

Synthesis and Characterization of *N*-Phenylated Wholly Aromatic Non-Cyclic Polyimides from *N,N'*-Diphenylphthalimidoyl Chlorides and Phthalic Acids

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ABSTRACT: A novel class of polyimides, *N*-phenylated wholly aromatic non-cyclic polyimides, was synthesized by the low-temperature solution and two-phase phase-transfer catalyzed polycondensations of new aromatic bis(imidoyl chloride)s, *N,N'*-diphenylisophthalimidoyl chloride and *N,N'*-diphenylterephthalimidoyl chloride, with aromatic dicarboxylic acids, isophthalic acid and terephthalic acid. The resulting polyimides were all white in color and had reduced viscosities of 0.11—0.14 dl g⁻¹. Compared with the conventional polyimides having cyclic imide structures, these *N*-phenylated non-cyclic polyimides exhibited better solubility in various organic solvents, reduced crystallinity and lower glass transition temperatures and thermal stability. The reduced viscosity of a typical polyimide decreased rapidly upon UV light irradiation, indicating the occurrence of photodegradation. Before the polymer synthesis, the effects of reaction medium, organic and inorganic bases and phase-transfer catalyst were studied on the solution and two-phase reactions of *N,N'*-diphenylisophthalimidoyl chloride with benzoic acid.

KEY WORDS *N*-Phenylated Wholly Aromatic Non-Cyclic Polyimides / *N,N'*-Diphenylphthalimidoyl Chlorides / Phthalic Acids / *N,N'*-Dibenzoyl-sophthalanilide / Polycondensation / Solubility / Thermal Behavior / Photosensitivity /

Wholly aromatic polyimides are finding numerous applications as high performance film and plastic materials in the high-technology fields such as electronic and aerospace industries, owing to their outstanding thermal, dimensional and chemical stabilities and excellent mechanical and electrical properties.¹ This important class of polymers all possesses imide groups in the form of cyclic structures in the backbone. However, little is known about the synthesis and properties of aromatic polyimides having non-cyclic imide structures.² Recently, Kurita *et al.*^{3,4} reported the synthesis of an open-chain polyimide with number-average molecular weight (M_n) of 1.25×10^4 g mol⁻¹ by the

solution polycondensation of an unique monomer benzyloxyamine with terephthaloyl chloride. In contrast to the conventional cyclic polyimides, this non-cyclic polyimide having bulky and flexible pendant benzyloxy groups has considerably low glass transition temperature (T_g) of 87°C and relatively low decomposition temperature around 200°C in air, but is quite readily soluble even in ordinary organic solvents.

Several synthetic routes have been thus far devised to produce *N*-substituted aromatic non-cyclic imides. These involve the reactions of imidoyl chlorides with carboxylic acids⁵ or their sodium salts⁶ and of amine⁷ or *N*-lithioamides⁸ with acid chloride. The first

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process is obviously much more convenient and led to better yields of products. *N,N*-Diaroylanilines, the simplest *N*-phenylated aromatic non-cyclic imides, are photosensitive.⁹ On ultraviolet (UV) light irradiation *N,N*-dibenzoylaniline is easily cleaved to give photo-Fries type of degradation products effectively.

In the present article, we report the detailed study on the synthesis and characterization of fully *N*-phenylated wholly aromatic non-cyclic polyimides (VI) by the polycondensation of novel *N,N'*-diphenylphthalimidoyl chlorides (I) with phthalic acids (V). These wholly aromatic polymers with pendant phenyl groups are expected to be soluble in organic solvents and have high thermal stability and UV light sensitivity.

EXPERIMENTAL

Materials

Isophthalanilide and terephthalanilide were prepared by the conventional condensation of the corresponding phthaloyl chlorides with aniline. Benzoic acid (II) and isophthalic acid (Va) were recrystallized from water and methanol, respectively. Terephthalic acid (Vb) was reprecipitated from aqueous sodium hydroxide into dilute hydrochloric acid. Solvents such as *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), *N*-methyl-2-pyrrolidone (NMP), chloroform and nitrobenzene and triethylamine (TEA) were distilled immediately before use. Phase-transfer catalysts such as tetra-*n*-butylammonium bromide (TBAB), benzyltriethylammonium bromide (BTEAB) and dibenzo-18-crown 6-ether (DB-18-C-6) and other reagents including 1,8-diazabicyclo-[5.4.0]-7-undecene (DBU) were used as received.

