Condensation Polyimides from AB-Type Amino Anhydride Monomers

Zhi Yuan Wang,* Yu Qi, Timothy P. Bender, and Jian Ping Gao

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

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ABSTRACT: Starting from α-tetralone and maleic anhydride, novel AB-type amino anhydrides **3** and **5** were synthesized in good yields and obtained in high purity without self-condensation. The tetrahydro-[5]helicene monomer **3** could be readily polymerized in *m*-cresol to give polyimide **8** with high molecular weight. Although direct polymerization of the [5]helicene monomer **5** afforded only an insoluble oligomer, the high molecular weight [5]helicene-based polyimide **9** could be readily obtained as powders and thin films from the precursor polyimide **8** upon treatment with bromine at elevated temperatures. Young's moduli of thin films as assessed by TMA for polyimides **8** and **9** were 2.91 and 6.34 GPa at 25 °C, respectively. Random and regularly alternating copolymers of the AB monomer **5**, *m*-phenylenediamine, and 4,4′-(hexafluoroisopropylidene)diphthalic anhydride were made and showed improved solubility over the homopolymer **9**.

Introduction

To date, most condensation polyimides such as Du Pont's Kapton have been synthesized by polymerization of two difunctional monomers: a dianhydride and a diamine.[1] Accordingly, much effort has been directed toward the design and preparation of new dianhydrides and diamines. Unlike many condensation polymers that can be made from a bifunctional monomer, very few amino anhydride monomers and their corresponding AB-type polyimides are known and well characterized. This result is mainly attributed to the ease of self-condensation between the amine and anhydride groups. Two known amino anhydrides, 4-aminophthalic anhydride[2] and 4-aminonaphthalic anhydride,[3] were obtained by reduction of the corresponding nitro precursors, but it was difficult to isolate the former as a pure monomer due to rapid oligomerization during drying or heating prior to melting. As a result, 4-aminophthalic anhydride and its many derivatives were difficult to polymerize to high molecular weight.[2b,4] 4-Aminonaphthalic anhydride is stable during isolation and purification, but polycondensation of this amino anhydride is likely to lead to the formation of an insoluble rigid-rod polyimide. Direct polymerization of dimethyl 4-[4-(4-aminophenoxy)phenyl]-3,5,6-triphenylphthalate in *m*-cresol or neat only afforded a low molecular weight polyimide with an inherent viscosity of 0.13 dL/g.[5]

From a synthetic point of view, using an amino anhydride monomer can avoid the strict stoichiometric control needed in polycondensation, offering obvious advantages in the production and processing of polyimides derived from such materials. However, such an AB monomer has to be stable and unreactive at ambient temperatures so that purification is possible and yet, on the other hand, it must be sufficiently reactive at elevated temperatures to make polymerization to high molecular weight possible. These two requirements seem to be in stark contrast to one another.

Recently, we have been interested in incorporation of [5]helicene as the central component in a series of main-chain chiral polyimides. A simple polyimide containing a [5]helicene is the one derived from the polycondensation of an AB-type amino anhydride monomer (ca. **5**).

Frimer *et al.* recently reported the synthesis of a difunctional helicene, [5]helicene-5,6,9,10-tetracarboxylic dianhydride, which involves a photochemical cyclization.[6] It was further demonstrated that a soluble, high molecular weight polyimide could be made by solution polymerization of this [5]helicene dianhydride and 3,3′-(hexafluoroisopropylidene)dianiline.[7] The polyimides based on this novel dianhydride were found to have higher long-term thermal stability than PMR-15 thermoset resin.

Clearly, the construction of the helicene core is a crucial step in production of a [5]helicene-based monomer. Many known helicenes are unfunctionalized and are obtained in small quantities from a photochemical reaction in dilute solution. 5,6,9,10-Tetrahydro[5]helicene-7,8-dicarboxylic anhydride (**1**) is known[8] and can be readily prepared on a large scale (e.g., over 300 g) in high yield through a nonphotochemical route (Scheme 1). We have established a viable process (Scheme 2) for conversion of anhydride **1** into novel amino anhydrides and a series of [5]helicene-containing diamines. In this paper, we describe the synthesis and characterizations of the polyimides based on two amino anhydrides (**3** and **5**) and a diamine (**7**).

Experimental Section

Materials. *m*-Cresol, isoquinoline, α-tetralone, maleic anhydride, and bromine were purchased from Aldrich Chemical Co. and used as received. *m*-Phenylenediamine (Aldrich) was purified by sublimation prior to use. 4,4′-(Hexafluoroisopropylidene)diphthalic anhydride (6FDA) was purchased from Chriskev Inc. 1,1,2,2-Tetrachloroethane (TCE), dimethyl sulfoxide (DMSO), *N*,*N*-dimethylacetamide (DMAc), *N*-methyl-2-pyrrolidinone (NMP), *N*,*N*-dimethylformamide (DMF) and other common organic solvents (Aldrich) were reagent grade unless otherwise stated and were used as received.

