

Syntheses and Properties of Polyamides from Ether Diacid Having the Spirobichroman Unit

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ABSTRACT: A novel hexamethylspirobichroman (HMSBC) unit-containing dicarboxylic acid, 6,6'-bis(4-carboxyphenoxy)-4,4,4',4',7,7'-hexamethyl-2,2'-spirobichroman (**3**), was derived from nucleophilic substitution of *p*-fluorobenzonitrile with the phenolate ion of 6,6'-dihydroxy-4,4,4',4',7,7'-hexamethyl-2,2'-spirobichroman (**1**), followed by alkaline hydrolysis of the intermediate bis(ether nitrile). Using TPP and pyridine as condensing agents, a series of polyamides with inherent viscosities in the range of 0.82–1.14 dL/g were prepared by the direct polycondensation of dicarboxylic acid **3** with various aromatic diamines. All the obtained polymers were noncrystalline and soluble in various organic solvents such as *N,N*-dimethylacetamide (DMAc) and *N*-methyl-2-pyrrolidone (NMP). Except for the polymer derived from benzidine, the other polyamides could be solution cast into transparent and tough films, and their tensile strengths, elongations at break, and tensile moduli were in the range of 56–76 MPa, 4–59%, and 1.6–2.0 GPa, respectively. These polyamides had glass transition temperatures in the range of 183–200°C with 10% weight loss above 420°C. © 1997 John Wiley & Sons, Inc. *J Polym Sci A: Polym Chem* **35**: 1479–1486, 1997

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INTRODUCTION

Wholly aromatic polyamides have an attractive combination of high strength, high modulus, high dimensional stability, and thermal stability.^{1,2} However, because of the presence of rigid benzene ring and amide hydrogen bonding, most aromatic polyamides have high crystallinity, high melting or glass transition temperatures, and poor solubility in common organic solvents. Thus, they are difficult to process. Therefore, much effort^{3–10} has been spent on preparing soluble or tractable aromatic polyamides by changing the chemical na-

ture of the macrochain to some degree while maintaining their desired properties. Using ether-containing monomers such as bis(ether amine)s or bis(ether acid)s to prepare ether-containing polyamides is a commonly useful method. Various bis(ether amine)s^{7–12} or bis(ether acid)s^{13–17} could be prepared easily starting from aromatic nucleophilic substitution of a bis-phenoxide ion with an activated aromatic halide, such as *p*-chloronitrobenzene and *p*-fluorobenzonitrile.

The introduction of a spiro structure into the polymer backbone would be expected to facilitate less polymer–polymer interaction and increased main chain rigidity and, additionally, possibly less probability of main chain scission because of having multibonds. The present article reports a new dicarboxylic acid having the spirobichroman structure, 6,6'-bis(4-carboxyphenoxy)-4,4,4',4',7,7'-hexamethyl-2,2'-spirobichroman, and its de-

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rived new polyamides. The solubility, film forming ability, crystallinity, tensile properties and thermal properties of these polyamides are reported.

EXPERIMENTAL

Materials

6,6'-Dihydroxy-4,4',4',7,7'-hexamethyl-2,2'-spirobichroman (**1**) (TCI) and *p*-fluorobenzonitrile (TCI) were used as received. *N,N*-Dimethylformamide (DMF; Wako) was purified by distillation under reduced pressure over calcium hydride.

4,4'-Bis(4-aminophenoxy)biphenyl (**4g**; mp 198–199°C) was prepared by the aromatic nucleophilic substitution reaction of 4,4'-biphenol (Fluka) and *p*-chloronitrobenzene (TCI) in the presence of K_2CO_3 , giving a bis(*p*-nitrophenoxy) compound, followed by catalytic reduction by hydrazine and palladium.¹⁸ *p*-Phenylenediamine (**4a**; TCI) and benzidine (**4c**; TCI) were purified by sublimation. *m*-Phenylenediamine (**4b**; Janssen) was vacuum distilled before use. 4,4'-Oxydianiline (**4d**; TCI), 4,4'-methylenedianiline (**4e**; TCI), 1,4-bis(4-aminophenoxy)benzene (**4f**; TCI), and 4,4'-diaminobenzanilide (**4h**; Chriskev) were used without further purification.

