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Synthesis and Characterization of Partially Bio-Based Polyimides Based on Biphenylene-Containing Diisocyanate Derived from Vanillic Acid

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Abstract

A new bio-based biphenylene-containing diisocyanate, namely, 5,5'-diisocyanato-2,2',3,3'-tetramethoxy-1,1'-biphenyl (BDI) was synthesized starting from vanillic acid –a lignin-derived phenolic acid. A series of new partially bio-based polyimides was prepared by polycondensation of BDI with five commercially available aromatic dianhydrides. Polyimides exhibited good solubility in organic solvents and medium molecular weights (M_n (GPC, polystyrene standard) = 25,100-32,200 g mol⁻¹). Polyimides showed good thermal stability with 10 % degradation temperature and glass transition temperature in the range 459-473 °C and 262-329 °C, respectively.

1. Introduction

Aromatic polyimides represent an important class of high performance polymers due to their excellent thermal, mechanical and chemical resistance properties. Polyimides often replace glass and metals and are mainly used in industrial sectors such as automotive, aerospace, gas separation, electronic packaging, adhesives, etc [1–4].

Aromatic polyimides possess rigid chains and strong inter-chain interactions originating from their intra- and inter-chain charge transfer complex (CTC) formation and electronic polarization, which results in their poor solubility in organic solvents, and consequently possess difficulties in their processability [5]. Therefore, significant efforts have been made in the past to improve the solubility and melt processability of aromatic polyimides by structural modifications which include: i) incorporation of hinge atoms, alkylene or 'kinked' structure in polymer backbone [6–8] and, ii) incorporation of pendant bulky substituents or flexible groups [9–11]. The incorporation of 'kinked' units in polyimide backbone is of great interest because it results in solubility enhancement without much compromise on thermal characteristics [12].

The key monomers used for the synthesis of aromatic polyimides are diamines/diisocyanates and dianhydrides. Most of these monomers are derived from petroleum-based chemicals [13–15]. However, the use of petroleum resources for the synthesis of polymers is insecure because of their finite stocks, non-renewability and environmental issues [16–18]. In this context, academic and industrial research laboratories have focused the attention on monomers and polymers based on bio-resources such as starch, cellulose, lignin, cashew nut shell liquid (CNSL), terpenes and so on [11,18–23]. A range of difunctional monomers useful for the preparation of polymers such as (semi)aromatic polycarbonates, polyesters, polyamides and polyimides have been reported [10,11,20,24–26]. On the other hand, only limited examples of bio-based difunctional monomers such as diamines and diisocyanates suitable for synthesis of aromatic polyimides are available in the literature [6,9,11,27–37].

The objective of the present work was to synthesize biphenylene-containing diisocyanate, namely, 5,5'-diisocyanato-2,2',3,3'-tetramethoxy-1,1'-biphenyl (BDI) starting from vanillic acid –a lignin-derived phenolic acid. A series of partially bio-based aromatic polyimides containing 'twisted' biphenylene linkages was synthesized by polycondensation of BDI with five commercially available aromatic dianhydrides *viz.* 4,4'-oxydiphthalic anhydride, 3,3',4,4'-benzophenonetetracarboxylic dianhydride, 4,4'-(hexafluoroisopropylidene)diphthalic anhydride, 4,4'-biphenyltetracarboxylic dianhydride and pyromellitic dianhydride. Polyimides were characterized by FT-IR, ¹H NMR, ¹³C NMR spectroscopy, X-ray diffraction studies, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The effects of structure of dianhydride on solubility and thermal properties of polyimides were investigated.

2. Experimental

2.1 Materials

Vanillic acid (97 %) and Laccase from *Trametes versicolor* (0.5 U/mg), were purchased from Sigma-Aldrich, USA. 4,4'-Oxydiphthalic anhydride (ODPA) 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA), 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA) 4,4'-biphenyltetracarboxylic dianhydride (BPDA) and pyromellitic dianhydride (PMDA) (Sigma Aldrich, USA) were sublimed before use. 1,4-diazabicyclo[2.2.2]octane (DABCO) (Sigma Aldrich, USA) was recrystallized from n-hexane. Methyl iodide, sodium acetate (NaOAc), sodium hydroxide, potassium carbonate, hydrochloric acid, sulphuric acid, sodium azide, ethyl chloroformate, triethyl amine and solvents were obtained from Thomas Baker (India) and were used as received. Toluene, *N,N*-dimethylacetamide (DMAc) and *N,N*-dimethylformamide (DMF) were dried over calcium hydride and distilled prior to use.

2.2 Measurements

Melting points were recorded on Electrothermal MEL-TEMP apparatus. FT-IR spectra were obtained on a Perkin-Elmer Spectrum GX spectrometer using KBr. NMR spectra were recorded on a Bruker 200, 400 or 500 MHz spectrometer at resonance frequencies of 200, 400 or 500 MHz for ¹H NMR and 50, 100, 125 MHz for ¹³C NMR measurements using CDCl₃ or DMSO-d₆ as a solvent. HR-MS were obtained on a Thermo Scientific Q-Exactive, Accela 1250 pump. Inherent viscosity of polyimides was measured with 0.5 % (w/v) solution of polymer in DMAc at 30±0.1°C using Ubbelohde suspended level viscometer. Molecular weights and dispersity values of polyimides were determined on Thermo-Finnigan make gel permeation chromatography (GPC) using DMF as an eluent at a flow rate of 1 mL min⁻¹ at 25 °C. Sample concentration was 2 mg mL⁻¹ and narrow dispersity polystyrenes were used as calibration standards. X-Ray diffraction patterns of polyimides were recorded using dried polymer film on a Rigaku Dmax 2500 X-ray diffractometer at a tilting rate of 2° min⁻¹. Thermogravimetric analysis was carried out on Perkin Elmer: STA 6000, at a heating rate of 10 °C min⁻¹ under nitrogen atmosphere. Differential scanning calorimetry was performed on TA Instruments DSC Q100 system at a heating rate 10 °C min⁻¹ under nitrogen atmosphere.

