Synthesis and Properties of Polyimides, Polyamides and Poly(amide-imide)s from Ether Diamine Having the Spirobichroman Structure

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ABSTRACT: A novel spirobichroman unit containing dietheramine, 6,6′-bis(4-aminophenoxy)-4,4,4′,4′,7,7′-hexamethyl-2,2′-spirobichroman (3), was prepared by the nucleophilic substitution of 6,6′-dihydroxy-4,4,4′,4′,7,7′-hexamethyl-2,2′-spirobichroman with p-chloronitrobenzene in the presence of K_2CO_3 followed by hydrazine catalytic reduction of the intermediate dinitro compound. A series of polyimides were synthesized from diamine 3 and various aromatic dianhydrides by a conventional two-stage procedure through the formation of poly(amic-acid)s followed by thermal imidization. The intermediate poly(amic-acid)s had inherent viscosities of 1.00–2.78 dL/g. All the poly-(amic-acid)s could be thermally cyclodehydrated into flexible and tough polyimide films, and some polyimides were soluble in polar solvents such as N-methyl-2-pyrrolidone (NMP), N,N-dimethylacetamide (DMAc), and N,N-dimethylformamide (DMF). These polyimides had glass transition temperatures (T_g) in the range of 236–256°C, and 10% weight loss occurred up to 450°C. Furthermore, a series of polyamides and poly(amide-imide)s with inherent viscosities of 0.71–2.29 dL/g were prepared by direct polycondensation of the diamine 3 with various aromatic dicarboxylic acids and imide ring-containing dicarboxylic acids by means of triphenyl phosphite and pyridine. All the polyamides and poly(amide-imide)s were readily soluble in polar solvents such as DMAc, and tough and flexible films could be cast from their DMAc solutions. These polymers had glass transition temperatures in the range of 137–228°C and 10% weight loss temperatures in the range of 419–443°C in air and 404–436°C in nitrogen, respectively. © 1997 John Wiley & Sons, Inc. J Polym Sci A: Polym Chem 35: 1487–1497, 1997
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INTRODUCTION

Aromatic polyimides and polyamides have high thermal stability and an unique combination of other properties, and find uses in high-strength/high-modulus fibers and engineering resins.[1–7] Drawbacks of these polymers are their insolubility and intractability, which cause difficulties in

both synthesis and processing. This problem is circumvented in polyimides, especially in thin film formation, through processing of the soluble poly(amic-acid) precursors. High T_g resins are often made more tractable through the incorporation of flexibilizing groups and bulky units in the polymer backbone.[8–21] Solubility, glass transition temperature, and crystallinity can be adjusted by varying the nature of aromatic ring systems and the number of flexible linkages within the polymer main chain.

The introduction of a spiro structure into the polymer backbone would facilitate less polymer–
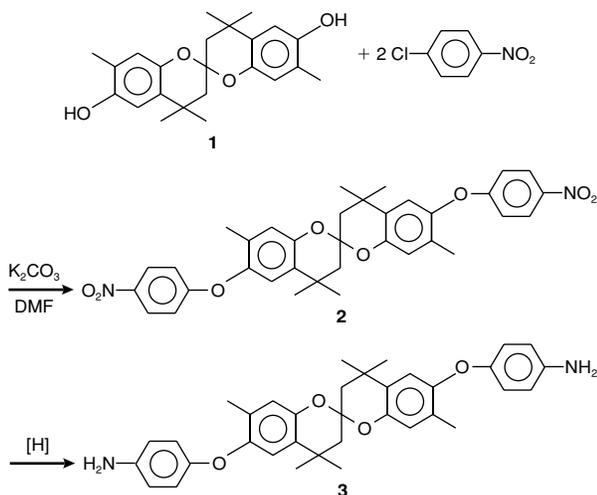
Scheme 1. Preparation of HMSBC-diamine.

polymer interaction and increased main chain rigidity and additionally, possibly a lower probability of main chain scission because of having multibonds. The objective of this research is to prepare and characterize the hexamethylspirobichroman (HMSBC) moiety-containing polyimides, polyamides, and poly(amide-imide)s on the basis of 6,6′-bis(4-aminophenoxy)-4,4,4′,4′,7,7′-hexamethyl-2,2′-spirobichroman (**3**) with various aromatic dianhydrides, dicarboxylic acids, and imide ring-containing dicarboxylic acids.

EXPERIMENTAL

Materials

6,6′-Dihydroxy-4,4,4′,4′,7,7′-hexamethyl-2,2′-spirobichroman (HMSBC-diol **1**) (TCI), p-chloronitrobenzene (TCI), 10% palladium on charcoal (Pd/C, Fluka), and hydrazine monohydrate (Wako) were used as received. N,N-Dimethylformamide (DMF, Wako), N,N-dimethylacetamide (DMAc), and pyridine were purified by distillation under reduced pressure in the presence of calcium hydride and stored over 4 Å molecular sieves. Triphenyl phosphite was purified by vacuum distillation. Calcium chloride (Wako) was dried under vacuum at 180°C for 10 h.

Reagent-grade aromatic tetracarboxylic dianhydrides such as 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA; **4b,** Oxychem), diphenylsulfone-3,3′,4,4′-tetracarboxylic dianhydride (DSDA; **4e,** New Japan Chemicals Co.), 4,4′-oxydiphthalic anhydride (ODPA; **4c,** Oxychem), and

2,2′-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA; **4f,** Chriskev) were used as received. Pyromellitic dianhydride (PMDA; **4a,** Aldrich) and 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA; **4d,** Aldrich) were recrystallized from acetic anhydride prior to use.

