

## Preparation and properties of polyimides, polyamides and poly(amide-imide)s based on a spirobichroman dietheramine

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### SUMMARY:

A novel diamine, 7,7'-bis(4-aminophenoxy)-4,4,4',4'-tetramethyl-2,2'-spirobichroman (**3**), was synthesized and used as a monomer with various aromatic tetracarboxylic dianhydrides, dicarboxylic acids and imide ring-containing dicarboxylic acids, to synthesize polyimides, polyamides and poly(amide-imide)s, respectively. The polyimides **5a–f** were prepared from diamine **3** and various aromatic tetracarboxylic dianhydrides via a conventional two-stage procedure. The intermediate poly(amic acid)s had inherent viscosities of 0,84–1,65 dL/g and could be thermally converted into transparent, flexible, and tough polyimide films. Some polyimides were readily soluble in polar solvents such as *N,N*-dimethylacetamide (DMAc) and *N*-methyl-2-pyrrolidone (NMP). The glass transition temperatures ( $T_g$ ) of these polyimides were in the range of 155–280 °C, and 10% weight loss temperatures were above 450 °C in air or nitrogen. Furthermore, a series of polyamides and poly(amide-imide)s having inherent viscosity between 0,40–1,69 dL/g were prepared by direct polycondensation of the diamine **3** with various aromatic dicarboxylic acids and imide ring-containing dicarboxylic acids. All the polyamides and poly(amide-imide)s were soluble in a variety of organic solvents and could be solution-cast into flexible and tough films. They had  $T_g$  values in the 150–237 °C range and showed no significant weight loss below 400 °C in air and nitrogen atmosphere.

### Introduction

Polyimides have found wide usage as films, coatings, adhesives, and matrix resins due to their excellent electrical and mechanical properties, high thermal and chemical stability, good solvent resistance, and dimensional stability<sup>1)</sup>. They are generally used as flexible circuitry substrates, interlayer dielectrics and passivation and protective coatings in high density electronic packaging devices. However, aromatic polyimides are usually insoluble and infusible; their glass transition or melting temperatures, being very high, practically in the same range as their decomposition, make their processing possible only from poly(amic acid) precursors. The commonly utilized two-stage polymerization process for the manufacture of polyimides from poly(amic acid)s still has certain limitations connected with the storage instability of poly(amic acid) solutions and with the elimination of released water and formation of microvoids in the final product. Therefore, many attempts have been made to improve the processing properties of aromatic polyimides, particularly their solubility and fusibility, by insertion of amide, ester, ether, or other flexibilizing linkages into the polymer backbone<sup>2–6)</sup>.

It has been generally recognized that flexible ether links inserted in the polyimide backbone improve the solubility and moldability while lowering the  $T_g$ . The structure of resulting polyimide is, therefore, expected to provide balanced properties of thermal stability and processability. This kind of polyimide structural modification was usually realized by incorporation of arylene ether segments into the diamine monomer. The approach to synthesize the bis(4-aminophenoxy) compound by a nucleophilic chlorodisplacement of an alkali metal bisphenolate with *p*-chloronitrobenzene, followed by reduction of the resulting dinitro compound, is very popular in the literature<sup>7-13</sup>). Combinations of the resulting "multi-ring" flexible bis(ether amine)s with dianhydrides, particularly for those containing a flexibilizing bridge between two phthalic anhydride moieties, usually resulted in polyimides with a lowered  $T_g$  and higher solubility.

The aromatic diol having tetramethyl-substituted spirobichroman (TMSBC) unit, 7,7'-dihydroxy-4,4,4',4'-tetramethyl-2,2'-spirobichroman (structure **1** in Scheme 1), can be readily obtained from the cyclocondensation of resorcinol with acetone in the presence of an acid catalyst<sup>14-16</sup>) and now is commercially available. The TMSBC-diol **1** might be used as the said antifading agent in a silver halide color photographic material which exhibits highly improved light fastness in magenta dye images<sup>17-20</sup>). The photographic films made of polyesters based on diol **1** have been described to lead to improved physical properties such as a higher glass transition temperature and dimensional stability in comparison with the analogues derived from bisphenol A<sup>21,22</sup>). To our knowledge, TMSBC-diol **1**-derived polymers other than polyesters have not been reported thus far. In the present article, the TMSBC-diol **1** will be extended to the bis(4-aminophenoxy) compound **3** (see Scheme 1), which will be subsequently built in a polyimide backbone.

We wish to report here the synthesis and the characterization of soluble polyimides from the novel bis(ether amine) **3**. Furthermore, the present work also deals with the synthesis and basic characterization of polyamides and poly(amide-imide)s based on the TMSBC-diamine **3** and various aromatic dicarboxylic acids or imide ring-bearing dicarboxylic acids. The introduction of a spiro structure into the polymer backbone would result in less polymer-polymer interaction and increased main chain rigidity and, additionally, possibly less probability of main chain scission because of having multibonds.

## Experimental part

### Materials

7,7'-Dihydroxy-4,4,4',4'-tetramethyl-2,2'-spirobichroman (**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 over 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, but pyromellitic dianhydride (PMDA; **4a**, Aldrich) and 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA; **4d**, Aldrich) were recrystallized from acetic anhydride prior to use.

