similar mechanical properties as that of the commercial product PA9T.

Dynamic Mechanical Analysis.

DMA was carried to characterize the resulting semiaromatic polyamides. As shown in

Figure 3, one obvious transition behaviors can be observed. It was defined as α

relaxation. It is well-known that the glass transition temperature (T_g) of a polymers

can be determined by α relaxation, as it is usually related to the segment movements

in the noncrystalline area [35]. The α relaxation temperatures of these semiaromatic

polyamides were found to be 150.6, 159.5, 171.3, 186.1 and 210.8 ^{o}C, respectively.

They are nearly the same as those obtained by the DSC method. The slight differences

are mainly attributed to the different responses of the polymers to these two

measurements. The α-relaxation temperatures (glass transition temperature) decreased

with the increase of carbon number of aliphatic chain (methylene) in the polymeric

backbone. **Figure 4** displays the storage modulus curves of BHPPE-(2-10). As listed

in **Table 2**, the semiaromatic polyamides exhibited high storage modulus of 2.1, 1.7,

1.8, 1.9 and 1.5 GPa. We also found that the polymers maintained above 70% storage

modulus (1.5 GPa) at 125 ^{o}C compared with that of samples at 40 ^{o}C, which indicates

that these semiaromatic polyamides have excellent mechanical properties.
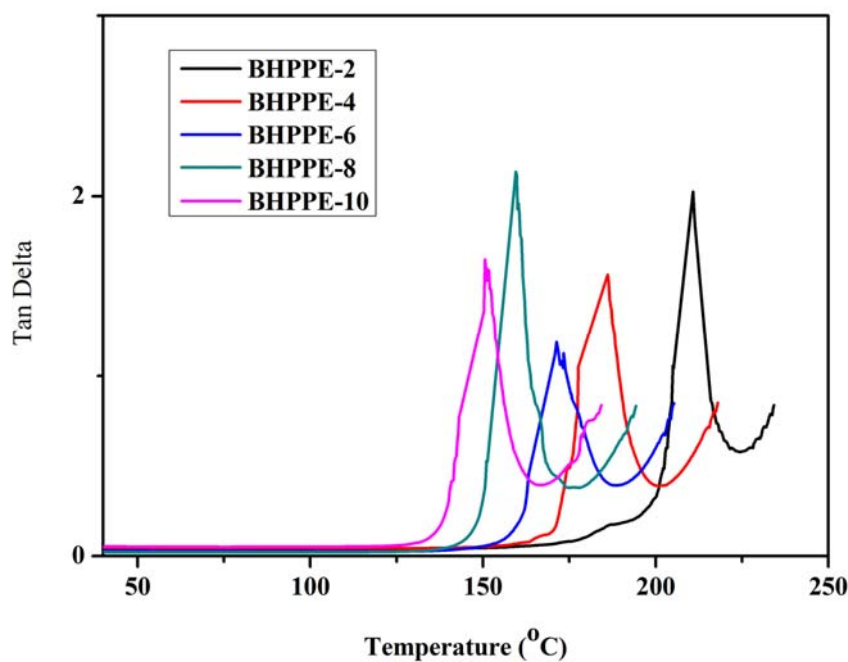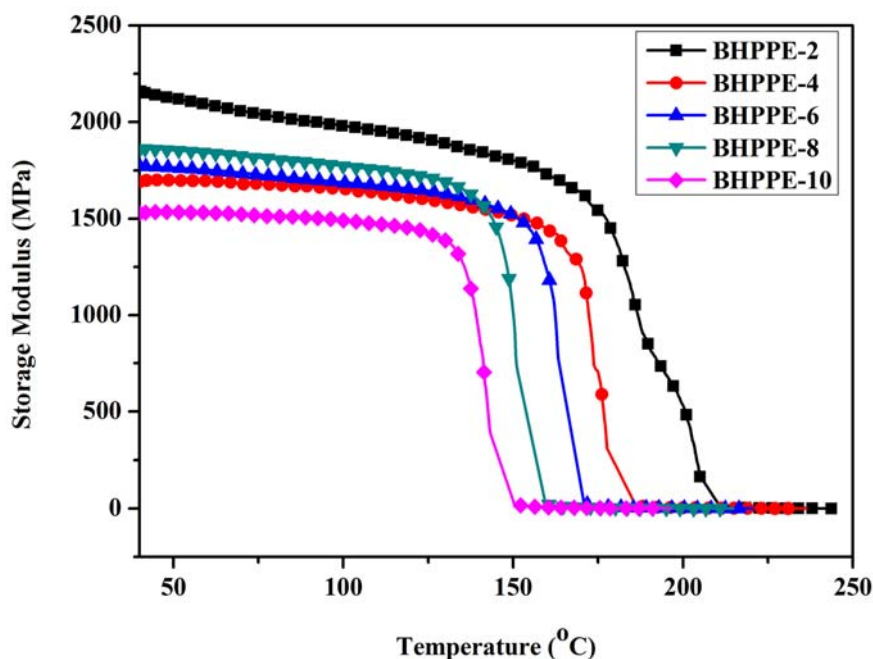

