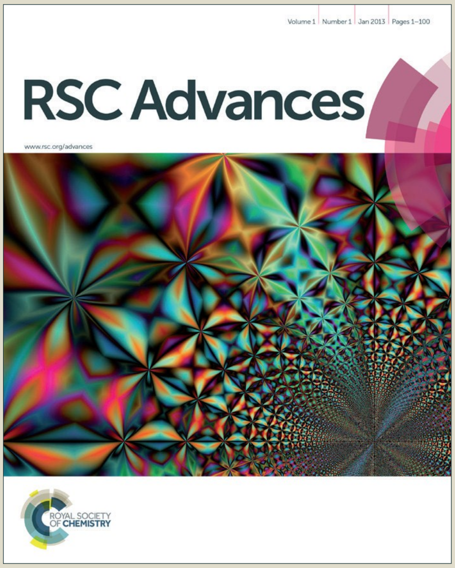
RSC Advances



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

RSC Advances Accepted Manuscript

Synthesis and Properties investigation of isophorone and ether units based semi-aromatic polyamides

Gang Zhang[1*], Yu-xuan Zhou[2], Yan Li[1], Xiao-Jun Wang[1], Sheng-Ru Long[1], Jie Yang[1,3*]

1. Institute of Materials Science & Technology, Analytical & Testing Center, Sichuan University, Chengdu 610064, P. R. China

2. College of Chemistry, Sichuan University, Chengdu, 610064, P. R. China

3. State Key Laboratory of Polymer Materials Engineering (Sichuan University), Chengdu, 610065, P. R. China

E-mail: gangzhang@scu.edu.cn ppsf@scu.edu.cn Fax: 86-28-8541-2866

Abstract: Difluoro-substituted monomer (N,N'-Bis(4-fluorobenzoyl) isophorone diamine (BFID) was prepared via interfacial reaction from isophorone diamine and 4-fluorobenzoic chloride. It was then conducted to react with hydroquinone (or resorcinol, 1,1-bis(4-hydroxyphenyl)-1-phenylethane (BHPPE)) to yield a series of semi-aromatic polyamides. For the synthesized semi-aromatic polyamides differential scanning calorimetry and thermogravimetric analysis confirmed high glass transition temperatures (T_g), between 217 and 239 °C and a good thermal stability with initial degradation temperatures (T_d) in the range 425 - 430 ^{o}C. Tensile test and dynamic mechanical analysis (DMA) results revealed the good mechanical properties for the semi-aromatic polyamides at ambient temperature and even at 200 °C. A complex viscosities at 310 ^{o}C for the semi-aromatic polyamide in the range of 990-1350 Pa·s could be observed when measured by rheological characterization, which suggests that they were suitable for melt process. The better solubility properties for the resultant semi-aromatic polyamides compared to the commercial ones were also found. All the results indicated the good processability for the synthesized semi-aromatic polyamides. Additionally, they were found to have almost the identical optical transmittance (*Tran*%: 83%-85% at 450 nm) as polycarbonate (PC) in the UV-visible region.

Keywords: synthesis; polyamides; rheology

Introduction

Polyamide such as nylon is a kind of famous thermoplastic polymer. It has been already widely used in many fields because of its excellent mechanical durability and high strength [1, 2]. However, aliphatic polyamide displays the limited thermal stability, especially when it is used in the shells of automobile engines and surface mount technology (SMT). In order to improve the thermal properties of aliphatic polyamides, incorporation of aromatic units into the polymer main chain acts as an efficient approach [3-7]. As we know the aromatic polyamides such as Aramid-1414 [8] and Aramid-1313 [9] exhibit excellent mechanical properties, good heat resistance, and high chemical and solvent resistance. However, their poor solubility and high glass

RSC Advances Accepted Manuscript

RSC Advances Accepted Manuscript

transition temperature result to the poor processability. To solve these problems, the application of semi-aromatic polyamides is regarded as a promising alternative method. Semi-aromatic polyamides are generally used to fill the "performance gap" between high performance polyamides and nylons [10]. But only several semi-aromatic polyamides such as the copolymer of PA6T [11], poly (nonamethylene terephthalamide) (PA9T) [12-15], poly (decamethylene terephthalamide) (PA10T), the product of Dupont, Solvay, Mitsui, Evonik and so on, are commercially available. The melt processing is impractical for those semi-aromatic polyamides which contain short chain (less than 7 methylenes) diamine because their melting temperature (T_m) (as shown in **Table 1**) was higher than the thermal degradation temperature. To improve their processability, some works to increase the semi-aromatic solubility by incorporation of bulky pendant groups [16, 17], noncoplanar biphenylene moieties [18], triazole units [19], azo groups [20, 21] and hyperbranched units [22, 23] into the polymer main chain have been reported. On the other hand, improving the melt processability (as shown in **Table 1**) by introduction of naphthalene rings [24], cyclodextrin unit [25], sulphone units [26], ester unit [27], sulfide groups [28], dicyclohexyl methane unit [29] and long carbon chain diamines [30, 31] [such as PA-10T [32], PA-12T [33] and PA-18T (T_m = 245 ^oC) and so on] into the polymer backbone could an alternately way.

The earlier literatures about semi-aromatic polyamides were usually focused on the study of thermal property of aggregation structure, while there were only quite few studies about their rheological and optical properties. Therefore, the aim of this work was synthesis of new semi-aromatic polyamides with improved mechanical and

RSC Advances Accepted Manuscript

thermal properties as well as their processability verified through investigation of their rheological and optical properties. To achieve this aim, we introduced the isophorone unit containing stable cyclohexane and side methyl group into the polymer chain. The ether bone (-O-) is thought to be a flexible linkage. It has already been introduced into the polymer main chain to yield high performance resins, such as poly (arylene ether ether sulfone) [34] and poly (arylene ether amide). Both of them are found to have excellent processability, mechanical and thermal properties. Additionally, the side group is usually expected to weaken the packing of the polymer chain and improve the optical properties. In this case, the finally synthesized semi-aromatic polyamides in this work would display a pronounced processability, mechanics, thermal properties, and optical performance.

Table 1 The melt temperature (T_m) and thermal degradation temperature (T_d) of traditional semi-aromatic polyamides

Polymer	T_m (°C)	T_d (°C)	Polymer	T_g (°C)	T_m (°C)	T_d (°C)
PA4T	430	350	PA18T	-	245	-
PA6T (homopolymer)	370	350	Semi-aromatic PA (with bulky pendant groups)	270	-	500
PA9T	305	464	Semi-aromatic PA (with biphenylene unit)	300	-	510
PA10T	315	472	Semi-aromatic PA (with naphthalene ring)	-	300	495
PA12T	295	429	Semi-aromatic PA (with ester unit)	110-140	219-260	-

In this work, we synthesized the semi-aromatic polyamides through the nucleophilic substitution reaction of bisphenol and difluorobenzamide monomers containing isophorone unit. The effects of chemical structure on these semi-aromatic polyamides' properties such as thermal properties, mechanics, and rheological as well as optical properties were investigated.

Experimental

Materials

4-Fluorobenzoic choride (4-FBC) (99.5%, Lanning Chemical Company Limited), BHPPE was synthesized as reported earlier by our group [35], sodium hydroxide (NaOH) (AR, SiChuan ChengDu ChangLian Chemical Reagent Company), N-methyl-2-pyrrolidone (NMP) (JiangSu NanJing JinLong Chemical Industry Company), PA6T-Dupont (DuPont Company, 18502 NC010), isophorone diamine and other reagents were obtained commercially.