Aromatic 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-naphthylenedicarboxylic 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 condensation of the potassium phenolate of hydroquinone and resorcinol, respectively, with *p*-fluorobenzonitrile, giving the corresponding bis(ether-nitrile)s, followed by alkaline hydrolysis<sup>23</sup>. The imide ring-containing diacids **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<sup>24,25</sup>. The bistrimellitides **7p** and **7q** were prepared by condensation of 4,4'-oxydianiline and hexamethylenediamine, respectively, with trimellitic anhydride in a mole ratio 1 : 2<sup>26</sup>.

#### 7,7'-Bis(4-nitrophenoxy)-4,4,4',4'-tetramethyl-2,2'-spirobichroman (2)

In a 500-mL flask, 25 g (0,073 mol) of diol **1** and 23,6 g (0,15 mol) of *p*-chloronitrobenzene were dissolved in 125 mL of dry DMF. Then, 23 g (0,166) of anhydrous potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) was added, and the suspension solution was refluxed at 160 °C for 8 h. The mixture was allowed to cool and then poured into 200 mL of ethanol-water (1 : 1 by vol.) to precipitate a yellow solid which was collected by filtration, repeatedly washed with methanol and water, and dried. Yield: 42,5 g (99%). The crude product was recrystallized from DMF as light yellow crystals; m. p.: 231–232 °C.

IR (KBr): 1 350 (sym. —NO<sub>2</sub> str.), 1 589 cm<sup>-1</sup> (asym. —NO<sub>2</sub> str.).

<sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) [Fig. 1-(B)]: δ = 1,4, 1,6 (methyl protons), 2,1 (methylene protons —CH<sub>2</sub>—), 6,4–8,1 ppm (aromatic protons).

C <sub>33</sub> H <sub>30</sub> N <sub>2</sub> O <sub>8</sub> (582,60):	Calc.	C 68,03	H 5,19	N 4,81
	Found	C 68,00	H 5,24	N 4,76

#### 7,7'-Bis(4-aminophenoxy)-4,4,4',4'-tetramethyl-2,2'-spirobichroman (3)

In a 1-L flask, 42 g (0,072 mol) of the dinitro compound **2** and 0,2 g of 10% Pd/C were suspended in 300 mL of ethanol and 135 mL of hydrazine monohydrate (NH<sub>2</sub>NH<sub>2</sub> · H<sub>2</sub>O). The suspension was refluxed for 4 h. The yellow suspension turned into a clear, dark green solution. The hot solution was then filtered to remove Pd/C. After cooling, the precipitated colorless needles were isolated and collected by filtration, washed with ethanol, and dried. Yield: 31.9 g (84.6 %); m. p.: 173–175 °C.

IR (KBr): 3 352, 3 426 (N—H str.), 2 964 cm<sup>-1</sup> (C—H str.).

<sup>1</sup>H NMR (CDCl<sub>3</sub>) [Fig. 1-(C)]: δ = 1,3, 1,5 (methyl protons), 2,0 (methylene protons), 3,4 (—NH<sub>2</sub>), 6,3–7,3 ppm (aromatic protons).

C <sub>33</sub> H <sub>34</sub> N <sub>2</sub> O <sub>4</sub> (522,64)	Calc.	C 75,84	H 6,56	N 5,36
	Found	C 75,78	H 5,36	N 5,30

### Synthesis poly(amic acid)s and the polyimides

The synthesis and characterization of poly(amic acid) **5a** and polyimide **6a** is described as a typical example: 0,2944 g (1,35 mmol) of PMDA (**4a**) was slowly added to a stirred solution of 0,7055 g (1,35 mmol) of TMSBC-diamine **3** in 9,5 mL (about 9 g) of dry DMAc at room temperature. Polymerization solution was continuously stirred for 1,5 h after the complete addition of PMDA, and a highly viscous poly(amic acid) solution of 10 wt.-% solid was obtained. The inherent viscosity of the resulting poly(amic acid) in DMAc was 1,65 dL/g, measured at a concentration of 0,5 g/dL at 30°C. The obtained poly(amic acid) solution of **5a** was poured into a  $\phi = 9$  cm glass culture dish, which was placed in a 90°C oven for 12 h to remove the solvent. The obtained semi-dried poly(amic acid) film was further dried and transformed into polyimide by sequential heating at 120°C for 20 min, 150°C for 20 min, 180°C for 10 min, 200°C for 10 min, and 250°C for 30 min. A tough and flexible film of about 0,1 mm thickness was stripped off from the glass surface by soaking in water.

IR spectrum of poly(amic acid) **5a** (film): 3000–3500 (broad, O—H and N—H str.), 1600–1720  $\text{cm}^{-1}$  (C=O str.)

IR spectrum of polyimide **6a** (film): 2920 (C—H str.), 1780, 1720 (imide ring C=O asym. and sym. str.), 1380 (C—N str.), 720  $\text{cm}^{-1}$  (imide ring deformation).

<b>6a</b> (C <sub>43</sub> H <sub>32</sub> N <sub>2</sub> O <sub>8</sub> ) <sub>n</sub> (704,73) <sub>n</sub>	Calc.	C 73,28	H 4,57	N 3,97
	Found	C 73,10	H 4,62	N 3,91

All the other TMSBC-poly(amic acid)s and polyimide films were prepared by a similar procedure.

