Introduction of a [5]Helicene Unit in Polyimides by Chemical and Thermal Transformations of Precursor Polymers

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ABSTRACT: Several [5]helicene-containing polyimides have been synthesized by chemical and thermal transformation of the precursor polyimides having the tetrahydro[5]helicene unit. The illustrated diamines **4a** and **4b** were polymerized with two dianhydrides (6FDA and s-BPDA) to form high molecular weight polyimides **5a,b** and **6a,b**, containing the tetrahydro[5]helicene core. These precursor polyimides showed good solubilities in common solvents and good thermal properties. Chemical transformation in solution or in the film form could be effected by treatment with bromine at elevated temperatures. The resulting [5]helicene-containing polyimides showed a marked increase in thermooxidative stability. The onset temperatures for 5% weight loss in air were over 500 °C for the [5]helicene-based polyimides, about 70 °C higher than those for the precursor polyimides. Furthermore, the [5]helicene-containing polyimides retained the high tensile (Young's) moduli of the precursor polyimides, indicating that the transformation did not result in any chain cleavage or cross-linking. The transformation to yield [5]helicene-containing polyimides could also be effected by heating at 400 °C in air. The thermally induced transformation was supported by the synthesis and transformation of a model compound.

Introduction

The application of the precursor strategy in polymer synthesis has recently attracted much attention. It is often employed when a desired polymer cannot be obtained by direct polymerization because of the lack of a suitable monomer or insolubility of the resulting polymer. In this case, a high molecular weight polymer is synthesized first as a precursor and subsequently converted into the desired polymer by a simple transformation. The transformation may be effected by a chemical process,[1] photochemical process[2] or thermal (heating) process.[3] The protecting or masking groups are also used in obtaining the soluble precursor polymers and later removed to yield the targeted insoluble polymers, such as poly(*p*-phenylene),[4] poly(phenylene sulfide),[5] poly(*p*-phenyleneterephthalamide),[6] poly(ether ether ketone),[7] and aromatic polyimides from poly(amic acid ester)s.[8]

The precursor approach has some advantages, particularly if the transformation can be done on the precursor polymer as a thin film or bulk part. Thus, the precursor polymer is processed to the desired form and transformed (or cured) to the final polymer product that often has improved solvent resistance and increased thermal stability compared to its precursor. However, there are certain requirements that should be considered. The process should ideally be simple and clean and leave no residue or byproduct. If byproducts are generated, as is likely in the case of chemical transformation, then they should be easily removed from the polymer. The transformation should not cause polymer degradation or unwanted cross-linking. Ideally, the transformation should be done in the solid state by a thermal process within the polymer processing temperature window.

We have recently reported the incorporation of a [5]helicene unit into a high molecular weight polyimide using a precursor approach.[9] It was found that an AB-type [5]helicene-based monomer, 3-amino[5]helicene-7,8-dicarboxylic anhydride (**C**) could not be directly polymerized to give a high molecular weight polyimide (**D**), due to insolubility of **D** in *m*-cresol (Scheme 1). However an analogue to **C**, 3-amino-5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic anhydride (**A**) gave a high molecular weight polyimide (**B**) by solution polymerization. By simple treatment of **B** in solution or the thin film with bromine at elevated temperatures, a high molecular weight [5]helicene-based polyimide **D** was obtained. Polyimide **D** showed excellent solvent resistance and improved thermal stability over polyimide **B**. We also showed therein that a [5]helicene-containing diamine (analogous to **4a**) could not be directly polymerized to give a high molecular weight polyimide.[9] It is therefore supposed that a series of polyimides containing the tetrahydro[5]helicene unit could serve as suitable precursors to a series of [5]helicene-containing polyimides.

Helicenes have some unique features not found in other polycyclic aromatic compounds. They contain overlapping terminal aromatic rings and are therefore chiral.[10] Helicene-containing polymers are likely to possess some interesting photochemical and electrochemical properties and high thermal stability due to the extended π-system. Frimer *et al.* reported the synthesis of a series of polyimides derived from a [5]helicene dianhydride.[11] The polyimides indeed showed excellent thermal stability, rivaling that of PMR-15[12] polyimide composite, and were insoluble in common organic solvents.