2.3 Synthesis of 5,5'-diisocyanato-2,2',3,3'-tetramethoxy-1,1'-biphenyl

Synthesis of methyl 4-hydroxy-3-methoxybenzoate (1)

Into a 250 mL two-necked round bottom flask equipped with a reflux condenser and an argon inlet were charged vanillic acid (8.4 g, 50 mmol), sulphuric acid (1 mL) and methanol (100 mL). The reaction mixture was refluxed for 12 h. After completion of reaction, excess methanol was removed under reduced pressure. The reaction mixture was dissolved in dichloromethane (100 mL). The dichloromethane solution was washed with water (2 × 100 mL), dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The crude product was filtered through short bed of silica column using petroleum ether: dichloromethane as an eluent to afford white solid.

Yield 8.65g (95 %); FTIR (KBr): 1692 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3 , δ/ppm): 3.90 (s, 3H), 3.95 (s, 3H), 6.05 (s, 1H), 6.94 (d, 1H), 7.56 (d, 1H), 7.66 (dd, 1H); ^{13}C NMR (50 MHz, CDCl_3 , δ/ppm): 51.9, 56.0, 111.8, 114.1, 122.2, 124.1, 146.2, 150.0, 166.9; HRMS (ESI) calculated for $\text{C}_9\text{H}_{10}\text{O}_4$ (M +H), 183.0657; found, 183.0652.

Synthesis of dimethyl 6,6'-dihydroxy-5,5'-dimethoxy-[1,1'-biphenyl]-3,3'-dicarboxylate (2)

Into a 3 L two-necked round bottom flask were charged methyl vanillate (15 g, 82.3 mmol), NaOAc buffer (1800 mL, 0.1 M, pH 5.0) and acetone (200 mL). The solution was saturated with O_2 for 5 min. Laccase from *Trametes versicolor* (124 mg) was added and the reaction mixture was stirred at room temperature for 24 h. The precipitate was filtered off and the product was dried overnight at 90 °C.

Yield 26.5g (89 %); FTIR (KBr): 3432, 1716 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3 , δ/ppm): 3.80 (s, 6H), 3.89 (s, 6H), 7.45 (s, 4H), 9.68 (br. s, 2H); ^{13}C NMR (50 MHz, CDCl_3 , δ/ppm): 51.7, 56.0, 110.9, 119.2, 124.5, 125.4, 147.6, 149.3, 166.1; HRMS ESI⁺: (M+H)⁺ m/z calculated for $\text{C}_{18}\text{H}_{19}\text{O}_8$: 363.1074, found: 363.1071.

Synthesis of dimethyl 5,5',6,6'-tetramethoxy-[1,1'-biphenyl]-3,3'-dicarboxylate (3)

Into a 500 mL two-necked round bottom flask equipped with a reflux condenser and an argon inlet were charged, dimethyl 6,6'-dihydroxy-5,5'-dimethoxy-[1,1'-biphenyl]-3,3'-dicarboxylate (8 g, 22.0 mmol), potassium carbonate (12.2 g, 88.3 mmol) and DMF (100 mL). The reaction mixture was heated at 100 °C for 1 h and then methyl iodide (7.8 g, 55.2 mmol) was added and heating was continued for 12 h. The reaction mixture was poured into ice cold water (1000 mL). The precipitate was filtered, dried and dissolved in dichloromethane (100 mL). The dichloromethane solution was washed with water (2 x 500

mL), dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography using petroleum ether: ethyl acetate (70:30 v/v) as an eluent to afford a white solid.

Yield 7.8g (91 %); FTIR (KBr): 1725 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3 , δ/ppm): 3.72 (s, 6H), 3.89 (s, 6H), 3.96 (s, 6H), 7.58 (d, 2H), 7.63 (d, 2H); ^{13}C NMR (50 MHz, CDCl_3 , δ/ppm): 52.1, 56.0, 60.8, 113.0, 125.0, 125.1, 131.7, 150.9, 152.4, 166.6; HRMS ESI⁺: (M+H)⁺ m/z calculated for $\text{C}_{20}\text{H}_{23}\text{O}_8$: 391.1387, found: 391.1383.

Synthesis of 5,5',6,6'-tetramethoxy-[1,1'-biphenyl]-3,3'-dicarboxylic acid (4)

Into a 500 mL two-necked round bottom flask equipped with a reflux condenser were charged dimethyl 5,5',6,6'-tetramethoxy-[1,1'-biphenyl]-3,3'-dicarboxylate (11.7 g, 30 mmol), sodium hydroxide (6 g, 150 mmol), methanol (100 mL) and water (100 mL). The reaction mixture was refluxed for 12 h and then methanol was removed under reduced pressure. The solution was diluted with water and acidified with aqueous hydrochloric acid (3M). The precipitate was filtered and dried in vacuum oven at 60 °C for 4 h and then recrystallized from aqueous ethanol.

Yield 10.3g (95 %); FTIR (KBr): 1671 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3 , δ/ppm): 3.61 (s, 6H), 3.91 (s, 6H), 7.38 (d, 2H), 7.57 (d, 2H), 12.95 (s, 2H); ^{13}C NMR (50 MHz, CDCl_3 , δ/ppm): 55.8, 60.2, 112.9, 124.1, 125.9, 131.3, 150.0, 152.1, 166.8; HRMS ESI⁺: (M+Na)⁺ m/z calculated for $\text{C}_{18}\text{H}_{18}\text{O}_8$ Na: 385.0894, found: 385.0892.

Synthesis of 5,5',6,6'-tetramethoxy-[1,1'-biphenyl]-3,3'-dicarbonyl diazide (5)

Into a 250 mL two-necked round bottom flask equipped with a reflux condenser, an argon inlet and an addition funnel were charged, 5,5',6,6'-tetramethoxy-[1,1'-biphenyl]-3,3'-dicarboxylic acid (7.2 g, 20 mmol) and a mixture of tetrahydrofuran: water (3:1 v/v, 100 mL). The reaction mixture was cooled to 0 °C and the solution of triethyl amine (12 g, 120 mmol) in tetrahydrofuran (20 mL) was added drop wise over a period of 15 min. To the reaction mixture, ethylchloroformate (12.8 g, 120 mmol) was added dropwise over a period of 10 min and stirred for 2 h. The solution of sodium azide (7.8 g, 160 mmol) in water (30 mL) was added drop-wise over a period of 10 min and the reaction mixture was stirred at 0 °C for 2 h and then at 25 °C for 4 h. Ice cold water (250 mL) was added gradually to the reaction mixture and solid was precipitated out. The precipitate was filtered and washed with water. The product was dissolved in dichloromethane (200 mL) and washed with water (150 mL),

dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure at 25 °C to afford a white solid.