N,N'-Bis(4-fluorobenzoyl) isophorone diamine (BFID) (Scheme 1)

BFID was prepared as the following: deionized water (1200 ml), isophorone diamine (170 g, 1 mol), NaOH (80 g, 2 mol) and sodium dodecyl sulfate (3 g, 0.01 mol) were added into a 5000 ml three-necked flask under stirring. When the mixture was dissolved, the solution of 4-FBC (320 g, 2.02 mol) dissolved in dichloromethane (2000 ml) was added dropwisely. After all the 4-FBC was added into the flask, the reaction mixture was stirred at ambient temperature for another 8 h. Afterwards, the mixture was filtered and washed with deionized water for 3 times. Then the crude

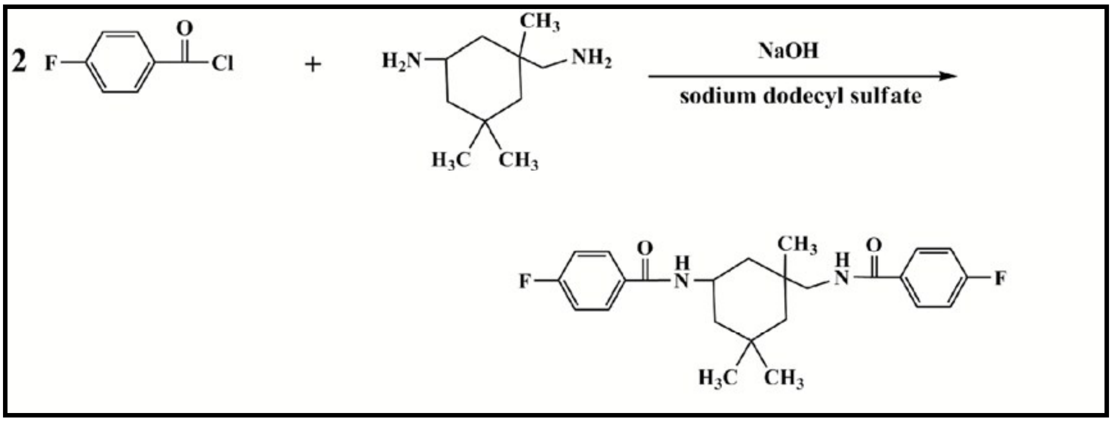
RSC Advances Accepted Manuscript

RSC Advances Accepted Manuscript

product was recrystallized from ethanol. Finally it was dried at 80 °C for about 24 h.

Yield: 347.3 g, 83.9%.

Elemental analysis (%): C, 69.63 (69.55); H, 6.82 (6.81); N, 6.67(6.76) (values in bracket are calculated data). FT-IR (KBr, cm^{-1}): 3308, 3239 (N-H in amide group), 1632 (-CONH-), 3074 (C-H aromatic ring), 2958 ($-CH_3$), 2910 ($-CH_2-$), 1605, 1550, 1503 (aromatic ring skeleton), 850 (para substitution of the benzene ring). ^{1}H-NMR [400 MHz, deuterated DMSO-d6/ TMS, ppm]: 0.933 (s, 3H, H1), 1.062-1.072 (d, 6H, H2), 1.138-1.253 (m, 4H, H3-H4), 1.539-1.568 (d, 2H, H5), 3.064-3.087 (t, 2H, H6), 4.136-4.187 (m, 1H, H7), 7.288-7.310 (d, 4H, H8), 7.880-7.942 (m, 4H, H9), 8.210-8.230 (d, 1H, H10), 8.376-8.407 (d, 1H, H11).



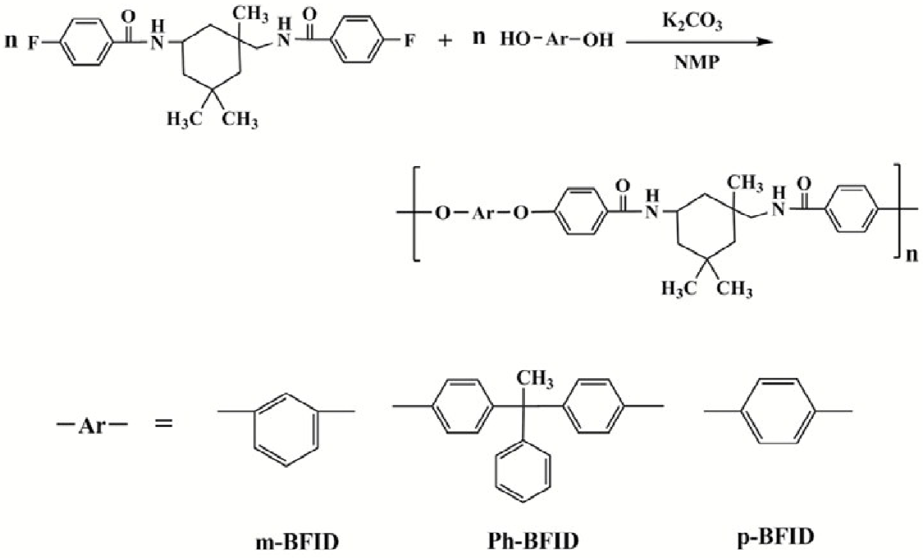
Scheme 1 Synthesis route of N,N’-Bis(4-fluorobenzoyl) isophorone diamine (BFID)

Polymer Synthesis

The polymerization was carried out as the following (**Scheme 2**). BFID (41.4 g, 0.1 mol), BHPPE (29.0 g, 0.1 mol), potassium carbonate (27.6 g, 0.2 mol), toluene (20 ml) and NMP (150 ml) were added into a 500 ml three-necked flask firstly. Then the flask was heated to 180 °C to remove the byproduct of water. Afterwards, the reaction

RSC Advances Accepted Manuscript

temperature was raised to 202 °C and kept for about 6 h to yield high molecular weight polymers. The reacted solution was poured into water to precipitate fibrous polymers. It was pulverized to powder and washed with hot water for 3 times. Then the crude product was dried at 100 °C for 24 h to yield pure resins. (Yield: 63.1 g, 95.1%). FT-IR (cm^{-1}): 3326 (N-H of amide group), 1640 (-CONH-), 3056 (C-H of benzene ring), 2951, 2914 (-CH_3), 1596, 1539, 1493 (benzene ring skeleton), 846 (para substitution of the benzene ring). ^{1}H-NMR [400 MHz, deuterated DMSO-d6)/ TMS, ppm]: 0.900 (s, 3H, H1), 1.027-1.049 (d, 6H, H2), 1.156-1.188 (m, 4H, H3-H4), 1.529 (s, 2H, H5), 2.112 (s, 3H, H6), 3.047 (s, 2H, H7), 4.148-4.169 (d, 1H, H8), 6.974-7.073 (m, 14H, H9-H12), 7.192-7.208 (m, 1H, H13), 7.217-7.281 (m, 2H, H14), 7.831-7.881 (m, 4H, H15), 8.104-8.123 (d, 1H, H16), 8.296 (s, 1H, H17).



Scheme 2 Synthesis routes of polymers (m-BFID, Ph-BFID and p-BFID)

m-BFID and p-BFID were synthesized with a similar procedure as that of Ph-BFID.

m-BFID: Yield: 45.6 g (94.3%). FT-IR (cm^{-1}): 3307 (N-H of amide group), 1637 (-CONH-), 3062 (C-H of benzene ring), 2949, 2855 (-CH_3), 1591, 1541, 1497 (benzene ring skeleton), 848 (para substitution of the benzene ring). ^{1}H-NMR [400 MHz, deuterated DMSO-d6/TMS, ppm]: 0.899 (s, 3H, H1), 1.027-1.050 (d, 6H, H2), 1.157-1.189 (m, 4H, H3-H4), 1.531 (s, 2H, H5), 3.048 (s, 2H, H6), 4.146-4.167 (d, 1H, H7), 6.732 (s, 1H, H8), 6.823-6.843 (d, 2H, H9), 7.051-7.090 (m, 4H, H10), 7.395-7.435 (m, 1H, H11), 7.848-7.898 (m, 4H, H12), 8.131-8.148 (d, 1H, H13), 8.320 (s, 1H, H14).

p-BFID: Yield, 45.5 g (94.1%). FT-IR (cm^{-1}): 3320 (N-H of amide group), 1637 (-CONH-), 3070 (C-H of benzene ring), 2951, 2865 (-CH_3), 1604, 1540, 1488 (benzene ring skeleton), 845 (para substitution of the benzene ring). ^{1}H-NMR [400 MHz, deuterated DMSO-d6/ TMS, ppm]: 0.914 (s, 3H, H1), 1.041-1.062 (d, 6H, H2), 1.161-1.202 (m, 4H, H3-H4), 1.536 (s, 2H, H5), 3.057 (s, 2H, H6), 4.156-4.172 (d, 1H, H7), 7.008-7.049 (m, 4H, H8), 7.118 (s, 4H, H9), 7.847-7.898 (m, 4H, H10), 8.119-8.139 (d, 1H, H11), 8.311 (s, 1H, H12).

