polymer

Synthesis and properties of polyimides derived from isomeric biphenyltetracarboxylic dianhydrides

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Abstract

2,2′,3,3′-Biphenyltetracarboxylic dianhydride (i-BPDA) was suggested as a monomer for the synthesis of soluble polyimides with high thermal stability, and an efficient method of its preparation has been developed. Polyimides derived from i-BPDA and aromatic diamines (i.e. 4,4′-oxydianiline, 2,2′-bis(trifluoromethyl)benzidine and 9,9′-fluorenylidene-4,4′-dianiline) showed high glass transition ($T_g > 330°C$) and degradation ($T_{d5} > 550°C$) temperatures, and were soluble in organic solvents (i.e. NMP, DMF, γ-butyrolacton, $CHCl_3$), although their mechanical properties were inferior to those of polyimides composed of semirigid 3,3′,4,4′-biphenyltetracarboxylic dianhydride (s-BPDA). Random copolymers, derived from i-BPDA and s-BPDA, retained superior mechanical properties of s-BPDA-based polyimides and showed improved solubilities, depending on the i-BPDA content. A regular increase of glass transition temperatures and a decrease of inherent viscosities of copolymers with increasing content of i-BPDA was observed, whereas the dielectric constants and degradation temperatures were found to be independent of the ratios of dianhydride units. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Biphenyltetracarboxylic dianhydrides; Aromatic polyimides; Polycondensation

1. Introduction

Aromatic polyimides have found various applications related to their excellent thermal and chemical stability, good mechanical properties, low dielectric constants and intrinsic purity [1]. They are considered as promising materials for electronics applications. However, many of the polyimides are insoluble in common solvents and should be processed via soluble precursors with subsequent thermal solid-state imidization. Since the so-obtained polymers may suffer from defects in chemical structure, partial depolymerization and bulk anisotropy, it may be prohibitive to their applications in high-precision devices.

To circumvent these problems, solutions of polyimides would be desirable, instead of precursors. Flexible links (e.g. $-O-$, $-SO_2-$, $-CH_2-$) or bulky groups (fluorenylidene, hexafluoropropylidene, etc.) are commonly employed as solubilizing moieties, but it often costs a decrease in thermal stability and chain stiffness of polyimides [2]. Alter-

natively, the solubilizing units may be derived from substituted biphenyls, increasing entropy factors due to rotational isomerism of benzene rings relative to aryl–aryl bond [3,4]. The relevant compounds of this class are biphenyltetracarboxylic dianhydrides (Scheme 1). Among them, 3,3′,4,4′-biphenyltetracarboxylic dianhydride (s-BPDA) was commercialized in the early 1980s and is widely used at present [5]. In contrast, an isomeric 2,2′,3,3′-biphenyltetracarboxylic dianhydride (i-BPDA) attracted much less attention, with only two publications in the open literature being found to date [6,7].

In the course of our work on thermally resistant low-dielectric organic materials, we were interested to examine i-BPDA-based polyimides, since their high thermal stability, good solubility and low anisotropy were anticipated. The recent publication of Ding and coworkers on a similar subject [7] prompted us to disclose results of our study. In this paper, we report: (i) the novel efficient synthesis of i-BPDA; (ii) the elucidation of the structure of the model compounds; (iii) the synthesis and properties of polyimides, derived from i-BPDA and common aromatic diamines; and (iv) the study of random copolymers based on i-BPDA/s-BPDA mixtures.

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s-BPDA
(symmetric)

a-BPDA
(asymmetric)

i-BPDA
(isomeric)
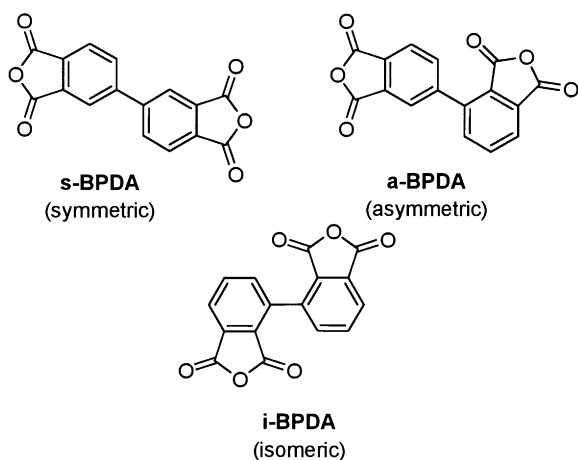
Scheme 1.

2. Experimental section

2.1. Materials

N,N-Dimethylformamide (DMF) was dried over CaH$_2$ and distilled under nitrogen prior to use. *m*-Cresol was dried over CaCl$_2$, then over 4 Å Linde type molecular sieves, distilled under reduced pressure and stored under nitrogen in the dark. *p*-Phenylenediamine (PDA) and *m*-phenylenediamine (MDA, both from Wako Chemicals) were purified by sublimation. 4,4′-Oxydianiline (ODA, from Mitsui Chemicals), 2,2′-bis(trifluoromethyl)benzidine (TFMB), 9,9′-fluorenylidene-4,4′-dianiline (FDA, both from Wakayama Seika Kogyo) and 3-chlorophthalic anhydride (from Mitsuboshi Chemicals) were used without additional purification. Other reagents were purchased from Wako Chemicals or Tokyo Kasei Kogyo and used as received.