Yield 6.5g (80 %); FTIR (KBr): 2143, 1680 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3 , δ/ppm): 3.75 (d, 6H), 3.96 (d, 6H), 7.55 (s, 2H), 7.61 (s, 2H); ^{13}C NMR (50 MHz, CDCl_3 , δ/ppm): 55.9, 60.8, 112.5, 124.9, 125.5, 131.4, 152.1, 152.5, 171.5; HRMS ESI⁺: (M+H)⁺ m/z calculated for $\text{C}_{18}\text{H}_{17}\text{N}_6\text{O}_8$: 413.1204, found: 413.2663.

Synthesis of 5,5'-diisocyanato-2,2',3,3'-tetramethoxy-1,1'-biphenyl (BDI)

Into a 100 mL two-necked round bottom flask equipped with a reflux condenser and a nitrogen inlet were charged, 5,5',6,6'-tetramethoxy-[1,1'-biphenyl]-3,3'-dicarbonyl diazide (1.9 g, 4.69 mmol) and dry toluene (25 mL). The reaction mixture was heated at 80 °C for 8 h. The toluene was removed under reduced pressure at 60 °C and white solid compound was obtained.

Yield 1.4g (85 %); FTIR (KBr): 2268 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3 , δ/ppm): 3.66 (d, 6H), 3.90 (d, 6H), 6.61 (s, 2H), 6.67 (s, 2H); ^{13}C NMR (50 MHz, CDCl_3 , δ/ppm): 56.0, 60.8, 108.7, 118.7, 124.5, 128.6, 132.3, 144.6, 153.2; HRMS ESI⁺: (M+H)⁺ m/z calculated for $\text{C}_{18}\text{H}_{17}\text{N}_2\text{O}_6$: 357.1081, found: 357.1079.

2.4 Synthesis of polyimides

A representative procedure for the synthesis of polyimides is described below:

Into a 50 mL two necked round bottom flask equipped with a magnetic stirrer bar, a nitrogen inlet and a reflux condenser were taken BDI (1 g, 2.8 mmol), aromatic dianhydride (2.8 mmol), DABCO (94 mg, 0.84 mmol) and benzonitrile (10 mL). The reaction mixture was heated at 140 °C for 10 h under nitrogen atmosphere. The reaction mixture was cooled to room temperature and poured into excess methanol and the precipitated polymer was filtered, washed with hot methanol and dried at 100 °C for 10 h under reduced pressure.

Synthesis of PI-1 by polycondensation of BDI with ODPA

FT-IR (KBr): 739, 1375, 1720, 1777 cm^{-1} ; ^1H NMR (500 MHz, DMSO-d_6 , δ/ppm): 3.75 (s, 6H), 3.92 (s, 6H), 7.00 (s, 4H), 7.45 (d, 2H), 7.97 (d, 2H); ^{13}C NMR (125 MHz, DMSO-d_6 , δ/ppm): 55.9, 60.3, 112.0, 113.6, 121.5, 124.9, 126.1, 127.2, 131.5, 134.5, 145.9, 152.5, 160.8, 166.1, 166.3.

Synthesis of PI-2 by polycondensation of BDI with 6-FDA

FT-IR (KBr): 736, 1375, 1731, 1771 cm^{-1} ; ^1H NMR (500 MHz, DMSO-d_6 , δ/ppm): 3.65 (s, 6H), 3.82 (s, 6H), 6.92 (s, 2H), 7.21 (s, 2H), 7.73 (s, 2H), 7.95 (d, 2H), 8.16 (d, 2H); ^{13}C NMR (125 MHz, DMSO-d_6 , δ/ppm): 55.9, 60.3, 112.1, 121.6, 123.6, 124.4, 126.8, 131.5, 132.6, 133.0, 135.8, 137.3, 146.1, 152.5, 166.0, 166.2.

Synthesis of PI-3 by polycondensation of BDI with BTDA

FT-IR (KBr): 723, 1378, 1725, 1780 cm^{-1} ; ^1H NMR (400 MHz, DMSO-d_6 , δ/ppm): 3.67 (s, 6H), 3.84 (s, 6H), 6.95 (s, 2H), 7.24 (s, 2H), 8.13 (s, 2H), 8.22 (br. d, 4H); ^{13}C NMR (125 MHz, DMSO-d_6 , δ/ppm): 56.1, 60.3, 112.0, 121.5, 123.8, 129.5, 131.5, 132.2, 134.8, 141.6, 146.0, 152.5, 166.3, 193.4

Synthesis of PI-4 by polycondensation of BDI with BPDA

FT-IR (KBr): 739, 1378, 1721, 1775 cm^{-1} ; ^1H NMR (400 MHz, DMSO-d_6 , δ/ppm): 3.70 (s, 6H), 3.87 (s, 6H), 6.97 (s, 2H), 7.23 (s, 2H), 8.03 (s, 2H), 8.3 (br. s, 4H); ^{13}C NMR (125 MHz, DMSO-d_6 , δ/ppm): 55.1, 59.9, 111.8, 113.3, 121.1, 124.5, 125.9, 127.0, 131.1, 134.6, 145.8, 152.3, 160.2, 166.0, 165.5

Synthesis of PI-5 by polycondensation of BDI with PMDA

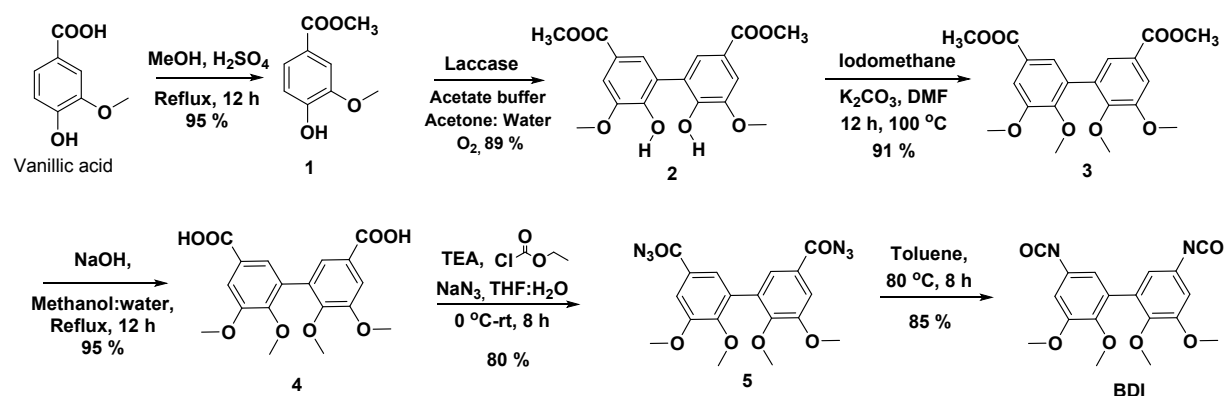
FT-IR (KBr): 725, 1378, 1727, 1784 cm^{-1} ; ^1H NMR (400 MHz, DMSO-d_6 , δ/ppm): 3.68 (s, 6H), 3.85 (s, 6H), 7.0 (s, 2H), 7.27 (s, 2H), 8.35 (s, 2H); ^{13}C NMR (125 MHz, DMSO-d_6 , δ/ppm): 56.0, 60.3, 112.0, 117.8, 121.5, 126.7, 131.5, 137.1, 146.1, 152.5, 165.5.