### Synthesis of polyamides and poly(amide-imide)s

*Synthesis of polyamide 8a:* A mixture of 0,2077 g (1,25 mmol) of terephthalic acid (**7a**), 0,6533 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 2,5 mL of NMP was heated with stirring at 110°C for 3 h. The resultant polymer solution was tricked slowly into methanol giving rise to a stringy 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 in DMAc containing 5 wt.-% LiCl was 0,79 dL/g, measured at a concentration of 0,5 g/dL at 30°C.

All other polyamides **8b–j** and poly(amide-imide)s **8k–q** were synthesized by an analogous procedure as above. The synthesis conditions and the inherent viscosities of the prepared polymers are listed in Tab. 2.

*Preparation of polymer 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 glass culture dish of 9 cm diameter, which was placed in a 90°C oven for 12 h to remove the solvent. Then, the obtained semi-dried polymer film was further dried at 100°C for 8 h under vacuum.

### Measurements

Infrared spectra were obtained on a Jasco FT/IR-7000 Fourier transform infrared spectrometer. <sup>1</sup>H NMR spectra were recorded on a Jeol JNM-PMX60 NMR spectrometer with tetramethylsilane (TMS) as an internal reference. 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<sup>3</sup>/min) at a heating rate of 20°C/min. Thermogravimetry (TG) data were obtained on a Rigaku Thermoflex TG-8110 coupled to a

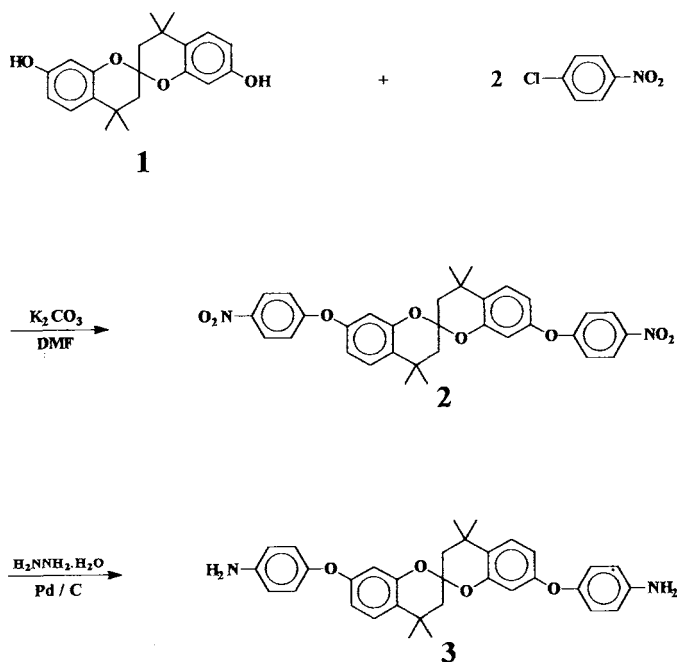
Rigaku TAS-100 thermal analysis station. Measurements were performed with  $10 \pm 2$  mg sample heated in flowing nitrogen or air ( $50 \text{ cm}^3/\text{min}$ ) at a heating rate  $20^\circ\text{C}/\text{min}$ . Wide-angle X-ray diffractograms were obtained on a Rigaku Geiger Flex D-Max IIIa, using Ni-filtered  $\text{CuK}_\alpha$  radiation (40 kV, 15 mA). The scanning rate was  $2^\circ/\text{min}$ . An Instron Universal tester Model 1130 with a load cell 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 average of at least five individual determinations was used.

## Results and discussion

### Synthesis of TMSBC-diamine **3**

The diamine **3** was prepared using a two-step reaction from TMSBC-diol **1** and *p*-chloronitrobenzene (Scheme 1). A conventional aromatic nucleophilic chlorodispla-

#### Scheme 1:



cement between diol **1** and *p*-chloronitrobenzene was carried out to produce the dinitro compound **2** in quantitative yield. The dinitro compound was then reduced with hydrazine monohydrate in refluxing ethanol in the presence of a 10% Pd/C catalyst. The yield was high (85%), and the purity was high enough to prepare polymers with

high molecular weights. The structures of intermediate dinitro compound **2** and diamine **3** were confirmed by elemental analysis, FT-IR,  $^1\text{H}$  NMR spectroscopy, and the results were in good agreement with proposed structures.