Characterization. ^{1}H and ^{13}C NMR spectra were recorded on either Varian Gemini-200 or Bruker-400 instruments using tetramethylsilane as an internal reference. Infrared measurements were performed on a Bomen Michelson 120 FTIR spectrometer. UV absorption was recorded on a Varian Cary 3 spectrophotometer. Low- and high-resolution mass spectra were obtained on VG 7070E and Kratos Concept IIH spectrometers, respectively. Melting points were obtained from a Fisher-Johns melting apparatus and were uncorrected or from a Seiko 220C differential scanning calorimeter (DSC) at a heating rate of 10 °C/min in nitrogen (200 mL/min). The

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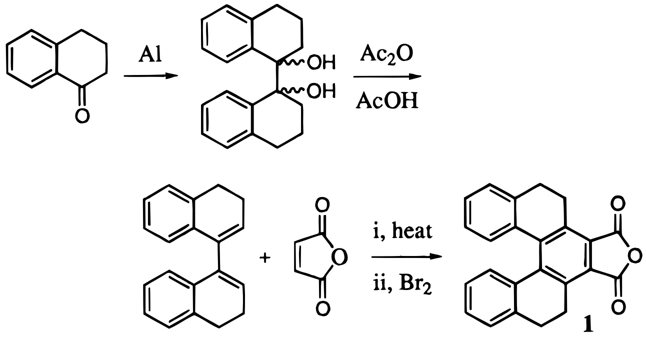
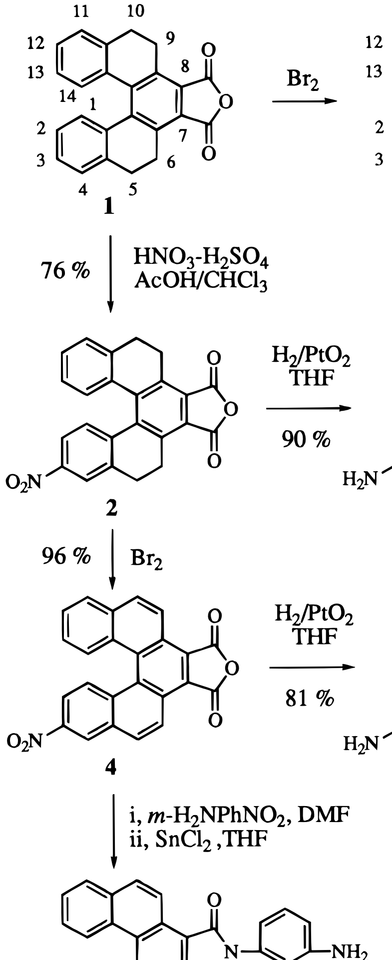
Scheme 1. Synthesis of 5,6,9,10-Tetrahydro[5]helicene-7,8-dicarboxylic Anhydride (1) from α-Tetralone



Scheme 2. Derivatizations of Anhydride 1



apparent molecular weights of the polymers were determined by gel permeation chromatography (GPC) relative to polystyrene standards using chloroform at ambient temperature at a flow rate of 1.0 mL/min; a UV detector was set at 254 nm. Intrinsic viscosities were measured in TCE or NMP at 30 °C using an Ubbelohde dilution viscometer. The glass transition temperatures were determined on a Seiko 220C DSC at a heating rate of 10 °C/min in nitrogen (200 mL/min). Thermal stabilities, as measured by weight loss, of the polymer samples were determined using a Seiko 120 TG/DTA analyzer from 25 to 1000 °C at a heating rate of 10 °C/min. Thin films were cast from TCE solution, dried at 200−250 °C under vacuum over 6 days, and cut into strips (length = 10 mm, width 2 mm, thickness = 0.01−0.03 mm). Young's moduli were obtained from the slope of the linear portion of the stress−strain plots (E') on a Seiko TMA/SS 120C TMA/SS analyzer. For E' at 25 °C, the parameters were offset load = 50 g, load amplitude = 5−10 g, and cycling frequency = 0.02 Hz. After the data at 25 °C were collected, the same films were used, without changing the parameters, to measure E' variation with temperature by heating to 450 °C at a ramp rate of 2 °C/min in nitrogen.

X-ray Structure Determination of 3. Crystal structure determination was performed at the department of chemistry of the University of Ottawa, Ottawa, Canada. A single crystal of **3** was grown from chloroform solution at ambient temperature and cut to dimensions of 0.2 mm × 0.2 mm × 0.2 mm. All the measurements were made on a Nonius diffractometer with Cu Kα radiation. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement using the setting angles of 25 reflections in the range $100 < 2\theta < 130°$ corresponded to a monoclinic cell with dimensions: $a = 8.4531$ (8) Å, $b = 23.854(3)$ Å, $c = 11.0902(11)$ Å, and $\beta = 103.275(8)°$. For $Z = 4$ and FW = 496.94, the calculated density is 1.517 g/cm^3. On the basis of the systematic absences, the space group was determined to be $P2_1/c$. The data were collected at −110 °C using the $\omega-2\theta$ scan technique to a maximum 2θ value of 128.4. The residuals are as follows: for significant reflections, $R_f = 0.063$, $R_w = 0.078$; for all reflections, $R_f = 0.076$, $R_w = 0.080$. A total of 5549 reflections was collected. The unique set contains only 3259 reflections. The standards were measured after every 150 reflections. No crystal decay was noticed. The data were corrected for Lorentz and polarization effects. No absorption correction was made. The structure was solved by direct methods. There are two molecules per asymmetric unit. All the phenyl groups were refined as rigid groups to increase the ratio of reflections/parameters. All the atoms were refined anisotropically except hydrogen. The hydrogen atoms were calculated assuming a distance C−H of 1.007 Å. Calculations were performed using the NRCVAX crystallographic software package.