3. Results and discussion

3.1 Synthesis of biphenylene-containing diisocyanate

Aromatic diisocyanates are useful class of monomers in polymer industry, as they find applications in the synthesis of various step-growth polymers such as polyurethanes, polyureas, polyimides, polyamides and so on. More than 90% market of diisocyanates is captured by aromatic diisocyanates. The most commonly used aromatic diisocyanates *viz.* toluene diisocyanate and methylenediphenyl diisocyanate are obtained from petroleum-derived chemicals. The reports on the synthesis of aromatic diisocyanates based on bio-derived chemicals are scanty except for furan derivatives *viz.* 2,5-diisocyanatofuran, bis(5-isocyanatofurfuryl)ether, diisocyanates containing difurylalkane moieties and CNSL-based diisocyanates [10,11,38,39]

In the present work, a new bio-based diisocyanate *viz.* 5,5'-diisocyanato-2,2',3,3'-tetramethoxy-1,1'-biphenyl (BDI) was designed and synthesized starting from vanillic acid as depicted in **Scheme 1**.



Scheme 1 Synthesis of biphenylene-containing diisocyanate starting from vanillic acid

In the first step, esterification of vanillic acid was carried out using methanol and catalytic amount of sulphuric acid to give methyl vanillate (1) which was subsequently dimerized using Laccase from *Trametes versicolor* as a catalyst in NaOAc buffer solution in acetone-water mixture (pH 5.0) [40,41]. The resulting diester 2 was alkylated by using iodomethane in the presence of potassium carbonate in DMF to afford methyl protected diester 3. The hydrolysis of diester 3 by using sodium hydroxide in water: methanol mixture afforded diacid 4. Diacylazide 5 was synthesized from diacid 4 by elegant one-pot Weinstock modification of the Curtius rearrangement. In this reaction, diacid 4 was treated successively with triethylamine, ethylchloroformate and sodium azide. The obtained diacyl azide 5 was converted into BDI by heating at 80 °C for 8 h in toluene *via* thermal Curtius rearrangement. The reaction was monitored by FT-IR spectroscopy. The disappearance of the band at 2143 cm^{-1} and 1680 cm^{-1} corresponding to azido and carbonyl group indicated the complete conversion of azido carbonyl into isocyanato group (**Figure-1**). The chemical structure of diisocyanate was established by FT-IR, ^1H NMR, ^{13}C NMR spectroscopy and HRMS. In FT-IR spectrum of BDI (**Figure 1**), the strong absorption band was observed at 2268 cm^{-1} corresponding to isocyanato group.

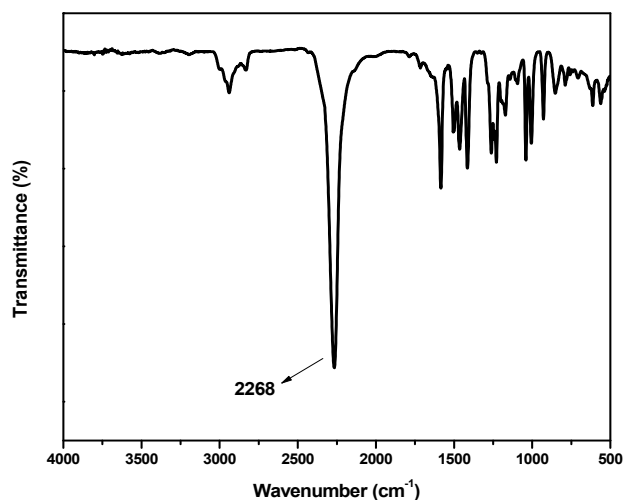


Figure 1 FT-IR spectrum of 5,5'-diisocyanato-2,2',3,3'-tetramethoxy-1,1'-biphenyl

^1H NMR spectrum of BDI is displayed in **Figure 2**. The aromatic protons exhibited two doublets at $\delta = 6.67$ ppm and 6.60 ppm corresponding to proton 'a' and 'b', respectively. Methoxyl group protons *meta* and *para* to isocyanato group exhibited two separate singlets at 3.90 ppm and 3.66 ppm, respectively. ^{13}C NMR spectrum of BDI along with the assignments is shown in **Figure 3**.