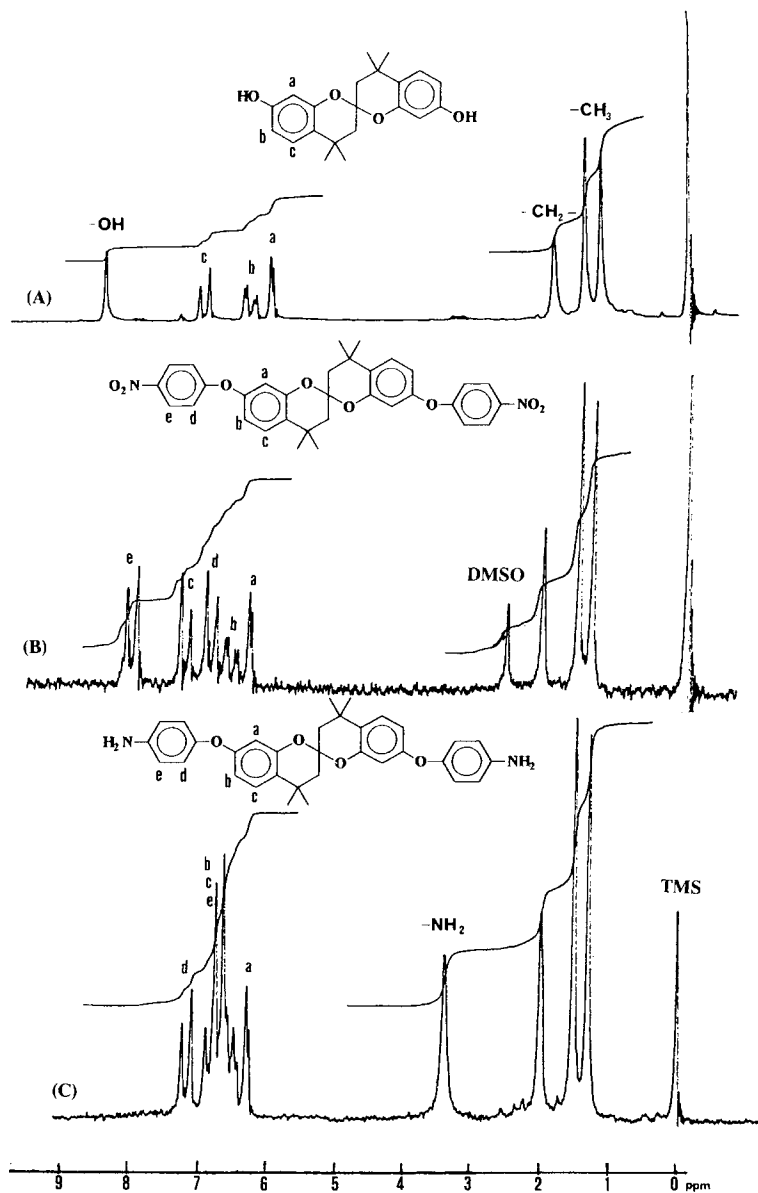


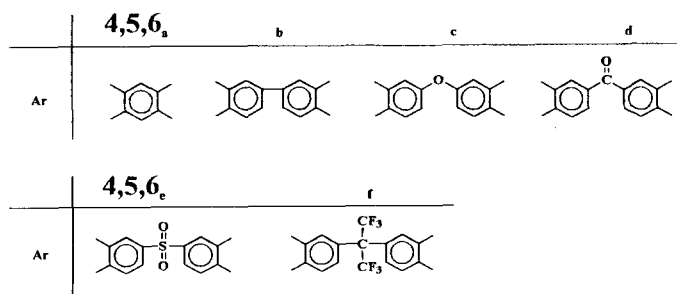
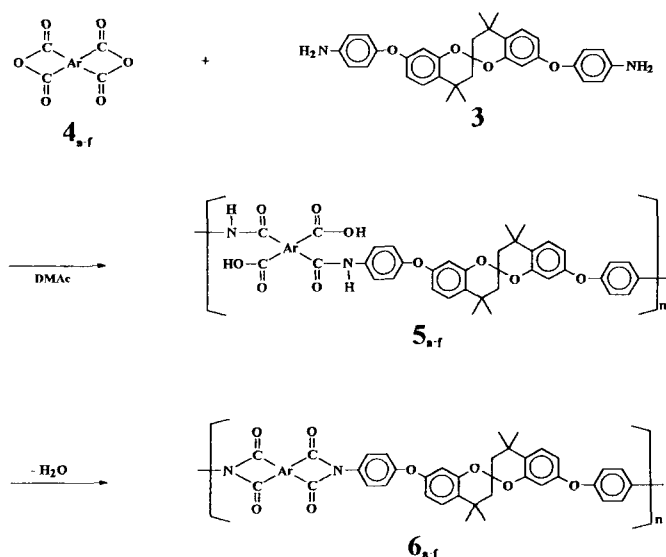
Fig. 1. 60 MHz  $^1\text{H}$  NMR spectra of (A) TMSBC-diol **1** in  $\text{CDCl}_3$ , (B) TMSBC-dinitro compound **2** in  $\text{DMSO}-d_6$ , and (C) TMSBC-diamine **3** in  $\text{CDCl}_3$

The IR spectrum of dinitro compound **2** showed characteristic bands near 1350 and 1590  $\text{cm}^{-1}$  peculiar to the nitro group, that of diamine **3** revealed a primary amine absorption pair around 3300–3500  $\text{cm}^{-1}$ . The  $^1\text{H}$  NMR spectra and assignment of protons of compounds **1**, **2** and **3** are given in Fig. 1. The spectra were consistent with the assigned structures. The formation of diamine **3** could be confirmed by the upfield shift of aromatic protons and the appearance of the resonance peak of amino protons at 3,6 ppm.