2.2. Equipment

X-ray diffraction data were collected by a Rigaku AFC5R diffractometer. Details of analysis can be found elsewhere [8]. UV–visible absorption spectra were measured on a Hitachi U-3410 spectrophotometer either from CH$_2$Cl$_2$ solutions or from neat polymer films. FTIR spectra were recorded on JEOL JIR-5500 from KBr pellets or films cast onto KBr plates. ^{1}H NMR spectra were obtained on JEOL JNM-EX90 (90 MHz) in CDCl$_3$ or DMSO-d_6, with TMS as an internal standard. Inherent viscosities of 0.5 g/dl polymer solutions in specified solvents were measured with an Ubbelohde viscosimeter at 30°C. Mass-spectra (MS) were recorded on JEOL Automass GC/MS apparatus. Gas chromatography (GC) data were obtained from Shimadzu GC-12C instrument, with He as a carrier gas. Gel permeative chromatography (GPC) analyses were performed on a Shimadzu LC-10AD chromatograph, using Tosoh TSK gel, with a solution of LiBr (3 mM) and H$_3$PO$_4$ (10 mM) in DMF as an eluent and standard polystyrene as a reference. Melt-ing points (m.p.) were determined on a Yanaco micro melting point apparatus. Thermogravimetric analyses (TGA) were performed on Seiko SSC-5200 under N$_2$ flow (200 ml/min) with the scanning rate of 10°C/min. Degradation temperatures (T_{d5}) were defined as points, at which 5% weight loss occurred. Differential scanning calorimetry (DSC) measurements were carried out on DuPont DSC-2000 under N$_2$ flow (30 ml/min) with the scanning rate of 20°C/min. Glass transition temperatures (T_g) were determined as inflection points of the baseline in the second heating. Dielectric constants (ϵ) of polyimide films (thickness ranged from 1.5 to 10 μm), sandwiched between two electrodes, were measured on Hewlett Packard 4284A precision LCR meter at 1 MHz, at a constant temperature (23°C) and relative humidity (50%).

2.3. Synthesis of monomers and model compounds

2.3.1. 3,3′-Bis(N-methylphthalimide) (2)

A 5-necked 3 l flask, equipped with an overhead mechanical stirrer, a Dean-Stark trap, a thermometer, nitrogen inlet and outlet, was charged with 3-chlorophthalic anhydride (182.6 g, 1.00 mol), sodium iodide (30.0 g, 0.20 mol) and dimethylacetamide (DMAc, 0.75 l). The mixture was stirred under flow of dry nitrogen until the complete dissolution of solids, then cooled below 10°C on the ice bath. Methylamine (40% aq. solution, 115 ml, ca. 1.5 mol) was added via the syringe, the reaction mixture was stirred for 20 min, then toluene (300 ml) was added, and the stirring was continued under N$_2$ flow at 155°C for 6 h, until no more water was collected in the Dean-Stark trap. Most of the residual toluene was distilled off, and the reaction mixture was allowed to cool to 80°C. A mixture of anhydrous NiCl$_2$ (3.89 g, 0.03 mol) and PPh$_3$ (52.5 g, 0.20 mmol) was added at once, the solution was stirred for 10 min, then Zn dust (98.5 g, 1.50 mol) was added. An exothermic reaction immediately followed, and it was complete within 5 min (*Caution!* Foaming). The supernatant liquid was poured into methanol (3 l) and stirred for 20 min. The solids in the reaction flask were rinsed with DMAc (100 ml), and washings were added to methanol. The precipitate was separated by filtration, washed with methanol, then with *n*-hexane and thoroughly pressed to dryness. The crude product was stirred with CH$_2$Cl$_2$ (1.5 l) until the dissolution of the organic part, residual Zn was filtered off, and the solvent was removed by the rotary evaporator, to afford bis-imide **2** (112.5 g, 70%) as a pale-yellow powder, m.p. 258–259°C (from ethyl acetate). IR (KBr, cm^{-1}): 1772, 1701, 1441, 1388, 1265, 1003. ^{1}H NMR (CDCl$_3$): 3.10 (s, 6 H), 7.56–7.99 (m, 6 H). MS: 320 (calc. for C$_{18}$H$_{12}$N$_2$O$_4$ 320.30). GC: 99.7% peak area.

2.3.2. 2,2′,3,3′-Biphenyltetracarboxylic acid (3)

3,3′-Bis(*N*-methylphthalimide) (**2**, 102.0 g, 0.32 mol) was added to the stirred solution of NaOH (150 g, 3.75 mol) in water (0.5 l), and the suspension was gradually