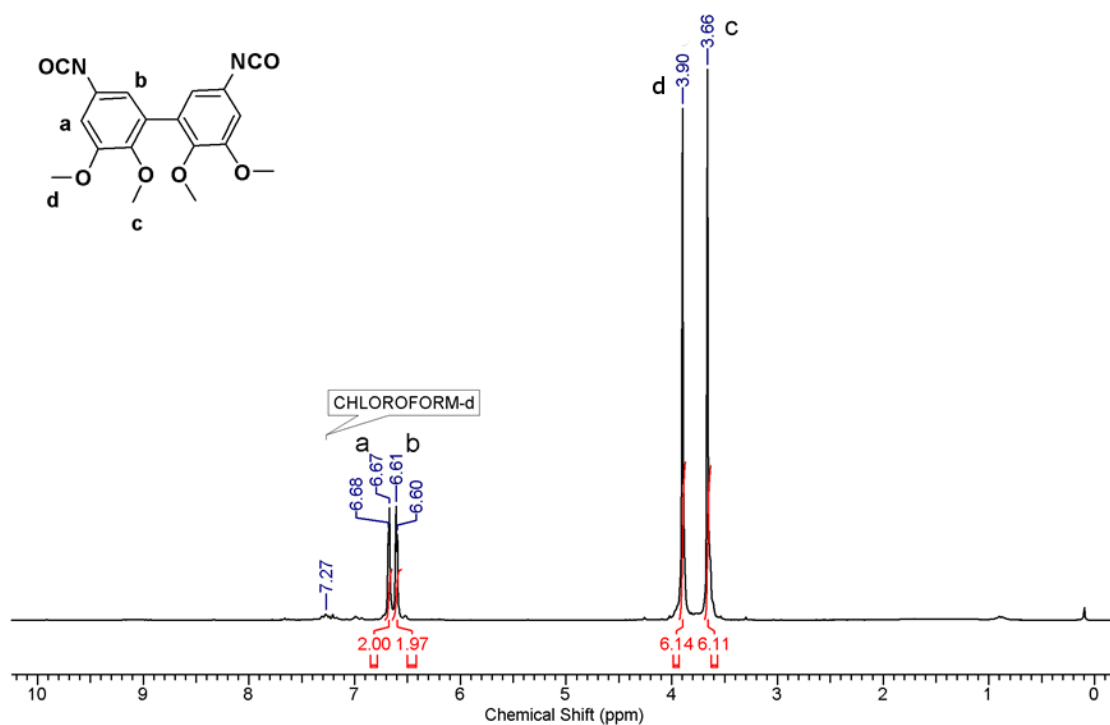


Figure 2 ^1H NMR spectrum of 5,5'-diisocyanato-2,2',3,3'-tetramethoxy-1,1'-biphenyl.

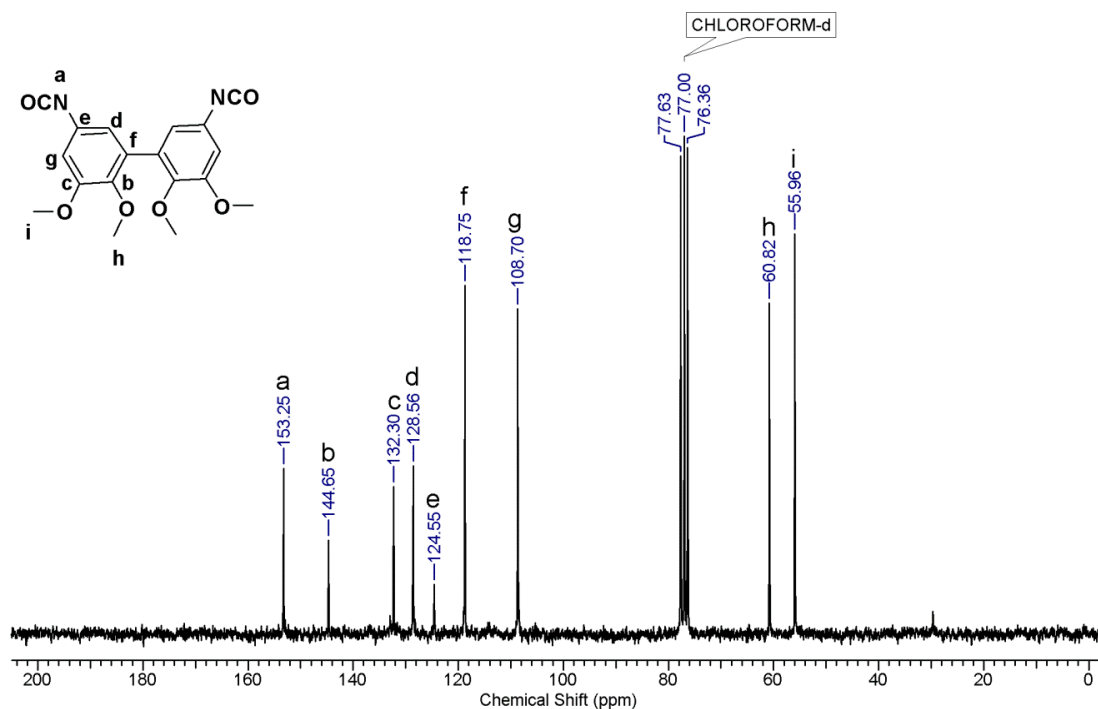
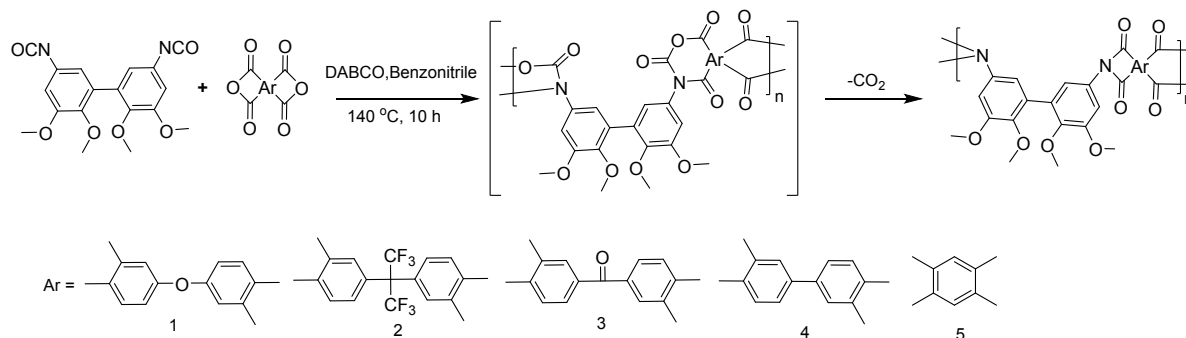


Figure 3 ¹³C NMR spectrum of 5,5'-diisocyanato-2,2',3,3'-tetramethoxy-1,1'-biphenyl

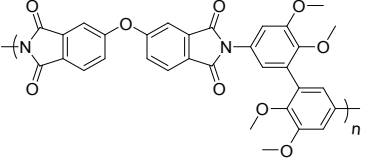
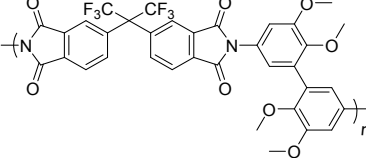
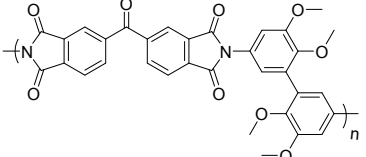
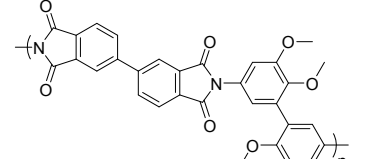
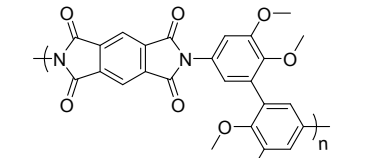
3.2 Polyimide synthesis