Monomer Synthesis. 5,6,9,10-Tetrahydro[5]helicene-7,8-dicarboxylic Anhydride (1). The reported procedure[8] was modified for large-scale preparation as follows: (a) In a 10 L reaction vessel α-tetralone (1200 g, 8.20 mol) was dissolved in 3.5 L of toluene and 2.0 L of absolute ethanol. To this solution were added aluminum foil (227 g, 8.40 mol, approximately 2 × 2 cm) and $HgCl_2$ (7.00 g, 25.0 mmol), and the solution was vigorously stirred with gentle heating. The reaction was sufficiently exothermic for the solvent to reflux. After 4 h, an aqueous HCl solution (800 mL of concentrated HCl diluted to 4 L) was added in one portion and the resulting heterogeneous mixture was allowed to stir overnight. The organic phase was decanted, dried over $MgSO_4$, and removed to yield the pinacol product as a slightly yellow solid. The remaining aqueous phase was extracted with diethyl ether (3 × 3 L). The ethereal extract was dried and removed to yield more product. The yield was 867 g (71%). This product (498 g, 1.70 mol) was mixed with 600 mL of acetic anhydride and 400 mL of acetic acid and refluxed overnight. The reaction was allowed to cool to room temperature, and the precipitate was filtered to give the corresponding diene (329 g, 74%). (b) The diene (329 g, 1.30 mol) and maleic anhydride (950 g, 9.70 mol) were placed in an Erlenmeyer flask and heated at 155 °C for 3 h. While still hot and homogeneous, the reaction mixture was dumped into 2.0 L of hot water with vigorous stirring. The resulting slurry was stirred for 2 h. The solid was filtered and divided into two portions which were then stirred in water (2 L each) overnight. The solid was filtered out and washed with 450 mL of glacial acetic acid. The solid was once again filtered out and dried. The corresponding Diels−Alder adduct was obtained (387 g, 85%). (c) The Diels−Alder product (385 g, 1.10 mol) was dissolved in chloroform (2.1 L) and stirred at room temperature in a 4 L, three-necked, round-bottomed flask fitted with a gas outlet routed to an aqueous KOH solution. To this chloroform solution was added Br_2 (440 g, 2.80 mol) in acetic acid (200 mL) dropwise over 1.5 h. The reaction mixture was allowed to stir at room temperature overnight. The precipitate was filtered out, washed with methanol (2 × 1.0 L), and dried (60−80 °C, 5 mmHg) to give anhydride **1:** 317 g (82% or 37% yield based on α-tetralone); mp 286−287 °C (lit.[8a] 282 °C, lit.[8b] 275 °C).

3-Nitro-5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic Anhydride (2). Anhydride **1** (30.0 g) was dissolved in 1.0 L of chloroform, to which was added 300 mL of acetic acid. The nitrating agent (300 g of 70% nitric acid and 250 g of concentrated sulfuric acid in 500 mL of acetic acid) was added dropwise to the above solution at room temperature (22 °C). The reaction continued for 4 h until TLC showed no more starting material. The solution was then poured onto 500 g of crushed ice with vigorous stirring. The yellow precipitate was collected. After washing twice with methanol and drying in a vacuum oven (60 °C, 5 mmHg), pure 3-nitro anhydride **2** (26.0 g, 76%) was obtained. Evaporation of the filtrate afforded 6.6 g (20%) of a mixture of isomeric 1- and 3-nitro products in about a 1:1 ratio. The 3-nitro product **2** could be recrystallized from a mixture of acetonitrile and dichloromethane as a yellow crystalline solid: mp 267.3 °C (DSC); IR (KBr, C=O) 1763, 1830 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.23 (1 H, d, J = 2.36 Hz), 7.80 (1 H, q, J = 2.36 Hz, J = 4.36 Hz), 7.34 (3 H, m), 7.01 (2 H, m), 4.02 (2 H, t, J = 19.3 Hz), 3.07 (4 H, m), 2.64 (2 H, m); ^{13}C NMR (50 MHz, $CDCl_3$) δ 162.78, 162.74, 147.31, 142.21, 140.95, 140.60, 140.42, 139.34, 138.37, 132.07, 130.92, 130.41, 129.90, 128.46, 126.91, 126.52, 125.65, 123.29, 123.13, 121.13, 28.26, 28.10, 24.18, 24.11; MS (EI, *m*/*e*, % relative intensity) 397 ($M^{\bullet+}$, 100).