Figure 3 The DMA curves (Tan delta) of BHPPE-(2-10).

Figure 4 The DMA curves (storage modulus) of BHPPE-(2-10).

Water Absorption

The water absorption of BHPPE-(2-10) was measured according to standard GB/T1034. The results are summarized in **Table 3**. As shown in **Table 3**, the water absorption of BHPPE-(2-10) were found to be 0.31%, 0.30%, 0.27%, 0.24% and 0.24%, respectively, which were close to that of the commercial product PA9T (0.17%). The results indicate that these semiaromatic polyamides have low water absorption, which is good for their dimensional and mechanical stability. We also found that the water absorption decreased with lengthening the aliphatic chain of the polyamides. The main reason was that the high content of methylene group can improve the hydrophobic property of the semiaromatic polyamides.

Table 3 The water absorption and dielectric properties of BHPPE-(2-10) compared to PA9T

Polymers	Water absorption (%)	Thickness (mm)	Dielectric constant			
			0.1 kHz	1 kHz	10 kHz	100 kHz
BHPPE-2	0.31	1.142	4.41	4.13	3.95	3.68
BHPPE-4	0.30	1.130	4.33	4.07	3.82	3.56
BHPPE-6	0.27	1.126	4.17	3.94	3.68	3.49
BHPPE-8	0.24	1.127	4.05	3.80	3.62	3.42
BHPPE-10	0.24	1.125	3.96	3.75	3.54	3.33
PA-9T	0.17	1.137	4.06	3.78	3.92	3.64

Dielectric Constant

Table 3 summmarizes the dielectric constants of BPPPE-(2-10), which are in the

range of 3.33-3.68 at 100 kHz. These low dielectric constants may be attributed to the

low polarizability of the C-H bonds of the alkyl groups and the low water absorption

of the polymers.

Thermal Properties of BHPPE-(2-10)

The thermal properties of BHPPE-(2-10) were examined by DSC and TGA. The

results are displayed in **Figures 5** and **6**, respectively. As shown in **Figure 5**, the Tg

values of BHPPE-(2-10) were in the range of 134.4-195.6 $^{\circ}$C (**Table 2**). They were

higher than that of commercial product such as PA9T (T_g= 126 $^{\circ}$C) and copolymers of

PA6T (T_g is about 135 $^{\circ}$C). Following decreasing carbon number of aliphatic chain,

BHPPE-2 exhibited the highest T_g value (195.6 $^{\circ}$C) in this series. We had not found

the melting endothermic peaks from the DSC curves. It suggests that the amorphous

nature of the resultant semiaromatic polyamides. That was different with the other