Monomer Synthesis

N,N'-Diphenylisophthalimidoyl Chloride (Ia). A mixture of isophthalanilide (9.48 g, 0.03 mol), thionyl chloride (100 ml) and a few drops

of pyridine was heated with stirring at reflux temperature for 3 h. The unreacted thionyl chloride was evaporated from the reaction solution to dryness under reduced pressure giving a crystalline mass. It was recrystallized from dry benzene to yield 7.62 g (72%) of needle-like slightly yellow crystals.

mp 150—151°C.

Infrared (IR) (KBr): 1640 cm⁻¹ (vs, C=N).

Anal. Calcd for C₂₀H₁₄N₂Cl₂: C, 68.00%; H, 4.00%; N, 7.93%. Found: C, 68.40%; H, 4.21%; N, 7.46%.

N,N'-Diphenylterephthalimidoyl Chloride (Ib). This monomer was similarly synthesized using terephthalanilide in place of isophthalanilide. Recrystallization from dry benzene afforded a 80% yield of yellow plates.

mp 195—197°C.

IR (KBr): 1650 cm⁻¹ (vs, C=N).

Anal. Calcd for C₂₀H₁₄N₂Cl₂: C, 68.00%; H, 4.00%; N, 7.93%. Found: C, 68.11%; H, 3.94%; N, 7.59%.

Model Reaction

A typical example of the model reaction is described.

N,N'-Dibenzoylisophthalanilide (IV) from Ia and II by Two-Phase Phase-Transfer Catalyzed Method. To a solution of benzoic acid II (0.610 g, 5 mmol) and DB-18-C-6 (15 mg) in 1 M aqueous potassium hydroxide (5.1 ml) was quickly added a solution of *N,N'*-diphenylisophthalimidoyl chloride Ia (0.883 g, 2.5 mmol) in nitrobenzene (8 ml), and the two-phase mixture was vigorously agitated at room temperature for 1.5 h. The reaction solution was diluted with nitrobenzene (20 ml), and the organic layer was separated, washed successively with dilute hydrochloric acid and water and dried over anhydrous magnesium sulfate. After the solvent was removed *in vacuo*, the crystalline residue was treated with a small amount of ether and dried. The yield was 1.19 g (91%). On recrystallization from ethanol, colorless needles were obtained.

mp 185—186°C.

IR (KBr): 1690 (vs, C=O) and 1670 cm^{-1} (shoulder, C=O).

Anal. Calcd for $\text{C}_{34}\text{H}_{24}\text{N}_2\text{O}_4$: C, 77.85%; H, 4.61%; N, 5.34%. Found: C, 77.85%; H, 4.58%; N, 5.45%.

Polycondensation

A typical example of the polycondensation is described.

Polyimide (VIb) from Ia and Vb by Low-Temperature Solution Method. A solution of terephthalic acid **Vb** (0.166 g, 1 mmol) and TEA (0.222 g, 2.2 mmol) in chloroform (3 ml) was chilled to 0°C, and to this cooled solution was added *N,N'*-diphenylisophthalimidoyl chloride **Ia** (0.353 g, 1 mmol) all at once. The mixture was stirred at that temperature for 1 h and at ambient temperature for 24 h under nitrogen flow, and then poured into methanol (300 ml) to precipitate the polymer. The white, powdery polymer was filtered, rinsed well with methanol and dried. The yield was 0.352 g (79%). The reduced viscosity (η_{red}) was 0.14 dl g^{-1} , measured at a polymer concentration of 0.5 g dl^{-1} in DMF at 30°C.

IR (KBr): 1690 cm^{-1} (vs, C=O).

Anal. Calcd for $(\text{C}_{28}\text{H}_{18}\text{N}_2\text{O}_4)_n$: C, 75.32%; H, 4.06%; N, 6.28%. Found: C, 73.79%; H, 4.04%; N, 6.16%.

Polyimides (**VIa**) and (**VIc**) were also synthesized by analogous procedures. The elemental analyses are as follows.