Table 1
Elemental analysis of polyimides

Entry	Dianhydride		Diamine	Method	Formula	Molecular weight		Elemental analysis (%)		
	i-BPDA (%)	s-BPDA (%)						C	H	N
1	100	0	PDA	Two-step	$(C_{22}H_{10}N_2O_4)_n$	$(366.33)_n$	Calc.	72.13	2.75	7.65
							Found	71.99	2.52	7.39
2	100	0	PDA	One-step	$(C_{22}H_{10}N_2O_4)_n$	$(366.33)_n$	Calc.	72.13	2.75	7.65
							Found	71.03	2.05	7.68
3	100	0	MDA	Two-step	$(C_{22}H_{10}N_2O_4)_n$	$(366.33)_n$	Calc.	72.13	2.75	7.65
							Found	71.26	2.19	7.65
4	100	0	MDA	One-step	$(C_{22}H_{10}N_2O_4)_n$	$(366.33)_n$	Calc.	72.13	2.75	7.65
							Found	71.47	2.50	7.35
5	100	0	ODA	Two-step	$(C_{28}H_{14}N_2O_5)_n$	$(458.42)_n$	Calc.	73.36	3.08	6.11
							Found	72.75	2.70	6.13
6	100	0	ODA	One-step	$(C_{28}H_{14}N_2O_5)_n$	$(458.42)_n$	Calc.	73.36	3.08	6.11
							Found	73.96	2.62	5.98
7	0	100	ODA	Two-step	$(C_{28}H_{14}N_2O_5)_n$	$(458.42)_n$	Calc.	73.36	3.08	6.11
							Found	73.28	2.63	6.08
8	12.5	87.5	ODA	Two-step	$(C_{28}H_{14}N_2O_5)_n$	$(458.42)_n$	Calc.	73.36	3.08	6.11
							Found	72.85	2.59	6.14
9	25	75	ODA	Two-step	$(C_{28}H_{14}N_2O_5)_n$	$(458.42)_n$	Calc.	73.36	3.08	6.11
							Found	73.23	2.50	6.08
10	50	50	ODA	Two-step	$(C_{28}H_{14}N_2O_5)_n$	$(458.42)_n$	Calc.	73.36	3.08	6.11
							Found	72.68	2.57	6.18
11	100	0	TFMB	Two-step	$(C_{30}H_{12}F_6N_2O_4)_n$	$(578.42)_n$	Calc.	62.29	2.09	4.84
							Found	63.70	1.36	4.93
12	100	0	TFMB	One-step	$(C_{30}H_{12}F_6N_2O_4)_n$	$(578.42)_n$	Calc.	62.29	2.09	4.84
							Found	64.04	1.57	4.73
13	0	100	TFMB	Two-step	$(C_{30}H_{12}F_6N_2O_4)_n$	$(578.42)_n$	Calc.	62.29	2.09	4.84
							Found	64.11	1.43	4.83
14	12.5	87.5	TFMB	Two-step	$(C_{30}H_{12}F_6N_2O_4)_n$	$(578.42)_n$	Calc.	62.29	2.09	4.84
							Found	64.22	1.52	4.78
15	25	75	TFMB	Two-step	$(C_{30}H_{12}F_6N_2O_4)_n$	$(578.42)_n$	Calc.	62.29	2.09	4.84
							Found	64.20	1.52	4.71
16	50	50	TFMB	Two-step	$(C_{30}H_{12}F_6N_2O_4)_n$	$(578.42)_n$	Calc.	62.29	2.09	4.84
							Found	64.33	1.53	4.84
17	20	80	TFMB	One-step	$(C_{30}H_{12}F_6N_2O_4)_n$	$(578.42)_n$	Calc.	62.29	2.09	4.84
							Found	64.82	1.78	4.96
18	25	75	TFMB	One-step	$(C_{30}H_{12}F_6N_2O_4)_n$	$(578.42)_n$	Calc.	62.29	2.09	4.84
							Found	62.85	1.79	4.72
19	50	50	TFMB	One-step	$(C_{30}H_{12}F_6N_2O_4)_n$	$(578.42)_n$	Calc.	62.29	2.09	4.84
							Found	64.80	1.80	4.82
20	100	0	FDA	Two-step	$(C_{41}H_{22}N_2O_4)_n$	$(606.62)_n$	Calc.	81.18	3.66	4.62
							Found	81.34	3.41	4.57
21	100	0	FDA	One-step	$(C_{41}H_{22}N_2O_4)_n$	$(606.62)_n$	Calc.	81.18	3.66	4.62
							Found	81.41	3.38	4.62

heated to boiling. Reaction was continued until the complete dissolution of solids, then for 1 h more. The resulting orange–yellow solution was acidified with conc. HCl to pH 7–8. Activated charcoal (2–3 teaspoons) was added, the mixture was boiled for 10 min, then filtered. The filtrate was heated to boiling, acidified with conc. HCl to pH $\leq$ 1 (375 ml of acid was consumed in both steps) and left to cool overnight. The precipitate was filtered off, washed with distilled water (200 ml) and dried, to afford tetra-acid **3** (105.3 g, ca. 95%) as a colorless powder. IR (KBr, cm^{-1}): 3430, 3082, 2638, 2546, 1722, 1697, 1284. ^{1}H NMR (DMSO-d_6): 7.40–7.67 (m, 4 H), 7.88 (dd, $J_1 = 7$ Hz, $J_2 = 2$ Hz, 2 H).

2.3.3. 2,2′,3,3′-Biphenyltetracarboxylic dianhydride (i-BPDA)

2,2′,3,3′-Biphenyltetracarboxylic acid (**3**, 69.0 g) was placed into a 3 l flask equipped with a magnetic stirrer bar and a Dean-Stark trap, with CaCl$_2$ tube attached at the outlet of the condenser. Xylene (1400 ml) and DMSO (150 ml) were added, and the reaction mixture was refluxed with stirring for 5 h, until no more water appeared in the trap. The hot solution was transferred into a 5 l beaker, diluted with xylene (700 ml) and placed onto the ice bath for 2 h. The precipitate was separated by filtration, washed with xylene, then with *n*-hexane and dried in vacuo, to afford i-BPDA (48.0 g, 80%, relative to **2**) as colorless crystals,
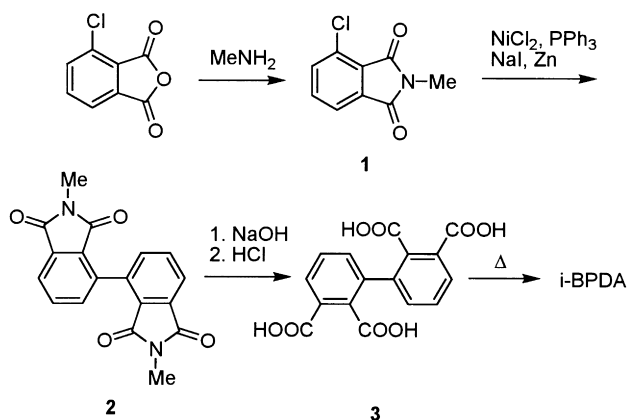
Scheme 2.

m.p. 272–273°C (from xylene/DMSO, literature [7] 268–269°C). IR (KBr, cm^{-1}): 1847, 1774, 1263, 1222, 906. ^{1}H NMR (DMSO-d_6): 8.03–8.30 (m). MS: 294 (calc. for $C_{16}H_6O_6$ 294.22). GC: > 99.8% peak area.

2.3.4. 3,3′-Bis(N-phenylphthalimide) (4) and 4,4′-bis(N-phenylphthalimide) (5)

Acetic acid (50 ml) and i-BPDA (2.94 g, 10 mmol) were placed in a 200 ml flask equipped with a reflux condenser and a magnetic stirred bar under nitrogen. Aniline (2.51 g, 27 mmol) was added via the syringe, the reaction mixture was refluxed with stirring for 3 h, then was left to cool overnight. The precipitate was collected by filtration, washed with methanol and dried in vacuo, to afford 3,3′-bis(N-phenyl)phthalimide (4, 4.00 g, 90%) as fine colorless crystals, m.p. 277–279°C (from sublimation) or 240.5–242°C (from melt). IR (KBr, cm^{-1}): 1774, 1713, 1377. Single crystals for X-ray diffraction analysis were obtained by slow sublimation of the powdered sample. 4,4′-Bis(N-phenylphthalimide) (5) was prepared by the same procedure from s-BPDA (2.94 g, 10 mmol) and aniline (2.51 g, 27 mmol) in 95% yield, m.p. 387–389°C (from sublimation).