Dicarboxylic acids such as terephthalic acid (**7a;** Wako), isophthalic acid (**7b;** Wako), 5-tert-butylisophthalic acid (**7c;** Aldrich), 4,4′-biphenyldicarboxylic acid (**7d;** TCI), 4,4′-oxydibenzoic acid (**7e;** TCI), 4,4′-sulfonyldibenzoic acid (**7f;** New Japan Chemical Co.), 4,4′-hexafluoroisopropylidenedibenzoic acid (**7g;** Chriskev), and 2,6-naphthalenedicarboxylic acid (**7h;** TCI) were used without further purification. 4,4′-(1,4-Phenylenedioxy)dibenzoic acid (**7i**) and 4,4′-(1,3-phenylenedioxy)dibenzoic acid (**7j**) were prepared by the condensation of the potassium phenolate of hydroquinone and resorcinol, respectively, with p-fluorobenzonitrile, giving the corresponding bis(ether-nitrile)s, followed by alkaline hydrolysis.[22] The imide ring-bearing dicarboxylic acids **7k–o** were prepared by condensation of the corresponding amino acids such as p-aminobenzoic acid, m-aminobenzoic acid, glycine, 6-aminocaproic acid, and 11-aminoundecanoic acid with trimellitic anhydride.[23,24] The two imide rings-preformed dicarboxylic acids **7p** and **7q** were prepared by the condensation of the 4,4′-oxydianiline and hexamethylenediamine with trimellitic anhydride in a mole ratio 1 : 2, respectively.[25]

Monomer Synthesis

6,6′-Bis(4-nitrophenoxy)-4,4,4′,4′,7,7′-hexamethyl-2,2′-spirobichroman (HMSBC–Dinitro Compound 2)

In a 250-mL flask, 9.8 g (0.0266 mol) of 6,6′-dihydroxy-4,4,4′,4′,7,7′-hexamethyl-2,2′-spirobi-
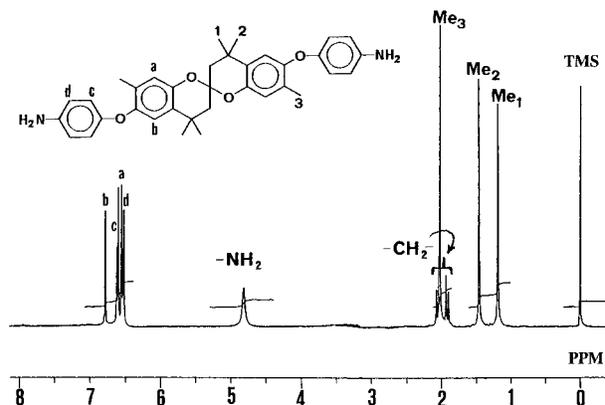
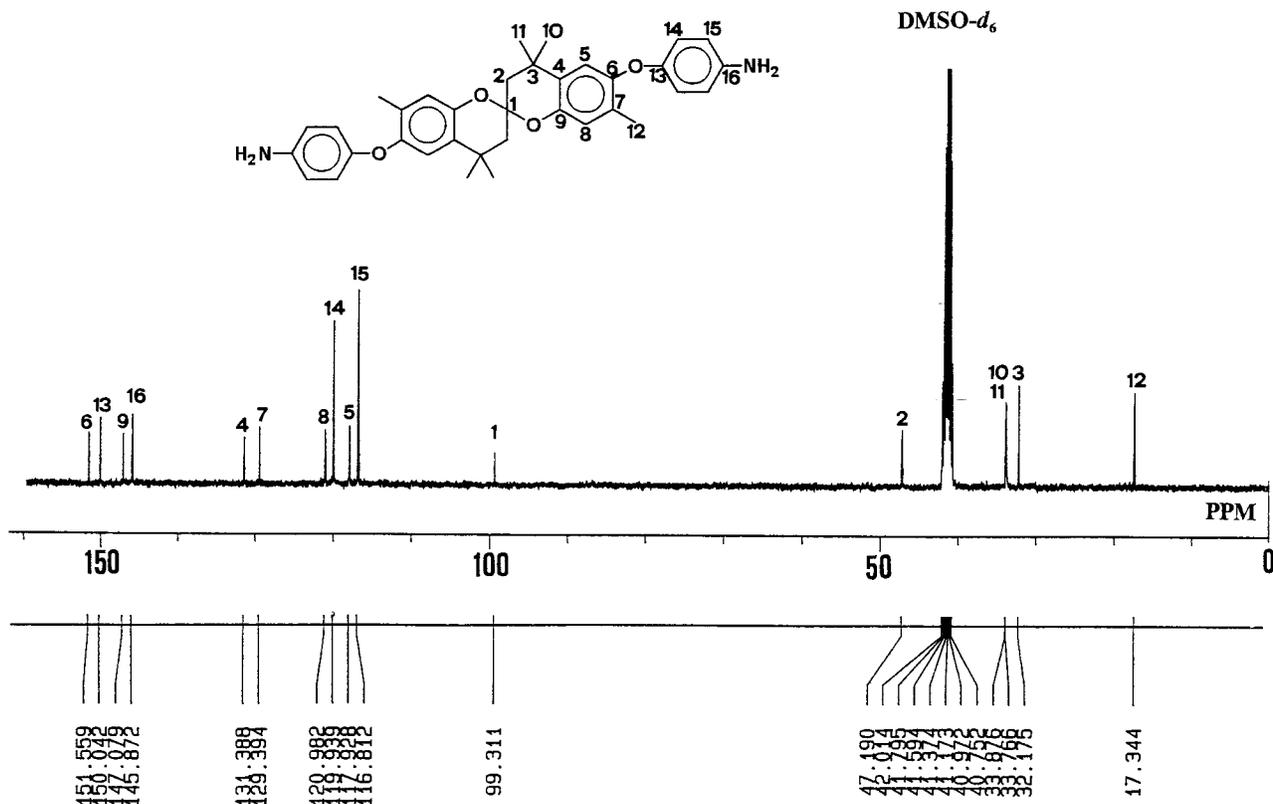**Figure 1.** The 400 MHz ^{1}H-NMR spectrum of HMSBC-diamine **3** in DMSO-d_6.