Polyimide VIa from Ia and Va.

Anal. Calcd for $(\text{C}_{28}\text{H}_{18}\text{N}_2\text{O}_4)_n$: C, 75.32%; H, 4.06%; N, 6.28%. Found: C, 73.94%; H, 4.17%; N, 6.16%.

Polyimide VIc from Ib and Vb.

Anal. Calcd for $(\text{C}_{28}\text{H}_{18}\text{N}_2\text{O}_4)_n$: C, 75.32%; H, 4.06%; N, 6.28%. Found: C, 73.35%; H, 4.15%; N, 6.18%.

UV Light Irradiation

The effect of UV light irradiation on the reduced viscosity of polyimide **VIb** was examined by using the polymer (50 mg) dissolved in DMAc (10 ml). The solution,

placed in an Ostwald viscometer made of quartz, was exposed to UV light at a distance of 10 cm at 20°C using an Ushio 400 W high-pressure mercury lamp, and the decrease in the viscosity of the exposed solution was measured with respect to time of irradiation.

Measurements

IR spectra were obtained on a JASCO IR-810 spectrophotometer as potassium bromide disks. Elemental analysis was conducted by a Perkin-Elmer 240C elemental analyzer. Weight-average molecular weight (M_w) and M_n were determined by gel permeation chromatography (GPC) with polystyrene standards on a Tosoh HLC CP-8000 System (columns: G4000HXL and G2000HXL polystyrene gel) using DMF containing 10 mmol l^{-1} of lithium bromide as eluent. Wide-angle X-ray diffraction diagrams were taken for pulverized specimens on a Rigaku Geigerflex Rad-rA X-ray diffractometer, using nickel-filtered Cu- K_α radiation (30 kV, 50 mA). Differential thermal analysis (DTA) and thermogravimetry (TG) were simultaneously performed on powder specimens by a Seiko SSC 5200H Thermal Analysis System in air at a heating rate of 10 K min^{-1} . Differential scanning calorimetry (DSC) was performed on powder specimens with a Perkin-Elmer DSC System 4 under nitrogen at a scan rate of 20 K min^{-1} . UV spectra were recorded in acetonitrile in the range 210–350 nm with a Hitachi 150-20 double beam spectrophotometer.

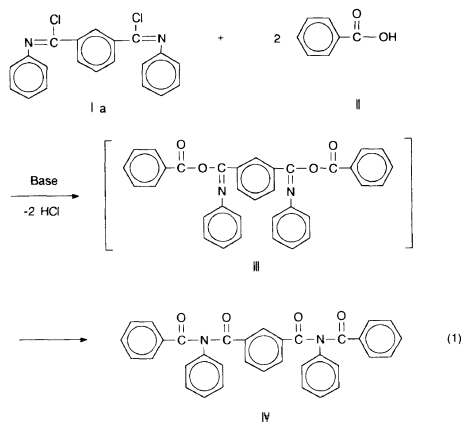
RESULTS AND DISCUSSION

Model Reaction

Novel monomers, *N,N'*-diphenylisophthalimidoyl chloride (**Ia**) and *N,N'*-diphenylterephthalimidoyl chloride (**Ib**), were crystalline solids.

In the model reaction of *N,N'*-diphenylisophthalimidoyl chloride **Ia** with benzoic acid (**II**), the initially formed isoimide (**III**) undergoes thermally-induced Chapman-type re-

arrangement to model compound, *N,N'*-dibenzoylisophthalanilide (**IV**), through a [1,3]benzoyl migration (eq 1).⁵



The reaction was carried out by using two different synthetic procedures, namely low-temperature solution and two-phase phase-transfer catalyzed methods. The respective reaction conditions and the yields of model compound **IV** are shown in Tables I and II. All these reactions proceeded rapidly and gave directly desired product **IV** in excellent yields.

