Synthesis and Properties of Polyimides Derived from 2,2′,3,3′-Biphenyltetracarboxylic Dianhydride

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Summary

2,2′,3,3′-Biphenyltetracarboxylic dianhydride (i-BPDA) was suggested as a monomer for the synthesis of soluble polyimides with keeping 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 and degradation 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 good mechanical properties of s-BPDA-based polyimides and showed improved solubilities, depending on 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 independent of ratios of dianhydride units.

Introduction

Aromatic polyimides represent an important class of high-performance polymers. Since the most of commercially available polyimides are insoluble in common solvents, they are usually processed via soluble precursors, that is not always suitable for some applications. A number of soluble or melt-processable polyimides is available, but their thermal resistance is inferior because of thermally labile flexible links in the backbones. Alternatively, the solubilizing units may be derived from thermally robust substituted biphenyls, employing entropy factors of rotational isomerism of imide planes [1,2]. The relevant compounds of this class are biphenyltetracarboxylic dianhydrides (Scheme 1). Polyimides derived from 3,3′,4,4′-biphenyltetracarboxylic dianhydride (s-BPDA) are known to be strong and the most thermally resistant among this class of polymers, but they are poorly soluble and highly anisotropic. It was expected that an introduction of twisted i-BPDA units may lead to the good solubility and low anisotropy of corresponding polyimides, with little damage of other useful properties.

s-BPDA
(symmetric)

a-BPDA
(asymmetric)

i-BPDA
(isomeric)
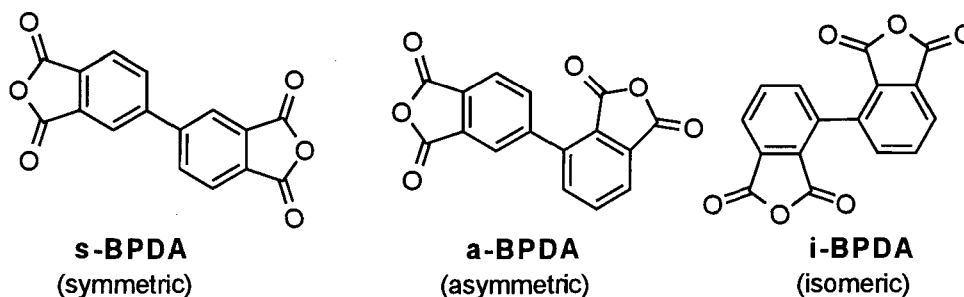
Scheme 1

Experimental

3,3′-Bis(N-methylphthalimide) (2). Methylamine (40 % aq. solution, 115 ml, *ca.* 1.5 mol) was added to the ice-cold nitrogen-purged solution of 3-chlorophthalic anhydride (182.6 g, 1.00 mol) and sodium iodide (30.0 g, 0.20 mol) in dimethylacetamide (DMAc, 0.75 l) via the syringe. The mixture was stirred for 20 min, then toluene (300 ml) was added, and stirring was continued under N_2 flow at 155 °C for 6 h, until no more water was collected in the Dean-Stark trap. The reaction mixture was cooled to 80 °C, then anhydrous $NiCl_2$ (3.89 g, 0.03 mol), PPh_3 (52.5 g, 0.20 mmol) and Zn dust (98.5 g, 1.50 mol) were added in succession. An exothermic reaction immediately followed, and it was complete within 5 min. The reaction mixture was poured into methanol (3 l), the precipitate was separated by filtration, washed with methanol, then with *n*-hexane, and dried. The crude product was stirred with CH_2Cl_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 $C_{18}H_{12}N_2O_4$ 320.30). GC: 99.7 % peak area.

2,2′,3,3′-Biphenyltetracarboxylic acid (3). A mixture of 3,3′-bis(*N*-methyl-phthalimide) (**2**, 102.0 g, 0.32 mol), NaOH (150 g, 3.75 mol) and water (0.5 l) was gently boiled 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, boiled with activated charcoal (2 - 3 teaspoons) for 10 min, then filtered. The filtrate was heated to boiling, acidified with conc. HCl to pH ≤ 1 and left to cool overnight. The precipitate was filtered off, washed with distilled water (200 ml) and dried, to afford tetraacid **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).