Figure 2.   The 100 MHz ^{13}C-NMR spectrum of HMSBC-diamine **3** in DMSO-d_6.

chroman (**1**) and 8.5 g (0.054 mol) of p-chloronitrobenzene were dissolved in 125 mL of dry DMF. Then, 8.3 g (0.06 mol) of anhydrous potassium carbonate (K_2CO_3) was added, and the suspension solution was refluxed at 150°C on an oil bath for 6 h. The mixture was allowed to cool and poured into 200 mL of 1 : 1 ethanol–water to precipitate a yellow solid, which was collected by filtration and washed thoroughly by methanol and water. The crude product was recrystallized from DMF, collected by filtration, and dried, giving a light yellow crystalline dinitro compound **2.** Yield: 14.6 g (90%); m.p. 256–258°C. IR (KBr): 1342 (sym. —NO_2 str.), 1593 cm^{-1} (asym. —NO_2 str.).

ANAL. Calcd for $C_{35}H_{34}N_2O_8$ (610.66): C, 68.84%; H, 5.61%; N, 4.59%. Found: C, 68.69%; H, 5.69%; N, 4.52%.

6,6′-Bis(4-aminophenoxy)-4,4,4′,4′,7,7′-hexamethyl-2,2′-spirobichroman (HMSBC–Diamine 3)

A mixture of 11 g (0.018 mol) of dinitro compound **2,** 0.1 g of 10% Pd/C, 200 mL of ethanol and 50 mL of hydrazine monohydrate was stirred at 100°C for 5 h forming a transparent solution. The resulting hot solution was filtered to remove Pd/C. After cooling, the precipitated white needle crystals of diamine **3** were isolated by filtration, washed by ethanol, and dried under vacuum at 100°C. Yield: 24 g (74.2%); m.p. 211–212°C. IR (KBr): 3434, 3358 (N—H str.), 1164, 1207 cm^{-1} (C—O str.). ^{1}H-NMR (DMSO-d_6): δ 1.20, 1.50 (s,

Table I.   Inherent Viscosity of Poly(amic acid)s and Polyimides Based on HMSBC-Diamine

Polymer	η_{inh}^a of Poly(amic-acid) (dL/g)	η_{inh}^a of Polyimide (dL/g)
5,6a	2.26	0.92
5,6b	2.02	—^{b}
5,6c	2.78	—^{b}
5,6d	1.32	—^{b}
5,6e	1.00	0.93
5,6f	2.60	1.03

^{a} Measured at a concentration of 0.5 g/dL in DMAc at 30°C using an Ubbelohde viscometer.
^{b} Insoluble in DMAc.
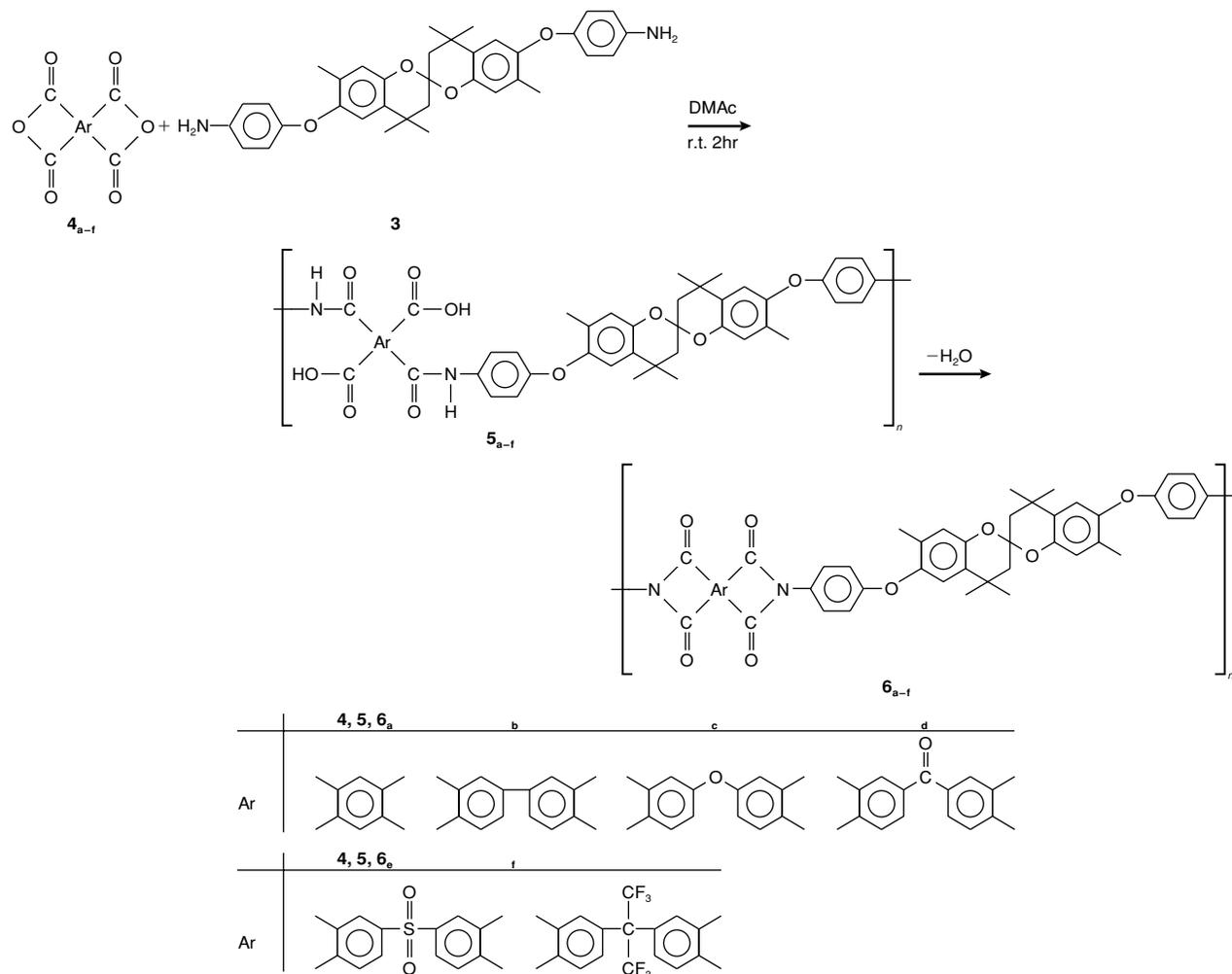
Scheme 2. Preparation of HMSBC-polyimides.

