

A Novel Diamine, 4'-Phenylphenyl 4-(3'', 5''-Diaminobenzoyloxy)-benzoate and Longer Side-chain Polyimide

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Abstract: This is a part of our systematic research work on polyimides with mesogenic unit side chain. In this study, a new 4'-phenylphenyl 4-(3'', 5''-diaminobenzoyloxy)benzoate and polyimide were synthesized, and characterized by FTIR, ¹H-NMR, inherent viscosity, mechanical properties, and solubility measurements. The diamine composed with mesogenic unit aryl ester groups and biphenyl group with longer L/D ratio, was synthesized by two key steps. Firstly, the hydroxy group of 4-hydroxybenzoic acid was protected by acetoxy group for avoiding self-polymerization of 4-hydroxybenzoic acid, and then selectively hydrolyzed after esterification of carboxyl. Secondly, a selective catalysis hydrogenation was adopted to prevent the aryl ester from deoxidation. Based on this diamine, a novel polyimide was prepared by polycondensation of 4'-phenylphenyl 4-(3'', 5''-diaminobenzoyloxy)benzoate and 4-aminophenyl ether(ODA) with 4, 4'-oxydiphthalic anhydride(ODPA) in N-methyl-2-pyrrolidone (NMP). The resulting polyimide with longer side chain showed better solubility and more regular structure. Its inherent viscosity is lower than that without side chains, but its modulus and strength not only maintained, even improved.

Keywords: Polyimide, film materials, side-chain, synthesis.

In our previous study, the polyimides with the side-chain were obtained from 3, 5-diaminobenzoic-4'-biphenyl ester(DABBE)¹. This kind of polyimide films showed some interesting properties, such as excellent solubility, lower density, and higher tensile strength. To understand the influence of various mesogenic units, making reference to those synthesis of polyimides with side-chain²⁻³, in this study, a novel diamine with higher length/diameter(L/D) ratio containing aryl ester group and biphenyl unit was synthesized. Based on it, a soluble polyimide was prepared by imidization⁴. The chemical structure of this new diamine was confirmed by FTIR and ¹H-NMR. A preliminary study on the properties of the novel polyimide from this diamine was conducted.

Experimental

4-Acetoxybenzoic acid **1**. 21.3 mL of acetic anhydride was dropped into the solution containing 17.2 g (0.1mol) of 4-hydroxybenzoic acid, 50 mL (6.25 mol/L) of NaOH

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aqueous solution and 100 mL of water, and the mixture was stirred for 30 min in an ice-bath, then 50 mL (6.25 mol/L) of HCl aqueous solution was added with stirring for another 30 min. A white precipitate was filtered and washed with water, purified by recrystallization from ethyl acetate. The pure **1** was obtained with mp 188-189°C (19.5 g, yield 84%) .

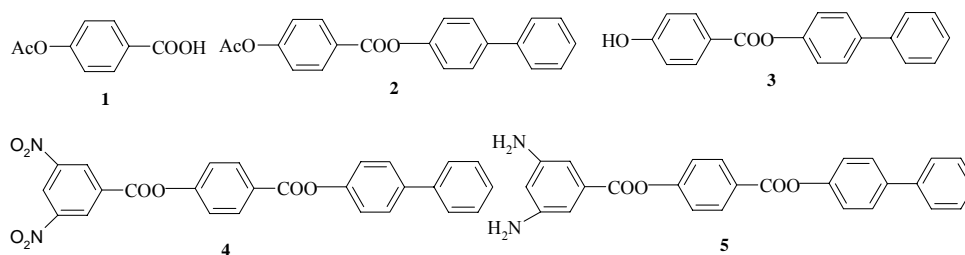
4'-Phenylphenyl 4-acetoxybenzoate 2. 16 g (0.1 mol) of **1** and approximately 6 mol equivalence of thionyl chloride were stirred at reflux for 5 hr, and then the excess thionyl chloride was removed. The acyl chloride product was subsequently dissolved in 40 mL dry THF, and then added dropwise to the stirred solution of 4-phenylphenol 17 g (0.1 mol) and pyridine (10 mL) in 100 mL of dry THF. The mixture was stirred for 12 hr and was subsequently poured into a large amount of water. A white precipitate was filtered, and purified by recrystallization from ethanol (mp.126-127°C, yield 87%). FTIR (KBr, cm^{-1}): 2922, 2850 (CH_3); 1754, 1734 ($\text{C}=\text{O}$); 1281, 1235 ($\text{C}-\text{O}-\text{C}$). $^1\text{H-NMR}$ (CDCl_3 , δ ppm): 2.35 (s, 3H, CH_3COO -); 7.23-7.66 (m, 11H, aromatic protons of biphenyl and *ortho* to acetoxy); 8.25 (d, 2H, $J=8.6$, aromatic protons *meta* to acetoxy).

4'-Phenylphenyl 4-hydroxybenzoate 3. 25 g (0.075 mol) of prepared **2** and 200 mL of ammonia (25%-28%) were stirred for 24 hr at room temperature, and then the dilute HCl aqueous solution was added. The precipitate was subsequently filtered and washed repeatedly with water, purified by recrystallization from ethanol (mp 245-246 °C; yield 90%). FTIR (KBr, cm^{-1}): 3395 ($-\text{OH}$); 1703 ($\text{C}=\text{O}$); 1282, 1217 ($\text{C}-\text{O}-\text{C}$). $^1\text{H-NMR}$ ($\text{C}_3\text{D}_6\text{O}$, δ ppm): 7.02 (d, 2H, $J=8.6$, aromatic H *ortho* to hydroxy); 7.33-7.76 (m, 9H, aromatic H of biphenyl); 8.08 (d, 2H, $J=9.1$, aromatic H *meta* to hydroxy); 9.38 (s, 1H, hydroxy).