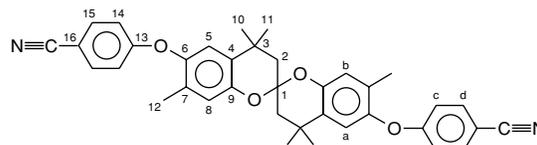
Calcium chloride was dried under vacuum at 180°C for 8 h prior to use. *N*-Methyl-2-pyrrolidone (NMP; TCI) and pyridine (Wako) were dehydrated by calcium hydride, distilled under reduced pressure, and stored over 4 Å molecular sieves. Triphenyl phosphite (TPP; Wako) was purified by distillation under reduced pressure.

Monomer Synthesis

Synthesis of HMSBC-Dinitrile **2**

HMSBC-diol **1** (10.3 g) was dissolved in a solution of DMF (40 mL) and toluene (70 mL) in a 300-mL round-bottomed flask equipped with a Dean–Stark trap. Anhydrous potassium carbonate (7 g) was added and the reaction mixture was heated until the solvent began to reflux at 140°C. Water (by-product of the reaction) was continuously removed via the Dean–Stark trap. The reflux temperature was maintained for 4–6 h until the accumulation of water was no longer evident in the Dean–Stark trap. Then the residual toluene was distilled off from the reaction system. The reaction mixture was allowed to cool to about 60°C, then *p*-fluorobenzonitrile (7 g) was added and the reac-

tion mixture was heated at a solvent reflux for a period of 4 h. The mixture was allowed to cool and subsequently added to water (300 mL) to precipitate a light yellow solid, which was collected by filtration and dried. The crude product was washed thoroughly with methanol to give 13.3 g (83%) of 6,6'-bis(4-cyanophenoxy)-4,4,4',4',7,7'-hexamethyl-2,2'-spirobichroman (**2**); m.p.: 242–243°C. IR (KBr): 2230 (C≡N str.), 1230, 1160 cm^{-1} (C—O str.) ¹H-NMR (CDCl₃): δ 7.58 (d, Hd, 4H), 6.96 (s, Hb, 2H), 6.90 (d, Hc, 4H), 6.63 (s, Ha, 2H), 2.12, 2.01 (AB doublets, —CH₂—, 4H), 2.01 (s, —CH₃ attached on the aromatic ring, 6H), 1.58, 1.32 ppm (s, —CH₃ attached on the aliphatic carbon, 12H). ¹³C-NMR (CDCl₃): δ 162.31 (C⁶), 147.63 (C⁹), 146.31 (C¹³), 134.13 (C¹⁵), 130.79 (C⁴), 129.38 (C⁷), 120.05 (C⁸), 118.93 (C⁵ and C≡N), 116.17 (C¹⁴), 104.82 (C¹⁶), 97.94 (C¹), 46.19 (C²), 32.29, 32.12 (C¹⁰, C¹¹), 30.82 (C³), 15.63 ppm (C¹²).

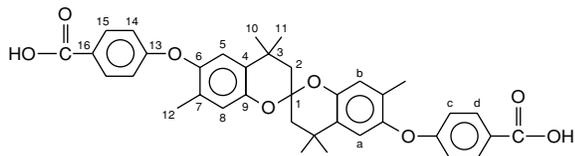


ANAL. Calcd for C₃₇H₃₄N₂O₄ (570.69): C, 77.87%; H, 6.00%; N, 4.90%. Found: C, 77.90%; H, 6.03%; N, 4.84%.