2.4. General procedure for the two-step synthesis of polyimides

Diamine (4–7 mmol) and DMF (22–27 ml) were placed in a 3-necked 100 ml flask equipped with a mechanical stirrer, nitrogen inlet and outlet. The reaction system was purged with dry nitrogen for 30 min at room temperature. An equimolar amount of powdered i-BPDA was added to the reaction solution at once. The final concentration of solids was 15% by weight. The reaction mixture was stirred under the steady flow of nitrogen at room temperature for 18 h. The resulting poly(amic acid) solution was transferred into the sample bottle and stored in the refrigerator at 0°C. The thermal imidization was accomplished by exposing solution-cast or spin-coated films at 80°C for 2 h, followed by the thermal treatment at 150°C (45 min), 200°C

(45 min), 250°C (45 min) and 300°C (45 min), in succession. Elemental analysis data of polyimides are given in Table 1.

2.5. General procedure for the one-step synthesis of polyimides

Diamine (4–6 mmol) and m-cresol (25–28 ml) were placed in a 3-necked 100 ml flask equipped with a mechanical stirrer, a Dean-Stark trap, nitrogen inlet and outlet. The reaction flask was purged with dry N$_2$ for 30 min, the mixture was stirred until the complete dissolution of amine, then an equimolar amount of powdered i-BPDA (or i-BPDA/s-BPDA mixture) and seven drops of isoquinoline were added. The final concentration of solids was 10–12% by weight. The mixture was stirred at 100°C until the complete dissolution of solids, then the temperature of an oil bath was gradually raised to 200°C within 1 h. The reaction mixture was stirred at these conditions for 15 h under the steady flow of nitrogen, and then poured into methanol (1 l). The precipitate was filtered off, washed freely with methanol, extracted with methanol in a Soxhlet extractor for 6 h and dried in vacuo, to afford powdered polyimide in 80–98% yield. Elemental analysis data of polyimides are given in Table 1.

3. Results and discussion

3.1. Synthesis of 2,2′,3,3′-biphenyltetracarboxylic dianhydride

According to the literature, i-BPDA can be obtained by the Ullmann coupling of dimethyl-3-iodophthalate with subsequent hydrolysis of tetra-ester and dehydration of tetra-acid [6,7]. However, this method suffers from harsh conditions (260°C in the bulk), tedious work up and poor reproducibility of the coupling reaction. Moreover, the starting 3-iodophthalates are not readily available and should be synthesized by multistep procedures in modest overall yields.

Some time ago, Ni-catalyzed dehalogenative coupling of aryl chlorides was established as a versatile method for the synthesis of symmetrical biaryls [9]. Ding et al. successfully applied this procedure to the preparation of s-BPDA from readily accessible 4-chlorophthalic anhydride [10], but failed to extend it to i-BPDA, claiming steric factor as a possible cause [7]. Being unaware of that failure, we were looking for the procedure based on the available 3-chlorophthalic anhydride. It was found that its derivatives (i.e. N-substituted phthalimides and dialkylphthalates) readily underwent coupling reactions to form 3,3′-bis(phthalimides) and 2,2′,3,3′-biphenyltetracarboxylates, respectively. The exothermic reaction of 3-chlorophthalimides was complete within minutes, while 1.5–2 h (at ca. 80°C) were required for the coupling of di-esters, independent of the scale. The only detected side reaction was the reductive

Table 2
Selected crystal data of model bis-imides

	Bis-imide **4**	Bis-imide **5**
Space group	$P2_1/n$	$P2_1/c$
Lattice parameters	$a = 12.140(2)$ Å	$a = 8.399(2)$ Å
	$b = 12.934(3)$ Å	$b = 6.890(4)$ Å
	$c = 14.212(3)$ Å	$c = 17.858(2)$ Å
	$\beta = 108.63(2)°$	$\beta = 90.87(1)°$
	$V = 2114.7(8)$ Å^3	$V = 1033.2(5)$ Å^3
Z value	4	2
D_{calc}	1.398 g/cm^3	1.428 g/cm^3
No. of reflections measured	6742	3608

Fig. 2. UV spectra of **4** (solid line) and **5** (broken line) in CH$_2$Cl$_2$ (10^{-5} M).

dehalogenation, which might occur in the presence of proton donors [9].

The multigram-scale procedure via imide protection has been designed (Scheme 2). Since it was unnecessary to isolate *N*-methyl-3-chlorophthalimide (**1**), protection and coupling steps were combined in a one-pot sequence, in which catalyst (NiCl$_2$, PPh$_3$ and NaI) and reducing agent (Zn dust) were added to the pre-formed solution of **1** in DMAc. According to GC, **1** was consumed within 4–6 min after addition of Zn, with evolution of much heat. Only **2** (80–88%) and the product of the side reaction, *N*-methylphthalimide (12–20%), were detected. The simple work up afforded bis-imide **2** as the only product in a good yield. Tetra-acid **3** was isolated after the alkaline hydrolysis of **2** and was converted to i-BPDA by heating in xylene/DMSO mixture. The latter method was found advantageous compared to the common dehydration in acetic anhydride, because it afforded highly pure and essentially colorless product in better yield.
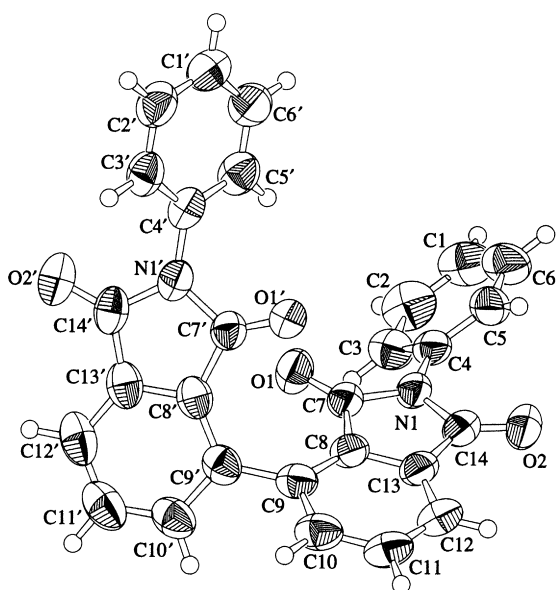
3.2. Synthesis, properties and structure of model compounds