4'-Phenylphenyl 4-(3'',5''-dinitrobenzoyloxy)benzoate 4. The product was obtained by 3,5-dinitrobenzoic acid and **3** according to the procedure described for **2**. It was recrystallized from 1,2-dichloroethane (mp 218-219 °C; yield 92%). FTIR (KBr, cm^{-1}): 1743, 1726 ($\text{C}=\text{O}$); 1547, 1344 (NO_2); 1258, 1205 ($\text{C}-\text{O}-\text{C}$). $^1\text{H-NMR}$ (CDCl_3 , δ ppm): 7.25-7.68 (m, 11H, aromatic H of biphenyl and *ortho* to 3'',5''-dinitrobenzoxy); 8.36 (d, 2H, $J=8.4$, aromatic H *meta* to 3'',5''-dinitrobenzoxy); 9.35 (s, 3H, aromatic H *ortho* to NO_2).

4'-Phenylphenyl 4-(3'',5''-diaminobenzoyloxy)benzoate 5. **4** (7 g, 0.014 mol) was charged in a hydrogenation reaction and a catalytic amount of Pd-C (5%) in 100 mL of

Scheme 1 Structures of compound **1**, **2**, **3**, **4**, and **5**



THF were added. The hydrogen was introduced continuously in 4-5 hr at about 80°C under 2 MPa pressure. The catalyst was then filtered off and the solution was poured into a large amount of water to obtain white diamine **5** with 85% yield. **5** was purified by recrystallization from ethanol (mp 195-196 °C; yield 65%). FTIR (KBr, cm⁻¹): 3426, 3344 (NH₂); 1736 (C=O); 1269, 1204 (C-O-C). ¹H-NMR (CDCl₃, δ ppm): 3.75 (s 4H, NH₂); 6.28 (s 1H, aromatic H between NH₂); 6.94 (s, 2H, aromatic H between NH₂ and C=O); 7.25-7.67 (m, 11H, aromatic H of biphenyl and *ortho* to 3'',5''-diaminobenzoyloxy); 8.29 (d, 2H, J=8.6, aromatic H *meta* to 3'',5''-diaminobenzoyloxy).

Preparation of polyimides. Poly(amic acid)s were prepared by low-temperature solution polycondensation of diamine and dianhydride. The diamines [ODA and **5** (or *m*-PDA) in mol ratio 3/1] were dissolved in dry NMP. After a stoichiometric amount of 4, 4'-oxydiphthalic anhydride (ODPA) was added, the stirring was continued for 12 hr at room temperature. The imidization mixture Ac₂O/pyridine (1/1 by volume) was added to the solution of PAA (5 mol of Ac₂O per repeating unit of the prepolymer), and stirred for 12 hr again, then poured into a large amount of ethanol to precipitate light yellow PI solid.

Results and Discussion

In order to introduce a higher length/diameter ratio mesogen side chain onto the polyimide main-chain, a new diamine containing mesogenic unit aryl esters and biphenyl group was obtained after 5 reaction steps (see **Scheme 1**). The synthesis of **3** and **5** were the key steps. In order to get compound **3**, the protection of hydroxy group was needed. Otherwise, the intermediate 4-hydroxybenzoyl chloride would self-polymerize. Ammonia (25%-28%) was chosen as selective hydrolyzation reagent, and the aryl ester was not touched. The yield of compound **3** was 90%. Another key step was the Pd-C catalysis hydrogenation of the dinitro groups in compound **4**. The final product was compound **5** with yield 85%.

In this study, the influence of length of side mesogenic units upon the structure and properties of polyimides was investigated. It showed that enhanced with introduction of the side chains could enhance the solubility considerably. Furthermore, the longer the side mesogenic unit, the more soluble the polyimide was. It was seen that ODPA/ODA-**5** was able to dissolve in hot DMF, and ODPA/ODA-DABBE only could be swelled (see **Table 1**).

Table 1 Solubilities of the polyimides in organic solvents

PI films	NMP		DMF		Chloroform		THF		<i>m</i> -Cresol	
	r	h	r	h	r	h	r	h	r	h
ODPA/ODA+m-PDA	-	-	-	-	-	-	-	-	-	-
ODPA/ODA+DABBE	-	++	-	+	-	-	-	-	+	++
ODPA/ODA+ 5	+	++	+	++	-	+	-	-	+	++

r, room temperature; h, heat

-, insoluble; +, swellable; ++, soluble

Table 2 Tensile mechanical properties of polyimide films

Sample code	η_{inh} (dL/g)	Strength at break (MPa)	Elongation at break (%)	Initial modulus (GPa)
ODPA/ODA+m-PDA	1.18	133	12	2.8
ODPA/ODA+DABBE	0.98	152	14	2.3
ODPA/ODA+5	0.82	139	15	2.0

Compared to DABBE, compound **5** had higher L/D ratio and lower reactivity. Therefore the polyimide ODPA/ODA-**5** displayed lower inherent viscosity and tensile strength than the polyimide ODPA/ODA-DABBE. Although both of their inherent viscosities were reduced in contrast with the polyimide ODPA/ODA-*m*-PDA, but their tensile strength was higher than that without side chain (see **Table 2**). And the polyimide with higher L/D ratio side mesogenic units (ODPA/ODA-**5**) could form a needle-like crystal in NMP at room temperature, and the structure of the crystals became more ordered with increasing the temperature. The further study on understanding the texture of the polyimide containing biphenyl unit is underway, and the results will be published later.

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