Synthesis of HMSBC-Diacid **3**

In a 500-mL flask were added dinitrile **2** (12 g, 0.02 mol), potassium hydroxide (25 g, 0.4 mol), and 1 : 1 volume mixture of water–ethanol (100/100 mL). The suspension was refluxed for 48 h to form a clear solution. The resulting hot clear solution was filtered to remove any insoluble impurities. After cooling, the filtrate was acidified by conc. HCl to pH = 2–3. The precipitated white product was collected on a filter, washed repeatedly with water until neutral, and dried in vacuum to give 9.8 g (77%) of 6,6'-bis(4-carboxyphenoxy)-4,4,4',4',7,7'-hexamethyl-2,2'-spirobichroman (**3**); m.p.: 358–363°C. IR (KBr): 2500–3500 (broad, O—H str.), 1682 (C=O str.), 1230, 1160 cm^{-1} (C—O str.). ¹H-NMR (DMSO-*d*₆): δ 7.92 (d, Hd, 4H), 7.14 (s, Hb, 2H), 6.87 (d, Hc, 4H), 6.66 (s, Ha, 2H), 2.14, 2.01 (AB doublets, —CH₂—, 4H), 1.96 (s, —CH₃ attached on the aromatic unit, 6H), 1.56, 1.30 ppm (s, —CH₃ attached on the aliphatic carbon, 12H). ¹³C-NMR

(DMSO- d_6): δ 166.71 (C=O), 161.85 (C⁶), 146.91 (C⁹), 146.29 (C¹³), 131.58 (C¹⁵), 130.50 (C⁴), 128.89 (C⁷), 124.10 (C¹⁶), 119.42 (C⁸), 119.20 (C⁵), 114.92 (C¹⁴), 97.69 (C¹), 45.06 (C²), 31.75 (C¹⁰, C¹¹), 30.30 (C³), 15.12 ppm (C¹²).



ANAL. Calcd. for C₃₇H₃₆O₈ (608.69): C, 73.01%; H, 5.96%. Found: C, 72.60%; H, 5.80%.

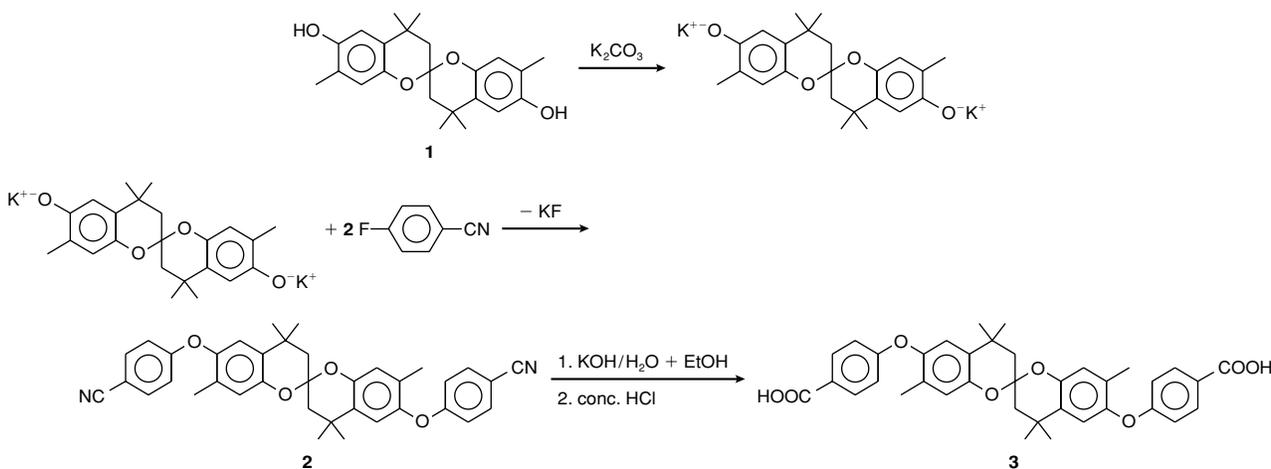
General Procedure for Polymer Synthesis

The synthesis and characterization of polyamide **5a** is described as a typical example:

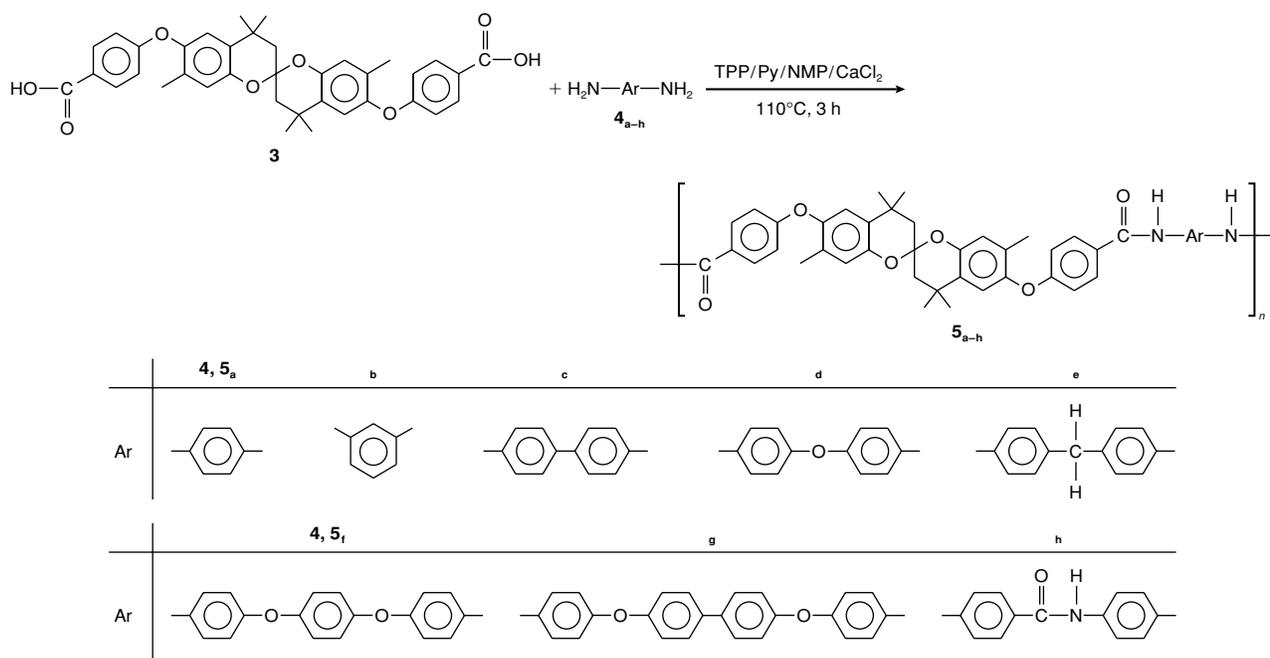
In a 50-mL flask, a mixture of HMSBC-diacid **3** (1.25 mmol, 0.7608 g), *p*-phenylenediamine (1.25 mmol, 0.1351 g), calcium chloride (0.3 g), triphenyl phosphite (TPP, 0.9 mL), pyridine (0.8 mL), and NMP (2.5 mL) was stirred at 110°C for 3 h. The resulting viscous reaction mixture was trickled slowly into stirring methanol to precipitate white fibrous product, which was washed thoroughly with methanol and hot water, collected on a filter, and dried. Yield: 0.88 g, 100%. The polymer had inherent viscosity of 0.90 dL/g, measured in DMAc containing dissolved 5 wt % LiCl on a concentration of 0.5 g/dL at 30°C. IR (film): 3312 (N—H str.), 1655 (C=O str.), 1226, 1170 cm⁻¹ (C—O str.).