A series of new partially bio-based polyimides containing ‘twisted’ biphenylene linkages were synthesized by polycondensation of BDI with aromatic dianhydrides *viz.* 4,4'-oxydiphthalic anhydride (ODPA), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA), 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA), 4,4'-biphenyltetracarboxylic dianhydride (BPDA) and pyromellitic dianhydride (PMDA) using DABCO as the catalyst in benzonitrile at 140 °C (**Scheme 2**). In this reaction, BDI and dianhydride reacted together to form seven-membered cyclic intermediate, which thermally decomposed to form polyimide with evolution of carbon dioxide. The reaction mixture was homogenous throughout the course of polymerization.



Scheme 2 Synthesis of biphenylene-containing polyimides by polycondensation of BDI with aromatic dianhydrides

Table 1 Synthesis of aromatic polyimides derived from 5,5'-diisocyanato-2,2',3,3'-tetramethoxy-1,1'-biphenyl (BDI) and aromatic dianhydrides

Code	Polyimide	η_{inh} (dLg ⁻¹) ^a	GPC ^b			T ₁₀ ^c (°C)	Char Yield at 800 °C (%)	T _g ^d (°C)
			M _n g/mol	M _w g/mol	Dispersity			
PI-1		0.35	25,100	49,500	2.0	459	50	262
PI-2		0.30	27,700	59,800	2.2	473	45	278
PI-3		0.35	27,400	69,200	2.5	466	52	277
PI-4		0.39	ns	ns	ns	472	55	300
PI-5		0.40	32,200	75,800	2.3	462	47	329

a η_{inh} was measured with 0.5 % (w/v) solution of polyimide in DMAc at 30 °C ± 0.1 °C.

b Measured by GPC in DMF, polystyrene was used as the calibration standard.

c Temperature at which 10 % weight loss was observed.

d T_g determined by DSC

ns GPC measurements could not be carried out due to insolubility of polymer in DMF

The results of polymerization reactions are summarized in **Table 1**. Inherent viscosity values and number average molecular weights of polyimides were in the range 0.30-0.40 dLg⁻¹ and 25,100-32,200 g mol⁻¹, respectively. The results of GPC and inherent viscosity measurements indicated the formation of medium molecular weight polymers. Molecular weight of polyimide derived from BDI and BPDA could not be measured due its partial solubility in DMF.

3.3 Structural characterization

The chemical structure of polyimides was confirmed by FT-IR, ¹H NMR and ¹³C NMR spectroscopy. A representative FT-IR spectrum of PI-5 is presented in **Figure 4**.

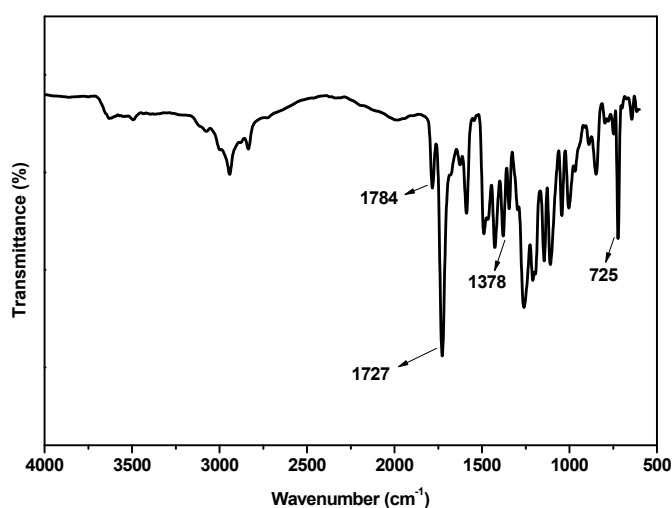


Figure 4 FT-IR spectrum of polyimide (PI-5) derived from BDI and aromatic dianhydride

The characteristic absorption bands for imide ring were observed at 1784 cm⁻¹ and 1727 cm⁻¹ which correspond to asymmetric and symmetric carbonyl stretching, respectively. Absorption band at 1378 cm⁻¹ corresponds to C-N stretching and absorption band at 725 cm⁻¹ was ascribed to imide ring deformation.

A representative ¹H NMR spectrum of polyimide derived from BDI and PMDA is shown in **Figure 5**. Aromatic protons of dianhydride moiety showed a singlet at $\delta = 8.35$ ppm. The two singlets appeared at 7.27 ppm and 7.0 ppm are attributed to proton labeled as 'b' and 'c', respectively. Methoxy protons *meta* and *para* to imide nitrogen showed singlet at 3.85 ppm and 3.68 ppm, respectively.

¹³C NMR spectrum of polyimide (PI-5) derived from BDI and PMDA is shown in **Figure 6** along with the assignments.