The IR spectrum of model compound **IV** exhibited a strong doublet at 1690 and 1670 cm^{-1} , which is characteristic of *N*-phenylated aromatic non-cyclic imide carbonyl

Table I. Reaction conditions and results of the preparation of model compound **IV** by low-temperature solution reaction

Run	Reaction conditions ^a		Yield %
	Solvent	Organic base	
1	DMAc	TEA	92
2	DMF	TEA	96
3	DMF	DBU	91
4	NMP	TEA	80
5	NMP	DBU	93
6	Chloroform	TEA	94

^a The reaction was carried out with **Ia** (1 mmol) and **II** (2 mmol) in a solvent (3 ml) in the presence of an organic base (2.2 mmol) at 0°C for 1 h and then at room temperature for 24 h under nitrogen.

stretching band in solid state.²

Polycondensation

Three types of *N*-phenylated wholly aromatic non-cyclic polyimides (**Via—Vlc**) were synthesized directly from combinations of *N,N'*-diphenylphthalimidoyl chlorides **Ia** and **Ib** and phthalic acids **Va** and **Vb** (eq 2).

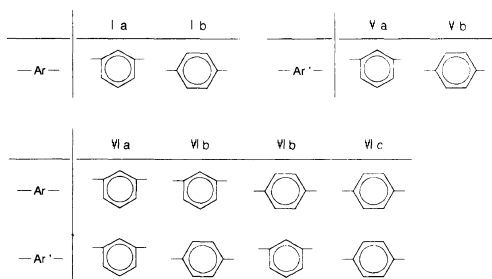
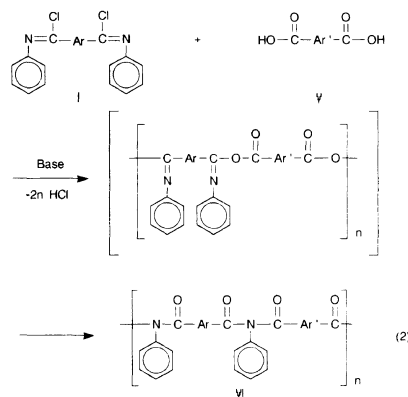


Table II. Reaction conditions and results of the preparation of model compound **IV** by two-phase phase-transfer catalyzed reaction

Run	Reaction conditions ^a		Yield %
	Phase-transfer catalyst	Inorganic base	
1	TBAB	NaOH	84
2	BTEAB	NaOH	77
3	DB-18-C-6	KOH	91

^a The reaction was carried out with **Ia** (2.5 mmol) and **II** (5 mmol) in nitrobenzene (8 ml) and 1 M aqueous alkaline hydroxide (5.1 ml) in the presence of a phase-transfer catalyst (15 mg) at room temperature for 1.5 h.

Table III. Reaction conditions and results of the synthesis of *N*-phenylated wholly aromatic non-cyclic polyimides **VI** by low-temperature solution polycondensation

Monomers		Reaction conditions ^a			Polymer		
Bis(imidoyl chloride)	Dicarboxylic acid	Solvent	Organic base	Remark ^b	Code	Yield	η_{red}^c
						%	dl g ⁻¹
Ia	Va	DMAc	TEA	S	VIa	78	0.06
Ia	Va	DMF	TEA	S	VIa	79	0.08
Ia	Va	DMF	DBU	S	VIa	92	0.07
Ia	Va	NMP	DBU	S	VIa	86	0.06
Ia	Va	Chloroform	TEA	S	VIa	82	0.13
Ia	Vb	DMF	TEA	P	VIb	72	0.07
Ia	Vb	DMF	DBU	P	VIb	89	0.06
Ia	Vb	Chloroform	TEA	P	VIb	79	0.14
Ib	Va	DMF	TEA	P	VIb	73	0.09
Ib	Va	Chloroform	TEA	P	VIb	82	0.12
Ib	Vb	DMF	TEA	P	VIc	71	0.09 ^d
Ib	Vb	Chloroform	TEA	P	VIc	73	0.11 ^d

^a The polymerization was carried out with **I** (1 mmol) and **V** (1 mmol) in a solvent (3 ml) in the presence of an organic base (2.2 mmol) at 0°C for 1 h and then at room temperature for 24 h under nitrogen.

^b Appearance of the polymerization mixture: S, homogeneous solution; P, polymer precipitation.

^c Reduced viscosity was measured at a polymer concentration of 0.5 g dl⁻¹ in DMF at 30°C.

^d Measured in HMPA.