semiaromatic polyamides reported earlier [28]. The main reason was that the introduction of large pendent benzene group limited the locomotion of molecular chain, so it could not arrange in order. As shown in **Figure 6**, the initial degradation temperatures ($T_{5\%}$) of BHPPE-(2-10) in nitrogen were 405, 417, 441, 442, and 443 ^{o}C, which are much higher than the glass transition temperature and close to those of PA9T (T_d= 464 ^{o}C) and PA10T (T_d= 472 ^{o}C). The char yield of BHPPE-(2-4) at 800 ^{o}C in nitrogen was about 28.3% and 7.5%. It was much higher than that of PA6T, PA9T. These results suggest that the thermal stability was almost maintained with incorporating the ether linkage and different number of methylene units into the polymeric backbone.
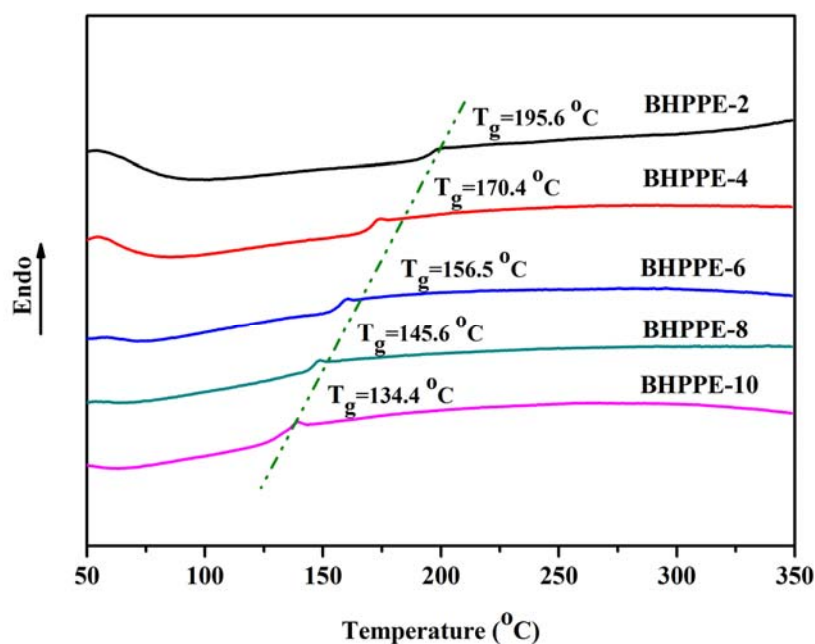

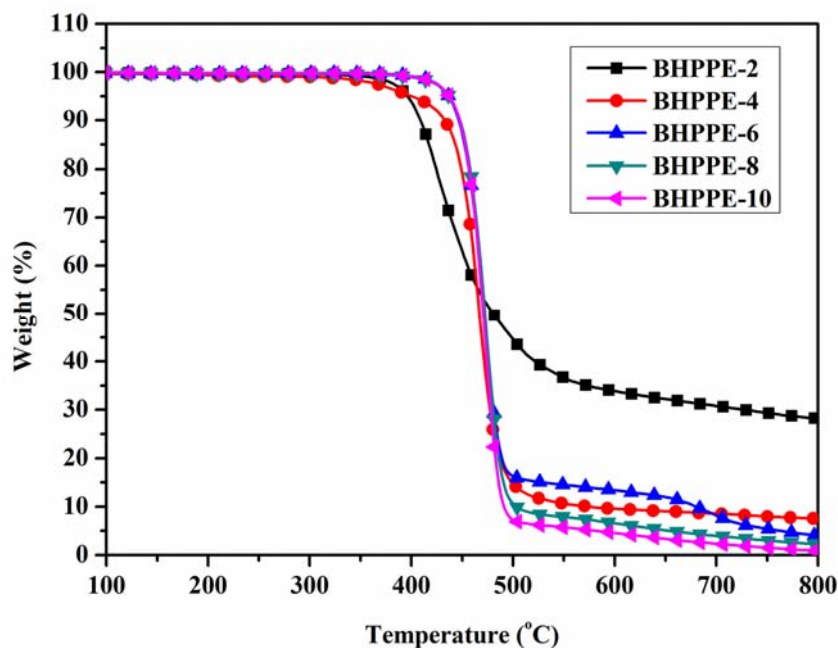**Figure 5** The DSC curves of BHPPE-(2-10) at a heating rate of 10 ^{o}C/min in N$_2$.

Figure 6 The TGA curves of BHPPE-(2-10) at a heating rate of 10 $^{\circ}$C/min in N_2.

Thermal degradation kinetics

The thermal decomposition behaviour of these semiaromatic polyamides was studied

with differential method (Kissinger method): it is the basis of the most powerful

methods for the determination of kinetic parameters. The changes in

thermogravimetic data, which caused by variation of heating rate were analysized.