### Polymer synthesis

The TMSBC-polyimides **6a–f** were prepared by a conventional two-stage polymerization from TMSBC-diamine **3** with various commercially available carboxylic dianhydrides (**4a–f**). The reaction scheme and code of the compounds are outlined in Scheme 2. The intermediate poly(amic acids) **5a–f** had moderate to high inherent

Scheme 2:



Tab. 1. Inherent viscosities of TMSBC-poly(amic acid)s and elemental analyses of TMSBC-polyimides

Poly(amic acid)s		Elemental analyses of polyimides					
code	$\eta_{inh}^{a)}$ in dL/g	code	Polymer formula (mol. wt.)		%C	%H	%N
<b>5a</b>	1.65	<b>6a</b>	$(C_{43}H_{32}N_2O_8)_n$ (704,73) <sub>n</sub>	Calc.	73.28	4.57	3.97
				Found	73.10	4.62	3.91
<b>5b</b>	0.89	<b>6b</b>	$(C_{49}H_{36}N_2O_8)_n$ (780.83) <sub>n</sub>	Calc.	75.37	4.65	3.59
				Found	75.02	4.69	3.50
<b>5c</b>	0.84	<b>6c</b>	$(C_{49}H_{36}N_2O_9)_n$ (796.83) <sub>n</sub>	Calc.	73.86	4.55	3.52
				Found	73.45	4.58	3.46
<b>5d</b>	1.14	<b>6d</b>	$(C_{50}H_{36}N_2O_9)_n$ (808.84) <sub>n</sub>	Calc.	74.25	4.49	3.46
				Found	74.01	4.56	3.38
<b>5e</b>	1.21	<b>6e</b>	$(C_{49}H_{36}N_2O_{10}S)_n$ (844,90) <sub>n</sub>	Calc.	69.66	4.29	3.31
				Found	69.33	4.34	3.28
<b>5f</b>	1.20	<b>6f</b>	$(C_{52}H_{36}N_2O_8F_6)_n$ (930.85) <sub>n</sub>	Calc.	67.10	3.90	3.01
				Found	66.78	3.98	2.98

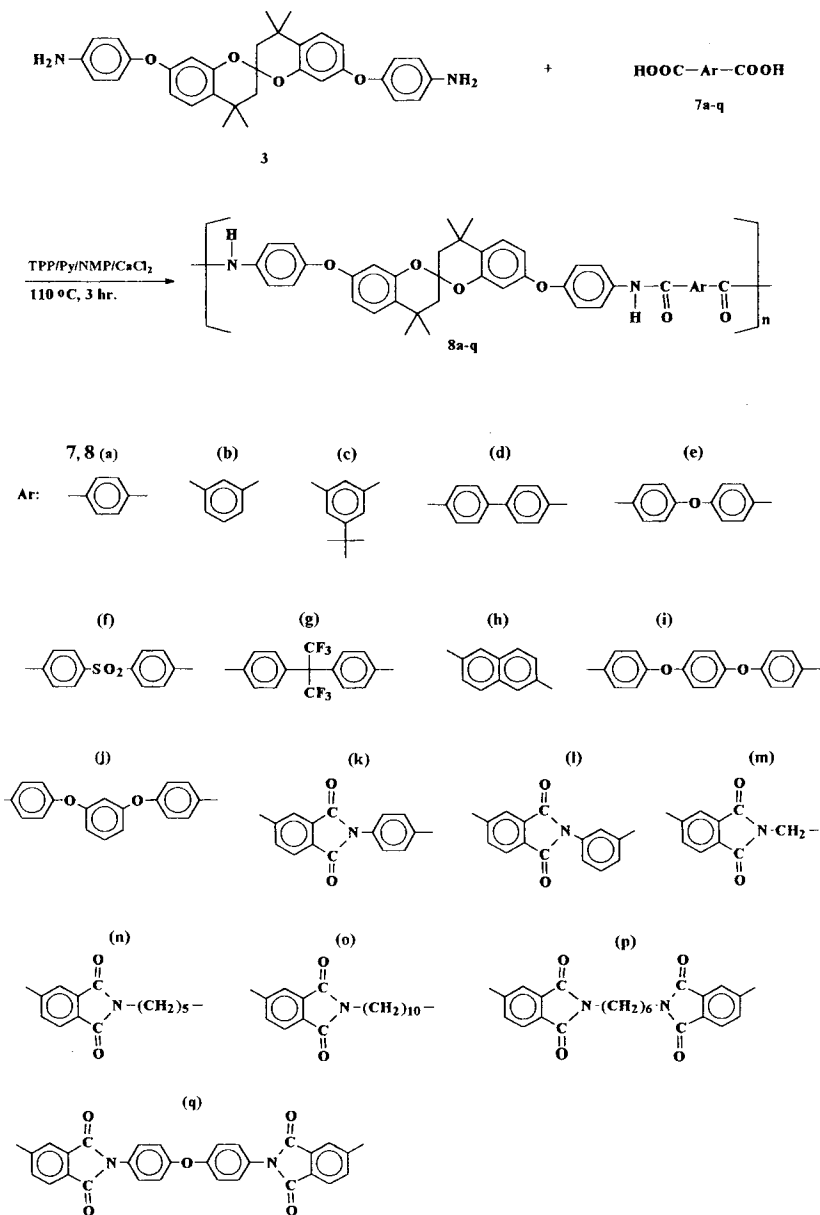
<sup>a)</sup> Measured at a concentration of 0.5 g/dL in DMAc at 30 °C using an Ubbelohde viscosimeter.

viscosities ranging from 0.84 to 1.65 dL/g, indicative of high molecular weights. Polyimides **6a–f** were obtained as flexible films by *in situ* thermocyclodehydrating the corresponding poly(amic acid) films. The structure of these polyimides was verified through elemental analysis and IR spectroscopy. As shown in Tab. 1, the results of elemental analysis of these polyimides agree well with the desired structures. The IR spectra of the polyimides have characteristic imide absorbance near 1780 and 1720  $cm^{-1}$  (coupled carbonyls), and 1100 and 720  $cm^{-1}$  (imide ring).