The structural features of repeating units in i-BPDA-derived polyimides were estimated from the model bis-imide **4**, which was synthesized by the reaction of i-BPDA with aniline. For comparison, the isomeric model compound **5** was also prepared from s-BPDA. The structure of both bis-imides was elucidated from single-crystal X-ray diffraction measurements (Table 2). As expected, steric hindrance forced phthalimide planes in **4** to be non-coplanar, adopting *syn* conformation of imide units, with a dihedral angle of 53° (Fig. 1). In contrast, imide rings in molecules of **5** were coplanar, and this compound crystallized in a bilayer

Fig. 1. Molecular structure of 3,3′-bis(*N*-phenylphtalimide) (**4**).
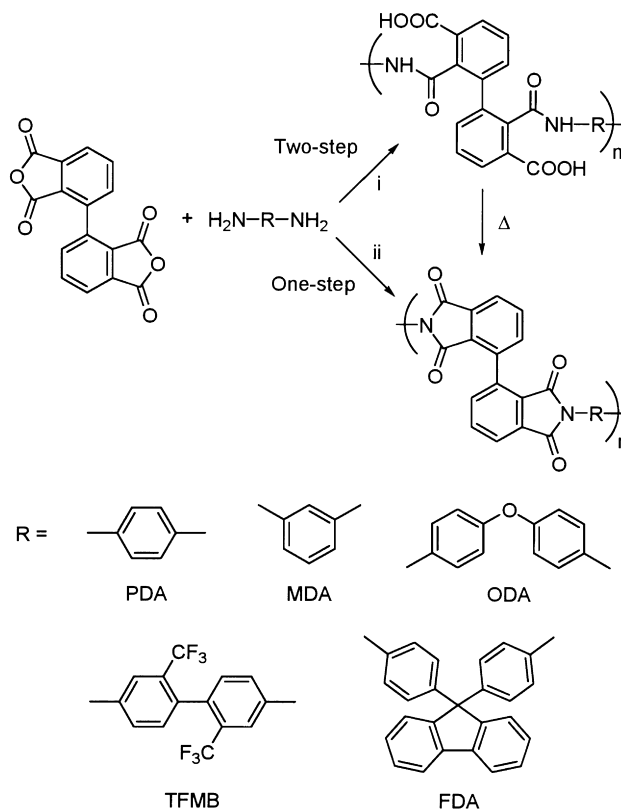
Scheme 3.

Table 3
Properties of polyimides, obtained by the two-step method

Designation	η_{inh}[a] (dl/g)	T_{d5}[b] (°C)	T_g (°C)	ϵ[c]	Film appearance, color[d]
i-BPDA–PDA	0.32	568	n.o.[e]		Highly brittle, dark-yellow
i-BPDA–MDA	0.43	552	n.o.		Highly brittle, brown
i-BPDA–ODA	0.56	553	326	3.22	Brittle, brown
i-BPDA–TFMB	0.25	583	346	2.79	Brittle, yellow
i-BPDA–FDA	0.40	576	n.o.	3.31	Brittle, yellow

[a] Measured for poly(amic acids) in DMF.
[b] Five percent weight loss in N_2.
[c] Dielectric constant at 1 MHz.
[d] Referred to a. 10 μm film.
[e] Not observed.

fashion [8]. The density of **4** was appreciably lower, compared with **5**, presuming lesser degree of intermolecular interactions. Values of melting points are in agreement with these data. UV spectra of model compounds indicated lower degree of conjugation for **4**, as may be concluded from the different intensities of their $\pi-\pi^*$ bands (Fig. 2).

Assuming a similar configuration of repeating units in polymers, an increase in solubility for polymers with i-BPDA moieties might be anticipated, because of the bigger number of conformational isomers and the presumed inability to crystallize. The decreased coloration of i-BPDA-based polyimides might be expected due to the broken conjugation in phthalimide units. At the same time, the trend of bis-imide **4** to adopt *syn* conformations may indicate a facile formation of undesired cyclic oligomers.

3.3. Synthesis and properties of polyimides derived from i-BPDA and common diamines

Polyimides from i-BPDA and commercially available diamines (both rigid-rod and bent) were synthesized by two methods (Scheme 3). In the two-step process, reactions of i-BPDA and diamines were performed in DMF at room temperature, to afford poly(amic acid) solutions. Polyimides were obtained as films after casting and thermal treatment of precursors (Table 3). Polyimides from one-step polycondensations were prepared by the reaction in hot *m*-cresol and isolated by the precipitation of reaction mixtures into methanol. Films were prepared (whenever possible) by the re-dissolution of powdered samples in *N*-methylpyrrolidinone (NMP), followed by the standard casting procedures (Table 4).

IR spectra of polyimides showed absorptions at ca. 1780 and 1720 cm^{-1}, which are characteristic of the cyclic imide groups. An absence of bands assignable to poly(amic acids) confirms the complete imidization by both the one-step and the two-step procedures. Expected structures were confirmed by elemental analyses. The moderate inherent viscosities of polymers would indicate either the decreased reactivity of sterically hindered i-BPDA or the peculiarities of molecular shapes, because globular conformations with low degree of entanglements should be favored for such twisted repeating units.