methyl groups attached on the aliphatic carbon), 2.03 (s, methyl groups attached on the aromatic unit), 1.93, 2.04 (d, —CH$_2$—), 4.70 (—NH$_2$), 6.47–6.78 ppm (aromatic protons). ^{13}C-NMR (DMSO-d_6): 151.56, 150.04, 147.08, 145.87, 131.39, 129.39, 120.98, 119.94, 117.93, 116.81 (aromatic carbons), 99.31 (spiro carbon), 47.19 (methylene carbons), 33.88, 33.77 (methyl carbons; methyl groups attached on the aliphatic carbon), 32.17 (quaternary carbon), 17.34 ppm (methyl carbons; methyl groups attached on the aromatic unit).

ANAL. Calcd for C$_{35}$H$_{38}$N$_2$O$_4$ (550.58): C, 76.35%; H, 6.95%; N, 5.08%. Found: C, 76.23%; H, 6.84%; N, 4.75%.

Polymer Synthesis

Polyimides

The synthesis of poly(amic-acid) **5a** and polyimide **6a** is described as a typical example: 0.2837 g (1.30 mmol) of PMDA (**4a**) was slowly added to a stirred solution of 0.7162 g (1.30 mmol) of HMSBC–diamine **3** in 9.5 mL (about 9 g) of dry DMAc. The solution was continuously stirred at room temperature for 2 h after the complete addition of PMDA, and a highly viscous poly(amic-acid) **5a** solution of 10 wt % solid was obtained. Its inherent viscosity in DMAc was 2.26 dL/g, measured at a concentration of 0.5 g/dL at 30°C. The obtained poly(amic-acid) solution was spread on a clean and heat-resistant glass dish, which was placed in a 90°C oven for 12 h to remove the solvent. The obtained semidried poly(amic-acid) film was further dried and transformed into polyimide by sequential heating: 120°C, 20 min; 150°C, 30 min; 180°C, 30 min; 200°C, 30 min; 250°C, 30 min. The film self-stripped from the glass substrate after cooling. IR spectrum of poly-(amic-acid) **5a** (film): 3000–3500 (broad, O—H and N—H str.), 1723, 1661 cm^{-1} (C=O str.).
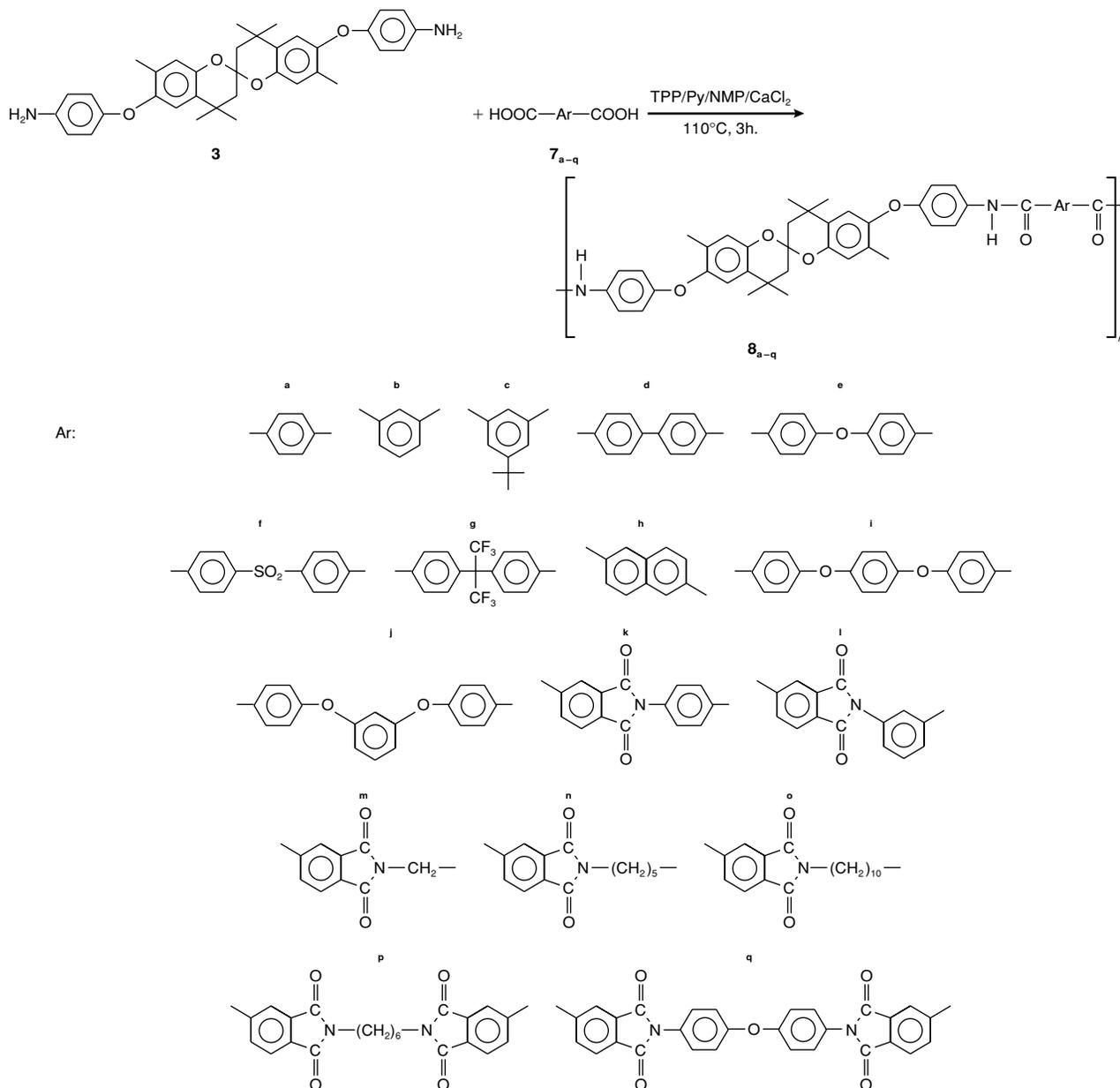
Scheme 3. Preparation of HMSBC-polyamides and poly(amide-imide)s.

IR spectrum of polyimide **6a** (film): 1779, 1729 (imide ring C=O asym. and sym. str.), 1379, 1118 (C—N str.), 1226, 1166 (C—O str.), 727 cm^{-1} (imide ring deformation).

