Polyimides Derived from Novel Unsymmetric Dianhydride

Hai Bin Zheng and Zhi Yuan Wang*

Department of Chemistry, Carleton University, 1125 Colonel By Drive, Ottawa, Ontario, Canada K1S 5B6

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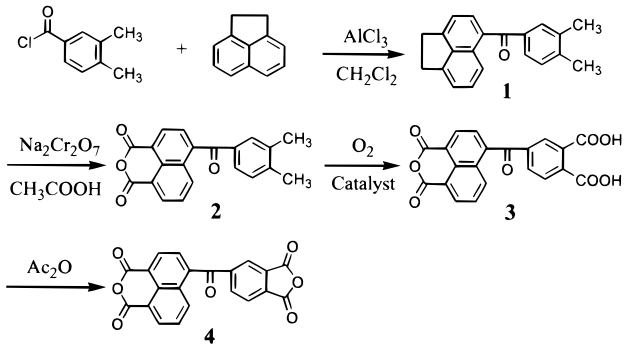
Much effort has been directed toward the design and synthesis of new dianhydride and diamine monomers for making the polyimides with desirable properties and functions. There are mainly two structural variations for aromatic dianhydride monomers: five-membered phthalic and six-membered naphthalic dianhydrides. To design a new dianhydride monomer, one of the approaches is to tailor the moiety that links either two phthalic anhydrides or two naphthalic anhydrides. For example, the dianhydride monomer used for Ultem poly(ether imide)s can be prepared via the condensation of methyl 4-nitrophthalimide and bisphenol A. Two naphthalic anhydrides can also be linked together through a variety of connectors such as arylene ether, sulfonyl, keto, and alkylene groups.[1] Another approach is to vary the relative position for catenation of the anhydride groups or introduce a kink in the structure of dianhydrides, as evidenced by examples such as 5,6-diphenylbenzene-1,2,3,4-tetracarboxylic dianhydride,[2] 2,2′-bis(trifluoromethyl)biphenyl-4,4′,5,5′-tetracarboxylic dianhydride,[3] and isomeric 3,3′-, 3,4′-, and 4,4′-oxydiphthalic anhydrides (ODPA).[4] These structural modifications for dianhydride monomers have led to new polyimides with improved solubility and other desirable properties.

Previous investigations have shown that polyimides derived from bis(naphthalic anhydride)s display superior chemical, thermal, and fire resistance, compared with the analogous polyimides derived from bis(phthalic anhydride)s.[1] However, the majority of polynaphthalimides based on bis(naphthalic anhydride)s have poor processability and low solubility in organic solvents, which hampers the one-step solution polymerization. Furthermore, a two-step polymerization of bis(naphthalic anhydride)s is difficult to proceed as the corresponding poly(amic acid) is unstable and the imidization readily occurs.[1]

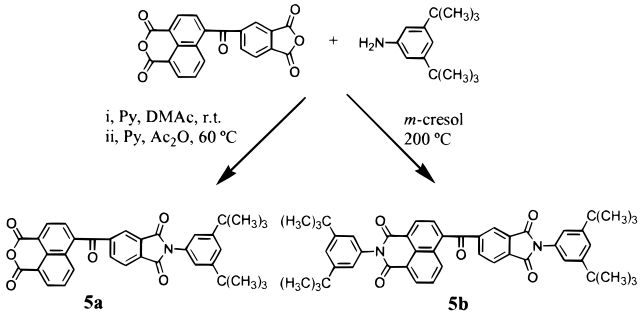
The molecular structure of 3,3′,4,4′-benzophenontetracarboxylic dianhydride (BTDA) is known to afford the polyimides with many desirable properties except for relative poor solubility.[5] Replacing one of phthalic anhydrides in BTDA with a naphthalic anhydride would give a new unsymmetric dianhydride which to our knowledge has not been reported in the literature. Since the new monomer is molecularly unsymmetric, the resulting polyimides should possess three possible diads in the main chain which lead to a better solubility than the BTDA- and bis(naphthalic anhydride)-based polyimides[6] and maintain other desirable properties such as high thermal stability (due to the naphthalimide unit). Furthermore, due to the presence of two different anhydrides, it is possible to control the structures and properties of copolyimides using BNTDA. Herein, we report the synthesis and polymerization of unsymmetric dianhydride **4** and preliminary investigation into the reactivity of BNTDA.

* To whom correspondence should be addressed. E-mail: wangw@ccs.carleton.ca.