Another reason for reduced molecular weights might be the formation of cyclic oligomers. GPC charts typically showed bimodal distributions, in which peaks at longer retention times would correspond to di- or trimers (Fig. 3). Some oligomeric fractions were separated by the treatment of crude polymers with chloroform (i-BPDA–FDA, oligo-

Table 4
Properties of polyimides, obtained by the one-step method

Designation	η_{inh}[a] (dl/g)	M_w[b] (M_w/M_n)	Yield[c] (%)	T_{d5}[d] (°C)	T_g (°C)	Film appearance, color[e]
i-BPDA–PDA			97	584	n.o.[f]	Yellow powder, no film forming.
i-BPDA–MDA	0.32[g]		98	578	337	Yellow powder, no film forming.
i-BPDA–ODA	0.39	66 900 (3.56)	94	575	332	Flexible, light-yellow
i-BPDA–TFMB	0.40	63 700 (6.72)	83	602	343	Brittle, colorless
i-BPDA–FDA	0.24	40 000 (2.63)	96 (68[h])	576	n.o.	Brittle, yellow

[a] Measured in NMP, unless otherwise noted.
[b] Measured by GPC in DMF, higher molecular weight peaks.
[c] Isolated yields.
[d] Five percent weight loss in N_2.
[e] Referred to a. 10 μm film.
[f] Not observed.
[g] Measured in *p*-chlorophenol at 60°C.
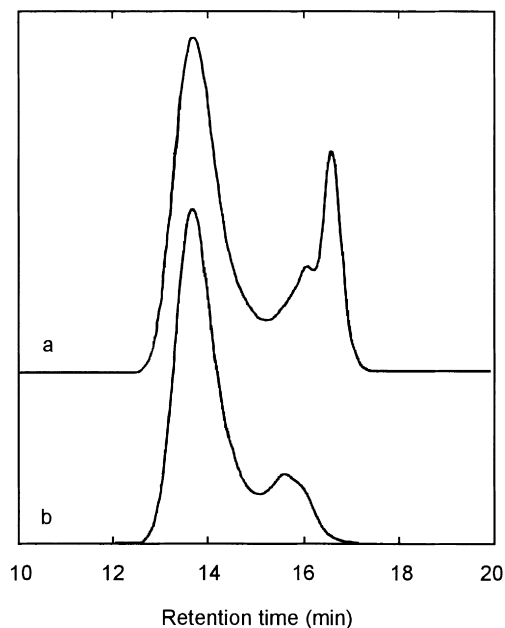[h] CHCl$_3$-soluble (polymeric) part.

Fig. 3. GPC traces of polyimides, obtained by the one-step method: (a) i-BPDA–ODA; and (b) i-BPDA–FDA.

mers precipitated) or by Soxhlet extraction with methanol (i-BPDA–TFMB, oligomers were extracted). IR spectra of these fractions were virtually indistinguishable from the spectra of the corresponding polymers. Since neither of the end groups were detected, an assignment of these products to cyclic species is likely.

Except for i-BPDA–PDA and i-BPDA–MDA, reported polyimides were soluble in a variety of solvents, including amides (NMP, DMF), γ-butyrolacton and chlorinated hydrocarbons, with i-BPDA–TFMB being soluble also in THF and acetone (Table 5). The latter observation conforms to the literature data concerning the solubilizing effect of trifluoromethyl groups [11]. Solutions of i-BPDA–ODA
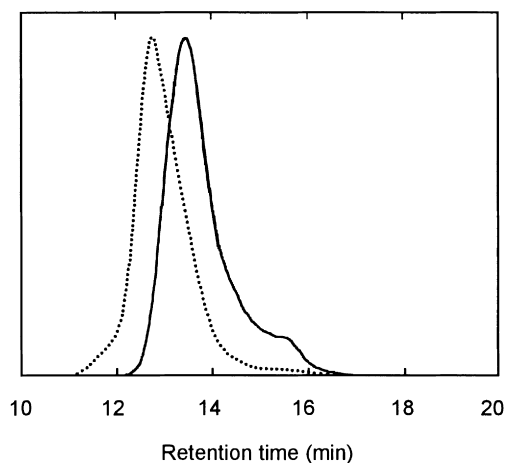

Fig. 4. GPC traces of homopolymer i-BPDA–TFMB (solid line) and copolymer i-BPDA(0.5)–s-BPDA(0.5)–TFMB (dotted line), obtained by the one-step method.
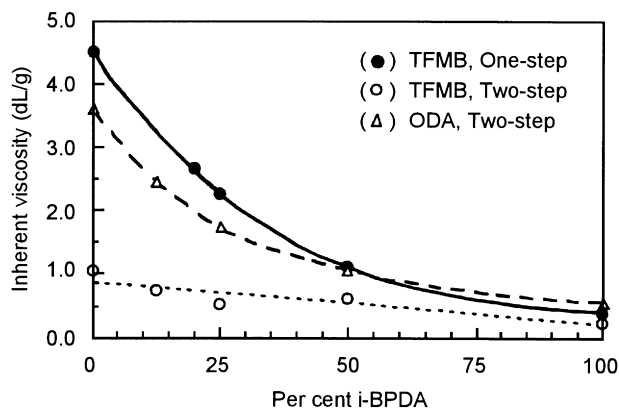

Fig. 5. Inherent viscosities of BPDA-derived homo- and copolyimides vs. content of i-BPDA units. Data of Ref. [13] are used for s-BPDA–TFMB homopolymer from the one-step procedure.

were rather unstable and turned to gels in time, except for solutions in phenolic solvents, which were stable for years. Initially, there was a possibility of reverse gelation by heating, but the gels gradually became irreversible and turbid. Probably, this process is related to the known spinodal decomposition-driven gelation of polymers in poor solvents, such as atactic polystyrene in decalin [12].

All the reported polyimides showed high glass transition ($T_g > 330°C$) and degradation ($T_{d5} > 550°C$) temperatures, depending on their diamine moieties. Polymers from one-step procedures were superior with respect to thermal stability, which may be assigned to the lower concentration of structural defects in solution-imidized species. The lesser coloration of polyimides from one-step procedures might be explained by the same reason. Dielectric constants of i-BPDA-derived polyimides were found close to the known values for isomeric polymers from s-BPDA [13,14].