3-Amino-5,6,9,10-tetrahydro-[5]helicene-7,8-dicarboxylic Anhydride (3). 3-Nitro anhydride **2** (1.00 g) was dissolved in 50 mL of THF containing 3 drops of water and 15 mg of PtO_2 catalyst. Under 40 psi of hydrogen, the nitro compound was reduced to the corresponding amine at room temperature in 3 h. The catalyst was filtered, and the solution was dried over $MgSO_4$. Removal of THF under reduced pressure (20 mmHg) and drying under vacuum (5 mmHg) at room temperature (22 °C) afforded a reddish solid (0.83 g, 90%). The product **3** was further purified by flash chromatography on a short column eluting with dichloromethane: 0.66 g (72%); mp 181−183 °C, 181.8 °C (DSC); IR (KBr, C=O) 1826, 1759 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.33 (2 H, m), 7.21 (1 H, m), 6.99 (2 H, m), 6.61 (1 H, d, J = 2.4 Hz), 6.28 (2 H, q, J = 2.4 Hz, J = 6.02 Hz), 3.91 (4 H m), 2.88 (4 H, m) 2.56 (2 H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.56, 163.42, 147.42, 141.59, 140.89, 140.57, 139.55, 139.27, 138.85, 133.50, 131.72, 131.27, 129.55, 128.89, 128.63, 128.41, 128.27, 127.85, 126.25, 126.00, 125.30, 125.14, 123.81, 123.43, 121.03, 113.40, 113.15, 112.79, 28.45, 28.28, 24.55, 24.25; MS (EI, *m*/*e*, % relative intensity) 367 ($M^{\bullet+}$, 100); HRMS calcd for $C_{24}H_{17}NO_3$ 367.1208, found 367.1196.

3-Nitro[5]helicene-7,8-dicarboxylic Anhydride (4). Anhydride **2** (5.00 g) was dissolved in 35 mL of 1,2-dichlorobenzene and heated to reflux at 180 °C. Br_2 (4.40 g) was added, and the color of bromine disappeared immediately. The reaction continued for 2 h. The solution was then cooled to room temperature and poured into 100 mL of methanol. The resulting yellow product **4** was collected and dried in a vacuum oven (60−80 °C, 5 mmHg): 4.72 g (96%); mp 300.7 °C (DSC); IR (KBr, C=O) 1838, 1763 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.10 (1 H, d, J = 8.76 Hz), 8.97 (1 H, d, J = 5.40 Hz), 8.95 (1 H, d,), 8.55 (1 H, d, J = 9.32 Hz), 8.28 (3 H, m), 8.08 (2 H, m), 7.73 (1 H, m), 7.40 (1 H, m); ^{13}C NMR (50 MHz, $CDCl_3$) δ 162.97, 146.68, 134.10, 133.69, 133.05, 133.01, 131.81, 131.76, 131.21, 131.00, 129.91, 129.46, 129.32, 128.73, 128.33, 127.73, 126.72, 126.40, 126.36, 124.27, 123.32, 120.93, 119.03; MS (EI, *m*/*e*, % relative intensity) 393 ($M^{\bullet+}$, 100).

3-Amino[5]helicene-7,8-dicarboxylic Anhydride (5). Nitro anhydride **4** (1.00 g) was dissolved in 75 mL of THF containing 3 drops of water and 15 mg of PtO_2 catalyst. Under 40 psi of hydrogen, the nitro compound was reduced to the corresponding amine at room temperature in 2 h. After filtration of the catalyst, the filtrate was dried over $MgSO_4$ and concentrated under reduced pressure. Hexane (20 mL) was then added to the residue to precipitate the product **5** which was usually pure enough for polymerization. It could be further purified by sublimation in vacuo at ca 200 °C to give a purple crystalline solid: 0.70 g (81%); mp 331.7 °C (DSC); IR (KBr, C=O) 1833, 1751 cm^{-1}; ^1H NMR (200 MHz, DMSO-d_6) δ 8.68 (1 H, d, J = 8.80 Hz), 8.55 (1 H, d, J = 8.84 Hz), 8.38 (1 H, d, J = 8.44 Hz), 8.28 (1 H, d, J = 8.80 Hz), 8.13 (1 H, d, J = 7.24 Hz), 7.99 (1 H, d, J = 8.82 Hz), 7.91 (1 H, d, J = 9.16 Hz), 7.68 (1 H, t, J = 6.96 Hz), 7.40 (1 H, t, 7.00 Hz), 7.03 (1 H, d, J = 2.36 Hz), 6.72 (1 H, q, J = 9.16 Hz, J = 2.36 Hz), 6.12 (2 H, s); ^{13}C NMR (50 MHz, $CDCl_3$) δ 163.84, 163.64, 149.85, 135.92, 132.96, 132.81, 130.55, 130.40, 130.22, 130.03, 129.92, 128.31, 128.10, 127.84, 126.99, 125.85, 125.63, 123.19, 123.02, 121.04, 120.21, 116.21, 107.11, 106.69; MS (EI, *m*/*e*, % relative intensity) 363 ($M^{\bullet+}$, 45); HRMS calcd for $C_{24}H_{13}NO_3$ 363.0895, found 363.0888.

Diamine 7. 3-Nitro[5]helicene-7,8-dicarboxylic anhydride **4** (412 mg, 1.04 mmol) was placed along with *m*-nitroaniline (233 mg, 1.68 mmol) in 20 mL of DMF and 5 mL of acetic acid and refluxed overnight. The reaction mixture was allowed to cool to room temperature, and the resulting precipitate was filtered out. The precipitate was washed with acetic acid (2 × 20 mL) and then methanol (2 × 40 mL) and dried to give the corresponding dinitro imide (400 mg, 62%) with a melting point of 254−257 °C.