2,2′,3,3′-Biphenyltetracarboxylic dianhydride (i-BPDA). A mixture of 2,2′,3,3′-biphenyltetracarboxylic acid (**3**, 69.0 g), xylene (1400 ml) and DMSO (150 ml) was refluxed with stirring for 5 h, until no more water appeared in the Dean-Stark trap. The

resulting colorless solution was 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, to afford i-BPDA (48.0 g, 80 %, relative to **2**) as colorless crystals, m.p. 272 - 273 °C (from xylene/DMSO). 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.

General procedure for the two-step synthesis of polyimides. Diamine (4 - 7 mmol) and N,N-dimethylformamide (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 dianhydride 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, then stored at 0 °C prior to use. The thermal imidization was accomplished by drying 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.

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 dianhydride and 7 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, then poured into methanol (1 l). The precipitate was filtered off, washed with methanol, extracted with methanol in a Soxhlet extractor for 6 h and dried *in vacuo*, to afford powdered polyimide.

Results and Discussion

In this work, homo- and copolymers were prepared from s-BPDA and i-BPDA. The former is commercially available, whereas the latter was synthesized from 3-chlorophthalic anhydride, with Ni-catalyzed dehalogenative coupling of aryl chlorides being the key step [3]. The multigram-scale procedure via imide protection of anhydride groups has been designed. Protection and coupling steps were combined in a one-pot sequence, in which catalyst and reducing agent were added to the pre-formed solution of N-methyl-3-chlorophthalimide (**1**) in DMAc. The simple workup afforded 3,3'-bis(N-methyl-

phthalimide) (2) as the only product in a good yield. Tetraacid 3 was isolated after the alkaline hydrolysis of 2, and it was converted to i-BPDA by heating in xylene/DMSO.

Polyimides were synthesized by two methods (Scheme 2). In the two-step process, reactions 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 1). Polyimides from one-step polycondensations were prepared by the reaction in hot *m*-cresol, with catalytic amounts of isoquinoline, and isolated by the precipitation of reaction mixtures into methanol (Table 2).

Scheme 2
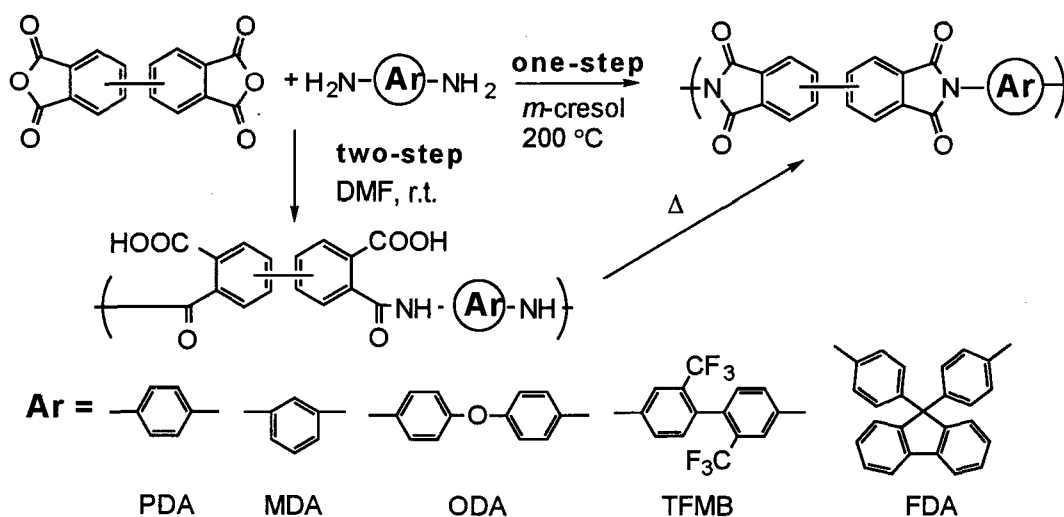
IR spectra of polyimides showed absorptions at *ca* 1780 and 1720 cm^{-1}, which are characteristic for cyclic imide groups. An absence ob bands assignable to poly(amic acid)s indicates their high degrees of imidization. An authenticity of polymers was further confirmed by elemental analysis.

Homopolymers derived from i-BPDA showed moderate inherent viscosities due to, probably, relatively low reactivity of sterically hindered i-BPDA. Moreover, GPC charts of these homopolymers typically showed bimodal distributions, in which peaks at longer retention times can be assigned to cyclic oligomers. These by-products are more abundant in case of one-step procedures, indicative of reversible polymerization-depolymerization high-temperature processes. Copolymerization with s-BPDA greatly improved both molecular weights and mechanical properties of polymers, and tough flexible films could be easily prepared.