We are interested in exploring the properties of helicenes within macromolecules and as a result are looking at a variety of ways for incorporation of helicenes into polymers. The AB-type monomer **A** offers only one route to a polymer system (e.g., polyimide **D**) by direct polycondensation. To explore other polyimides containing the [5]helicene unit, diamines **4a** and **4b** (Scheme 2) have been synthesized and a series of high molecular weight precursor polyimides **5a,b** and **6a,b** containing the tetrahydro[5]helicene unit (Scheme 2) have been made from these diamines. In this paper we describe a general approach for the chemical and

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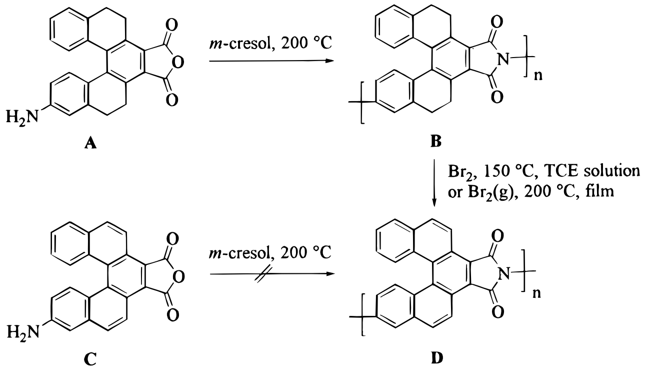
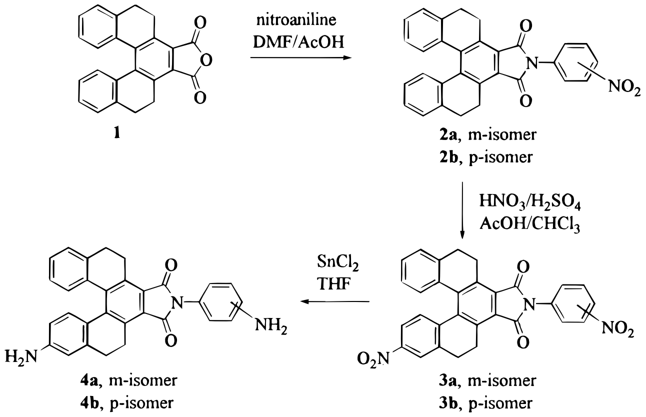
Scheme 1. Polyimides B and D Derived from AB-Type Monomers A and C



Scheme 2. Synthesis of Tetrahydro[5]helicene-Based Diamines 4a and 4b



thermal transformations of this series of precursor polyimides to [5]helicene-containing polyimides.

Experimental Section

Materials. The preparation of oligomeric **8a**, as a powder, has been previously reported.[9] *m*-Cresol, isoquinoline, *m*-nitroaniline, *p*-nitroaniline, and bromine were purchased from Aldrich Chemical Co. and used as received. 4,4′-(Hexafluoroisopropylidene)diphthalic anhydride (6FDA) and 3,3′,4,4′-biphenyltetracarboxylic dianhydride (s-BPDA) were polymer grade as purchased from ChrisKev Co. 4-*tert*-Butylphthalic anhydride (TBPA) was purchased from TCI America and used as received. 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 used as received. TCE-d_2 was purchased from CIL Isotopes and used as received.

Characterization. ^{1}H and ^{13}C NMR spectra were recorded on either a Varian Gemini-200 or a Bruker-400 instrument 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- (EI) and high-resolution mass spectra (HRMS) were obtained on VG 7070E and Kratos Concept IIH spectrometers, respectively. Melting points were obtained with a Fisher-Johns apparatus and are uncorrected. The apparent molecular weights of selected 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 set at 254-nm wavelength was used for detection. Inherent viscosities were measured in *N*-methyl-2-pyrrolidinone (NMP) solution at 30 °C using an Ubbelohde dilution viscometer, flow times were in excess of 2 min. The glass transition temperatures were determined on a Seiko 220C DSC at a heating rate of 3 °C/min in nitrogen (200 mL/min) in oscillating mode. Thermal stabilities of the polymer samples were determined using a Seiko 120 TG/DTA analyzer run from 25 to 800 °C at a heating rate of 10 °C/min. Thin films were cast from TCE solution, dried at 200−250 °C under vacuum (5 mmHg) over 14 days, and cut into strips (length = 10 mm, width = 2 mm, thickness = 0.01−0.03 mm). Young's moduli of thin films were obtained on a Seiko TMA/SS 120C TMA/SS analyzer. The films were tested by measuring the stress and strain while applying a sinusoidal load program. For Young's modulus at 25 °C, the parameters were set as: offset load = 20 g, load amplitude = 10 g, and cycling frequency = 0.05 Hz. Young's moduli were obtained from the slope of the linear portion of the stress−strain plots (E'). After the data were collected, the same film was used without changing the parameters to measure Young's modulus variation with temperature by heating to 450 °C at a rate of 3 °C/min in static air. After the film was slowly cooled to room temperature, a second measurement of Young's modulus variation with temperature was performed on the same film without changing the parameters, by heating to 450 °C at a rate of 3 °C/min in static air.

Monomer Synthesis. Imides 2a and 2b. Anhydride **1** (20.0 g, 56.8 mmol) and *m*- or *p*-nitroaniline (11.8 g, 85.2 mmol) was placed in a mixture of 100 mL of DMF and 50 mL of acetic acid. The heterogeneous reaction mixture was heated at reflux overnight. The homogeneous reaction mixture was dumped into 300 mL of vigorously stirred dilute HCl solution. The resulting precipitate was filtered and washed with dilute HCl (200 mL), water until the washings were neutral to litmus, and finally methanol (2 × 100 mL). After drying in air and then at 50 °C under vacuum (5 mmHg), the corresponding imide was obtained.