The resulting dinitro compound (5.215 g, 10.16 mmol), without further purification, was placed along with $SnCl_2{\cdot}2H_2O$ (23.26 g, 103.1 mmol) in THF (500 mL) and refluxed overnight. The resulting homogeneous solution was dumped into water (500 mL) containing sodium carbonate (20 g). The resulting fine red precipitate was filtered and boiled in THF (150 mL) for 1 h. The undissolved off-white solid was filtered from the blood red solution and washed with 100 mL of THF. The combined red THF solutions were dried over $MgSO_4$ and concentrated under vacuum to afford diamine **7** as a red powder: 3.85 g (84%); mp 278 °C dec; ^1H NMR (400 MHz, DMSO-d_6) δ 8.90 (1 H, d), 8.78 (1 H, d), 8.33 (1 H, d), 8.16 (1 H, d), 8.05 (1 H, d), 7.89 (2 H, t), 7.60 (1 H, t), 7.33 (1 H, t), 7.18 (1 H, t), 6.99 (1 H, d), 6.6−6.7 (4 H, m), 5.94 (2 H, s), 5.35 (2 H, s); ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.22, 168.18, 149.25, 135.30, 132.55, 132.35, 132.06, 130.29, 130.04, 129.74, 129.18, 129.08, 129.00, 128.02, 127.87, 127.67, 126.11, 125.98, 125.18, 123.44, 122.53, 121.17, 120.79, 120.71, 115.64, 114.79, 113.42, 112.96, 106.81; MS (EI, *m*/*e*, % relative intensity) 453 ($M^{\bullet+}$, 100); HRMS calcd for $C_{30}H_{19}N_3O_2$ 453.1477, found 453.1488.

Model Chemical Transformation. [5]Helicene-7,8-dicarboxylic Anhydride (6). To a refluxing solution of anhydride **1** (1.00 g, 2.84 mmol) in TCE (10 mL) was added Br_2 (1.13 g, 7.10 mmol) dropwise over 10 min. After 1 h the reaction solution was cooled to room temperature and poured into 50 mL of hexane. The resulting yellow precipitate was collected by filtration, washed twice with hot hexane, and dried in a vacuum oven (5 mmHg) at 130 °C. The pure anhydride **6** was obtained as a yellow solid and could be further recrystallized from DMAc: 0.96 g (97%); mp 276−277 °C, 275.7 °C (DSC) (lit.[8a] >360 °C); IR (KBr, C=O) 1839, 1756 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.91 (1 H, d, J = 8.76 Hz), 8.39 (1 H, d, J = 8.56 Hz), 8.15 (1 H, d, J = 8.76 Hz), 8.02 (1 H, d, J = 8.04 Hz), 7.64 (1 H, t d, J_1 = 1.00 Hz, J_2 = 8.04 Hz), 7.31 (1 H, t d, J_1 = 1.00 Hz, J_2 = 8.56 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) d 163.52, 133.77, 132.90, 131.00, 130.43, 129.54, 128.80, 128.33, 126.53, 126.38, 125.68, 120.96; MS (EI, *m*/*e*, % relative intensity) 348 ($M^{\bullet+}$, 64.1), 276 (100); HRMS calcd for $C_{24}H_{12}O_3$ 348.0786, found 348.0798.

Polymer Synthesis. Polyimide 8. Monomer **3** (0.50 g) was dissolved in 8.5 mL of *m*-cresol in a three-neck, round-bottomed flask fitted with a nitrogen inlet, a nitrogen outlet, and a magnetic stirrer. The solution was stirred at 200 °C under a flow of nitrogen overnight. The resulting viscous solution was cooled to 100 °C and then poured into 200 mL of methanol. The yellow polymer was collected by filtration. Washing with hot acetone several times and drying in a vacuum oven (5 mmHg) at 150 °C overnight gave polyimide **8**: 0.43 g (92%); IR (KBr, C=O) 1764, 1712 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.23 (7 H, m), 4.12 (2 H, s), 2.99 (4 H, d), 2.62 (2 H, s); M_w = 188 000 (GPC), M_w/M_n = 2.23; $[\eta]$ = 0.84 dL/g (TCE, 30 °C). T_d (5% weight loss in nitrogen) = 499 °C; E' = 2.91 GPa (25 °C), 2.36 GPa (200 °C).

Polyimide 9. (a) Chemical Transformation in Solution. The powdered polyimide **8** (0.10 g) was dissolved in 7.5 mL of TCE and heated to reflux. Br_2 (5 drops) was added to the solution while refluxing. A yellow precipitate formed spontaneously. The reaction continued for 1 h at the same temperature. The solution was then cooled to room temperature. The resulting polyimide **9** was collected by filtration, washed with acetone several times, and dried at reduced pressure (5 mmHg) at 150 °C for 2 days. The powdered polymer **9** (0.95 g, 96%) was placed in a round-bottomed flask and was heated at 350 °C for 40 min under a nitrogen atmosphere. IR (KBr, C=O): 1767, 1716 cm^{-1}. T_d (5% weight loss in nitrogen) = 495 °C. The test for bromine was negative.