This method can be used to determine the activation energy of solid state reactions

from plots of the logarithm of the heating rate versus the inverse of the temperature at

the maximum reaction rate in constant heating rate experiments, which does not need

a precise knowledge of the reaction mechanism, using the following equation (2):

$$\ln\left(\frac{\beta}{T_{max}^2}\right) = \left\{\ln\frac{AR}{E} + \ln\left[n(1-\alpha_{max})^{n-1}\right]\right\} - \frac{E}{RT_{max}} \qquad (2)$$

where β is the heating rate, T_{max} is the temperature corresponding to the inflection

point of the thermal degradation curves at the maximum reaction rate, A is the

pre-exponential factor, α_{max} is the maximum conversion, and n is the reaction order.

The activation energy E can be calculated from the slope from the plot of $\ln(\beta/T^2_{max})$

versus $1000/T_{max}$ and fitting to a straight line. The thermal degradation curves

obtained at different heating rate: 5, 10, 20, 40 ^{o}C/min are shown in **Figure 7**. The

values of the maximum decomposition rate (T_{max}) are shown in **Table 4**. **Figure 8**

shows the curves of Kissinger method applied to experimental data at different

heating rates. The activation energy (as shown in **Table 5**) of the decomposition of

BHPPE-(2-10) was calculated from a straight line fit of a plot of $\ln(\beta/T^2_{max})$ versus

$1000/ T_{max}$. The value obtained from **Figure 8** for the activation energy (E) of

BHPPE-(2-10) was in the range of 180.1-275.9 kJ/mol, respectively. The activation

energy increased with lengthening the aliphatic chain of the semiaromatic polyamides.

It suggests that the long aliphatic chain is beneficial for the thermal stability of these

semiaromatic polyamides. The reaction order (n) can be calculated by the peak value

of TGA secondary derivative curves. Then we can obtain the pre-exponential factor
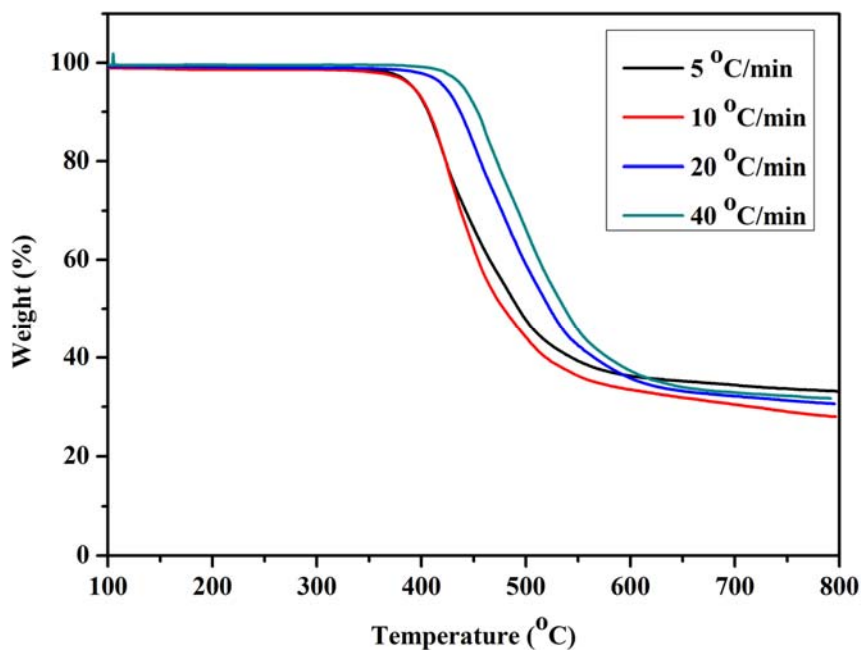
(lnA) value from equation (2).

Figure 7 TGA curves of BHPPE-2 at a heating rate of 5 ^{o}C/min, 10 ^{o}C/min, 20 ^{o}C/min, 40 ^{o}C/min in N$_2$.