All other HMSBC-poly(amic-acid)s and corresponding polyimide films were prepared by a similar manner.

Polyamides and Poly(amide-imide)s

The synthesis of polyamide **8a** is described as a typical example: A mixture of 0.2077 g (1.25 mmol) of terephthalic acid (**7a**), 0.6882 g (1.25 mmol) of diamine **3,** 0.3 g of calcium chloride, 0.9 mL of triphenyl phosphite (TPP), 0.8 mL of pyridine, and 2 mL of NMP was heated with stirring at 110°C for 3 h. The resultant polymer solution was trickled slowly into methanol giving rise to a white fibrous precipitate, which was washed thoroughly with methanol and hot water, collected by filtration and dried. Yield 0.79 g (99%). The inherent viscosity of the obtained polyamide **8a** in DMAc containing 5% LiCl was 0.79 dL/g, measured at a concentration of 0.5 g/dL at 30°C.

Table II. Preparation Conditions and Inherent Viscosities of Polyamides and Poly(amide-imide)s Based on HMSBC-Diamine

Polymer	Amount of Reagents Used[a]				η_{inh}^{b} (dL/g)
	NMP (mL)	Py (mL)	TPP (mL)	$CaCl_2$ (g)	
8a	2.0 + 1.0[c]	0.8	0.9	0.3	1.65
8b	2.0	0.8	0.9	0.3	0.79
8c	2.0	0.8	0.9	0.3	0.73
8d	3.0 + 3.0	1.0	0.9	0.5 (+0.2 g LiCl)	1.52
8e	2.5	0.8	0.9	0.3	0.90
8f	2.0 + 2.0	0.8	0.9	0.3	1.11
8g	2.5 + 1.0	0.8	0.9	0.3	1.18
8h	2.5 + 2.0	0.8	0.9	0.3	2.29
8i	2.5	0.8	0.9	0.3	1.23
8j	2.5	0.8	0.9	0.3	1.09
8k	3.0	1.0	0.9	0.3	0.91
8l	3.0	1.0	0.9	0.4	1.02
8m	3.0	1.0	0.9	0.4	1.05
8n	3.0	1.0	0.9	0.4	1.15
8o	3.0	1.0	0.9	0.4	0.71
8p	3.0	1.0	0.9	0.4	1.25
8q	5.0 + 1.0	1.5	0.9	0.5 (+0.3 g LiCl)	1.19

[a] 1.25 mmol of each diacid and diamine monomer was used; reaction temperature = 110°C; reaction time = 3 h.
[b] Measured at a concentration of 0.5 g/dL in DMAc-5% LiCl at 30°C using a Cannon−Fenske viscometer.
[c] "2.0 + 1.0" means that an initial amount of 2 mL was used and additional amount of 1 mL was added when the reaction medium was too viscous to stir.