2a: 55% yield; mp 215−219 °C; IR (KBr) 1763, 1712 cm^{-1} (C=O, imide); ^{1}H NMR (400 MHz, $CDCl_3$) 2.58 (m, 1H), 2.94 (m, 1H), 4.14 (m, 1H), 6.95 (t, 2H), 7.1−7.3 (m, 6H), 7.67 (t, 1H), 7.86 (d, 1H), 8.24 (d, 1H), 8.43 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 24.37, 28.56, 121.68, 122.34, 125.29, 125.97, 127.86, 128.70, 129.71, 130.33, 132.27, 133.26, 133.40, 139.19, 139.64, 139.88, 148.55, 167.07; MS (EI, *m*/*e*, relative intensity %) 472 ($M^{•+}$, 100.0).

2b: 78% yield; mp 244−248 °C; IR (KBr) 1764, 1713 cm^{-1} (C=O, imide); ^{1}H NMR (400 MHz, $CDCl_3$) 2.58 (m, 1H), 2.96 (m, 2H), 4.16 (m, 1H), 6.95 (t, 1H), 7.19 (m, 2H), 7.33 (d, 1H), 7.75 (d, 1H), 8.35 (d, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 24.35, 28.54, 124.32, 125.28, 125.99, 126.62, 127.87, 128.73, 130.32, 133.38, 137.92, 139.16, 139.68, 139.97, 146.31, 166.65; MS (EI, *m*/*e*, relative intensity %) 472 ($M^{•+}$, 36.7).

Dinitro Intermediates 3a and 3b. The imide **2a** or **2b** (10.0 g, 21.0 mmol) was dissolved in 160 mL of chloroform. To this solution was added 32 mL of acetic acid with stirring, and the homogeneous solution was cooled to 10 °C. To this stirred solution was added dropwise over a period of 1 h a chilled (0 °C) mixture of 12.7 g of HNO_3 (70%), 16.2 g of H_2SO_4 (96%), and 12.5 mL of acetic acid The reaction mixture was then allowed to warm to room temperature, and the two-phase reaction medium was stirred vigorously. The reaction was followed by TLC (SiO_2, 10% acetone in hexane) and was stopped when TLC showed no starting imide (3−6 h). The reaction mixture was placed in a separatory funnel without partitioning and washed with water (3 × 150 mL). The organic phase was dried over sodium sulfate and concentrated under vacuum to yield a yellow solid (two spots on TLC). Two successive precipitations of the crude product in 95% ethanol from hot chloroform solution gave the desired dinitro product in 80% yield. The dinitro product was reduced without further purification. **3a**: mp > 300 °C; MS (EI, *m*/*e*, relative intensity %) 517 ($M^{•+}$, 100.0). **3b**: mp > 300 °C; MS (EI, *m*/*e*, relative intensity %) 517 ($M^{•+}$, 100.0).

Diamines 4a and 4b. The dinitro compound **3a** or **3b** (21.0 g, 40.0 mmol) and $SnCl_2{\cdot}2H_2O$ (94.5 g, 0.40 mol) was placed in 300 mL of THF. After reflux for 5 h, the initially yellow and heterogeneous mixture had turned to a homogenous blood red solution. The solution was poured slowly into an aqueous solution containing 50 g of sodium carbonate. A white precipitate was formed and was filtered from the blood red solution. The red filtrate was placed in a separatory funnel and extracted with 200 mL of chloroform. The aqueous phase was then extracted with 200 mL of chloroform. The white precipitate was stirred with THF (200 mL), and the mixture was filtered. The THF washings and chloroform extracts were combined and concentrated under reduced pressure. The residual solution (100 mL) was then passed through a pad of silica gel to remove remaining inorganic salts. The filtrate was concentrated under reduced pressure to yield a red solid, which was dissolved in a minimum amount of TCE and loaded onto a column packed with silica gel (6 cm × 20 cm). The column was first eluted with 4 L of dichloromethane and then with 8 L of chloroform. The chloroform fraction was collected and concentrated under vacuum to give the diamine **4a** or **4b** as a red solid.

4a: 9.1 g (50%); mp 290 °C (dec); IR (KBr) 3466, 3374 (NH$_2$),1754, 1703 cm^{-1} (C=O imide); ^{1}H NMR (400 MHz, DMSO-d_6) 2.4 (m, 2H), 2.8 (m, 4H), 3.9−4.0 (m, 2H), 5.29 (s, 2H), 5.48 (s, 2H), 6.16 (d, 1H), 6.4 (m, 2H), 6.55 (t, 1H), 6.61 (d, 1H), 6.78 (d, 1H), 7.00 (t, 1H), 7.12 (t, 1H), 7.18 (t, 1H), 7.26 (d, 1H), 7.35 (d, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) 23.64, 23.93, 27.74, 28.08, 111.45, 111.97, 112.89, 113.35, 114.70, 120.62, 123.28, 125.35, 125.49, 127.63, 127.71, 128.79, 128.90, 130.96, 132.61, 133.78, 135.86, 136.85, 137.92, 138.56, 139.70, 140.24, 149.14, 149.31, 167.27, 167.37; HRMS calcd for $C_{30}H_{23}N_3O_2$ 457.1790, found 457.1784.