Characterization

The intrinsic viscosities of m-BFID, Ph-BFID and p-BFID were tested at 30 ± 0.1 ^{o}C with the dilute solution of polymers in NMP. The values were calculated with the following equation:

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

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

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

RSC Advances Accepted Manuscript

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), Their effective molecular weight ranges 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 ^{o}C. Polystyrene standards were used for calibration.

The samples of monomers were measured with an elemental analyzer (EURO EA-3000). 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 10 ^{o}C/min in nitrogen atmosphere. The polymer powder was processed into the sheet shape by a hydraulic press at 310 ^{o}C (pressure: 8 MPa) for 30 min. Then the sheets were cut into specific shapes for the different tests. The samples having dimensions 50.0 mm × 3 mm × 1.0 mm (length × width × thickness) were prepared for tensile tests. The samples with dimensions 30.0 mm× 3.7 mm× 1.0 mm (length× width × thickness) were prepared for DMA experiments. The disks (diameter: 3 cm and thick: 1mm) were prepared for parallel-plate rheological measurements. An Instron Corporation 4302 instrument was used to study the stress-strain behavior of the samples. Dynamic mechanical analysis (DMA) was performed on a TA-Q800 apparatus operating in tensile mode at a

RSC Advances Accepted Manuscript

RSC Advances Accepted Manuscript

frequency of 1 Hz with a heating rate of 5 °C/min. A Parallel plate rheometer (Bohlin Gemini 200, Britain) was fitted with 2.5 cm diameter stainless steel parallel plates. Temperature (temperature scanning rate: 5 °C/min, shear strain: 2%, shear frequency: 1 Hz) and time (shear strain: 2%, shear frequency: 1 Hz) 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 and time during processing. The optical transmittance of the polymers at 200-800 nm was characterized by UV-vis spectroscopy (U-2310Ⅱ) (The samples were prepared with a casting method to form a thickness of 10-13 μm film). The solubility of the polymers in various solvents was tested at ambient temperature and the temperatures with boiling points of the solvents.

Results and Discussion

Synthesis and Chemical Structure of monomer semi-aromatic difluorobenzamide monomer (BFID)

The monomer BFID was synthesized with an interfacial reaction at ambient temperature without any catalyst (shown in **Scheme 1)**. From the FT-IR spectra of monomers **(Figure 1),** we found the characteristic absorptions of -CONH-, stretching of C-H (Aromatic ring), aliphatic chain, vibration of C-F and para-substituted benzene rings were near 3300, 1630 cm^{-1}, 3070 cm^{-1}, 2960 cm^{-1}, 1320 cm^{-1} and 850 cm^{-1}, respectively. The ^{1}H-NMR spectrum of BFID is showed in **Figure 2**. The signals at 8.210 - 8.230 and 8.376 - 8.407 ppm were ascribed to amide protons. While the signals near 7.2 - 8.0 ppm were characteristic protons of aromatic moiety. The signals ranging from 0.9 to 4.2 ppm were attributed to aliphatic chain protons. Both of the results (FT-IR and ^{1}H-NMR) confirm the occurrence of the reaction between amine and chloride units.

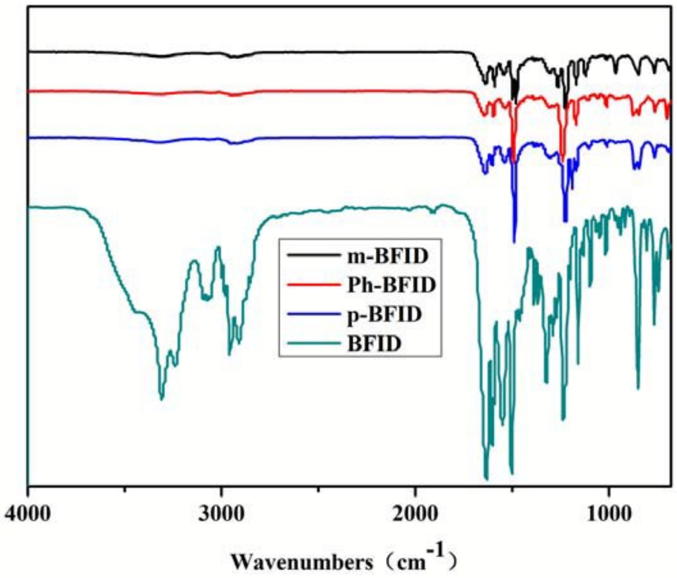


Figure 1 The FT-IR spectra of BFID and m-BFID, Ph-BFID and p-BFID.

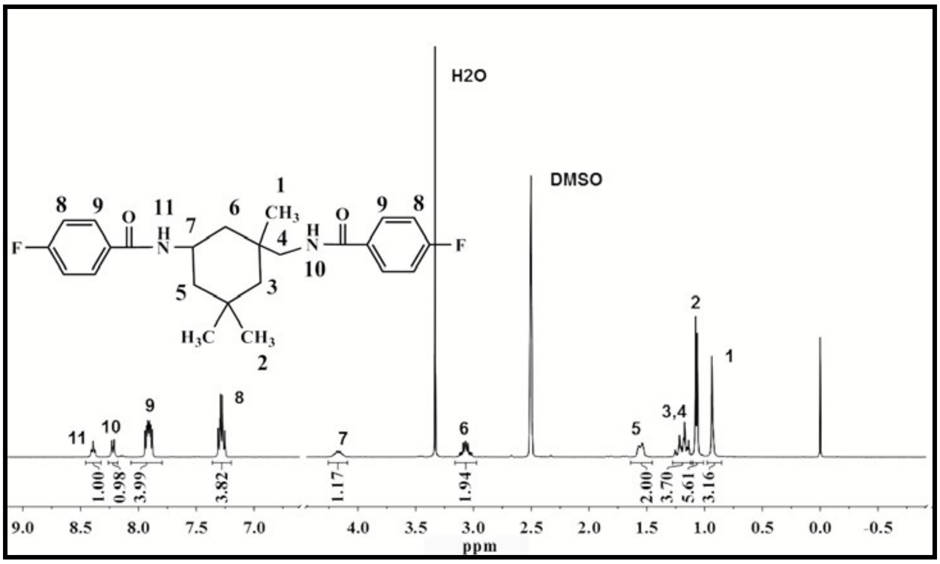


Figure 2 The ^{1}H-NMR spectrum of BFID.

Synthesis of m-BFID, Ph-BFID and p-BFID

The polymerization was carried out by nucleophilic substitution reaction with K_2CO_3 as the base. The reaction temperature was kept from 140 °C to 202 °C. Firstly, the

RSC Advances Accepted Manuscript

RSC Advances Accepted Manuscript

reaction was maintained at 140 - 160 °C to remove the byproduct of water. Then it was raised up to 180 - 202 °C to get polymers with high molecular weight. The η_{int} values of m-BFID, Ph-BFID and p-BFID determined by the method of intrinsic viscosity were in the range of 0.89 - 1.21 dL/g (**Table 2**) while their M_w values measured by GPC were in the range of 1.40-1.68×10^5. It indicates that synthesized polymers exhibited the similar molecular weight as that of the commercial available products.