3.4. Synthesis and properties of i-BPDA/s-BPDA random copolymers

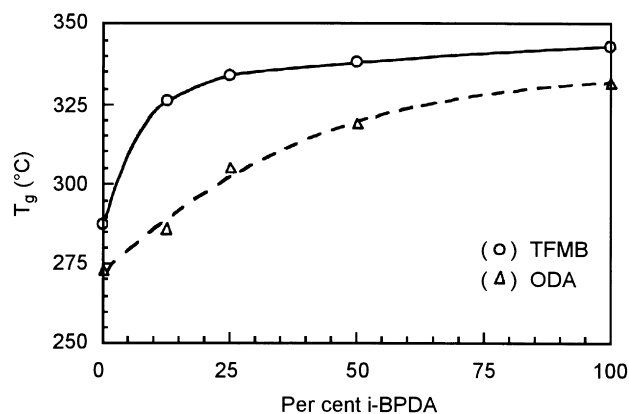Recently, the semiconductors community paid a considerable

Fig. 6. Glass transition temperatures of BPDA-derived homo- and copolyimides vs content of i-BPDA units.

Table 5
Solubility of i-BPDA-derived polyimides (+ soluble; ± partially soluble; — insoluble; (g) forms gel on standing)

	p-Chlorophenol	m-Cresol	NMP	DMF	γ-Butyrolacton	Chloroform	Cyclohexanone	THF	Acetone
i-BPDA–PDA	±	—	—	—	—	—	—	—	—
i-BPDA–MDA	±	±	±	±	—	—	—	—	—
i-BPDA–ODA	+	+	+ (g)	+ (g)	±	+ (g)	±	±	—
i-BPDA–TFMB	+	+	+	+	+	+	+	+	+
i-BPDA–FDA	+	+	+	+	+	+	+	±	±

attention to fluorinated polyimides, since their low dielectric constants, low moisture uptake and good thermal stability make them perspective candidates to interlayer dielectrics [15–17]. The novel i-BPDA–TFMB polyimide is attractive, because it combines high thermal stability and high T_g with solubility in non-toxic solvents. However, its mechanical properties are rather poor. Strong films can be afforded from s-BPDA–TFMB isomer, but it is soluble only in hot phenolic solvents [13]. Moreover, spin-coated films of this polymer are highly anisotropic [18], while isotropic materials are required. One can expect the suitable combination of properties from copolymers, based on i-BPDA/s-BPDA mixtures. A series of copolyimides was obtained from TFMB and various combinations of i-BPDA and s-BPDA by the same procedures as those for homopolymers. In addition, copolymers with ODA units were synthesized by the two-step method (Table 6).

In agreement with the literature data [13,19], homopolymers with s-BPDA units were soluble only in hot phenolic solvents, with a strong tendency to gelation on cooling, while examined copolyimides formed stable solutions in m-cresol at room temperature. This improvement was achieved by replacing just 1/8 of s-BPDA units by their twisted isomers (i-BPDA). Among the less toxic solvents, NMP showed the best solvation power. Only i-BPDA(0.125)–s-BPDA(0.875)–ODA (Table 6, entry 2) was partly soluble, while other copolymers could be

dissolved in warm NMP up to 10 wt.%. Similar to homopolymer i-BPDA–ODA, gelation was observed on cooling the solutions of the corresponding copolymers. The TFMB-containing copolyimides formed rather stable solutions in NMP, but were partly soluble or turned to gels in DMF and γ-butyrolacton.

An introduction of s-BPDA units led to the apparent changes in the molecular weights of the polymers. Nearly a 5-fold increase in M_w was detected by GPC for i-BPDA(0.5)–s-BPDA(0.5)–TFMB (Table 6, entry 11) compared with i-BPDA–TFMB homopolymer, to be 299 400 (M_w/M_n 6.72) vs. 63 600 (M_w/M_n 6.95), respectively (Fig. 4). Other copolyimides were not soluble enough to be characterized by GPC, but their inherent viscosities showed the same trend, increasing regularly with higher ratios of s-BPDA to i-BPDA (Fig. 5). High inherent viscosities were obtained from polyimides with TFMB units, when one-step procedures were applied. The failure to reproduce their values by the two-step method may be due to low nucleophilicity of TFMB [20], which is responsible for its moderate reactivity at ambient temperatures and/or in aprotic solvents.

A prominent effect of dianhydride ratios on glass transition temperatures indicates higher stiffness of backbones with i-BPDA units (Fig. 6). This effect is characteristic of polymers with sterically hindered substituents and restricted motion of main chains [3]. Thermal stabilities of both

Table 6
Properties of random copolyimides derived from isomeric biphenyltetracarboxylic dianhydrides

Entry	i-BPDA (%)	s-BPDA (%)	Diamine	Method	η_{inh}[a] (dl/g)	T_{d5}[b] (°C)	T_g (°C)	ϵ[c]	Film appearance, color[d]
1	0	100	ODA	Two-step	3.61	554	273	3.11	Tough, flexible, yellow
2	12.5	87.5	ODA	Two-step	2.46	563	286	3.11	Tough, flexible, yellow
3	25	75	ODA	Two-step	1.73	563	305	3.27	Flexible, yellow
4	50	50	ODA	Two-step	1.07	558	319	3.33	Flexible, yellow
5	0	100	TFMB	Two-step	1.04	575	287	2.39	Flexible, yellow
6	12.5	87.5	TFMB	Two-step	0.74	573	326	2.76	Flexible, yellow
7	25	75	TFMB	Two-step	0.52	583	334	2.70	Brittle, yellow
8	50	50	TFMB	Two-step	0.63	585	338	2.87	Brittle, yellow
9	20	80	TFMB	One-step	2.65	591		2.84	Tough, flexible, colorless
10	25	75	TFMB	One-step	2.26	583			Tough, flexible, colorless
11	50	50	TFMB	One-step	1.12	589			Tough, flexible, colorless