4b: 10.0 g (55%); mp 290 °C (dec); IR (KBr) 3460, 3371 (NH$_2$); 1754, 1698 cm^{-1} (C=O imide); ^{1}H NMR (400 MHz, DMSO-d_6) 2.35 (m, 2H), 2.8 (m, 4H), 3.9 (m, 2H), 5.33 (s, 1H), 5.51 (s, 1H), 6.16 (d, 1H), 6.50 (s, 1H), 6.64 (m, 2H), 6.77 (d, 1H), 7.0 (m, 3H), 7.17 (t, 1H), 7.25 (d, 1H), 7.33 (d, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) 23.71, 24.00, 27.837, 28.18, 111.51, 112.04, 113.50, 119.87, 120.72, 123.42, 125.53, 127.72, 128.42, 128.87, 131.02, 133.86, 135.80, 136.75, 137.81, 138.62, 139.62, 140.30, 148.64, 149.32, 167.89, 167.91; HRMS calcd for $C_{30}H_{23}N_3O_2$ 457.1790, found 457.1821.

Typical Procedure for Polymerization. Diamine **4a** (1.381 g, 3.000 mmol) and 6FDA (1.341 g, 3.000 mmol) were placed in a 100 mL three-necked round-bottomed flask equipped with a N$_2$ inlet and a Dean-Stark trap fitted with a N$_2$ outlet, followed by 45 mL of *m*-cresol and 24 drops of isoquinoline under a strong N$_2$ stream. The flask was then placed in a preheated oil bath at 210 °C. The initially red solution quickly faded to give a yellow-orange solution. Polymerization was stopped after 6−8 h by pipeting the hot solution into 600 mL of vigorously stirred methanol. The resulting fibrous polyimide was collected by filtration, washed twice with methanol (600 mL), filtered off, and finally washed with methanol (600 mL) overnight. Polymer **5a** was dried under vacuum (5 mmHg) for 4 days at 150 °C.

End-Capped Polyimide 7. Diamine **4a** (0.458 g, 1.000 mmol), 6FDA (0.4273 g, 0.960 mmol), and TBPA (8.5 mg, 0.040 mmol) were polymerized as above. After 6 h the hot solution was poured into 300 mL of vigorously stirred methanol. The resulting fibrous polymer was collected by filtration, and washed with methanol (300 mL), filtered off, and finally washed with methanol (300 mL) overnight. Polyimide **7** was dried under vacuum (5 mmHg) for 4 days at 150 °C.

Model Thermal Transformation. A finely divided powder of 5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic anhydride (**1**, 20 mg) was placed in a sealed glass tube (10 cm long, 0.5 cm ID) with an atmosphere of air. The tube was then placed in a preheated oven at 300 °C. After 2.5 h the tube was removed and cooled to room temperature. The contents were dissolved in chloroform, and some insoluble material was filtered off. The filtrate was dried over MgSO$_4$, and the solvent was removed under reduced pressure to give [5]helicene-7,8-dicarboxylic anhydride (**9**, 17−18 mg, 86−91%). This product has been previously characterized by IR, ^{1}H NMR, ^{13}C NMR, MS, HRMS, and DSC.[9]

Polymer Transformation. 1. Chemical Transformation Using Gaseous Bromine (Typical Procedure). A thin film of **5a** (0.01−0.03 mm thick, 50 mm × 10 mm) was placed in a glass tube (3 cm id × 15 cm) fitted with a vacuum outlet and a bromine inlet. The tube was evacuated with water aspiration and placed in a preheated oil bath at 180 °C and allowed to stand for 1 h. The vacuum source was disconnected and gaseous bromine (~50 mL) was let into the tube. Bromine and HBr were evacuated, and bromine was refilled every hour for a period of 4 h. After 4 h, IR showed the reaction to be complete and the tube was evacuated for a further 2 h, while being maintained at 180 °C. The tube was cooled to room temperature, and the film was removed.

2. Chemical Transformation Using Bromine in Solution (Typical Procedure). Polyimide **5a** (300 mg, 0.34 mmol) was dissolved in 15 mL of TCE in a 50 mL round-bottomed flask fitted with a dropping funnel and a reflux condenser. To this refluxing solution, a solution of bromine (130 mg, 0.72 mmol) in 5 mL of TCE was added dropwise over 30 min. White fumes evolved that were acidic to moist litmus. After 2 h, IR spectroscopy confirmed the reaction to be complete and the hot reaction mixture was poured into 200 mL of methanol. The resulting powder was filtered and stirred in 200 mL of methanol overnight. Polyimide **8a** (298 mg, 100%) was collected by filtration and dried under vacuum overnight (100 °C, 5 mmHg).