Measurements

IR spectra were recorded with a Jasco FT/IR-7000 Fourier transform infrared spectrometer. ¹³C- and ¹H-NMR spectra were determined on a Jeol EX-400 NMR spectrometer (¹H: 399.65 MHz, ¹³C: 100.40 MHz) with perdeuterodimethyl sulfoxide (DMSO- d_6) as an external reference and with tetramethylsilane (TMS) as an internal reference, respectively. The inherent viscosities were measured with a Cannon–Fenske viscometer thermostated at 30°C. Differential scanning calorimetry (DSC) measurements were conducted using a Sinku Riko DSC-7000 coupled to a Sinku Riko TA-7000 thermal analyzer in flowing nitrogen of 30 cm³/min at a heating rate of 10°C/min. Glass transition temperatures were taken as the midpoint of the change in slope of the baseline on the second DSC heating trace after quick cooling prior to the scan. Thermogravimetry (TG) was conducted with a Rigaku Thermoflex TG-8110 coupled to a Rigaku TAS-100 thermal analysis station. Measurements were performed with 9–11 mg sample heated in flowing nitrogen or air of 50 cm³/min at a heating rate of 20°C/min. The wide-angle x-ray scattering measurements were carried out with a Rigaku Geiger Flex D-Max IIIa x-ray diffractometer, using Ni-filtered CuK α radiation (40 kV, 15 mA) and the scanning rate of 2°/min. Tensile properties were determined from stress–strain curves obtained by an Instron Universal tester Model 1130 with a load cell of 5 kg. A gauge of 2 cm and a crosshead speed of 5 cm/min were used here. The measurements were made at room temperature using solution-cast film speci-



Scheme 1.



mens (0.5 cm wide, 6 cm long, and about 0.1 mm thick), and an average of at least five individual determinations was used.

RESULTS AND DISCUSSION

Monomer Synthesis

According to the synthetic pathways outlined in Scheme 1, HMSBC-diacid **3** was prepared in good

Table I. Preparation Conditions and Inherent Viscosities of Polyamides Based on HMSBC-Diacid

Polymer	Amount of Reagents Used ^a				η_{inh}^b (dL/g)
	NMP (mL)	Py (mL)	TPP (mL)	CaCl ₂ (g)	
5a	3.0	0.8	0.9	0.3	0.90
5b	2.0	0.8	0.9	0.3	0.83
5c	3.5	0.8	0.9	0.3	1.03
5d	2.5	0.8	0.9	0.3	1.27
5e	3.0	0.8	0.9	0.3	0.94
5f	3.0	0.8	0.9	0.3	1.14
5g	4.5	1.0	0.9	0.4	0.82
5h	3.5	1.0	0.9	0.4	1.06

^a 1.25 mmol of each diacid and diamine monomer were used; reaction temperature = 110°C; reaction time = 3 h. Py: pyridine.

^b Measured at a concentration of 0.5 g/dL in DMAc-5 wt % LiCl at 30°C.

yield by a nucleophilic fluorodisplacement of *p*-fluorobenzonitrile with the dipotassium bisphenolate of HMSBC-diol **1**, giving the intermediate HMSBC-dinitrile **2**, followed by alkaline hydrolysis and acidification. The structures of compounds **2** and **3** were ascertained through elemental analysis and IR, ¹H-NMR, and ¹³C-NMR spectroscopy. The cyano group in compound **2** was evident from the peak at 2230 cm⁻¹ in the IR spectrum. While **2** was converted into **3**, the C≡N stretching vibration disappeared, but a broad O—H absorption appeared in the region of 2500–3500 cm⁻¹ and C=O stretching absorption appeared near 1688 cm⁻¹. The corresponding ¹³C-NMR spectra of dinitrile **2** and diacid **3** are reproduced in Figure 1. Almost all carbon atoms gave separate and assignable resonances. The most obvious features of the spectra are the shifts of the resonance signals for the cyano carbon and its adjacent carbon C¹⁶. The C¹⁶ of dinitrile **2** is shielded by the anisotropic field induced by the π electrons of C≡N, and, hence, C¹⁶ has resonance at higher field than the other aromatic carbons. After the cyano group was hydrolyzed to the carboxyl group, the resonance signal of C¹⁶ moved to lower field (from 104.82 to 124.10 ppm) due to the lack of anisotropic shielding, the original signal at 118.93 ppm assigned to cyano carbon disappeared, and the reso-