Serial polyamides **8a–j** and poly(amide-imide)s **8k–q** were synthesized by direct polycondensation of TMSBC-diamine **3** with the equivalent diacids by means of triphenyl phosphite and pyridine<sup>27</sup>). The structures of the diacids and polymers are illustrated in Scheme 3. Using the conditions listed in Tab. 2, all the resulting polymers remained in solution throughout the polymerization. They were isolated as white (for polyamides) or yellow fibers (for poly(amide-imide)s) upon precipitation in methanol. The inherent viscosities of these polymers stay in the range of 0.52–1.69 dL/g. Although the synthesis conditions have not been optimized, the molecular weights of the obtained polymers are high enough to permit casting good-quality, coherent, creasable films. The structure of the polyamides and poly(amide-imide)s was ascertained by the IR spectra. The amide groups in polymer backbone were identified through the wide absorptions around 3300  $cm^{-1}$ , characteristic of N–H, and the band at 1630  $cm^{-1}$ , which is due to C=O in the amide group. The strong bands appearing at 1780, 1720, and 720  $cm^{-1}$  were assigned to the imide ring.



Scheme 3:



Tab. 2. Synthesis conditions and inherent viscosities of polyamides and poly(amide-imide)s based on TMSBC-diamine

Polymer	Amount of reagents used <sup>a)</sup>				$\eta_{inh}^{b)}$ in dL/g
	NMP in mL	Py in mL	TPP in mL	CaCl <sub>2</sub> in g	
<b>8a</b>	2,0	0,8	0,9	0,3	0,79
<b>8b</b>	1,5	0,8	0,9	0,3	0,64
<b>8c</b>	1,5	0,8	0,9	0,3	0,53
<b>8d</b>	3,0	1,0	0,9	0,5 (+0,2 g LiCl)	1,00
<b>8e</b>	2,0	0,8	0,9	0,3	0,52
<b>8f</b>	2,0	0,8	0,9	0,3	0,79
<b>8g</b>	2,5	0,8	0,9	0,3	0,84
<b>8h</b>	2,0	0,8	0,9	0,3	1,69
<b>8i</b>	2,5	0,8	0,9	0,3	0,85
<b>8j</b>	2,5	0,8	0,9	0,3	0,75
<b>8k</b>	2,5	0,8	0,9	0,3	0,62
<b>8l</b>	2,5	0,8	0,9	0,4	0,78
<b>8m</b>	2,5	0,8	0,9	0,4	1,07
<b>8n</b>	2,5	0,8	0,9	0,3	0,85
<b>8o</b>	2,5	0,8	0,9	0,3	0,40
<b>8p</b>	3,0	1,0	0,9	0,4	0,89
<b>9q</b>	5,5	1,5	0,9	0,5 (+0,3 g LiCl)	0,72

<sup>a)</sup> Amount of each diacid and diamine monomer = 1,25 mmol; reaction temperature = 110 °C; reaction time = 3 h.

<sup>b)</sup> Measured at a concentration of 0,5 g/dL in DMAc-5 wt.-% LiCl at 30 °C using a Cannon-Fenske viscometer.

### Properties of polymers

The solubility of all the polymers was investigated qualitatively, and the results are summarized in Tab. 3. Among polyimides **6a–f**, DSDA- and 6FDA-based polyimides **6e** and **6f** have high solubility in organic solvents. The high solubility of the 6FDA polyimide is believed to be due to the significantly lower cohesive energy of the 6FDA segment than that of the other dianhydrides. On the other hand, the good solubility of the DSDA polyimide can be related to the introduction of the polar sulfone group, which increased the affinity between the polymer chain and the solvent molecules. For polyamides **8a–j** and poly(amide-imide)s **8k–q**, all of them are readily soluble in DMAc, NMP, and *m*-cresol, and most of them are also soluble in DMF and THF; however, DMSO seems to be a poor solvent for these polymers. The good solubility of these polymers may be apparently due to the incorporation of the bulky, nonlinear spirochroman moieties and the ether group along the main chain.