Scheme 1. Synthesis of Unsymmetric Dianhydride (BNTDA)



Scheme 2. Model Reactions of Dianhydride 4 and 3,5-Di-*tert*-butylaniline



1-Benzoylnaphthalene-3′,4,4′,5-tetracarboxylic dianhydride (BNTDA, **4**) was readily synthesized in four steps from acenaphthene and 3,4-dimethylbenzoyl chloride (Scheme 1). The acylation reaction of acenaphthene with 3,4-dimethylbenzoyl chloride produced compound **1** in 93% yield. Oxidation of compound **1** with an excess of sodium dichromate in acetic acid gave compound **2** in 84% yield, which was further oxidized with oxygen in the presence of cobalt acetate and bromoacetic acid to afford compound **3** in 68% yield. In the above three reactions, the product of each reaction was pure enough for the subsequent reaction. Dehydration of compound **3** with acetic anhydride gave dianhydride **4**.[7] The pure monomer was obtained by recrystallization from 1,2-dichlorobenzene or by sublimation under vacuum. Its structure was unambiguously confirmed by IR, ^{1}H, and ^{13}C NMR spectroscopies and high-resolution mass spectrometry.

The model reaction of monomer **4** with 3,5-di-*tert*-butylaniline was first carried out in DMAc in the presence of pyridine at room temperature (Scheme 2). After 3 h, additional pyridine and acetic anhydride were added, and the temperature rose to 60 °C. After another 3 h, the reaction was stopped, and anhydride−imide **5a** was isolated in 92% yield. When the same reaction was carried out for 4 h in *m*-cresol at 200 °C, anhydride−imide **5a** was found to be formed faster than diimide **5b**, and the latter was eventually isolated in 96% yield. The structures of model compounds **5a** and **5b** were confirmed by IR, ^{1}H, and ^{13}C NMR spectroscopies and mass spectrometry. The melting points of compounds

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Table 1. Characterizations of Polyimides 6a−d, 8a−c, and 9

polymer	η_{inh},[a] dL/g	T_g,[b] °C	T_d,[c] °C	solubility[d]			
				NMP	DMAc	TCE	$CHCl_3$
6a	N/M	N/O	476	−	−	−	−
6b	0.73	360	478	+	−	+	±
6c	0.56	285	500	+	−	+	±
6d	0.44	370[e]	522	+	+	+	+
8a	0.63	312	523	+	−	+	−
8b	N/M	319	511	±	−	±	−
8c	1.12	282	514	+	−	+	−
9[f]	N/M	293	544	−	−	−	−

[a] Inherent viscosity measured in NMP at 30 °C. N/M = not measured due to low solubility in organic solvents listed in the table. [b] Obtained from the second DSC scan at a heating rate of 10 °C/min in nitrogen. N/O = not observed. [c] 5% weight loss at a heating rate of 10 °C/min in nitrogen. [d] Measured at room temperature. Key: +, soluble; ±, partially soluble; −, insoluble. [e] Obtained from the first scan of ODSC at a heating rate of 3 °C/min in nitrogen. [f] Made from BTDA and ODA.

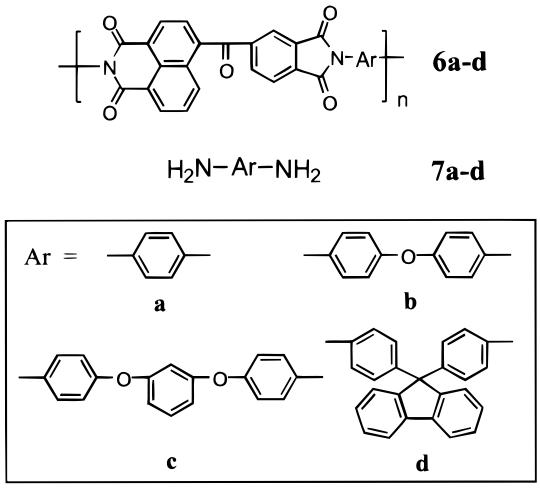


Figure 1. Polyimides **6a**−**d**.

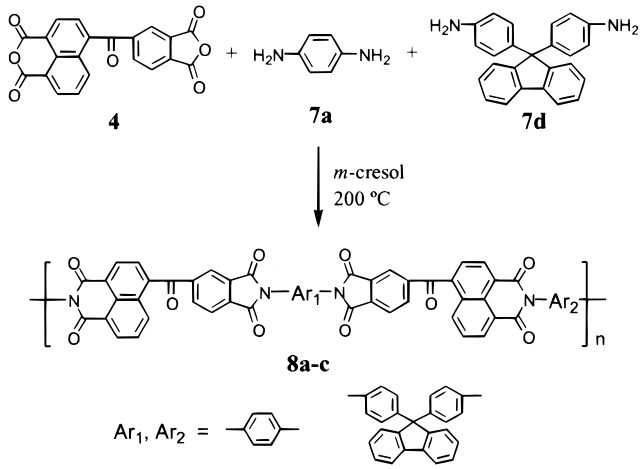
5a and **5b** were 306.1 and 169.4 °C, respectively. Comparing the IR spectrum of BNTDA, model compound **5a** shows two peaks at 1774 and 1742 cm^{-1} for the naphthalic anhydride and two peaks at 1782 and 1722 cm^{-1} corresponding to the phthalimide group. Model compound **5b** shows three carbonyl peaks at 1781, 1723, and 1673 cm^{-1} due to the naphthalimide, phthalimide, and ketone groups. The ^1H NMR spectrum of compound **5a** displays a distinct peak at δ 1.37 ppm for the methyl group, while two peaks at δ 1.40 and 1.37 ppm are shown for two magnetically nonequivalent methyl groups in compound **5b**. The ^{13}C NMR spectra are also consistent with the structures of compounds **5a** and **5b**. Thus, the model reactions demonstrated that reactivity of the five-membered ring anhydride is different from the six-membered ring anhydride, and the former is more reactive than the latter.