Table 4 The maximum thermal degradation temperatures of BHPPE-(2-10)

Heating rates	T$_{max}$ (^{o}C)				
	BHPPE-2	BHPPE-4	BHPPE-6	BHPPE-8	BHPPE-10
5 ^{o}C/min	421	465	468	471	471
10 ^{o}C/min	432	472	476	482	483
20°C/min	452	485	494	501	500
40 ^{o}C/min	465	498	513	516	515
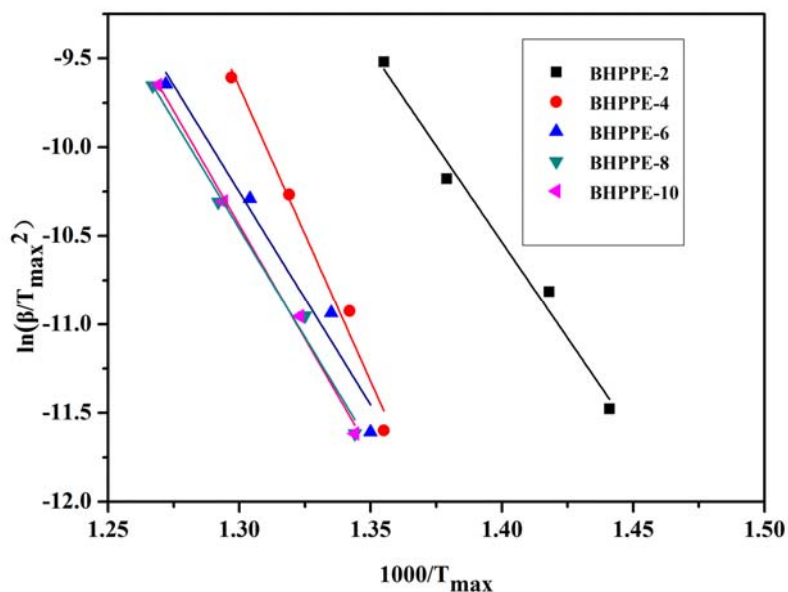
Figure 8 Kissinger method applied to experimental data at a heating rate of 5 $^{\circ}$C/min, 10 $^{\circ}$C/min, 20 $^{\circ}$C/min, 40 $^{\circ}$C/min of BHPPE-(2-10)

Table 5 Results of BHPPE-(2-10) according to Kissinger method

Polymers	Activation energy E (KJ/mol)	Degradation order (n)	Pre-exponential factor lnA (min^{-1})
BHPPE-2	180.1	1.2	22.9
BHPPE-4	185.9	2.7	23.4
BHPPE-6	199.9	2.3	23.9
BHPPE-8	203.6	2.2	24.5
BHPPE-10	213.4	2.2	26.1

Rheological Properties of Polymers

A parallel plates rheometer was used to study the effects of the structure of resulting polyamides on their rheological properties. As shown in **Figure 9**, the complex viscosities of BHPPE-(2-10) were in the range of 32-1890 Pa·s at different temperature (250-320 $^{\circ}$C). We found that when a long aliphatic chain was introduced into the main chain of the polyamide, the complex viscosity of the polymer increased,

and the longer the polyamide aliphatic chain, the higher the viscosity. This result mainly arises because the interactions between molecules become stronger as the polymer molecular chains become longer. Consequently, more entangled points should exist, and the complex viscosity of the polymer melts should get much higher. Also we studied the effects of shear frequency (0.01-55 Hz, 290 ^{o}C) on the complex viscosities of the resultant polyamides (**Figure 10**). The viscosities ranged from 94.4 to 1488 Pa·s at different shear frequency. The melts of these polyamides exhibited much more stability under high shear rates. In addition, we found that the complex viscosities of samples which contained long aliphatic chain had much larger change. It suggests the sensitivity of the resins to the shear frequency increases with lengthening the aliphatic chain of the semiaromatic polyamides. The rheological study (both of temperature and frequency sweep) revealed that the resultant semiaromatic polyamides had good processability.
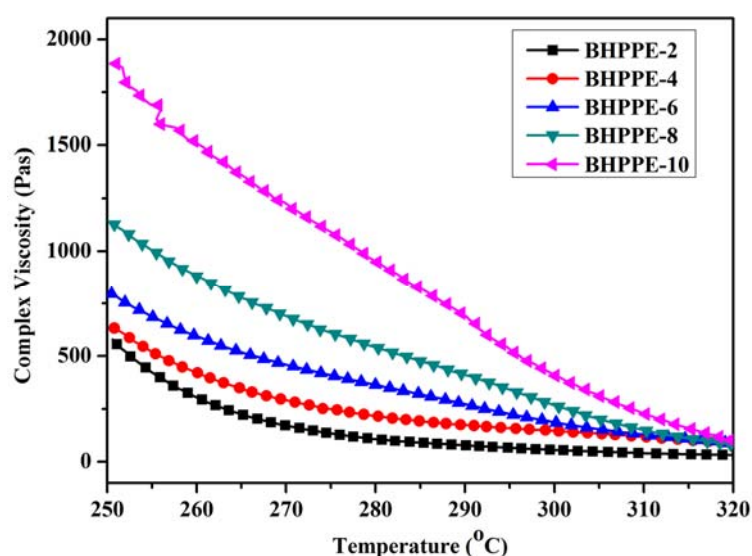