Table III summarizes the results obtained through low-temperature solution polycondensation. In these reactions, with one exception for the synthesis of polymer **VIa** precipitation of the polymers took place as the reaction progressed. The *N*-phenylated wholly aromatic non-cyclic polyimides thus formed were white powdery materials and had low reduced viscosity values less than 0.14 dl g⁻¹, regardless of the reaction conditions. No significant effects of the reaction solvents and organic bases employed were also observed with regard to the yield of polymers. Therefore, the low viscosities are attributed to the inherent low reactivity of difunctional phthalic acids **V**, compared to the high reactivity of monofunctional benzoic acid **II**. The GPC curve indicated that the M_w and M_n values of polyimide **VIb** with a reduced viscosity of 0.14 dl g⁻¹ were 7.07×10^3 and 4.55×10^3 g mol⁻¹, respectively, and the polydispersity index M_w/M_n was 1.55. In the case of another DMF-soluble polyimide **VIa** with a reduced viscosity of 0.13 dl g⁻¹, the

M_w and M_n values were 5.00×10^3 and 4.05×10^3 g mol⁻¹, respectively, and the M_w/M_n was 1.23. The polyimides were also synthesized by utilizing two-phase phase-transfer catalyzed polycondensation technique. The results obtained, however, were almost the same as those of the solution polycondensation described above.

Polymer Properties

The solubility of the polyimides in various organic solvents was tested by using 25 mg of the polymers in 1 ml of solvents and the results are presented in Table IV. *N*-Phenylated wholly aromatic non-cyclic polyimide **VIb** was readily soluble at ambient temperature in polar aprotic solvents such as DMAc, DMF, hexamethylphosphoramide (HMPA) and NMP. Furthermore, polyimide **VIa** only possessing unsymmetrical *m*-phenylene units in the backbone also dissolved in a wide variety of common organic media such as acetone, chloroform, tetrahydrofuran, *m*-cresol, and pyridine. Al-

Table IV. Solubility of *N*-phenylated wholly aromatic non-cyclic polyimides **VI** in various organic solvents^a

Solvent	Polymer		
	VIa	VIb	VIc
Acetone	+	—	—
Chloroform	+	—	—
Ethyl acetate	—	—	—
Methanol	—	—	—
Tetrahydrofuran	+	—	—
<i>m</i> -Cresol	+	±	±
Pyridine	+	±	—
DMAc	+	+	—
DMF	+	+	—
HMPA	+	+	+
NMP	+	+	±

^a +, soluble at room temperature; ±, partially soluble or soluble on heating; —, insoluble.

though both the polymers were of relatively low molecular weights, this high solubility compared with that of the usual aromatic polyimides with cyclic imide structures is probably attributed to the existence of both the open-chain imide group and bulky pendant phenyl substituent. The latter generally lowers markedly the polymer packing density. However, polyimide **VIc** containing exclusively symmetrical *p*-phenylene linkages was either partially or hardly soluble even in the polar aprotic solvents except HMPA. The limited solubility is presumably due to its rigid backbone structure.

Wide-angle X-ray diffraction studies of the polymers revealed that polyimide **VIc** had a fair degree of crystallinity, whereas polyimides **VIa** and **VIb** were essentially amorphous. The amorphous nature of the latter two polymers reflects in their excellent solubility.

The thermal behavior data of the polymers are listed in Table V. The DTA curves of amorphous polyimides **VIa** and **VIb** in air gave an endothermic shifts of base line assigned to be T_g , followed by an endothermic shift above 300°C that corresponded to the onset of decomposition in the TG curves. The DTA

Table V. Thermal properties of *N*-phenylated wholly aromatic non-cyclic polyimides **VI**

Polymer	T_g^a	T_m^b	DT_5^c	DT_{10}^d	RW^e
	°C	°C	°C	°C	%
VIa	143	— ^f	362	376	38
VIb	174	— ^f	372	384	41
VIc	185	271	367	380	36

^a Glass transition temperature was determined by DSC under nitrogen at a scan rate of 20 K min⁻¹.

^b Melting temperature was determined by DSC.

^c Temperature at which 5% weight loss was recorded by TG in air at a heating rate of 10 K min⁻¹.

^d Temperature at which 10% weight loss was recorded.

^e Residual weight at 500°C.