Table 2 Intrinsic viscosity (η_{int}) and molecular weights of polymers (m-BFID, Ph-BFID and p-BFID)

Polymers	η_{int} (dL/g)	M_n (g/mol)	M_w (g/mol)	PDI (M_w/M_n)
m-BFID	1.02	6.74×10^4	1.52×10^5	2.25
Ph-BFID	0.89	5.63×10^4	1.40×10^5	2.49
p-BFID	1.21	8.31×10^4	1.68×10^5	2.02

Chemical Structure of polymers

The chemical structures of m-BFID, Ph-BFID and p-BFID were characterized by FT-IR and ^{1}H-NMR. As shown in **Figure 1,** the characteristic absorptions of amide group appeared near 3320 and 1640 cm^{-1}. In contrast with the monomer BFID, the absorption of C-F vibration near 1320 cm^{-1} disappeared and a new absorption of ether units near 1100 cm^{-1} attributed to ether units stretching was observed. It confirms the polymerization of bisphenol and BFID. **Figure 3** shows the ^{1}H-NMR spectra of m-BFID. The signals of aromatic ring protons are in the range of 6.7 - 8.14 ppm. The signals at 8.148 and 8.320 ppm are assigned to amide unit. The signals at 6.5-8.5 ppm belong to the aromatic protons. The signals at 0.7- 4.5 ppm are characteristic protons of the aliphatic moiety. The ratio of corresponding integral curves was 3:6:2:2:2:2:1:1:2:4:1:4:1:1. Combined with the FT-IR and elemental analysis results suggest that the polymerization proceeds as described in **Scheme 2**. The chemical structures of Ph-BFID and p-BFID were also characterized by the ^{1}H-NMR (**Figure 4 and Figure 5**) and FT-IR spectra and the results confirmed their structures were still the same as what we have designed.

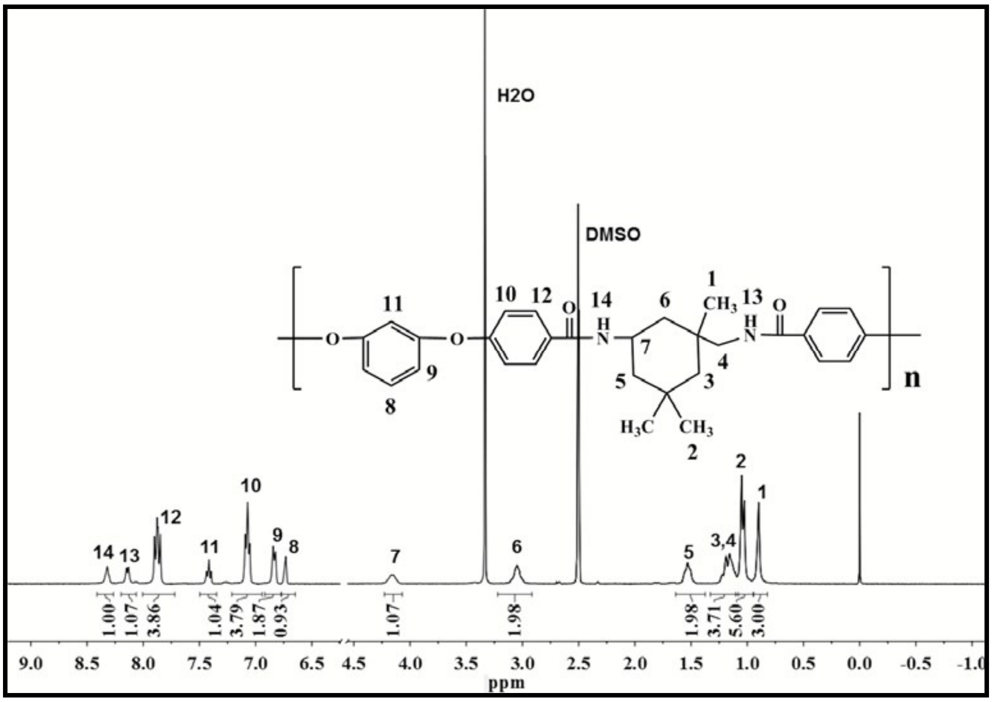


Figure 3 The ^{1}H-NMR spectrum of m-BFID.

RSC Advances Accepted Manuscript

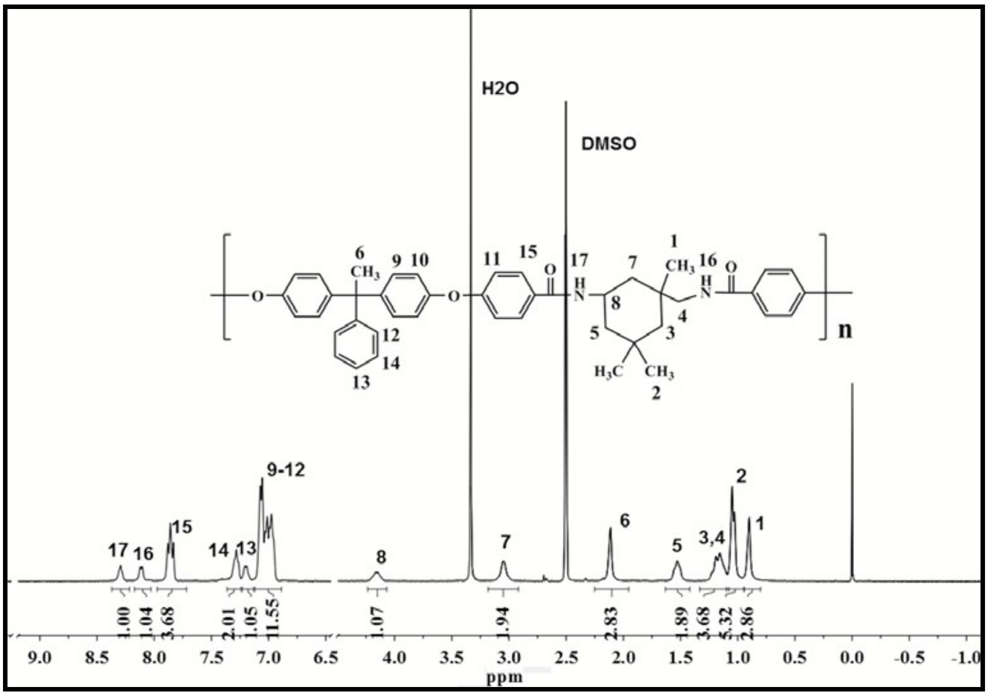


Figure 4 The ^{1}H-NMR spectrum of Ph-BFID.

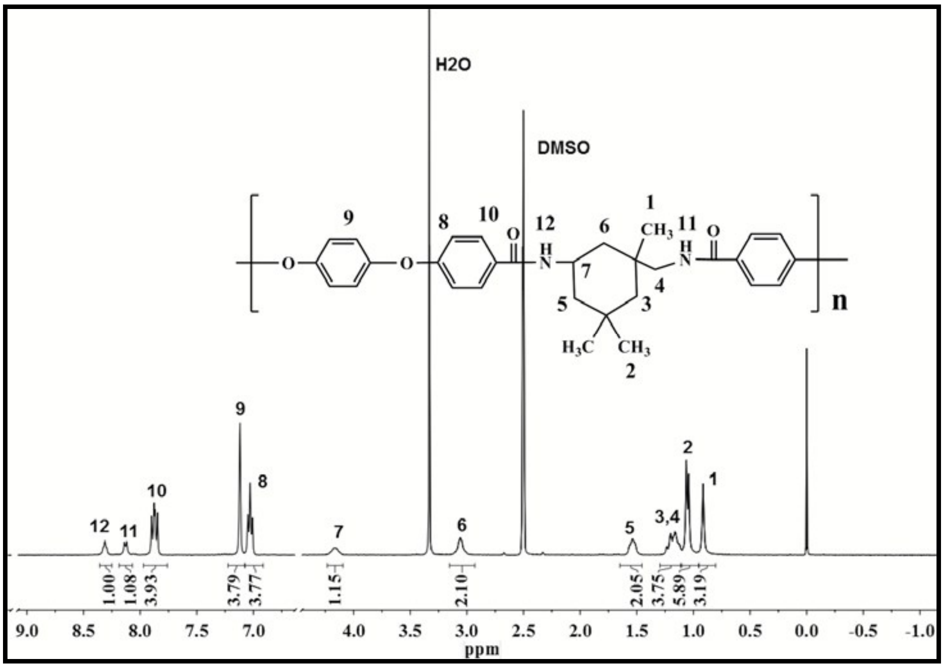


Figure 5 The ^{1}H-NMR spectrum of p-BFID.