Except for i-BPDA-PDA and i-BPDA-MDA, i-BPDA-derived 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. In contrast, homopolymers with s-BPDA units were soluble only in hot phenolic

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solvents, with 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 less toxic solvents, NMP showed the best solvation power. Solubility of copolymers in other solvents was dependent on the content of i-BPDA units, as well as on diamine. Similar to homopolymer i-BPDA-ODA, gelation was observed on cooling solutions of corresponding copolymers. TFMB-containing copolyimides formed rather stable solutions in NMP, but were partly soluble or turned to gels in DMF and γ-butyrolacton.

Table 1. Properties of polyimides obtained by the two-step method.

Entry	Diamine	i-BPDA (%)	s-BPDA (%)	η_{inh}^{a} (dL/g)	T_{d5}^{b} (°C)	T_{g}^{c} (°C)	ε^{d}
1	PDA	0	100	2.13	564		2.79
2	- " -	100	0	0.32	564	*n.o.*	
3	MDA	0	100	1.51	548		3.58
4	- " -	100	0	0.43	552	*n.o.*	
5	ODA	0	100	3.61	555	273	3.11
6	- " -	12.5	87.5	2.46	563	286	3.11
7	- " -	25	75	1.73	563	305	3.27
8	- " -	50	50	1.07	558	319	3.33
9	- " -	100	0	0.56	553	326	3.22
10	TFMB	0	100	1.04	575	287	2.39
11	- " -	12.5	87.5	0.74	573	326	2.76
12	- " -	25	75	0.52	583	334	2.70
13	- " -	50	50	0.63	585	338	2.87
14	- " -	100	0	0.25	583	346	2.79
15	FDA	0	100	0.58	575		3.27
16	- " -	100	0	0.40	576	*n.o.*	3.31

Table 2. Properties of polyimides obtained by the one-step method.

Entry	Diamine	i-BPDA (%)	s-BPDA (%)	η_{inh} (dL/g)	M_{ω}^{e} (M_w/M_n)	T_{d5} (°C)	T_g (°C)
1	PDA	100	0			584	*n.o.*
2	MDA	100	0	0.32^f		578	337
3	ODA	0	100	3.01^f		575	276
4	-"-	100	0	0.39	66900 (3.56)	575	332
5	TFMB	20	80	2.65		591	
6	-"-	25	75	2.26		583	
7	-"-	50	50	1.12	299400 (6.95)	589	
8	-"-	100	0	0.40	63700 (6.72)	602	343
9	FDA	100	0	0.24	40000 (2.63)	576	*n.o.*

a) Inherent viscosity, measured in DMF at 0.5 g/dL, 30 °C (referred to PAA for the two-step method); b) 5 % weight loss in N_2, measured by DTA; c) glass transition temperature, measured by DSC; d) out-of-plane dielectric constant, determnined by capacitance measurements at 1 MHz, 23 °C, 50 % relative humidity; e) determined by GPC in DMF/LiBr/H_3PO_4; f) measured in p-chlorophenl at 60 °C; *n.o.* = not observed

All reported polyimides showed high glass transition (T_g > 330 °C) and degradation (T_{d5} > 550 °C) temperatures, depending on their diamine moieties. A prominent effect of dianhydride ratios on glass transition temperatures indicates higher stiffness of backbones with i-BPDA units. This effect is characteristic for polymers with sterically hindered substituents and restricted motion of main chains [1]. Thermal stabilities of both i-BPDA and s-BPDA units are rather similar, judging from similar degradation temperatures of copolyimides of different compositions. Polymers from one-step procedures were superior in respect to the thermal stability, that may be assigned to the lower concentration of structural defects in solution-imidized species. Corresponding films are less colored by the similar reason. Dielectric constants seem to be actually independent of i-BPDA/s-BPDA ratios, with the only exception of homopolymer s-BPDA-TFMB (Table 1, Entry 10), which is known to be highly anisotropic [4,5]. Copolymers of i-BPDA, s-BPDA and TFMB showed the best combination of processability, thermal resistance, mechanical properties, optical transparency and low dielectric constant, that makes them potential candidates for electronics applications.

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. 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 acids) and the one-step direct polycondensation in *m*-cresol. The most of polymers exhibited excellent thermal properties and improved solubilities, compared with their analogues, 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 2,2′-bis(trifluoromethyl)benzidine (TFMB) were readily soluble in NMP, exhibited dielectric constants of 2.8 and formed tough, flexible, nearly colorless films.

References and Notes

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