^f No T_m was observed.

curve of crystalline polyimide **VIc** showed an endothermic shift of base line at 185°C (T_g) and two endothermic peaks at 270°C (melting temperature (T_m)) and above 300°C (decomposition), respectively. The T_m was observed only for polyimide **VIc** which confirms its above-mentioned crystalline nature. The T_g s and/or T_m of polyimides **VIa**, **VIb**, and **VIc** determined by DSC were 143, 174 and 185°C, and 271°C, respectively. This increasing order in T_g corresponds well to the increasing order of symmetry and rigidity of the polymer backbones. All these polyimides did not lose weight up to 300°C in air, and the initial 5% (DT_5) and 10% weight losses (DT_{10}) were recorded in the temperature ranges of 362–372°C and 376–384°C, respectively. The residual weight (RW) at 500°C was about 40% for all of these polyimides. The thermal stability is far superior to that of the open-chain polyimide reported by Kurita *et al.*,^{3,4} but evidently inferior to those of the ordinary aromatic cyclic polyimides and even to those of the fully *N*-phenylated wholly aromatic polyamide-esters,¹⁰ polyamides,^{11,12} and polyurethanes.¹³ This might be ascribed partly to their insufficient molecular weights.

Figure 1 shows the influence of UV light irradiation at 20°C on the reduced viscosity of

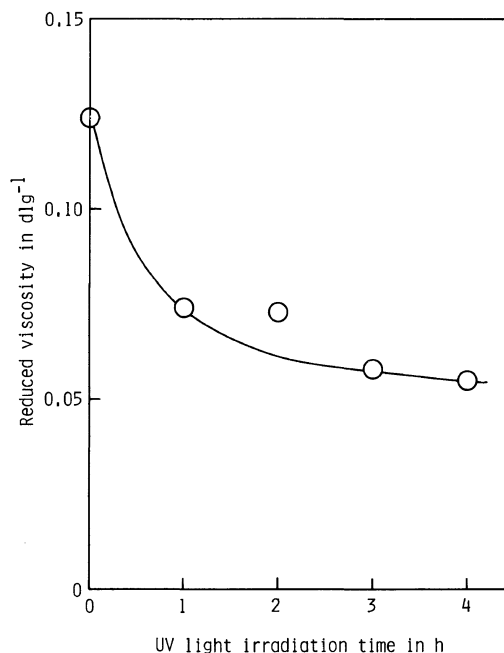


Figure 1. Effect of UV light irradiation at 20°C on the reduced viscosity of polyimide **VIb** in DMAc.

typical polyimide **VIb** in DMAc. The viscosity decreased rapidly with incremental irradiation time accompanied by the yellow coloration of the solution. This phenomenon indicates the photolytic degradation of the *N*-phenylated wholly aromatic non-cyclic polyimide. A viscosity decrease to one-half its initial value was observed after 3 h of the irradiation. The UV spectrum of acetonitrile-soluble polyimide **VIa** is illustrated in Figure 2 together with that of model compound **IV**. The spectra were quite similar to each other and revealed a broad absorption peak with an absorption maximum around 235 nm along with a shoulder near 280 nm.

In conclusion, wholly aromatic non-cyclic polyimides having bulky *N*-phenyl substituents were synthesized by the polycondensation of *N,N'*-diphenylphthalimidoyl chlorides with phthalic acids. This unique type of wholly aromatic polymers is characterized by high

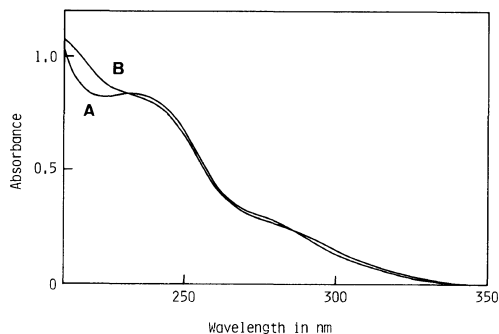


Figure 2. The UV spectra of (A) model compound **IV** and (B) polyimide **VIa** measured at a concentration of $2 \times 10^{-5} \text{ mol l}^{-1}$ in acetonitrile at 20°C.

solubility in various organic solvents, moderate thermal stability and photosensitivity toward UV light.

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