[a] Measured in DMF (two-step, referred to PAA) or m-cresol (one-step).
[b] Five percent weight loss in N_2.
[c] Dielectric constant at 1 MHz.
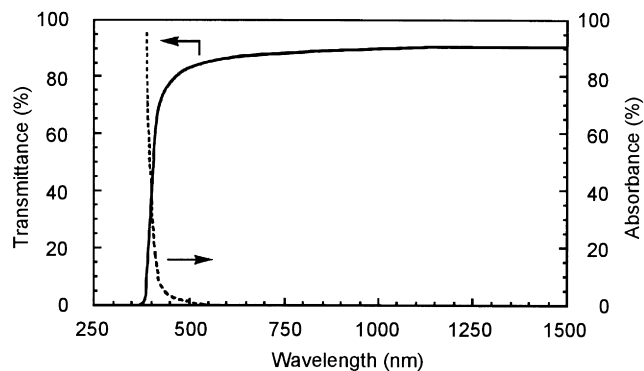[d] Referred to ca. 10 μm film.

Fig. 7. Optical spectrum of film of i-BPDA(0.2)–s-BPDA(0.8)–TFMB copolyimide (thickness 14 μm), obtained by the one-step method.

i-BPDA and s-BPDA units are rather similar, judging from the similar degradation temperatures of copolyimides of different compositions. Dielectric constants are actually independent of i-BPDA/s-BPDA ratios, with the only exception of homopolymer s-BPDA–TFMB (Table 6, entry 5). The low ϵ value for the latter might be due to the well-documented anisotropy of rigid-rod polyimides, which is enhanced by spin-coating and thermal imidization processes. The difference between in-plane and out-of-plane components of dielectric constants may be as high as 0.5–0.7 [21,22]. The latter component is determined by capacitance measurements and it is lower because of preferable in-plane orientation of dipoles.

Films of good mechanical and optical quality were cast from NMP solutions of i-/s-BPDA–TFMB copolyimides. Polymers from one-step procedure were advantageous. UV–visible spectra of the films showed broad transparency windows and low absorbance in the wide frequency range (Fig. 7). The use of NMP as a casting solvent seems crucial, because solutions in *m*-cresol, apart from their toxicity, yielded colored films with appreciable content of residual solvent. According to TGA, up to 5 wt.% of *m*-cresol remained in the film after 1 day in vacuum at 250°C, while films cast from NMP were solvent-free after 2 h drying in vacuum at 200°C.

4. Conclusions

2,2′,3,3′-Biphenyltetracarboxylic dianhydride (i-BPDA) was proposed as the thermally stable unit for the construction of polyimides with improved processabilities. The efficient multigram-scale method of its synthesis has been established. The structure of model 3,3′-bis(*N*-phenylphthalimide) has been elucidated from single-crystal X-ray analysis. Imide planes of this model compound adopted non-coplanar conformation with a dihedral angle of 53°. Polyimides, derived from i-BPDA and a number of aromatic diamines were synthesized by two methods, i.e. the two-step procedure via poly(amic acid s) and the one-step direct polycondensation in *m*-cresol. Most of the polymers exhibited excellent thermal properties and improved solubilities, compared with their analogs, derived from s-BPDA. The poor mechanical properties of i-BPDA-based polyimides were improved by copolymerization with s-BPDA. Random copolyimides from i-BPDA, s-BPDA and TFMB were readily soluble in NMP, exhibited dielectric constants of 2.8 and formed tough, flexible, nearly colorless films.

Acknowledgements

References

[1] Bessonov MY, Koton MM, Kudryavtsev VV, Laius LA. Polyimides: thermally stable polymers. New York: Consultants Bureau, 1987.
[2] de Abajo J, de la Campa JG. Adv Polym Sci 1999;140:23.
[3] Li F, Fang S, Ge JJ, Honigfort PS, Chen JC, Harris FW, Cheng SZD. Polymer 1999;40:4571.
[4] Li F, Ge JJ, Honigfort PS, Fang S, Chen JC, Harris FW, Cheng SZD. Polymer 1999;40:4987.
[5] Itaaki H, Yoshimoto H. J Org Chem 1973;38:76.
[6] Kenner J, Mattews AM. J Chem Soc 1914;105:2479.
[7] Tong Y, Huang W, Luo J, Ding M. J Polym Sci, Polym Chem Ed 1999;37:1425.
[8] Okuyama K, Rozhanskii I, Goto K. Acta Crystallogr C 1999;55:424.
[9] Colon I, Kelsey DR. J Org Chem 1986;51:2627.
[10] Ding M, Wang Z, Yang Z, Zhang J. US Patent 5081281, 1992.
[11] Bruma M, Fitch JW, Cassidy PE. J Macromol Sci, Rev Macromol Chem Phys 1996;C36:119.
[12] Wellinghoff S, Shaw J, Baer E. Macromolecules 1979;12:932.
[13] Arnold FE, Cheng SZD, Hsu SLC, Lee CJ, Harris FW, Lau SF. Polymer 1992;40:4987.
[14] Rozhanskii I, Matsubara M, Goto K. Unpublished data.
[15] Matsuura T, Ishizawa M, Hasuda Y, Nishi S. Macromolecules 1992;25:3540.
[16] Feiring AE, Auman BC, Wonchoba ER. Macromolecules 1993;26:2779.
[17] Hougham G, Tesoro G, Shaw J. Macromolecules 1994;27:3642.
[18] Li F, Savitski EP, Chen JC, Yoon Y, Harris FW, Cheng SZD. Polym Prepr (ACS Polym Series) 1997;38(I):368.
[19] Inoue H, Sasaki Y, Ogawa T. J Appl Polym Sci 1996;60:123.
[20] Ando S, Matsuura T, Sasaki S. Polym J 1997;29:69.
[21] Boese D, Lee H, Yoon DY, Swallen JD, Rabolt F. J Polym Sci, Polym Phys Ed 1992;30:1321.
[22] Hardaker SS, Samuels RJ. J Polym Sci, Polym Phys Ed 1997;35:777.