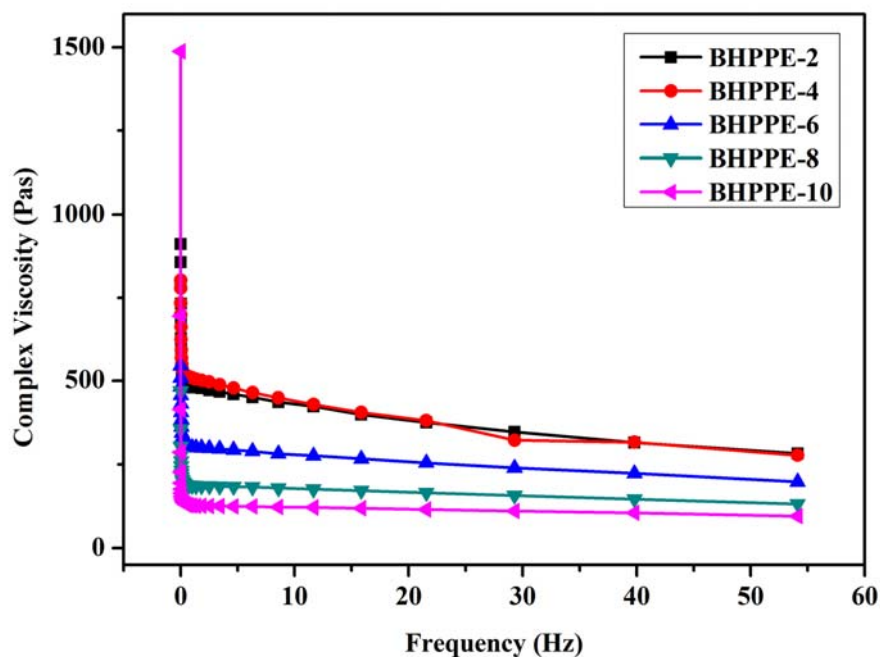**Figure 9** Plot of complex viscosities versus temperature for BHPPE-(2-10).

Figure 10 Plot of complex viscosities versus shear frequency for BHPPE-(2-10).

Flame-retardancy

The LOI values of BPPPE-(2-4) are summarized in **Table 6**, they were 34 and 30, respectively. We found that BPPPE-2 had the most large LOI value than that of BPPPE-(4-10). **Table 6** also lists the UL-94 data for BPPPE-(2-10). The flame-retardancy of BPPPE-(2-4) could reach V-1 and V-2 grade, repectively. While the commercial products such as PA6T and PA9T were combustible. Combing with the results of LOIs and UL-94 data, we find that the introduction of aromatic ring and short aliphatic chain into the semiaromatic polyamides chain is beneficial for its flame-retardancy. The main reason is that the high content of char yield formed during combustion of BPPPE-(2-4) segregated the samples from air, so its flame-retardancy was improved.

Table 6 LOIs and UL-94 data for BHPPE-(2-10)

Sample	LOI	1st buring time /s	2st buring time /s	Drpping	UL-94 grade
BHPPE-2	34	7.8	5.6	No	V-1
BHPPE-4	30	18.2	13.3	No	V-2
BHPPE-6			Combustible		
BHPPE-8			Combustible		
BHPPE-10			Combustible		

Solubilites

Table 7 reports the solubilities of BPPPE-(2-10). These materials were found to be soluble in the strong polar solvents such as NMP, DMF, DMSO and so on. They had better solubility than that of PA6T and PA9T. However, they were insoluble formic acid, toluene, 1, 4-dioxane, HCl, phosphoric acid and so on. Compared to alkyl polyamides (PA6), BPPPE-(2-10) showed better corrosion resistance.