Thermal Properties of m-BFID, Ph-BFID and p-BFID

The thermal properties of m-BFID, Ph-BFID and p-BFID were tested by DSC **(Figures 6)** and TGA **(Figures 7)**. As presented in **Figure 6**, the glass transition

RSC Advances Accepted Manuscript

RSC Advances Accepted Manuscript

temperature of m-BFID, Ph-BFID and p-BFID were 217, 224 and 239 °C, respectively (seen in **Table 3**). They were higher than that of PA9T (T_g= 126 °C) and copolymers of PA6T (T_g is about 135 °C). p-BFID exhibited the highest T_g value (239 °C) in this series. From the DSC curves, no melting endothermic peak was found. The incorporation of large bulkyl group reduces the movement of the polymer chain, thus it exhibits an amorphous nature. Figure 7 is the thermo-degradation curves of m-BFID, Ph-BFID and p-BFID. The initial degradation temperatures ($T_{5\%}$) of m-BFID, Ph-BFID and p-BFID in nitrogen were 425, 438and 430 °C, respectively. They are close to that of PA9T (T_d= 464 °C) and PA10T (T_d= 472 °C), and much higher than the glass transition temperature of themselves. The result suggests that their thermal stability is good and suitable for melt process.

Table 3 Thermal and mechanical properties of m-BFID, Ph-BFID and p-BFID and PA9T

Polymers	T_g (°C)		$T_{5\%}$ (°C)	Tensile strengths (MPa)	Young's Modulus (GPa)	Elongation at break (%)	Storage Modulus at 200 °C (GPa)
m-BFID	217	226 [a]	425	85±5.0	1.7±0.20	17.0±3.0	1.1
Ph-BFID	224	235 [a]	438	73±8.0	1.7±0.27	16.2±4.8	1.0
p-BFID	239	246 [a]	430	91±6.0	1.9±0.11	15.5±2.9	1.1
PA9T	115	-	464	86 ±4.0	2.7±0.16	4.2 ±2.6	-

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

RSC Advances Accepted Manuscript

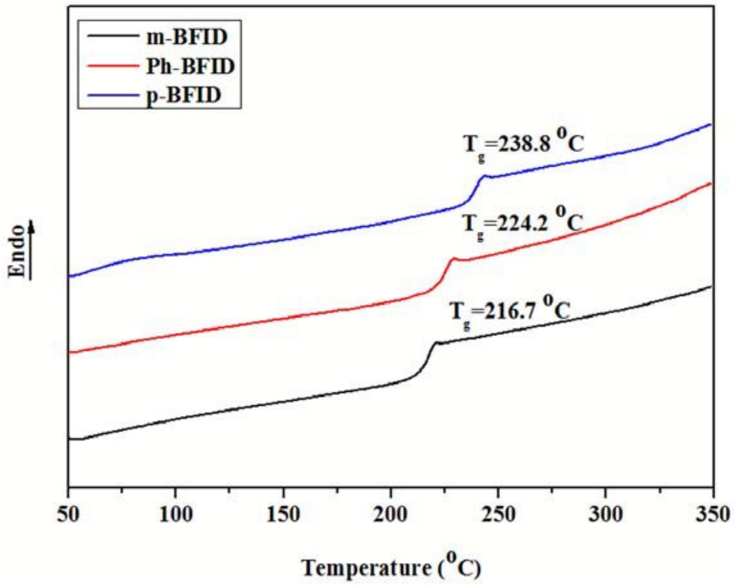


Figure 6 The DSC curves of m-BFID, Ph-BFID and p-BFID at a heating rate of 10 °C/min in N_2.

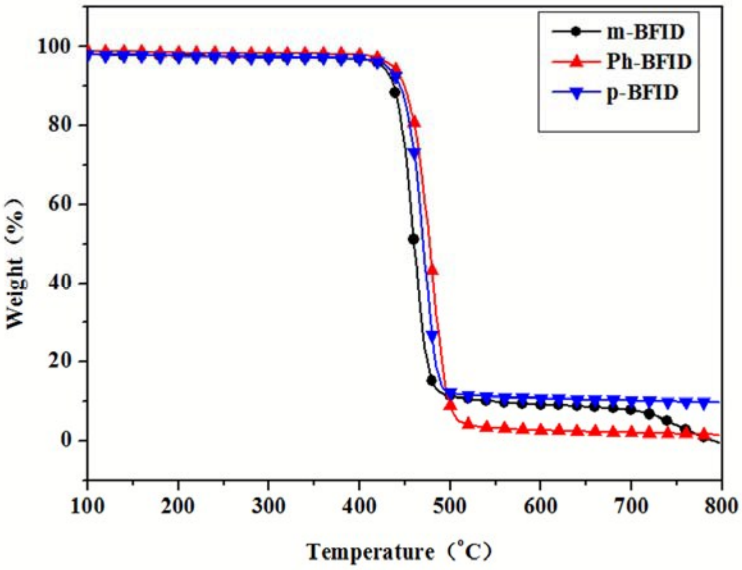


Figure 7 The TGA curves of m-BFID, Ph-BFID and p-BFID at a heating rate of 10 °C/min in N_2.

Mechanical Properties

The tensile strength of m-BFID, Ph-BFID and p-BFID were tested by universal testing machine and summarized in **Table 3**. The average tensile strengths of the polymers were 85, 73 and 91 MPa, respectively. The elongation at break ranged from 15.5 to 17.0%. It suggests that m-BFID, Ph-BFID and p-BFID have similar tensile strength as PA9T. The thermal mechanical properties of the resulting polyamides were characterized by DMA. As shown in **Figure 8**, one obvious transition peak can be observed. It was defined as α relaxation or glass transition temperature. The α relaxation temperatures of these semi-aromatic polyamides were 226, 235 and 246 ^{o}C, respectively. These T_g values were slightly higher than those tested by DSC. The storage modulus curves of m-BFID, Ph-BFID and p-BFID are displayed in **Figure 9**, the semi-aromatic polyamides showed high storage modulus of 1.60, 1.32 and 1.57 GPa, respectively. It was also found that the storage modulus of these semi-aromatic polyamides was kept about 1 GPa at 190 ^{o}C, indicating the good thermal mechanical performance for these semi-aromatic polyamides.

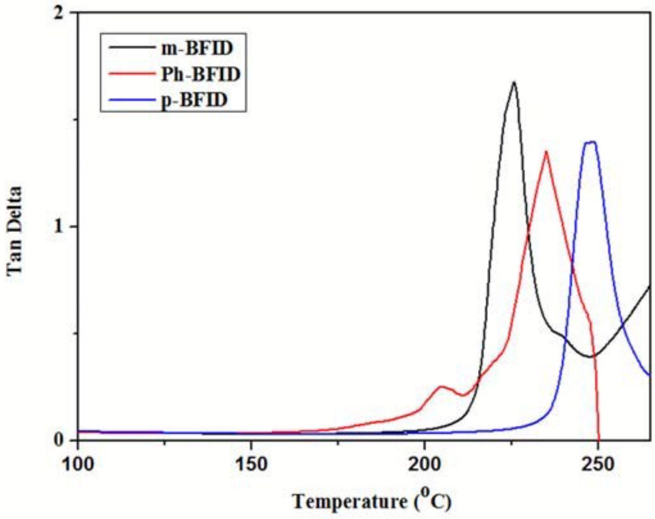


Figure 8 The DMA curves (Tan delta) of m-BFID, Ph-BFID and p-BFID.