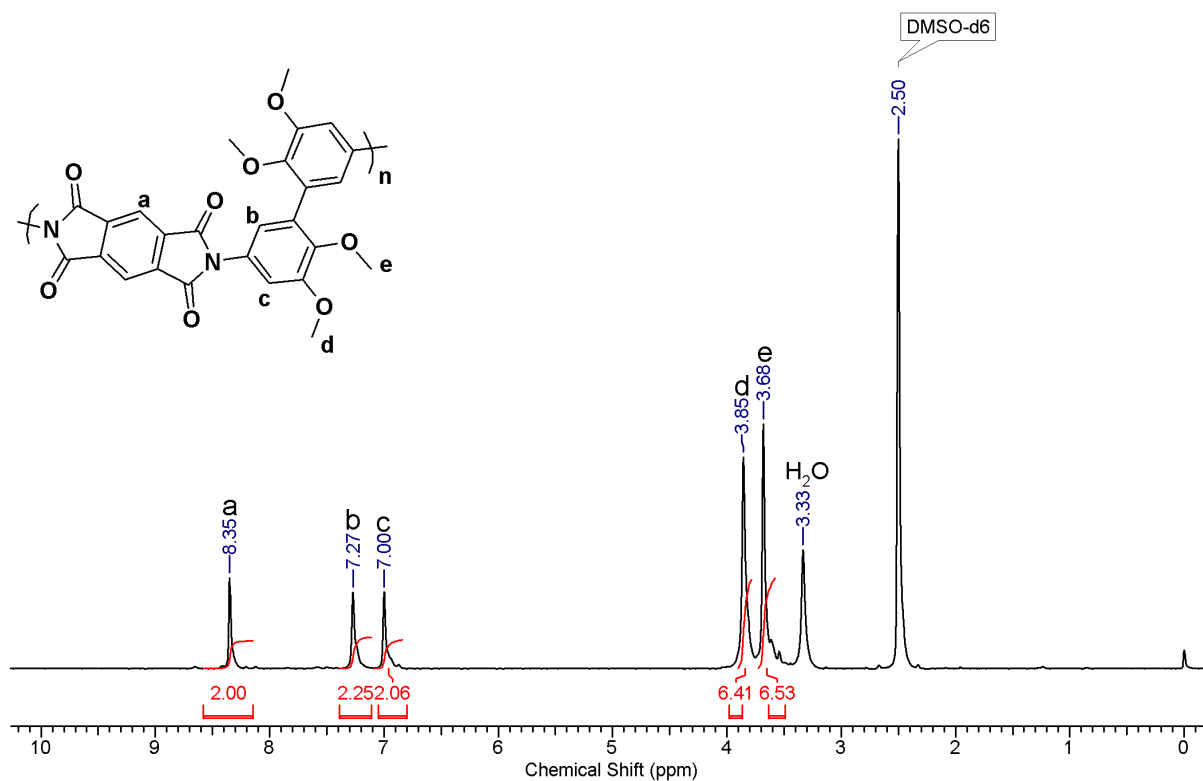


Figure 5 ^1H NMR spectrum of polyimide (PI-5) derived from BDI and PMDA in DMSO-d_6

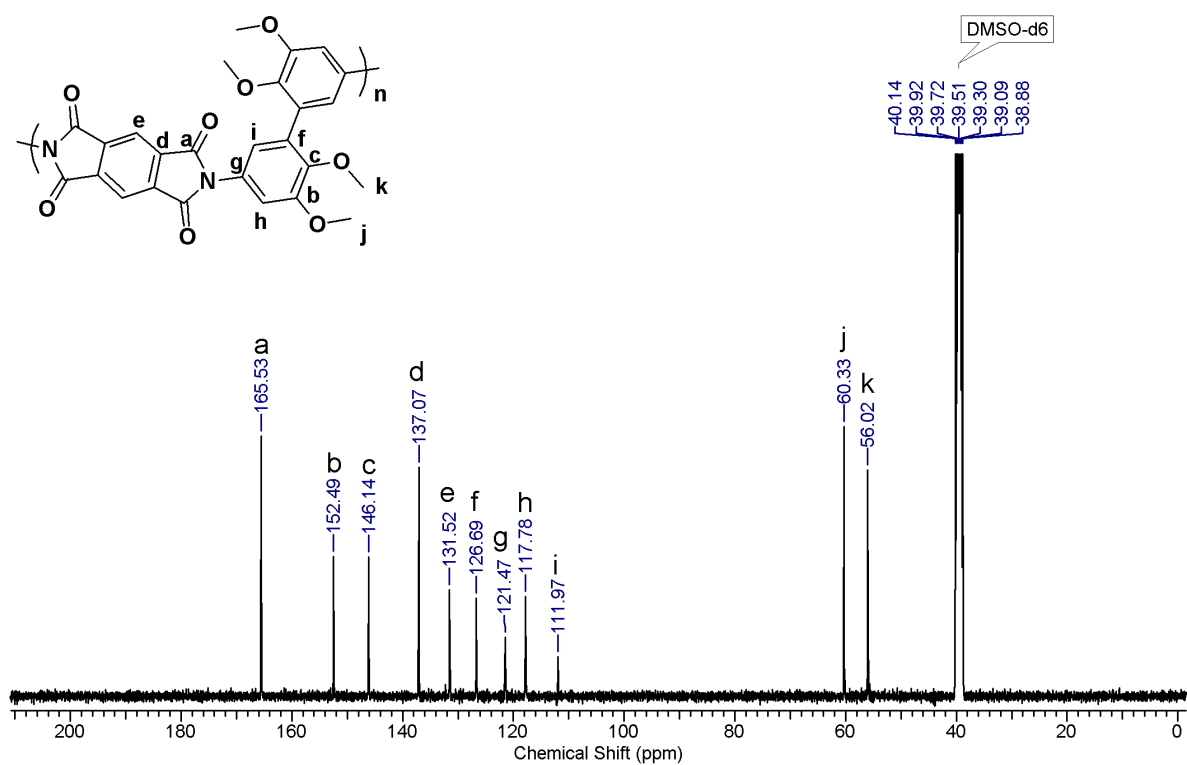


Figure 6 ^{13}C NMR spectrum of polyimide (PI-5) derived from BDI and PMDA in DMSO-d_6 .

3.4 Solubility of polyimides

The solubility of polyimides was tested at 3 wt % (w/v) concentration in various organic solvents and the data is summarized in **Table 2**.

Table 2 Solubility data of polyimides derived from BDI and aromatic dianhydrides.

Polyimide	Dianhydride	Dichloromethane	Chloroform	DMF	DMAc	NMP	DMSO	Pyridine
PI-1	ODPA	++	++	++	++	++	++	++
PI-2	6FDA	++	++	++	++	++	++	++
PI-3	BTDA	--	--	++	++	++	++	++
PI-4	BPDA	--	--	--	++	++	++	++
PI-5	PMDA	--	--	++	++	++	++	++

++ : soluble at room temperature; -- : insoluble at room temperature.

All the polyimides were soluble in polar organic solvents such as DMSO, DMAc, NMP and pyridine at room temperature. The solubility of biphenylene-containing polyimides could be ascribed to the zig-zag structure and the presence of methoxy groups which bring about disordering in the packing of the polymer chains. In addition, polyimides derived from 6FDA and ODPA were also soluble in halogenated solvents such as chloroform and dichloromethane. In case of 6FDA-based polyimide (PI-2), the presence of bulky CF_3 substituents, which increased the disorder in the chains and hindered close packing thereby decreasing the intermolecular interactions, is the cause of further enhancement in solubility characteristics [42]. ODPA-derived polyimide (PI-1) showed excellent solubility due to the presence of flexible ether linkages in the polymer backbone.