3. Thermal Transformation (General Procedure, Powder or Thin Film). The polyimide (100 mg) in a Pyrex dish (5 cm id., 0.75 cm deep) was placed in a preheated oven at 400 °C for 15 min, after which time the IR spectroscopy showed the reaction to be complete. The sample was removed and cooled to room temperature. The yield was quantitative.

Results and Discussion

Monomer Synthesis. We have previously described the large-scale (300 g) preparation of **1**.[9] The mononitration of symmetric **2a** and **2b** is the key to our synthetic route. Imidization of **1** before nitration was chosen because the dinitro compounds **3a** and **3b** were easier to purify than the mononitrated product of **1**. Imidization with the corresponding nitroaniline followed by selective mononitration gave the dinitro compounds in moderate yields. The pure dinitro **3a** and **3b** were not very soluble in common organic solvents, making spectroscopic characterizations difficult. Subsequent reduction with tin(II) chloride gave the unsymmetric diamines **4a** and **4b** in good yields. The diamines were bright orange amorphous solids and decomposed at 290 °C. They could be handled and purified in air for a prolonged period of time without showing signs of deterioration (i.e., no color change). The diamines **4a** and **4b** gave spectral data in excellent agreement with the proposed structures, including high-resolution mass spectrometry. The chemical shifts of the amino hydrogens were around 5.3 and 5.5 ppm. Even though **4a** and **4b** are unsymmetric, each amino group can be thought to have almost equal reactivity based on the chemical shift of the amino protons.[13] This leads to the formation of three possible diads (ca. head-to-head, tail-to-tail, or tail-to-head) in the polyimide backbone.[14]

Polyimide Synthesis. It was previously shown that tetrahydro[5]helicene polyimides have good solubility in organic solvents.[9] Therefore, one-step polymerizations were performed in *m*-cresol at 210 °C. Two dianhydrides (6FDA and *s*-BPDA) were polymerized with both **4a** and **4b** to produce a series of high molecular weight polyimides **5a**,**b** and **6a**,**b** (Figure 1). Polymerizations were stopped 2 h after a piece of flexible film could be cast from the polymerization solution. For the polyimides derived from 6FDA (**5a** and **6a**) the polymerizations went to completion after approximately 6 h, as indicated by GPC.

All the polyimides were obtained as slightly yellow fibrous powders. The UV/vis spectra of representative polymers **5a** and **6a** showed a maximum absorption at 370 nm in TCE. The cast thin films from TCE solution after drying were slightly darker and closer to yellow/orange in color. Table 1 lists the solubilities and inherent viscosities of polyimides **5a**,**b** and **6a**,**b**. Inher-

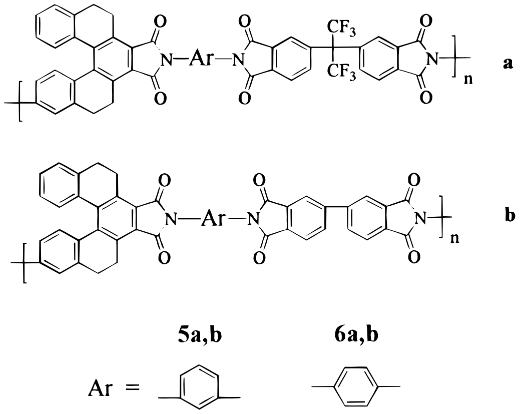


Figure 1. Polyimides **5a**,**b** and **6a**,**b** containing the tetrahydro[5]helicene unit.

Table 1. Solubilities and solution viscosities of tetrahydro[5]helicene-containing polyimides 5a,b and 6a,b[a]

	5a	5b	6a	6b
$[\eta]_{inh}$[b] (dL/g)	0.48	0.55	0.41	n/m[c]
$CHCl_3$	+	±	+	−
TCE	+	+	+	+
NMP	+	+	+	±
DMF	+	±	+	−
DMAc	+	±	+	±
DMSO	+	−	+	−
pyridine	+	+	+	±
chlorobenzene	±	−	±	−
conc. H_2SO_4	+	+	+	+

[a] Key: soluble (+), partially soluble (±), not soluble (−) at ambient temperatures (0.5 g/dL) [b] Measured in NMP solution (0.5 g/dL) at 30.0 °C. [c] n/m: not measured due to low solubility in NMP.

ent viscosities (0.41−0.48 dL/g, 0.5 g/dL in NMP) indicate that the polyimides are of high molecular weight. The polyimides showed good solubility in common organic solvents like TCE and NMP. The 6F-containing polyimides **5a** and **6a** were even soluble in chloroform and pyridine at ambient temperatures. GPC analysis showed a weight-average molecular weight of 80 000 for polyimide **5a** (**4a**/6FDA), relative to polystyrene standards. The apparent weight-average molecular weight (35 300) of polyimide **6a** (**4b**/6FDA) was relatively lower, even though their inherent viscosities were almost the same (0.48 dL/g for **5a** and 0.41 dL/g for **6a**).