Table II. Solubility Behavior^a of Polyamides Based on HMSBC-Diacid

Polymer	Solvent ^b					
	DMAc	NMP	DMF	DMSO	<i>m</i> -Cresol	THF
5a	+	+	+	+	+	—
5b	+	+	+	+	+	+
5c	+	+	—	—	—	—
5d	+	+	+	+	+	—
5e	+	+	+	+	+	+
5f	+	+	+	+	+	+
5g	+	+	+	+h	+	+
5h	+	+	—	—	—	—

^a +: soluble at room temperature; +h: soluble on heating; —: insoluble even on heating.

^b DMAc: *N,N*-dimethylacetamide; NMP: *N*-methyl-2-pyrrolidone; DMF: *N,N*-dimethylformamide; DMSO: dimethyl sulfoxide; THF: tetrahydrofuran.

nance of carbonyl carbon occurred at the farthest downfield (166.71 ppm).

Polymers Synthesis

The polyamides were synthesized by the Yamazaki–Higashi direct polycondensation method.¹⁹ By using TPP and pyridine as condensing agents, dicarboxylic acid **3** was directly polycondensated with various aromatic diamines **4a–i** in the NMP solution containing dissolved CaCl₂ (Scheme 2). According to the reaction conditions listed in Table I, all polycondensation reactions proceeded homogeneously throughout the reaction forming transparent and viscous polyamide solutions. The polyamides were isolated as white fibers upon precipitation in methanol, and they had inherent viscosities in the range of 0.82–1.14 dL/g. The structure of the polyamides was verified by IR spectroscopy. The polyamide displays characteristic absorbances of amide group near 3310 (N—H

str.) and 1655 cm⁻¹ (C=O str.), and of ether linkage between 1220–1170 cm⁻¹.

Properties of Polymers

As shown in Table II, all the polyamides were soluble in polar solvents such as DMAc and NMP. Except for polyamides **5c** and **5h**, the other polyamides were also soluble in DMF and DMSO, and in less polar *m*-cresol. Some of them were even soluble in THF. The high solubility can be attributed to the presence of ether links and bulky non-linear HMSBC-structure, which disrupts chain packing and intermolecular hydrogen bonding. The crystallinity of the prepared polyamides was evaluated by wide-angle x-ray diffraction measurements. It was found that all the polyamides showed a completely amorphous diffraction pattern due to the reasons cited above.

Except for polyamide **5c**, the other polyamides could be solution cast into flexible, creasable films

Table III. Tensile Properties of HMSBC-Polyamide Films^a

Polymer	Strength at Yield Point (MPa)	Strength at Break Point (MPa)	Elongation at Break Point (%)	Initial Modulus (GPa)
5a	—	56	4	2.1
5b	—	76	8	2.0
5d	72	73	59	1.8
5e	72	73	63	1.7
5f	73	65	16	1.7
5g	—	75	7	1.6
5h	—	73	9	2.0

^a Films were cast from polymer solutions of DMAc.

from the given solvents. The tensile properties of the DMAc-casted films of these polymers are given in Table III. They have yield or tensile strengths in the range of 56–76 MPa and initial moduli in the 1.6–2.1 GPa range. Elongations-to-break are relatively low (4–16%), except for polymers **5d** and **5e**, which show distinct yield points in their stress–strain curves and moderate elongation-to-break (59–63%).