All other polyamides (**8b– j**) and all the poly-(amide-imide)s (**8k–q**) were synthesized by an analogous procedure as above.

Preparation of Polyamide and Poly(amide-imide) Films

About 0.8 g of a polyamide or poly(amide-imide) sample was dissolved in 8 mL of DMAc. The solution was poured into a diameter = 9 cm glass culture dish, which was placed in a 90°C oven for 12 h to remove the solvent. Then, the obtained semidried polymer film was further dried at 100°C for 8 h under vacuum.

Measurements

Infrared spectra were recorded on a Jasco FT/IR-7000 Fourier transform infrared spectrometer. ^{1}H- and ^{13}C-NMR spectra were determined on a JEOL EX-400 NMR spectrometer with tetramethylsilane (TMS) as an internal reference and perdeuterodimethyl sulfoxide (DMSO-d_6) as an ex-

ternal reference, respectively. The inherent viscosities were measured with an Ubbelohde or Cannon−Fenske viscometer at 30°C. The differential scanning calorimetry (DSC) was performed on a Sinku Riko DSC-7000 coupled to a Sinku Riko TA-7000 in flowing nitrogen (30 cm^3/min) at a heating rate of 20°C/min. Thermogravimetry (TG) data were obtained on a Rigaku Thermoflex TG-8110 coupled to a Rigaku TAS-100 thermal analysis station. Measurements were performed with 10 ± 2 mg sample heated in flowing nitrogen or air (50 cm^3/min) at a heating rate 20°C/min. Wide-angle x-ray diffractograms were obtained on a Rigaku Geiger Flex D-Max III$_a$, using Ni-filtered CuKα radiation (40 kV, 15 mA). The scanning rate was 2°/min. An Instron Universal tester Model 1130 with a load cell of 5 kg was used to study the stress−strain behavior of the samples. A gauge of 2 cm and a strain rate of 5 cm/min were used for this study. The measurements were performed at room temperature using solution-cast film specimens (0.5 cm wide, 6 cm long, and about 0.1 mm thick), and an aver-

Table III.   Solubility Behavior[a] of Polyimides, Polyamides, and Poly(amide-imide)s Based on HMSBC-Diamine

Polymer	Solvent[b]					
	DMAc	NMP	DMF	DMSO	m-Cresol	THF
6a	+h	+	+h	−	−	−
6b	−	−	−	−	−	−
6c	−	−	−	−	−	−
6d	−	−	−	−	−	−
6e	+	+h	+	−	−	+
6f	+	+	+	+h	−	+
8a	+	+	+h	−	−	−
8b	+	+	+	+h	+	+
8c	+	+	+	−	+	+
8d	+	+	−	−	+	−
8e	+	+	−	−	+	+
8f	+	+	+h	−	+	+
8g	+	+	+	+h	+	+
8h	+	+	−	−	+	+
8i	+	+	−	−	+	+
8j	+	+	+	−	+	+
8k	+	+	−	−	+	+
8l	+	+	+	−	+	+
8m	+	+	+	−	+	+
8n	+	+	+	−	+	+
8o	+	+	+	−	+	+
8p	+	+	+	−	+	+
8q	+	+	+	−	+	+

[a] +: soluble at room temperature; −: insoluble at room temperature or on heating; +h: soluble on heating.
[b] DMAc: N,N-dimethylacetamide; NMP: N-methyl-2-pyrrolidone; DMF: N,N-dimethylformamide; DMSO: dimethyl sulfoxide; THF: tetrahydrofuran.

age of at least five individual determinations was used.

RESULTS AND DISCUSSION

Monomer Synthesis

According to the synthetic route outlined in Scheme 1, 6,6′-bis(4-aminophenoxy)-4,4,4′,4′,7,7′-hexamethyl-2,2′-spirobichroman (**3**) was prepared by an aromatic nucleophilic substitution reaction of 6,6′-dihydroxy-4,4,4′,4′,7,7′-hexamethyl-2,2′-spirobichroman (**1**) with p-chloronitrobenzene in a mole ratio 1 : 2 in the presence of anhydrous potassium carbonate in DMF, giving 6,6′-bis(4-nitrophenoxy)-4,4,4′,4′,7,7′-hexamethyl-2,2′-spirobichroman (**2**), and subsequent reduction of the dinitro compound using palladium as the catalyst and hydrazine monohydrate as the reducing agent. The nitro group of com-

pound **2** giving two characteristic bands at 1342 and 1592 cm^{-1} in its IR spectrum. After reduction, the characteristic absorption of nitro groups disappeared and the amino groups showed the pair of N—H stretching bands at 3428 and 3354 cm^{-1}. The ^{1}H- and ^{13}C-NMR spectra of diamine **3** are given in Figures 1 and 2. These spectra are in good agreement with the desired structure.