RSC Advances Accepted Manuscript

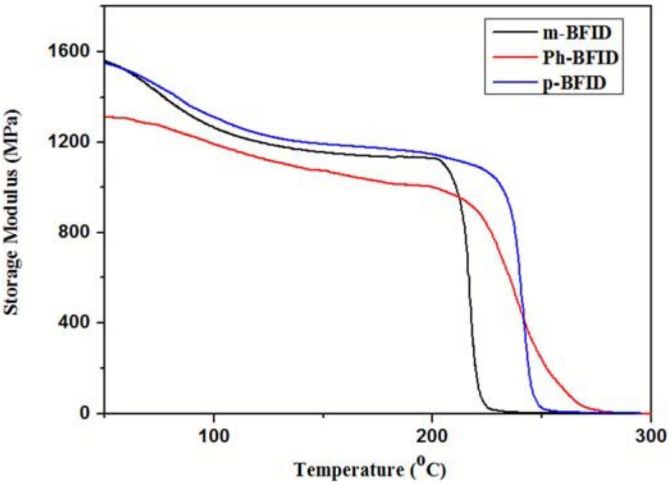


Figure 9 The storage modulus of m-BFID, Ph-BFID and p-BFID.

Rheological Properties of Polymers

Rheological measurements were carried out to investigate the resulting polyamides' rheological properties. We studied the effects of testing time (0-1830 s at 330 °C) on the complex viscosities of these semi-aromatic polyamides and PC (**Figure 10**). The complex viscosities of m-BFID, Ph-BFID and p-BFID exhibited a slight dependence on time. The viscosities values of the resultant semi-aromatic polyamides kept almost unchanging during the whole testing while the increase for the complex viscosities of PC and especially for PA6T-Dupont (as shown in Figure 11) could be observed. It indicates that these polyamides had better melt stability than PC and PA6T-Dupont. We also found that the complex viscosities of m-BFID, Ph-BFID, p-BFID, PC and PA6T-Dupont at different temperature (from 300 °C to 360 °C) were in the range of 177 - 4830 Pa·s (**Figure 12**). It gives the basic information for the melt processing parameters selection, e.g. 310 °C (990-1350 Pa·s) could be used as the suitable melt process temperature. Ph-BFID was found to have the lowest viscosity among these

RSC Advances Accepted Manuscript

samples. It suggests that when a bulky side unit was incorporated into the polyamide backbone, the complex viscosity decreased. The main reason of this phenomenon is attributed that the bulky groups decrease the inter-chain interaction.

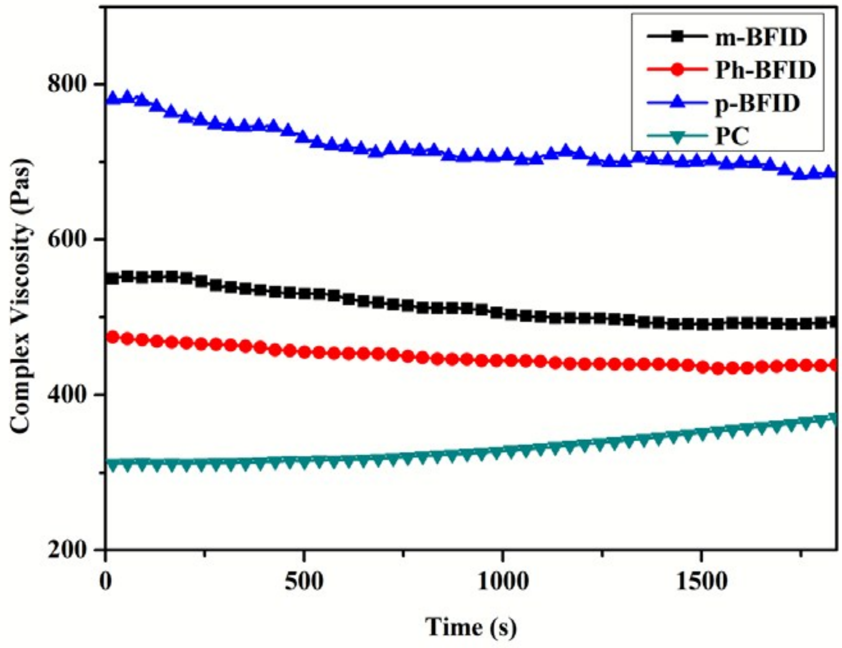


Figure 10 Plot of complex viscosities versus time (at 330 ^{o}C) for m-BFID, Ph-BFID, p-BFID and PC.

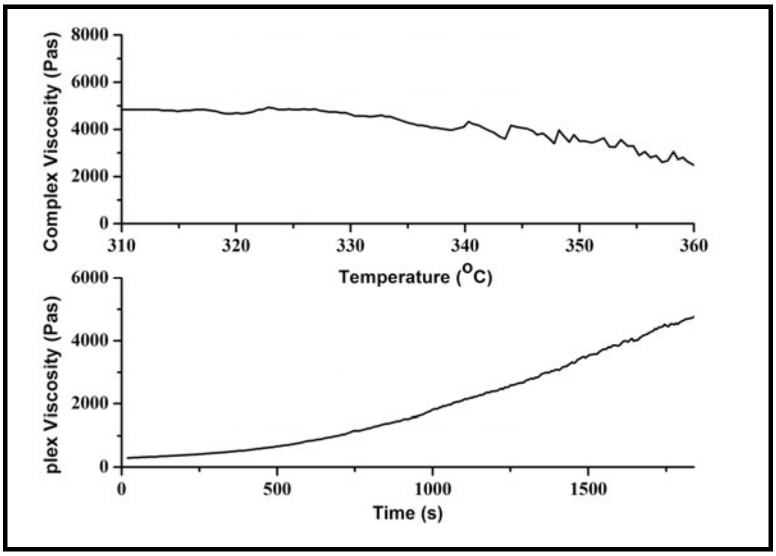


Figure 11 Plot of complex viscosities versus time and temperature for PA6T-Dupont.

RSC Advances Accepted Manuscript

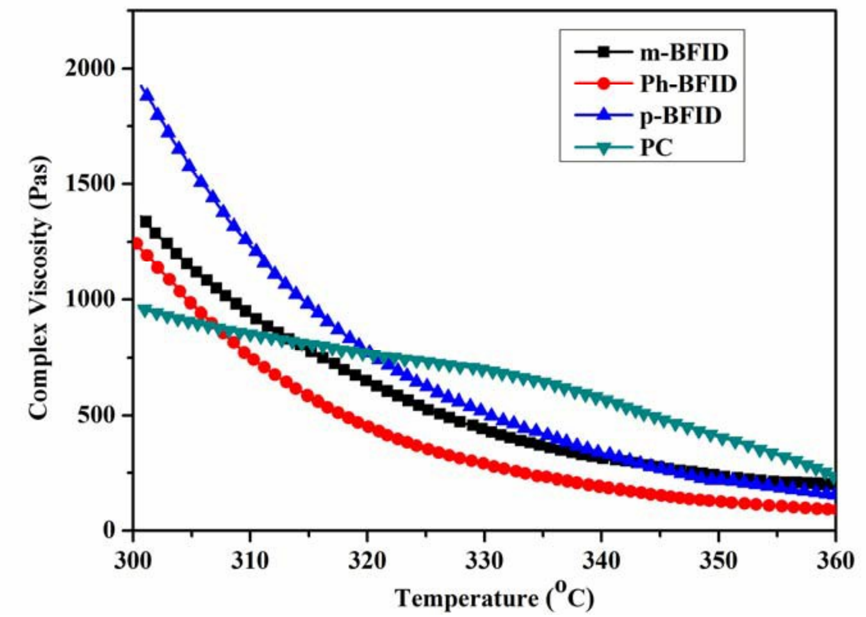


Figure 12 Plot of complex viscosities versus temperature for m-BFID, Ph-BFID, p-BFID and PC.