Table 7 Solvents resistance of BPPPE-(2-10) and PA6

Solvents	Polymers					
	PA6	BPPPE-2	BPPPE-4	BPPPE-6	BPPPE-8	BPPPE-10
concentrated sulfuric acid	+	+	+	+	+	+
formic acid	+	-	-	-	-	-
NMP	-	+	+	+	+	+
CF$_3$COOH	+	+	+	+	+	+
HCl (6 mol/L)	-	-	-	-	-	-
phosphoric acid	+	-	-	-	-	-
NaOH (1 mol/L)	-	-	-	-	-	-
acetone	-	-	-	-	+-	+-

chloroform	-	-	-	-	+-	+-
DMSO	-	+	+	+	+	+
1, 4-Dioxane	-	-	-	-	-	-
Toluene	-	-	-	-	-	-
Phenol + Tetrachloroethane	-	-	-	-	-	-

*+: soluble at room temperature; +-: swelling; -: insoluble with heating.

Conclusions

Semiaromatic difluorobenzamide monomers with different number methylene units were synthesized to develop a series of semiaromatic polyamides [BHPPE-(2-10)]. The semiaromatic polyamides were prepared by nucleophilic polycondensation. The effects of the chemical structure of the semiaromatic polyamides on polymers' physical performance were investigated in detail. The properties of the semiaromatic polyamides could be improved by changing the structure of aliphatic diamine. The glass transition temperature and water absorption were found to decrease with increasing aliphatic chain length in the polymers. In contrast, the thermal stability and complex viscosity of these polyamides continuously increased. These polyamides showed good thermal, mechanical properties and processability (including solution processing and melt processing). The resultant semiaromatic polyamides are suitable for melting process even the number of repeat units (methylene) in the aliphatic diamine that reacted with BHPPE is 2. With this method, a kind of semiaromatic polyamides which exhibited excellent performance can be obtained. And it can be produced by much more affordable and cheap diamines (such as 1,2-ethanediamine

and 1,6-hexanediamine) than that of PA9T. Additionally, we found that a part of the

resultant polymers [BHPPE-(2-4)] possessed natural flame-retardancy that the

traditional semiaromatic polyamides did not have. Thus, these semiaromatic

polyamides can be good candidates as components for heat resistant thermoplastic

engineering materials especially in some harsh environments which need resins be

thermo-stable and retardant.

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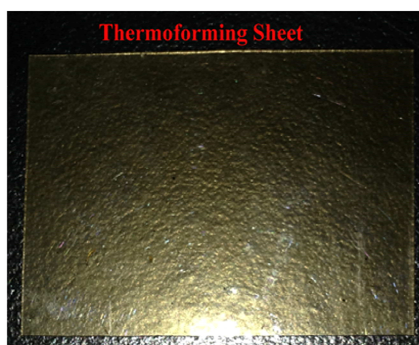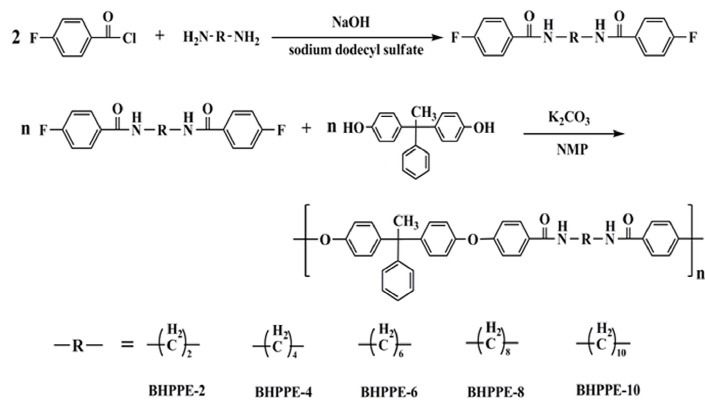
The resultant semi-aromatic polyamides showed excellent mechanical, processability,

thermal and retardant property.