The development of crystallinity in these polymers was not expected because of the presence of the approximately orthogonal chroman planes in the backbone. The X-ray diffraction patterns and the DSC curves confirmed that all the polymers are

Tab. 3. Solubility<sup>a)</sup> of polyimides, polyamides and poly(amide-imide)s based on TMSBC-diamine

Polymer	Solvent <sup>b)</sup>					
	DMAc	NMP	DMF	DMSO	<i>m</i> -cresol	THF
<b>6a</b>	-	-	-	-	-	-
<b>6b</b>	-	+h	-	-	+	-
<b>6c</b>	-	+	-	-	+	+
<b>6d</b>	-	-	-	-	-	-
<b>6e</b>	+	+	+	+	+	-
<b>6f</b>	+	+	+	-	+h	+
<b>8a</b>	+	+	-	-	+	-
<b>8b</b>	+	+	+	+	+	+
<b>8c</b>	+	+	+	-	+	-
<b>8d</b>	+	+	+	-	+	-
<b>8e</b>	+	+	+	-	+	+
<b>8f</b>	+	+	+	-	+	+
<b>8g</b>	+	+	+	+	+	+
<b>8h</b>	+	+	-	-	+	+
<b>8i</b>	+	+	+	-	+	+
<b>8j</b>	+	+	+	+h	+	+
<b>8k</b>	+	+	+	-	+	+
<b>8l</b>	+	+	+	-	+	+
<b>8m</b>	+	+	+	+	+	+
<b>8n</b>	+	+	+	-	+	+
<b>8o</b>	+	+	+	-	+	+
<b>8p</b>	+	+	-	-	+	+
<b>8q</b>	+	+	+	-	+	+

<sup>a)</sup> +: soluble at room temperature; -: insoluble at room temperature and on heating; +h: soluble on heating.

<sup>b)</sup> DMAc: *N,N*-dimethylacetamide; DMF: *N,N*-dimethylformamide; NMP: *N*-methyl-2-pyrrolidone; DMSO: dimethyl sulfoxide; THF: tetrahydrofuran.

noncrystalline. These results also correspond to their high solubility. All the polyamides and poly(amide-imide)s could be cast into flexible and tough films from DMAc, and these films were subjected to tensile test. As shown in Tab. 4, these polymer films exhibited a tensile strength range of 46–82 MPa, an elongation-to-break range of 4–30%, and an initial modulus range of 1,3–2,0 GPa. Part of the films behaved as ductile materials, yielding under stress and revealing moderate extension before breaking. The polyimide films behaved as strong and hard materials; they exhibited tensile strengths between 68–117 MPa, elongation-to-break between 3–7%, and initial moduli between 1,6–2,5 GPa.

The thermal stability of the polymers was evaluated by thermogravimetry (TG). Some TG data such as 10 wt.-% loss temperatures and char yield at 800 °C in nitrogen are included in Tab. 5. Fig. 2 shows the TG curves of a representative poly-

Tab. 4. Tensile properties of polyimide, polyamide<sup>a)</sup>, and poly(amide-imide)<sup>a)</sup> films

Polymer	Strength at yield point in MPa	Strength at break point in MPa	Elongation at break point in %	Initial modulus in GPa
<b>6a</b>	–	68	3	2.2
<b>6b</b>	–	77	3	2.5
<b>6c</b>	–	85	7	2.0
<b>6d</b>	–	117	6	1.6
<b>6e</b>	–	82	6	1.9
<b>6f</b>	–	79	6	2.0
<b>8a</b>	–	52	8	1.5
<b>8b</b>	–	67	4	2.0
<b>8c</b>	–	50	3	2.0
<b>8d</b>	84	65	13	1.9
<b>8e</b>	74	54	16	1.9
<b>8f</b>	73	56	13	1.9
<b>8g</b>	74	55	23	1.3
<b>8h</b>	73	65	30	2.0
<b>8i</b>	–	79	8	1.8
<b>8j</b>	–	82	8	1.9
<b>8k</b>	70	63	8	1.8
<b>8l</b>	–	72	6	1.7
<b>8m</b>	–	72	9	1.4
<b>8n</b>	65	46	10	1.5
<b>8o</b>	–	67	6	1.6
<b>8p</b>	–	70	7	1.6
<b>8q</b>	–	78	11	2.0

<sup>a)</sup> Films were cast from polymer solutions in DMAc.

imide, **6a**, in air and nitrogen. The behavior of decomposition below 500 °C in air and in nitrogen of this polymer was similar, and in air the rate of weight loss slowed down at 500–600 °C, probably owing to oxidation or crosslinking of aliphatic segments in the TMSBC structure of the polymer. In air, the oxidative degradation continued above 600 °C and **6a** decomposed completely near 700 °C. However, there were 43.6 wt.-% residual char left when heated to 800 °C in nitrogen. All other polyimides showed a similar thermal behavior, and all the polyimides lost 10% weight above 450 °C, with 26.0–46.3% char residue remaining at 800 °C in nitrogen atmosphere. The relatively lower char residue for polyimides obtained from DSDA and 6FDA may be associated with the degradation of the sulfonyl and hexafluoroisopropylidene bridging groups.

The 10% weight loss temperatures of the polyamides appeared in the range of 415–428 °C in nitrogen and of 418–435 °C in air. They left 28.3–51.5% char yield at 800 °C in nitrogen. The sulfone-containing polyamide **8f** also exhibited the least char yield. The 10% weight loss temperatures of poly(amide-imide)s **8k–q** were in the range of 393–436 °C in air and of 397–449 °C in nitrogen.