(b) Chemical Transformation of a Film. The polyimide film **8** cast from TCE solution was placed in a glass container fitted with a vacuum outlet and a gas inlet. The container was evacuated by a water aspirator (20−30 mmHg) and was heated in a sand bath at 270 °C for 3 h. A small amount of bromine vapor was then introduced into the container through the gas inlet. After Br_2 was kept inside for 20 min at 270 °C, the vacuum was applied by a water aspirator (20−30 mmHg) for 2 h to remove both bromine and HBr. The film **9** was then allowed to cool to room temperature and characterized. IR (KBr, C=O): 1767 and 1716 cm^{-1}. T_d (5% weight loss in nitrogen) = 537 °C. E' = 6.34 GPa (25 °C), 5.48 GPa (200 °C).

Polyimide 10. (a) By random Copolymerization. 3-Amino[5]helicene-7,8-dicarboxylic anhydride **5** (373 mg, 1.00 mmol), *m*-phenylenediamine (115 mg, 1.00 mmol), and 6FDA (459 mg, 1.00 mmol) were placed along with 15 mL of *m*-cresol and 8 drops of isoquinoline in a 50 mL three-necked, round-bottomed flask under a strong nitrogen stream. The reaction mixture was stirred overnight at 200 °C, and the viscous red solution was poured into methanol (300 mL) while still hot to give a brownish yellow powder. The polymer powder was filtered off and washed with methanol (2 × 300 mL) and dried at 150 °C under vacuum (5 mmHg) overnight. $[\eta]$ = 0.39 dL/g (NMP, 30 °C). T_d (5% weight loss in nitrogen) = 493 °C.

(b) By Alternating Copolymerization. Diamine **7** (458 mg, 1.00 mol) and 6FDA (453 mg, 1.00 mmol) were placed along with 15 mL of *m*-cresol and 8 drops of isoquinoline in a three-necked, round-bottomed flask under a strong nitrogen stream. The polymerization was kept overnight at 200 °C. The viscous red solution was poured into methanol (300 mL) while still hot to give a brownish yellow powder. The polymer powder was filtered off and washed with methanol (2 × 300 mL) and dried at 150 °C under vacuum (5 mmHg) overnight. IR (KBr, C=O): 1723, 1770 cm^{-1}. $[\eta]$ = 0.23 dL/g (TCE, 30 °C); T_d (5% weight loss in nitrogen) = 493 °C.

Results and Discussion

Monomer Synthesis. Since the monofunctionalized [5]helicene precursor **1** was readily prepared from α-tetralone and maleic anhydride in three steps (Scheme 1),[8] subsequent mononitration of compound **1** having two equally reactive terminal benzene rings became the key to our procedure. Selective mononitration was found to be best carried out in a mixture of acetic acid and chloroform using 70% nitric acid and concentrated sulfuric acid as a nitrating agent (Scheme 2). Under such reaction conditions, the pure nitro anhydride **2** could be obtained in 76% yield after simple workup, plus a 1:1 mixture (20% yield) of **2** and its 1-nitro regioisomer (see the numbering system of [5]helicene anhydride **6** in Scheme 2). Reduction of the nitro group by hydrogenation using PtO_2 in THF afforded the amino anhydride **3** which could be further purified by short-column flash chromatography. The [5]helicene-based monomer **5** was derived from compound **4** which was obtained from the nitro anhydride **2** upon aromatization by treatment with elemental bromine in refluxing *o*-dichlorobenzene (Scheme 2). Both AB-type monomers **3** and **5** are obtained in high purity and can be stored in a dry container over months without any deterioration. To demonstrate the versatility of our synthetic approach, the [5]helicene-based diamine **7** was prepared from the nitro anhydride **4** by reaction with *m*-nitroaniline and subsequent reduction with tin(II) chloride.

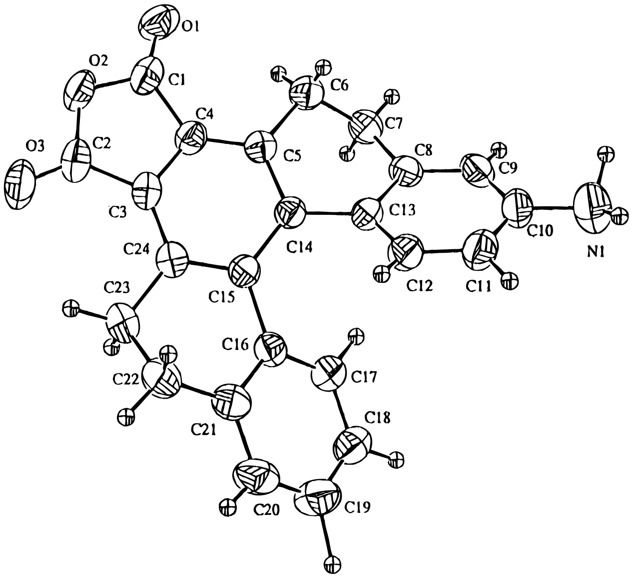


Figure 1. X-ray crystal structure of amino anhydride **3**.