On the basis of the results from model reactions, one-step polymerizations of dianhydride **4** with various aromatic diamines **7a**−**d** (Figure 1) were then carried out in *m*-cresol in the presence of a small amount of isoquinoline at 200 °C. High molecular weight polyimides **6b**−**d** (Figure 1) were readily formed in 16 h, except for polyimide **6a** which precipitated out during polymerization.

Polyimides **6b**−**d** had an inherent viscosity ranging from 0.44 to 0.73 dL/g in NMP at 30 °C (Table 1). The complete imidization during polymerization was confirmed by IR. The IR spectrum of monomer **4** shows three peaks at 1856, 1779, and 1737 cm^{-1} for the naphthalic and phthalic anhydrides, while the IR spectra of these polyimides display three imide peaks at 1781, 1724, and 1673 cm^{-1} similar to that of diimide **5b**. Polyimides **6b**−**d** were found to be soluble in *m*-cresol, *N*-methylpyrrolidinone (NMP), and 1,1,2,2-tetrachloroethane (TCE) at ambient temperatures. Some were even soluble in chloroform and *N*,*N*-dimethylacetamide (DMAc). Compared with polyimide **9** derived from BTDA and 4,4′-oxydianiline (ODA), polyimides derived from BNTDA are significantly more soluble in organic solvents. Apparently, such an improvement in solubility can be attributed to the unsymmetric structure of BNTDA and the resulting three possible diad microstructures within the polyimide backbone. The glass transition temperatures (T_g) of polyimides **6a**−**d** were measured by differential scanning calorimetry (DSC). The T_g of polyimides **6b, 6c**, and **6d** were 360, 285, and 370 °C, respectively. The T_g of polyimide **6a** was not detectable by DSC. In comparison with the T_g (293 °C) of polyimide **9**, the T_g value of BNTDA-based analogue **6b** increased by 67 °C. Evidently, the increase in T_g is attributed to the large and rigid naphthalimide unit in the polymer. The onset temperature for 5% weight loss for polyimides **6a**−**d** was above 476 °C in nitrogen.

The model reaction (Scheme 2) also revealed the difference in reactivity between the two anhydrides in BNTDA under certain reaction conditions. At ambient temperatures, phthalic anhydride is reactive toward an aromatic amine, but naphthalic anhydride is inert. Even at elevated temperatures, the former reacts faster than the latter. Conceivably, under controlled conditions it is possible to obtain structurally ordered copolyimides using BNTDA with two different diamines in one-step polymerization. Thus, three copolymerization experiments were carried out using different sequences for addition of BNTDA, *p*-phenylenediamine (**7a**), and 4,4′-(9-fluorenylidene)dianiline (**7d**) (Scheme 3). In the first run, all three monomers were added at the beginning, which presumably produced a random copolyimide **8a**. In the second run, diamine **7a** and BNTDA were mixed first and reacted for 2 h with gradual increase of reaction temperatures from 25 to 200 °C, followed by addition of diamine **7d**. The resulting copolyimide **8b** was expected to be a nearly perfect alternating copolymer (with Ar_1 being *p*-phenylene, Scheme 3). Finally, addition sequence of diamines **7a** and **7d** reversed, and copolyimide **8c** (with Ar_2 being *p*-phenylene) was expected to be different from **8b**. Indeed, three copolyimides **8a**−**c** showed different solubility in organic solvents and different T_g values (Table 1). Among three copolyimides, copolyimide **8b** had the highest T_g (319 °C) and the lowest solubility. The T_g (282 °C) of copolyimide **8c** was 37 °C lower than that of **8b** but was much more

Scheme 3. Synthesis of Copolyimides 8a−c by Different Monomer Addition Sequences



Copolyimide	Monomer Addition Sequence
8a	Add **4**, **7a** and **7d** together.
8b	Add **4** and **7a**, r.t.- 200 °C in 2 h; then add **7d**.
8c	Add **4** and **7d**, r.t.- 200 °C in 2 h; then add **7a**.

soluble (Table 1). Apparently, the difference in T_g and solubility can be attributed to the different alternating sequences within the polymer main chain that are caused by unsymmetric BNTDA. Copolyimide **8a** also showed the presence of a relatively high content of alternating sequence, as its T_g (312 °C) was close to that of alternating copolyimide **8b**.