3.5 X-Ray diffraction studies

X-Ray diffractograms of polyimide films based on BDI and aromatic dianhydrides are reproduced in **Figure 7**. X-Ray diffractograms of polyimides showed a broad halo at around $2\theta = 10-30^\circ$ suggesting that all the polymers were amorphous. The amorphous nature of polyimides could be attributed to the presence of methoxy substituents situated at the *meta*

and *para* position to the nitrogen of imide group and the zig-zag structure. These structural features decrease interchain interactions thus disturbing the chain packing.

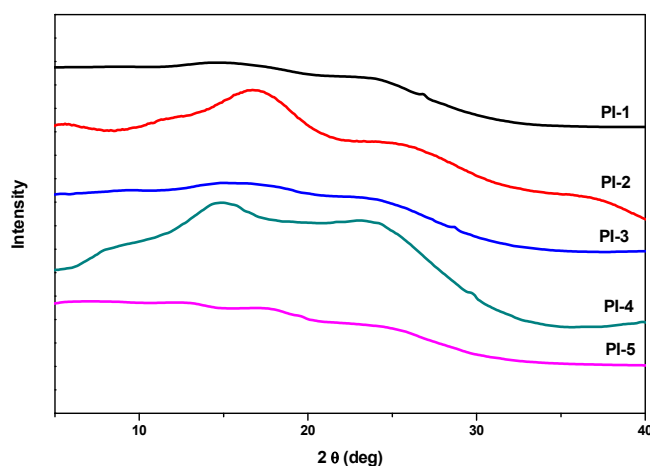


Figure 7 X-Ray diffractograms of polyimides derived from BDI and aromatic dianhydrides

3.6 Thermal properties of polyimides

Thermal characteristics of polyimides were evaluated by TGA and DSC at heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ under nitrogen atmospheres. TG and DSC curves are shown in **Figure 8** and **Figure 9**, respectively and results are summarized in **Table 1**.

Polyimides showed 10 % wt. loss and char yield at $800\text{ }^{\circ}\text{C}$ in the range $459\text{-}473\text{ }^{\circ}\text{C}$ and 45-55 %, respectively. A representative differential thermogravimetric (DTG) analysis curve of polyimide PI-2 is included in **Figure 8**. DTG curves of polyimides indicated two-stage degradation: the first stage degradation was presumably due to the cleavage of methoxy groups whereas the second stage degradation was observed due to decomposition of polyimide backbone.

It is interesting to compare the char yields of polyimides. In the series of polyimides, polyimide based on 6FDA (PI-2) showed the lowest char yield (45%). This could be due to the less thermally stable $-\text{C}(\text{CF}_3)_2-$ group, which gets lost in the form of $\cdot\text{CF}_3$ radicals [43]. Polyimide based on BPDA (PI-4) showed highest char yield (55%) which is in line with its highest aromatic character.

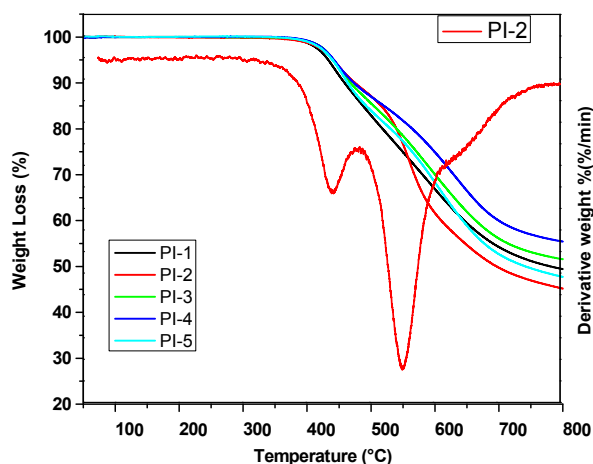


Figure 8 TG curves of polyimides derived from BDI and aromatic dianhydrides and DTG curve of PI-2.

T_g values of polyimides were in the range 262-329 °C and the order is: ODPA<6FDA<BTDA<BPDA<PMDA. Generally, the T_g value increases with increasing the chain rigidity of the polymer[44]. Therefore, highest T_g value (329 °C) was observed for polyimide (PI-5) based on PMDA due to highly rigid backbone. On the other hand, lowest T_g value (262 °C) was logically observed for polyimide (PI-1) based on ODPA due to the presence of flexibilizing ether linkages [42].

Overall, the results of polyimide synthesis and their properties indicated that BDI is a welcome addition to the family of bio-based difunctional monomers suitable for the synthesis of organo-soluble aromatic polyimides with satisfactory thermal properties.

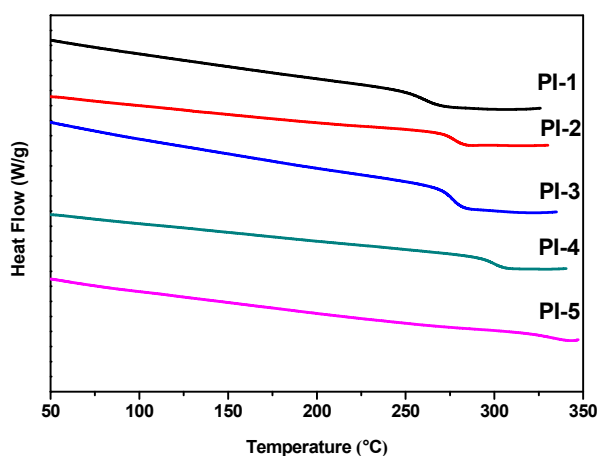


Figure 9 DSC curves of polyimides derived from BDI and aromatic dianhydrides

4. Conclusions

A new aromatic diisocyanate, namely, 5,5'-diisocyanato-2,2',3,3'-tetramethoxy-1,1'-biphenyl (BDI) was synthesized starting from vanillic acid and was polycondensed with five commercially available aromatic dianhydrides to obtain a series of partially bio-based polyimides. Polyimides displayed medium molecular weights and good solubility in organic solvents. T_{10} and T_g values of polyimides were in the range 459-473 °C and 262-329 °C, respectively indicating their good thermal properties. The biphenylene-containing polyimides could be considered as promising high performance bio-based materials.

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