To estimate absolute molecular weight, end-capped polyimide **7** was synthesized using 4-*tert*-butylphthalic anhydride as an end-capping agent (Figure 2). Polymer **7** had the same inherent viscosity as the corresponding uncapped polymer **5a** (0.48 dL/g in NMP at 30.0 °C) and the same apparent molecular weight by GPC (M_w = 71 900, M_n = 40 900). The resonance at 1.40 ppm in the ^{1}H NMR spectrum (400 MHz, TCE-d_2) of polymer **7** was assigned to the *tert*-butyl group, supported by correlation (using HETCOR spectroscopy) with the *tert*-butyl resonance in the ^{13}C NMR spectrum. The *tert*-butyl resonance was integrated relative to the resonance at 4.16 ppm corresponding to one proton in each of the ethylene bridges of the tetrahydro[5]helicene unit (or two protons per repeat unit). Based on the NMR data, calculation showed that polyimide **7** on average contained 69 repeat units or had a number-average molecular weight of 60 500. Since the polyimides **5a**,**b** and **7** derived from **4a** had similar solution viscosities, they should have number-average molecular weights of about 60 000.

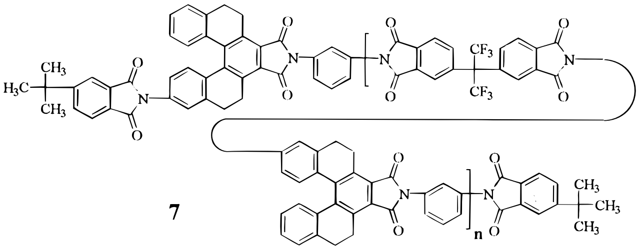


Figure 2. End-capped polyimide **7**.

Table 2. Thermal Properties and Young's Moduli of Polyimides 5a,b and 6a,b

		5a	5b	6a	6b
T_d[a] (°C)	N_2	471	498	490	491
	air	439	463	432	*g*
T_g (°C)	TMA[b]	*e*	380	386	*f*
	ODSC[c]	371	365	384	*g*
E' [d] (GPa)		1.99	0.40	0.59	*f*

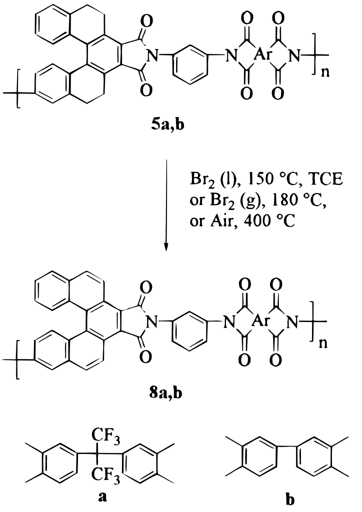
[a] Onset temperature for 5% weight loss, as assessed by TG at a heating rate of 10 °C/min. [b] Taken as a maximum of tan δ and measured on a 2 × 10 mm thin film at a heating rate of 3 °C/min. [c] Observed on the C_p curve of the ODSC scan. [d] Young's modulus at 25 °C measured by TMA on a 2 × 10 mm thin film in static air. [e] A maximum of tan δ was not observed. [f] Thin film was too brittle for measurement. [g] Not measured.

The thermal and mechanical properties of **5a**,**b** and **6a,b** (Table 2) were assessed by oscillating differential scanning calorimetry (ODSC), thermogravimetry (TG), and thermomechanical analysis (TMA). Polyimide **6b** could not produce a solution cast film because of limited solubility. The glass transition temperatures (T_g) for these polyimides were not detectable using standard DSC experiments but were detectable in the deconvoluted ODSC scan and were also detected by DMA. During the DMA experiment a loss of modulus could clearly be seen in the E' curve and the T_g was taken as a maximum in the tan δ curve. The T_g values were in the range 368−386 °C by ODSC and DMA. For polymer **5b** (**4a**/*s*-BPDA) only a very weak tan δ peak was observed, presumably because of its rigid structure. The T_g values taken as a maximum of tan δ in the TMA experiment were in good agreement with the T_g values observed by ODSC, with the exception of one case. A maximum of tan δ could not be observed for polymer **5a** (**4a**/6FDA) because of a change in modulus that occurred at the glass transition. The E' curve shows clearly a loss of modulus followed by a sharp increase in modulus above T_g. While this behavior was characteristic for this series of polymers, this was the only case where an increase in modulus occurred before a maximum of tan δ was observed. This increase in modulus was not retained upon slow cooling of the polymer film to room temperature.