The results presented herein demonstrated the uniqueness of unsymmetric dianhydride BNTDA and its potential in controlling the microstructures of polyimides and synthesizing segmented block copolymers.

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(7) (a) In the flask equipped with a condenser, a nitrogen gas inlet, and a stirrer, acenaphthene (2.50 g, 16.21 mmol), 3,4-dimethylbenzoyl chloride (2.73 g, 16.21 mmol), and dichloromethane (20 mL) were placed. Anhydrous aluminium chloride (2.38 g, 17.83 mmol) was then added slowly to the stirred solution while maintaining a temperature of 0 °C. After complete addition, the reaction temperature was allowed to gradually increase to room temperature. The reaction mixture was poured onto crushed ice. The organic layer was partitioned, washed with water, and dried over anhydrous magnesium sulfate. On removal of the solvent, compound **1** was obtained as a white solid, which could be recrystallized from acetonitrile: 4.32 g (93%); mp 122−123 °C. HRMS for $C_{21}H_{18}O$: calcd, 286.1363; found, 286.1358. IR (KBr): 2918 (C−H), 1646 cm^{-1} (C═O). ^1H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, 1 H, J = 8.44 Hz), 7.58 (d, 2 H), 7.45 (m, 2 H), 7.29−7.12 (m, 3 H), 2.26 (s 1 H), 2.23 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.45, 150.92, 146.09, 142.06, 139.54, 136.93, 136.71, 132.11, 131.42, 131.27, 129.90, 129.47, 129.43, 128.24, 121.56, 120.11, 117.87, 30.49, 30.39, 20.06, 19.77. (b) Compound **1** (1.00 g, 3.49 mmol) was treated with $Na_2Cr_2O_7 \cdot 2H_2O$ (4.16 g, 14.0 mmol) in acetic acid (10 mL) for 4 h at 100 °C and then poured into water (50 mL). The precipitate was filtered, washed with water and acetic acid, and dried at 100 °C in an oven overnight. The product was purified by recrystallization from acetic acid to give compound **2**: 0.97 g (84%). IR (KBr): 1773, 1738 (naphthalic anhydride), 1656 cm^{-1} (C═O). ^1H NMR (200 MHz, $CDCl_3/CF_3COOD$): 8.69−8.64 (m, 2 H), 8.41−8.36 (d, 1 H), 7.85−7.80 (m, 2 H), 7.63 (s, 1 H), 7.53−7.49 (d, 1 H), 7.25−7.21 (d, 1 H). ^{13}C NMR (50 MHz, $CDCl_3/CF_3COOD$): δ 199.1, 161.8, 161.5, 147.0, 144.1, 138.4, 135.1, 134.3, 133.9, 133.2, 132.5, 132.1, 130.8, 129.6, 129.4, 129.1, 127.9, 120.1, 118.5, 20.5, 19.8. (c) In a three-necked flask equipped with a condenser, a gas inlet, and a stirrer, compound **2** (0.50 g) was dissolved in 15 mL of refluxing acetic acid (120 °C). Cobalt acetate tetrahydrate (0.37 g) and bromoacetic acid (0.21 g) were added. The oxygen was then bubbled into the reaction solution for 8 h. After the reaction solution was cooled to room temperature, it was poured into water (50 mL). The precipitate was collected by filtration, washed with water, and dried in an oven at 100 °C (0.40 g, 68% yield). The crude acid **3** was dissolved in 8 mL of acetic anhydride and heated to reflux. When the solution became clear, it was cooled to room temperature. The monomer **4** was filtered, washed with dry toluene, and dried in an oven 100 °C, which can be further purified by recrystallization from 1,2-dichlorobenzene or by sublimation: 0.33 g (85% yield); mp 272 °C (DSC). IR: 1856, 1779, 1737 (naphthalic and phthalic anhydrides), 1672 cm^{-1} (ketone). HRMS for $C_{21}H_8O_7$: calcd, 372.0270; found, 372.0261. ^1H NMR (400 MHz, DMSO-d_6): δ 8.61−8.57 (m, 2 H), 8.40−8.38 (dd, 1 H, J = 8.52, 0.96 Hz), 8.05−7.90 (m, 4 H), 7.82−7.80 (d, 1 H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 190.50, 168.37, 167.24, 160.47, 160.26, 141.15, 138.58, 137.66, 132.77, 132.65, 132.48, 132.14, 131.17, 130.14, 128.92, 128.79, 128.60, 128.17, 121.69, 119.80.

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