Optical properties

Here, the effects of incorporation of side methyl group on the polymers' transmittance were investigated. The optical properties of m-BFID, Ph-BFID and p-BFID films and comparative polycarbonate (PC) sample, such as the cutoff wavelength (λ_{cutoff}), the optical transmittance at 400 nm ($Tran_{400}$) and 450 nm ($Tran_{450}$) are summarized in **Table 4**. As shown in **Figure 13,** the λ_{cutof} of m-BFID, Ph-BFID and p-BFID films and comparative sample (PC) were 291, 292, 299 and 276 nm, respectively. The transparencies of the prepared polyamides films measured at 400 and 450 nm were 80.87-84.03% and 83.16-85.84%, respectively. It indicates that the resultant semi-aromatic polyamides had better transmittance than traditional polyamides such as PA6 and PA66. Comparing with PC, it also suggests that the resultant polyamides have almost the identical transmittance. It could be a promising candidate material for advanced optical device which need both good optical and thermal properties.

RSC Advances Accepted Manuscript

Table 4. Optical properties of m-BFID, Ph-BFID and p-BFID

Polymers	d (μm)	λ_{cutoff} (nm)	T_{400} (%)	T_{450} (%)
m-BFID	9.2	291	84.03	85.84
Ph-BFID	9.3	292	83.99	85.22
p-BFID	9.0	299	80.87	83.16
PC	9.2	276	86.57	87.32

d: the thick of films; λ_{cutoff} : the cutoff wavelength; $Tran_{400}$, $Tran_{450}$: the transmittance of films at 450 nm and 450nm.

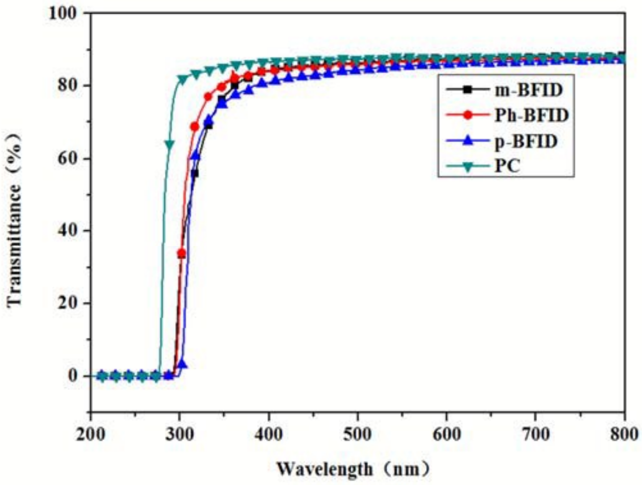


Figure 13. UV-Vis spectra of m-BFID, Ph-BFID and p-BFID films.

Solubilites

The solubilities of the resultant semi-aromatic polyamides are summarized in **Table 5**. It was found that these materials were soluble in strong polar solvents such as DMAC, DMSO, NMP and so on. It suggests that they had better solubility than traditional semi-aromatic polyamides such as PA6T and PA9T. While comparing with alkyl polyamides, the formic acid, phosphoric acid, acetone, solution of NaOH (1M) etc. can not dissolve these semi-aromatic polyamides. That indicates they had better corrosion resistance than aliphatic polyamides such as PA6 and PA66.

RSC Advances Accepted Manuscript

Table 5 Solvents resistance of m-BFID, Ph-BFID and p-BFID and PA6

Solvents	Polymers			
	PA6	m-BFID	Ph-BFID	p-BFID
concentrated sulfuric acid	+	+	+	+
formic acid	+	-	-	-
NMP	-	+	+	+
CF_3COOH	+	+	+	+-
HCl (6 mol/L)	-	-	-	-
phosphoric acid	+	-	-	-
NaOH (1 mol/L)	-	-	-	-
acetone	-	-	-	-
chloroform	-	-	-	-
DMAC	-	+	+	+
DMSO	-	+	+	+
1, 4-Dioxane	-	-	-	-
Toluene	-	-	-	-
Phenol + Tetrachloroethane	-	-	-	-

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

Conclusions

Difluoro-benzamide monomer containing isophorone unit was synthesized with a facile interface reaction. It was then used to react with bisphenol by nucleophilic polycondensation to synthesize a kind of semi-aromatic polyamides. The resultant semi-aromatic polyamides displayed good mechanical property, high thermal stabilities (such as T_g higher than 225 ^oC, $T_{5\%}$ around 430 ^oC), good processability

RSC Advances Accepted Manuscript

(including solution processing and melt processing) and melt stability when compared with the commercial materials. Additionally, these polyamides exhibited the good optical performance that the traditional semi-aromatic polyamides did not have. The cutoff wavelength and transmittance of the resultant resin films (~9 μm thickness) were around 290 nm and 85% (450 nm), respectively. Therefore, these semi-aromatic polyamides could be potentially used as heat resistant thermoplastic materials especially when the transparency was required.

Acknowlegement: This work was supported by research grants from the Youth Fund Natural Science Foundation of China (21304060).

References

(1) José, M. G. ; Félix, C.; García, F. S. ; José, L. de la P. High-performance aromatic polyamides. *Prog. in Polym. Sci.* **2010**, *35*, 623-638.

(2) Crespo, L.; Sanclimens, G.; Pons, M.; Giralt, E.; Royo, M.; Albericio, F. Peptide and Amide Bond-Containing Dendrimers. *Chem. Rev.*, **2005**, *105*, 1663-1681.

(3) Zhang, G.; Bai, D. T.; Li, D. S.; Long, S. R.; Wang, X. J.; Yang, Jie. Synthesis and properties of polyamides derived from 4,6-bis(4-chloroformylphenylthio) pyrimidine and 3,6-bis(4-chloroformylphenylthio) pyridazine. *Polym. Intern.* **2013**, *62*: 1358-1367.

(4) Du, S. M.; Wang, W. B.; Yan,Y.; Zhang, J.; Tian, M.; Zhang L. Q.; Wan, X. H. A facile synthetic route to poly(p-phenylene terephthalamide) with dual functional groups. *Chem. Commun.,* **2014**, *50*, 9929-9931.

(5) Williams, J. C.; Meador, M. Ann B.; McCorkle, L.; Mueller, Carl.; Wilmoth, N. Synthesis and Properties of Step-Growth Polyamide Aerogels Crosslinked with

RSC Advances Accepted Manuscript

Triacid Chlorides. *Chem. Mater.* **2014**, *26*, 4163-4171.

(6) Hsiao, S. H.; Chen, C. W.; Liou, G. S. Novel aromatic polyamides bearing pendent diphenylamino or carbazolyl groups. *J. Polym. Sci., Part A: Polym. Chem.*, **2004**, *42*, 3302-3313.

(7) Liou, G. S.; Lin, H. Y.; Yen, H. J. Synthesis and characterization of electroactive hyperbranched aromatic polyamides based on A2B-type triphenylamine moieties. *J. Mater. Chem.* **2009**, *19*, 7666-7673.

(8) Rao, Y.; Waddon, A. J.; Farris, R. J. Structure-property relation in poly(p-phenylene terephthalamide) (PPTA) fibers. *Polymer* **2001**, *42*, 5937-5946.

(9) Ferreiro, J. J.; dela, C. J. G.; Lozano, A. E.; de, A. J. Polyisophthalamides with heteroaromatic pendent rings: synthesis, physical properties, and water uptake. *J. Polym. Sci. Part A: Polym. Chem.* **2005**, *43*, 5300-5311.