Polymer Synthesis

The poly(amic-acid)s (**5a–f**) having inherent viscosities in the range of 1.00–2.78 dL/g (Table I) were prepared by ring-opening polyaddition of HMSBC-diamine **3** with various aromatic dianhydrides (Scheme 2) in DMAc at room temperature. After thermal cyclodehydration, all the poly(amic-acid) films could be converted into good, creasable polyimide films. Polyimides **6a, 6e,** and **6f** were soluble in DMAc and had been characterized

Table IV. Tensile Properties of Polyimide, Polyamide and Poly(amide-imide) Films

Polymer	Strength at Yield Point (MPa)	Strength at Break Point (MPa)	Elongation at Break Point (%)	Initial Modulus (GPa)
6a	87	85	27	1.7
6b	102	97	11	1.7
6c	—	97	9	2.2
6d	—	115	11	1.8
6e	—	110	10	1.8
6f	—	104	7	2.0
8a	64	88	83	1.4
8b	69	63	73	1.6
8c	84	70	14	1.9
8d	—	94	63	1.8
8e	67	60	51	1.4
8f	68	59	33	1.6
8g	71	75	69	1.5
8h	65	77	61	1.5
8i	65	66	71	1.5
8j	63	64	88	1.4
8k	75	71	37	1.7
8l	75	67	28	1.8
8m	74	60	15	2.0
8n	66	55	35	1.5
8o	66	54	13	1.3
8p	67	64	88	1.5
8q	70	69	53	1.4

by inherent viscosities in the range of 0.92–1.03 dL/g. The IR spectrum of the representative polyimide **6a** showed the characteristic absorptions at 1779, 1729, 1379, 1226, 1166, 1118, and 727 cm^{-1}. The bands around 1779 and 1729 cm^{-1} were attributed to the asymmetrical and symmetrical stretching vibration of carbonyl groups of imide ring, and those around 1379 and 1118 cm^{-1} were assigned to the C—N stretching. Band of ring bending appeared at approximately 727 cm^{-1}. Absorptions of C—O stretching were observed at 1226 and 1166 cm^{-1}.

According to a Yamazaki–Higashi phosphorylation polyamidation technique,[26] polyamides **8a–j** and poly(amide-imide)s **8k–q** were prepared by the direct polycondensation of diamine **3** with various dicarboxylic acids **7a–j** or imide ring-preformed dicarboxylic acids **7k–q** in the NMP solution containing dissolved CaCl$_2$, using TPP and pyridine as condensing agents (Scheme 3). By using the reaction conditions as listed in Table II, polyamides and poly(amide-imide)s had inherent viscosities in the range of 0.71–2.29 dL/g and were obtained with quantitative yields. All the polymers could be solution cast into flexible and

tough films, indicating the formation of high molar masses. The expected structures of these polymers were verified by IR spectroscopy. The characteristic absorptions of amide groups were observed at about 3316 cm^{-1} (N—H stretching) and 1657 cm^{-1} (C=O stretching). The C—O stretching vibration absorptions occurred near 1158 and 1216 cm^{-1}. The spectrum also revealed the aliphatic C—H stretching absorption at 2962 cm^{-1}.

Properties of Polymers

The solubility behavior of all the polymers in various solvents is given in Table III. Among polyimides **6a–f,** those derived from the dianhydride containing sulfone (DSDA; **4e**) or hexafluoroisopropylidene (6FDA; **4f**) bridging group exhibited higher solubility; for example, polyimides **6e** and **6f** were soluble in polar aprotic solvents such as DMAc, NMP, and DMF, and even in less polar solvents such as THF. The good solubility of polyimide **6f** is believed to be related to the significantly low cohesive energy of the 6FDA segment, while that of DSDA-based polyimide (**6e**) may be due to the increased affinity to solvent molecules

caused by the presence of polar sulfonyl groups. An unexpected result is that the pyromellitimide-based **6a** was soluble in NMP, and in hot DMAc or DMF. However, the reason is not fully understood. The other polyimides (**6b–d**) were insoluble in all the solvents tested.

All the polyamides **8a–j** were readily soluble in DMAc and NMP. With the exception of **8d, 8e, 8h,** and **8i,** the other polyamides were also soluble in DMF. Almost all the polyamides also dissolved easily in less polar solvents such as *m*-cresol and THF. However, DMSO is a poor solvent for these polymers. All the poly(amide-imide)s (**8k–q**) also exhibited excellent solubility. Almost all of them were easily soluble in DMAc, NMP, DMF, *m*-cresol, and THF, but insoluble in DMSO.

All the polymers were proved to be nearly completely amorphous as evidenced by their wide-angle x-ray diffraction patterns. The amorphous nature and high solubility of these polymers can be mainly explained by the presence of bulky nonlinear spirobichroman units. Due to these groups, the packing of macromolecular chains in tight structures is probably disturbed and, consequently, the solvent molecules can penetrate easily to solubilize the chains.

All of the new polymers possess outstanding film-forming properties. Transparent flexible films have been obtained by solution casting from DMAc on glass substrates. The tensile properties of these polymer films were included in Table IV. The polyimides **6a** and **6b** showed yield points on their stress–strain curves, and their tensile strengths at yield point were 87 and 102 MPa. This series of polyimide films had tensile strength at break point, elongation-to-break, and tensile modulus in the range of 85–115 MPa, 7–27%, and 1.7–2.2 GPa, respectively. These results indicate that most of these polyimides belong to strong and hard polymer materials. Almost all the films obtained from polyamides **8a–j** and poly(amide-imide)s **8k–q** behaved as ductile materials, with a distinct yield point in their stress–strain curves and moderate elongation at break point. The yield strengths, tensile strengths, elongation-to-break, and tensile moduli of these films were in the range of 63–84 MPa, 54–94 MPa, 13–88%, and 1.3–2.0 GPa, respectively.