Unlike 3- and 4-aminophthalic anhydrides which do not show any melting points by gradual heating, the amino anhydrides **3** and **5** displayed sharp melting points, 181.8 °C by DSC or 181−183 °C for **3** and 331.7 °C by DSC for **5**. At temperatures higher than their melting points condensation took place rapidly to yield water and oligoimides. These amino anhydrides are stable in refluxing chloroform and TCE but become reactive in polar solvents such as DMSO, DMAc, and NMP at elevated temperatures. The helicene-based monomer **5** could be sublimed under vacuum at ca. 200 °C without any self-condensation. The structures of monomers **3** and **5** were confirmed by spectroscopic means (IR, NMR, MS). The structure of **3** was confirmed by a single crystal X-ray diffraction analysis (Figure 1). The crystal structure shows that the two terminal benzene rings are non-coplanar with an interplanar angle of 50.9°. The amino and anhydride groups are connected by a conjugated biphenyl moiety to form a “push-and-pull” system.

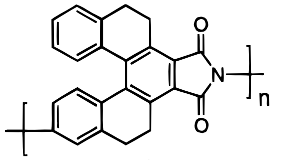
Polyimide Synthesis. Polyimide 8. Rigid aromatic polyimides (e.g., PMDA/ODA) due to poor solubility are applied as poly(amic acid) solutions in amide-type solvents which are subsequently cured at elevated temperatures to effect imidization. This two-step process only allows the use of these polyimides as thin films

Table 1. Solubilities of Polyimides 8 and 10[a]

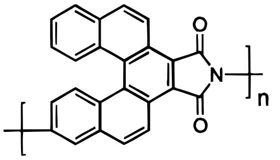
polyimide	$CHCl_3$	TCE	DMF	DMSO	DMAc	NMP	*m*-cresol	THF	pyridine
8	±	+	−	−	−	±	+	−	±
10, random	−	±	±	±	±	+	+	±	−
10, alternating	−	+	±	±	+	+	+	±	+

[a] Measured at room temperature. Key: +, fully soluble; ±, partially soluble; −, insoluble.

or coatings and also may induce significant stress in the films. Solution polymerization is more desirable to produce bulk polyimides, but the monomer and the resulting polyimide must have good solubility in common polymerization solvents like NMP and *m*-cresol. Presumably, the twisted terphenyl moiety and aliphatic ethylene units were able to impart good solubility to monomer **3** and polyimide **8**. One-step polymerization was carried out in *m*-cresol at 6% solid content in the presence of a small amount of isoquinoline at 200 °C. The water formed was removed together with a small amount of *m*-cresol with a stream of nitrogen. High molecular weight polyimide **8** could be readily obtained in about 18 h. Polyimide **8** is readily soluble in TCE and has limited solubility in chloroform and NMP at ambient temperatures (Table 1). It had a weight-average molecular weight of 188 000 by GPC relative to polystyrene and a polydispersity index of 2.23. The intrinsic viscosity was 0.84 dL/g in TCE at 30 °C.



8



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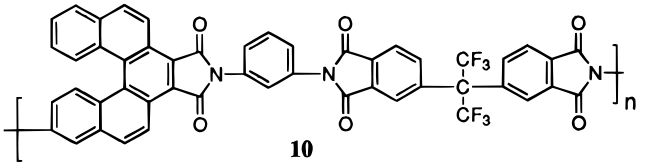

10

Polyimide **8** was characterized by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and thermomechanical analysis (TMA). A glass transition temperature (T_g) could not be detected by DSC or TMA up to 450 °C, indicative of the high rigidity of the polymer backbone. Despite the presence of the aliphatic moieties, polyimide **8** displayed good thermal stability. The onset temperature for 5% weight loss was at 499 °C in nitrogen and at 455 °C in air, as assessed by TGA. A clear, flexible and tough film could be cast from the TCE solution of **8**. Young's modulus of the nonoriented, amorphous film was measured to be 2.91 GPa at 25 °C and 2.36 GPa at 200 °C using TMA in the tensile stress−strain mode.

Polyimide 9. Solution polymerization of monomer **5** was attempted in *m*-cresol at 200 °C, but a low molecular weight insoluble polymer was formed prematurely. However, high molecular weight polymer **9** could be obtained using a precursor polymer. As a model reaction, we found that the tetrahydro-[5]helicene anhydride **1** could be converted quantitatively into [5]-helicene anhydride **6** upon treatment with bromine at elevated temperatures in TCE. This aromatization reaction was found to be best carried out by adding bromine to the substrate at elevated temperatures (e.g., 150 °C−180 °C in TCE or *o*-dichlorobenzene). The reactions run at lower temperatures or from room temperatures to high temperature afforded the desired product in low yield and brominated byproducts. A plausible explanation for successful aromatization of the tetrahydro[5]helicene is that, at high temperatures, bromine is homolytically cleaved to generate the bromine radical which abstracts and then replaces the hydrogen radical at the benzylic position. The subsequent elimination of HBr from the bromide intermediate occurs spontaneously at high temperature to form a carbon−carbon double bond. On the basis of this aromatization method, polyimide **8** is an ideal precursor for the synthesis of polyimide **9**. Thus, upon addition of bromine to refluxing TCE solution of polyimide **8**, yellow polyimide **9** precipitated out immediately. This polymer transformation was also performed in the solid state. A free-standing thin film of **8** was treated with bromine vapor at high temperature (ca. 270 °C) and converted into polyimide **9** without thermal or chemical degradation. Lassaign's test[9] on polyimide **9** gave a negative result, indicating the absence of bromine. The completion of the chemical transformation or aromatization was unambiguously confirmed by FTIR. Figure 2 shows the IR spectra of the precursor polyimide **8**, oligomer **9** made by solution polymerization of **5** and the polyimide film **9** derived from **8**. The aliphatic C−H bands were clearly seen close to the right side of the 3000 cm^{-1} line for polyimide **8** (spectrum a) and were absent for polyimide **9** (spectrum c). The spectra of the powdered oligomer **9** and the polymer film **9** are superimposible.