The thermal properties of polyamides **5a–h** were determined by differential scanning calorimetry (DSC) and thermogravimetry (TG). Figure 2 shows typical TG curves for the representative polyamide **5a** in air and in nitrogen. Polyamide **5a** started to lose weight around 400°C. In nitrogen, this polymer had a char yield of 46.3% at 800°C. The polyamide showed a two-step weight loss profile in air. It appeared that they first lost their aliphatic segments and then underwent degradation of the aromatic residues. As shown in Table IV, the temperature at which their 10% weight losses occurred ranged from 419 to 437°C in air and from 419 to 438°C in nitrogen. Their char yields at 800°C in nitrogen were in the range of 40.6–52.1%.

Glass transition temperatures (T_g) of these polyamides were determined from the DSC thermograms of samples that had been heated to 300°C and rapidly quenched prior to the run. The DSC thermograms of structurally rigid polyamides **5c** and **5h** did not show any discernible baseline shifts. The other polyamides showed a strong glass transition in the 201–221°C range on their

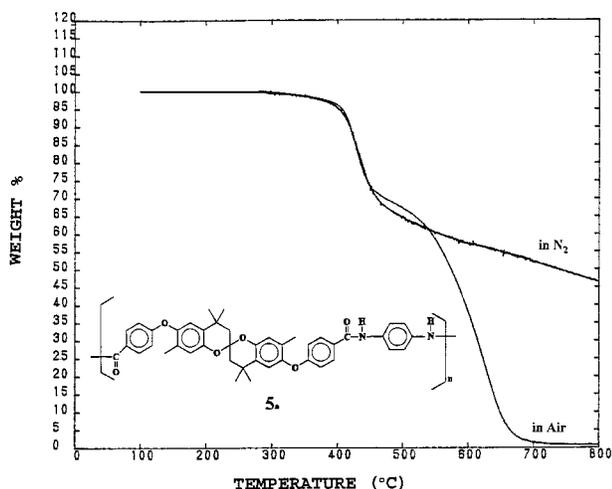


Figure 2. TG curves of polyamide **5a** in air and nitrogen (heating rate: 20°C/min).

Table IV. Thermal Properties of Polyamides Based on HMSBC-Diacid

Polymer	T_g^a (°C)	Decomposition Temperature ^b (°C)		Char Yield ^c (%)
		in N ₂	in Air	
5a	221	419	419	46.5
5b	209	419	432	42.7
5c	— ^d	435	436	47.2
5d	212	426	432	40.6
5e	201	423	430	48.1
5f	207	434	432	42.8
5g	201	438	437	52.1
5h	—	423	425	43.9

^a Base line shift in the second heating DSC trace, with a heating rate of 10°C/min in nitrogen.

^b Temperature at which 10% weight loss was recorded by TG at a heating rate of 20°C/min.

^c Residual wt % at 800°C in nitrogen.

^d No discernible transitions was observed.

second DSC heating traces. The large window between T_g and the decomposition temperature makes these polymers attractive for practical processing.

CONCLUSIONS

A novel dicarboxylic acid, 6,6'-bis(4-carboxyphenoxy)-4,4,4',4',7,7'-hexamethyl-2,2'-spirobichroman (HMSBC-diacid **3**), was prepared in high yields and high purity by nucleophilic substitution of 6,6'-dihydroxy-4,4,4',4',7,7'-hexamethyl-2,2'-spirobichroman with *p*-fluorobenzonitrile, followed by alkaline hydrolysis of the intermediate dinitrile. A series of novel polyamides with high molecular weights have been prepared by direct polycondensation of diacid **3** with various aromatic diamines by means of triphenyl phosphite and pyridine. Due to the presence of the bulky, nonlinear spirobichroman structure in the polymer backbone, the prepared polyamides are noncrystalline and are readily soluble in various organic solvents, which is very convenient for their processing. Flexible and tough films have been obtained by solvent casting. They showed a reasonable thermal stability and a large window between decomposition and glass transition temperatures. Thus, these polymers may be potential

condidates for high-performance thermoplastic materials.

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