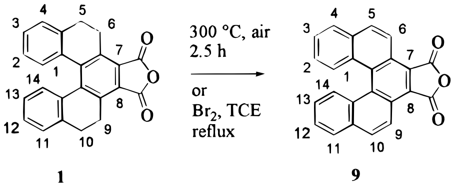
All four polyimides (**5a**,**b** and **6a**,**b**) showed high thermal stability in nitrogen and decreased thermooxidative stability in air (Table 2). An isothermal aging experiment was conducted on polymer **5a** (**4a**/6FDA) for 4 days in nitrogen (200 mL/min). On extended heating at 400 °C, the resulting rate of mass loss was found to be 1.5%/day (0.06%/h).

Young's modulus measurements at 25 °C showed that polyimides **5b** and **6a** had unusually low moduli (E' = 0.40−0.59 GPa), whereas polymer **5a** had a Young's modulus of 1.99 GPa (Table 2) comparable to most known polyimides. The thin film of **5b** (**4a**/*s*-BPDA) was somewhat brittle and could not be folded or creased without breaking.

Scheme 3. Chemical and Thermal Transformation of Precursor Polyimides 5a,b to [5]Helicene-Containing Polyimides 8a,b



Scheme 4. Chemical and Thermal Transformation of Model Compound 1 to Compound 9



Polymer Transformation. 1. Chemical Transformation. We have previously reported the use of elemental bromine at elevated temperatures to effect the chemical transformation of tetrahydro[5]helicene to [5]helicene (Schemes 1 and 4). The technique has been shown not to leave bromine within the polyimide.[9] The two precursor polymers **5a**,**b** were chosen in this work because they were of high molecular weight and were soluble enough to cast into a thin film from TCE solution. The resulting [5]helicene-containing polyimides **8a**,**b** were otherwise unattainable by direct polymerization of a [5]helicene-containing diamine and a dianhydride. For example, polycondensation 6FDA with the corresponding diamine afforded only oligomeric **8a**.[9]

Bromine was effective in quantitatively transforming precursor polyimides **5a**,**b** to [5]helicene-containing polyimides **8a**,**b** (Scheme 3). The transformation could be effected by treatment of either the polyimide thin film with an excess of gaseous bromine at 180 °C or a TCE solution of the polyimide with a slight excess of liquid bromine. The complete conversion of the tetrahydro[5]helicene unit in the precursor polymers was verified by IR spectroscopy. Upon aromatization, the corresponding [5]helicene polyimides showed the complete disappearance of the C−H aliphatic stretch (near 2800 cm^{-1}) in their IR spectra.

It is expected that the wholly aromatic [5]helicene-based polyimide would possess a greater thermal stability than the precursor polyimides containing aliphatic moieties. There was only a slight increase in the thermal stability of polyimides **8a**,**b** in a nitrogen atmosphere, but a rather large increase in air (Tables 2 and 3) as compared to **5a**,**b**. For example, the thermooxidative stability increased quite dramatically upon chemical transformation of **5a** to **8a**, as indicated by the onset temperature for 5% weight loss in air increasing from 439 °C for **5a** to 512 °C for **8a**.

Table 3. Comparison of Thermal Stabilities of Polyimides 5a,b and 8a,b

		5a	8a	ΔT	5b	8b	ΔT
$T_d{}^a$ (°C)	N$_2$	471	515	44	498	529	31
	air	439	515	76	463	531	68

[a] Onset temperature for 5% weight loss as assessed by TG.

There was no change in the Young's modulus of **5a** upon transformation to **8a** (1.99 GPa), indicating that the polymer transformation did not result in any chain cleavage or cross-linking. Due to the meta catenation and 6F linkage, polyimide **8a** can be expected to be the most flexible in this series of polyimides. For the more rigid **8b**, the film after chemical transformation became very brittle and the modulus could not be measured. This indicates that the introduction of the wholly aromatic [5]helicene unit can greatly increase the stiffness of the polyimide backbone.

Certainly, bromine is not the only reagent that can convert tetrahydro[5]helicene to [5]helicene. It is known that 9,10-dihydrophenanthrene, which constitutes part of the tetrahydro[5]helicene unit, can be oxidized to phenanthrene using a variety of oxidizing agents. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and nitrobenzene or elemental oxidizing agents such as S, Se, and Te have been used in the aromatization of 9,10-dihydrophenanthrene and its analogues.[15] In the case of dehydrogenation using sulfur, the mechanism is thought to involve radical abstraction of the benzylic hydrogen by a sulfur radical.[15] A similar mechanism likely plays a role in the aromatization of tetrahydro[5]helicene, as in the case of the transformation of 5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic anhydride to [5]helicene-7,8-dicarboxylic anhydride using bromine.[9] At elevated temperatures, bromine homolytically cleaves to generate a bromine radical, which can abstract a benzylic hydrogen atom and substitute at the same position. Thermal elimination of HBr results in aromatization. It has also been shown that the same transformation can be effected using a stoichiometric amount of *N*-bromosuccinimide in TCE solution at 140 °C.[16]