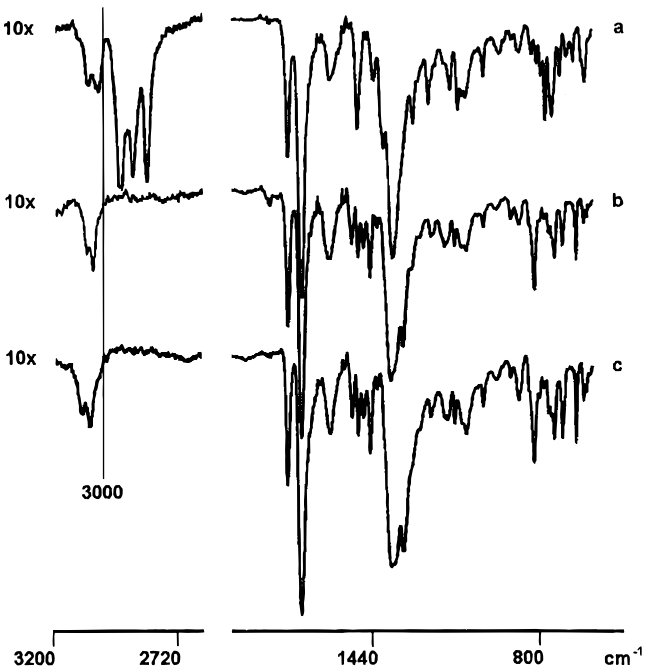

Figure 2. IR spectra of (a) polyimide **8**, (b) oligomer **9** (derived from **5**), and (c) polyimide **9** (derived from **8**). The region between 2720 and 3200 cm^{-1} is magnified 10 times.

Due to the presence of the helicene moiety, the film of polyimide **9** showed a higher thermal stability than that of polyimide **8** in nitrogen, with the onset temperature for 5% weight loss in nitrogen at 537 °C. But in air polyimide **9** (both powder and film) and polyimide **8** had the same onset temperature for 5% weight loss occurring at 455 °C. The tensile modulus (6.34 GPa at 25 °C) of the film of polyimide **9** was higher than that of polyimide **8** (2.91 GPa) and remained high (5.48 GPa) even at 200 °C. No T_g for **9** could be detected by DSC or TMA up to 500 °C, because of its highly rigid backbone.

Polyimide 10. To obtain a soluble [5]helicene-containing polyimide, copolymerization was performed. We have previously found that for some rigid rod-like copolyimides, a regularly alternating copolymer is more soluble than the random analogue with the same chemical composition.[10] Therefore, two routes to the incorporation of the [5]helicene monomer **5** into a copolyimide were explored. One involves direct random copolymerization of **5**, a diamine and a dianhydride. Thus, polycondensation of **5**, *m*-phenylenediamine and 6FDA in equal molar amounts was carried out in *m*-cresol at 200 °C. The random copolymer **10** remained soluble during polymerization and was obtained as a brownish-yellow powder with an intrinsic viscosity of 0.39 dL/g in NMP at 30 °C.

In the second route, an alternating copolyimide can be obtained by polymerization of a dianhydride and a diamine derived from the AB monomer **5**. Thus, diamine **7** was required to synthesize the alternating copolyimide **10**. This diamine was easily obtained from compound **4** by reaction with *m*-nitroaniline and subsequent reduction (Scheme 2). Polymerization of diamine **7** and 6FDA in *m*-cresol afforded the alternating copolyimide **10** with an intrinsic viscosity of 0.23 dL/g in TCE at 30 °C. The alternating copolyimide **10** has the same chemical compositions as the random copolymer and, as expected, is indeed more soluble. For example, the alternating copolymer is readily soluble in TCE, DMAc, NMP and even pyridine at ambient temperatures, whereas the random copolymer is only soluble in NMP (Table 1). Both copolymers had an onset decomposition temperature at 493 °C for 5% weight loss in nitrogen by TGA. The T_g values were not detectable by DSC up to 400 °C.

Conclusions

To the best of our knowledge, this is the first case of an AB-type amino anhydride monomer (e.g., **3**) that can be obtained in high purity and polymerized to the corresponding polyimide in high molecular weight. Therefore, it is highly possible that other interesting aromatic amino anhydrides could be designed, synthesized, and polymerized. It was also demonstrated that a [5]helicene moiety could be incorporated into the polyimide main chain by copolymerization or by chemical transformation of a precursor polymer in solution or in the solid state. Chemical resolution of the racemic helicene-based monomers necessary for making optically active helicene-based polyimides is in progress.

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References and Notes

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