(10) Zulfiqar, S.; Kausar, A.; Rizwan, M.; Sarwar, M. I. Probing the role of surface treated montmorillonite on the properties of semi-aromatic polyamide/clay nanocomposites. *Appl. Surf. Sci.,* **2008**, *255*, 2080-2086.

(11) Ballistreri, A.; Garozzo, D.; Giuffrida, M.; Maravigna, P. Thermal decomposition processes in aliphatic-aromatic polyamides investigated by mass spectrometry. *Macromolecules* **1986**, *19*, 2693-2699.

(12) Uddin, A. J.; Ohkoshi, Y.; Gotoh, Y.; Nagura, M.; Hara, T. Influence of moisture on the viscoelastic relaxations in long aliphatic chain contained semiaromatic polyamide, (PA9-T) fiber. *J. Polym. Sci. Part B: Polym. Phy.* **2003**, *41*, 2878-2891.

(13) Uddin, A. J.; Ohkoshi, Y.; Gotoh, Y.; Nagura, M.; Hara, T. Melt spinning and laser-heated drawing of a new semiaromatic polyamide, PA9-T fiber. *J. Polym. Sci.*

RSC Advances Accepted Manuscript

Part B: Polym. Phy. **2004**, *42*, 433-444.

(14) Uddin, A. J.; Gotoh, Y.; Ohkoshi, Y.; Nagura, M.; Endo, R.; Hara T. Hydration in a new semiaromatic polyamide observed by humidity-controlled dynamic viscoelastometry and X-ray diffraction. *J. Polym. Sci. Part B: Polym. Phy.* **2005**, *43*, 1640–1648.

(15) Uddin, A. J.; Ohkoshi, Y.; Gotoh, Y.; Nagura, M.; Endo, R.; Hara T. Effects of take-up speed of melt spinning on the structure and mechanical properties of maximally laser drawn PA9-T fibers. *Inter. Polym. Proce.* **2006**, *21*, 263-271.

(16) Liaw, D. J.; Hsu, P. N.; Chen, W. H.; Lin, S. L. Synthesis and Properties of New Soluble Polyamides Derived from 2,2’-Dimethyl-4,4’-bis(4-carboxyphenoxy) biphenyl. *Macromolecules.* **2002,** *35*, 4669-4676.

(17) Zhang, G.; Zhou,Y. X.; Kong,Y.; Li, Z. M.; Long, S. R.; Yang, J. Semiaromatic polyamides containing ether and different numbers of methylene (2-10) units: synthesis and properties. *RSC Advances*, **2014**, *4*, 63006-63015.

(18) Liaw, D. J.; Chang, F. C.; Leung, M. K.; Chou, M. Y.; Muellen, K. High thermal stability and rigid rod of novel organosoluble polyimides and polyamides based on bulky and noncoplanar naphthalene-biphenyldiamine. *Macromolecules* **2005**, *38*, 4024-4029.

(19) Ivanysenko, O.; Strandman, S.; Zhu, X. X. Triazole-linked polyamides and polyesters derived from cholic acid. *Polym. Chem.,* **2012**, *3*, 1962-1965.

(20) Huang, H. Y.; Lee, Y. T.; Yeh, L. C.; Jian, J. W.; Huang, T. C.; Liang, H. T.; Yeh, J. M.; Chou, Y. C. Photoactively electroactive polyamide with azo group in the main chain via oxidative coupling polymerization. *Polym. Chem.* **2013**, *4*, 343-350.

RSC Advances Accepted Manuscript

(21) Matsunaga, D.; Tamaki, T.; Ichimura, K. Azo-pendant polyamides which have the potential to photoalign chromonic lyotropic liquid crystals. *J. Mater. Chem.* **2003**, *13*, 1558-1564.

(22) Shabbir, S.; Zulfiqar, S.; M.; Sarwar, M. I. Amine-terminated aromatic and semi-aromatic hyperbranched polyamides: synthesis and characterization. *J. Polym. Res.* **2011**, *18*, 1919-1929.

(23) Shabbir, S.; Zulfiqar, S.; Zahoor, A.; M.; Sarwar, M. I. Pyrimidine based carboxylic acid terminated aromatic and semiaromatic hyperbranched polyamide-esters: synthesis and characterization. *Tetrahedron* **2010**, *66*, 7204-7212.

(24) Yang, S. H.; Fu, P.; Liu, M. Y.; Wang, Y. D.; Li, Z. P.; Zhao, Q. X. Synthesis, characterization and thermal decomposition of poly(decamethylene 2,6-naphthalamide). *Expre. Polym. Lett.* **2010**, *4*, 346-354.

(25) Shabanian, M.; Kang, N. J.; Liu, J. W.; Wagenknecht, U.; Heinrichbd, G.; Wang, D. Y. Bio-based semi-aromatic polyamide/functional clay nanocomposites: preparation and properties. *RSC Adv.,* **2014**, *4*, 23420-23427.

(26) Shabanian, M.; Kang, N. J.; Wang, D. Y.; Wagenknecht, U.; Heinrich, G. Synthesis, characterization and properties of novel aliphatic–aromatic polyamide/functional carbon nanotube nanocomposites via in situ polymerization. *RSC Adv.* **2013**, *3*, 20738-20745.

(27) Wilsens, Carolus H. R. M.; Deshmukh, Yogesh S.; Noordover, Bart A. J.; Rastogi, S. Influence of the 2,5-Furandicarboxamide Moiety on Hydrogen Bonding in Aliphatic-Aromatic Poly(ester amide)s. *Macromolecules* **2014**, *47*, 6196-6206.

(28) Zhang, G.; Huang, G. S.; Li, D. S.; Wang, X. J.; Long, S. R.; Yang, J. Facile Synthesis of Processable Semiaromatic Polyamides Containing Thioether Units. *Ind.*

RSC Advances Accepted Manuscript

RSC Advances Accepted Manuscript

Eng. Chem. Res. **2011**, *50*, 7056-7064.

(29) Moisa, S.; Landsberg, G.; Rittel, D.; Halary, J.L. Hysteretic thermal behavior of amorphous semi-aromatic polyamides. *Polymer* **2005**, *46*, 11870-11875.

(30) Yang, S. H., Fu, P., Liu, M. Y., Wang, Y. D., Zhang, Y. C., Zhao, Q. X. Synthesis, characterization of polytridecamethylene 2,6-naphthalamide as semiaromatic polyamide containing naphthalene-ring. *Expre. Polym. Lett.* **2010**, *4*, 442-449.

(31) Wang, W. Z.; Wang, X. W.; Li, R. X.; Liu, B. Y.; Wang, E. G.; Zhang, Y. H. Environment-Friendly Synthesis of Long Chain Semiaromatic Polyamides with High Heat Resistance. *J. Appl. Polym. Sci.* **2009**, *114*, 2036-2042.

(32) Novitsky, T. F.; Lange, C.A.; Mathias, L.J.; Osborn, S.; Ayotte, R.; Manning, S. Eutectic melting behavior of polyamide 10,T-co-6,T and 12,T-co-6,T copolyterephthalamides. *Polymer* **2010**, *51*, 2417-2425.

(33) Liu, M. Y.; Li, K. F.; Yang, S. H.; Fu, P.; Wang, Y. D.; Zhao, Q. X. Synthesis and Thermal Decomposition of Poly(dodecamethylene terephthalamide). *J. Appl. Polym. Sci.,* **2011**, *122*, 3369-3376.

(34) Song, Y.; Wang, J.Y.; Li, G. H.; Sun, Q. M.; Jian, X. G.; Teng, J.; Zhang, H. B. Synthesis, characterization and optical properties of cross-linkable poly(phthalazinone ether ketone sulfone). *Polymer* **2008**, *49*, 724-731.

(35) Zhang, G.; Xing, X. J.; Li, D. S.; Wang, X. J.; Yang, J. Effects of thioether content on the solubility and thermal properties of aromatic polyesters. *Industrial & Engineering Chem. Res.* **2013**, *52*, 16577-16584.