2. Thermal Transformation. It is likely that oxygen may also effect the transformation of tetrahydro[5]helicene to [5]helicene, given that oxygen at high temperatures would also abstract a benzylic hydrogen atom. To this end, 5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic anhydride (**1**) was placed in a sealed tube containing air and heated at 300 °C for 2.5 h (Scheme 4). Compound **1** was converted to [5]helicene-7,8-dicarboxylic anhydride (**9**) in high yield in the presence of oxygen. Confirmation of the thermal transformation was done using ^{1}H NMR (400 MHz, CDCl$_3$). Assignment of the individual proton resonances of **1** was done using the COSY and NOESY experiments, the details of which are supplied in the Supporting Information for this article.

Simple heating in air was also sufficient to transform tetrahydro[5]helicene-containing polyimides **5a**,**b** to [5]helicene-containing polyimides **8a**,**b**. The transformation was confirmed using FTIR. The IR spectra of the transformed polymer powder of **5a** shows the characteristic disappearance of the aliphatic C−H stretch around 2800 cm^{-1}, as described earlier.[9] When the IR spectrum of polyimide **8a**, made by thermal treatment of **5a**, is compared with oligomeric **8a**, the fingerprint

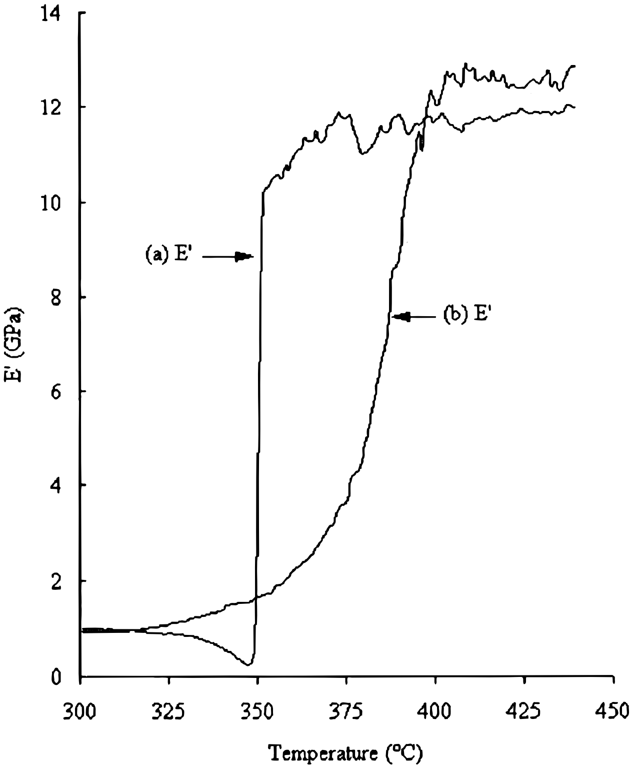


Figure 3. TMA curves of polyimide **5a**: (a) first scan; (b) second scan.

region of **8a** is superimposable on the same region of oligomeric **8a** (obtained by direct polycondensation).[9] Furthermore, a powder of polyimide **5a** was shown to be unaffected by heating in nitrogen at 400 °C for 15 min, as confirmed by IR.

Thermal transformation also occurred, when a film of **5a** was subjected to repeated heating to 450 °C in static air during DMA analyses (Figure 3). In the first scan (from 25 to 450 °C), polyimide **5a** displayed a glass transition as indicated by a loss of modulus and an increase in the tan δ curve (not shown). On second scanning no glass transition was observed; however, the film still showed a large increase in modulus (Figure 3). It is known that oligomeric **8a** had no glass transition below 450 °C by ODSC analysis. The IR spectrum of the thin film of **5a** after the first DMA measurement did not show the characteristic aliphatic C—H bands at 2800 cm^{-1}. Similar results were obtained using polyimide **5b**, which could also be converted by heating in air to **8b**, as confirmed by IR.

Conclusion

The tetrahydro[5]helicene-containing polyimides derived from diamines **4a** and **4b** showed good solubility in common solvents and good thermal properties. These precursor polyimides were then transformed into polyimides containing the more rigid [5]helicene unit by chemical treatment (in solution or solid state) or by heating (in the solid state) at temperatures around 400 °C in air. The transformed polyimides showed a marked increase in thermooxidative stability and solvent resistance. This thermooxidative transformation method may be applicable to other air oxidizable systems.

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Supporting Information Available: Textual material regarding the confirmation of **4a**,**b** and of the transformation of **1** to **9**, ^{1}H NMR spectra of **1** and **9**, and the NOESY spectrum of **9** (5 pages). Ordering information is on any current masthead.

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