Tab. 5. Thermal properties of TMSBC-polyimides, polyamides, and poly(amide-imide)s

Polymer	$T_g^{a)}$ in °C	Decomposition temperature <sup>b)</sup> in °C		Char yield <sup>c)</sup> in %
		in N <sub>2</sub>	in air	
<b>6a</b>	280	478	475	43,6
<b>6b</b>	220	490	492	46,3
<b>6c</b>	232	474	476	37,0
<b>6d</b>	244	476	483	46,6
<b>6e</b>	258	451	455	26,0
<b>6f</b>	267	485	477	31,5
<b>8a</b>	216	418	418	43,9
<b>8b</b>	157	419	426	42,2
<b>8c</b>	215	421	427	44,4
<b>8d</b>	215	420	423	51,5
<b>8e</b>	196	422	423	45,2
<b>8f</b>	194	416	419	28,3
<b>8g</b>	190	428	429	43,3
<b>8h</b>	210	415	418	47,1
<b>8i</b>	183	425	435	46,3
<b>8j</b>	198	424	434	49,7
<b>8k</b>	237	413	428	49,3
<b>8l</b>	193	436	449	46,5
<b>8m</b>	201	393	397	48,2
<b>8n</b>	171	435	435	35,8
<b>8o</b>	150	411	414	37,6
<b>8p</b>	162	429	432	42,9
<b>8q</b>	217	422	446	53,4

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 weight % at 800 °C in nitrogen.

The polymers'  $T_g$ 's were determined from the DSC traces of samples heated to 400 °C and rapidly quenched prior to the run. All the polymers showed a strong baseline shift on their second DSC heating traces. The temperature at the midpoint of the baseline shift was defined as  $T_g$ . The  $T_g$  values of all the polymers are also summarized in Tab. 5.

The series of TMSBC-polyimides **6a–f** had  $T_g$ 's in the range of 220–280 °C. The PMDA-based polyimide **6a** showed the highest  $T_g$  because of the rigid pyromellitimide unit. BPDA- and OPDA-based polyimides (**6b** and **6c**) exhibited a relatively lower  $T_g$ , possibly owing to higher flexibility of their dianhydride residues. Polar sulfone and bulky hexafluoroisopropylidene groups reduce the mobility of the polymer chain. Therefore, DSDA polyimide (**6e**) and 6FDA polyimide (**6f**) revealed a high  $T_g$ .

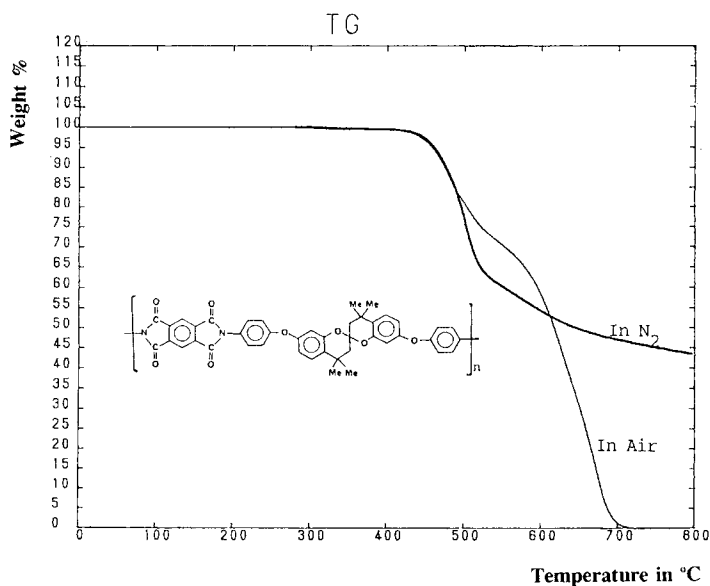


Fig. 2. TG curves for TMSBC-polyimide **6a**, with a heating rate of 20 °C/min

The  $T_g$ 's of the polyamide series (**8a–j**) were ranging from 157 to 216 °C. The polyamide **8b**, based on isophthalic acid, showed the lowest  $T_g$ , i.e., 157 °C. Polyamide **8c** had  $T_g$  48 °C higher than its analogue **8b** because of the presence of *tert*-butyl groups. In general, except the polyamide **8b**, in this series of polyamides, the effect of the diacid moiety on the  $T_g$  is small. For the TMSBC-poly(amide-imide) **8k–q** series, the  $T_g$ 's showed up between 150–237 °C. Polymers having flexible polymethylene segment, such as **8n–p**, revealed lower  $T_g$ 's.

## Conclusions

The diamine 7,7'-bis(4-aminophenoxy)-4,4,4',4'-tetramethyl-2,2'-spirobichroman (**3**) was prepared in high purity and high yield by the two-step reaction from *p*-chloronitrobenzene and 7,7'-dihydroxy-4,4,4',4'-tetramethyl-2,2'-spirobichroman. High-molar-mass polyimides, polyamides, and poly(amide-imide)s have been obtained from the polycondensation of diamine **3** with various aromatic tetracarboxylic dianhydrides, aromatic dicarboxylic acids, and imide ring-bearing dicarboxylic acids, respectively. Some polyimides were soluble in organic solvents in spite of their high  $T_g$  values. All the polyamides and poly(amide-imide)s exhibited excellent solubility in a variety of organic solvents. All the polymers are amorphous and can be processed into transparent, flexible and tough films. These polymers showed  $T_g$ 's in the range of 150–280 °C and had a reasonable thermal stability. High solubility and not too high  $T_g$ 's indicate that most of the polymers are readily processable from solution or melt even at high molar masses. Thus, the improved processability of these polymers makes them an attractive high-performance material.

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