The thermal properties of the polymer films were determined by using both TG and DSC (Table V). The T_g values of these polymers were in a moderate temperature range of 137–256°C. The results indicate that they are potentially useful thermoplastic resins. The moderate T_g values of

Table V. Thermal Properties of Polyimides, Polyamides, and Poly(amide-imide)s Based on HMSBC-Damine

Polymer	T_g^a (°C)	Decomposition[b] Temperature (°C) in N$_2$	in Air	Char[c] Yield (%)
6a	248	464	472	41.9
6b	256	462	474	43.5
6c	240	457	471	38.8
6d	236	465	468	46.7
6e	256	448	454	30.6
6f	240	467	483	28.3
8a	180 (396)[d]	427	436	39.8
8b	213	423	430	38.2
8c	193	430	437	42.5
8d	182 (392)[d]	429	437	40.9
8e	222	434	443	40.6
8f	227	421	423	37.5
8g	169	426	437	43.8
8h	218	422	435	42.3
8i	200	427	443	41.8
8j	181	429	441	43.6
8k	228	424	434	44.8
8l	221	422	430	42.7
8m	211	404	419	51.3
8n	147	419	424	32.5
8o	137	421	424	28.4
8p	156	436	434	37.0
8q	220	433	440	50.3

[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] Temperature at endotherm peak on the first DSC heating trace.

these polymers are primarily attributed to the low rotational energy barrier around ether linkages. Among these polymers, polyimides **6a–f** revealed relatively higher T_gs (236–256°C) than polyamides **8a–j** or poly(amide-imide)s **8k–q.** It is reasonable because of the rigid nature of the imide unit. Poly(amide-imide) **8n–p** had relatively lower T_gs, in the range of 137–156°C, than the other polymers owing to the presence of flexible polymethylene segment in the backbone.

As summarized in Table V, the polymers showed less thermal stability compared to the known wholly aromatic analogues. Ten percent weight loss was observed at 404–467°C in a nitrogen and 419–483°C in an air atmosphere, which is reasonably high for an aliphatic-aromatic poly-
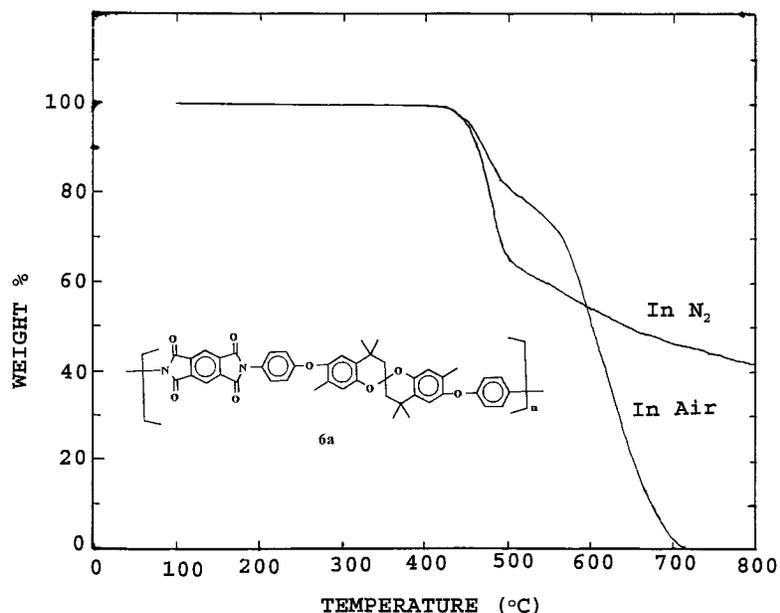
Figure 3. TG thermograms of polyimide **6a** in nitrogen and air, with a heating rate of 20°C/min.

mer owing to its alicyclic structure. Moreover, it is interesting to note that in almost all cases the temperature at which 10% weight loss occurred in air is higher than that in nitrogen. Figure 3 shows typical TG thermograms for the representative polyimide **6a** in air and in nitrogen. Polyimide **6a** started to loss weight around 420°C. In nitrogen, this polymer left 41.6% char residue when heated to 800°C. The polyimide showed a two-stage weight loss profile in air. It appeared that the polymer first lost its aliphatic segments and then underwent aromatic residue degradation. It also can be seen from these TG thermograms that the decomposition rate in air is lower than in nitrogen in the temperature range 420–500°C. This may be attributed to some possible oxidative interchain crosslinking between aliphatic segments of the polymer chain when thermally degraded in air.

CONCLUSIONS

A novel diamine monomer, 6,6′-bis(4-aminophenoxy) - 4,4,4′,4′,7,7′ - hexamethyl - 2,2′ -spirobichroman (**3**), has been prepared in high yields and high purity starting from 6,6′-dihydroxy-4,4,4′,4′,7,7′-hexamethyl-2,2′-spirobichroman and *p* -chloronitrobenzene. High-molar-mass polyimides, polyamides, and poly(amide-imide)s have

been prepared in quantitative yields from this diamine with conventional aromatic dianhydrides, dicarboxylic acids, and imidodicarboxylic acids. Some polyimides and all the polyamides and poly-(amide-imide)s were soluble in organic solvents. All the polymers were noncrystalline, and tough and flexible films could be cast from solution. The T_gs of the polymers ranged from 137 to 256°C but were well below the decomposition temperatures (above 400°C). Because of these properties, these polymers generally exhibited good thermal processabilities. Thus, the present polymers may be considered as potential candidates for high performance engineering thermoplastics.

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