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Preparation and Properties of Novel Aromatic Polyamides from Diamines Containing 4,5-Imidazolediyl Structure

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ABSTRACT

Novel aromatic polyamides were prepared from aromatic diamine containing 4,5-imidazolediyl unit, either by low temperature solution polycondensation or by direct polycondensation. Used diamines were 4,5-bis(4-aminophenyl)-2-phenylimidazole **1**, 4,5-bis[4-(4-aminophenyl)]-2-(4-methylphenyl)imidazole **2** and 4,5-bis[4-(4-aminophenoxy)phenyl]-2-phenylimidazole **3**. The obtained aromatic polyamides were produced with moderate to high inherent viscosity and soluble in polar aprotic solvents such as *N,N*-dimethylacetamide (DMAc), 1-methyl-2-pyrrolidone (NMP), *N,N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO). Thermogravimetric analysis showed those polymers were stable up to 422°C in nitrogen atmosphere. The glass transition temperature (T_g)s of the polymers derived from diamine **3** were in the range between 243 and 275°C, and these values were approximately 120–160°C lower than those analogue polyamide **I** series containing no phenoxy units. The properties of polyamide **I** series are also compared with those of analogue polymers that order of aromatic nuclei and amide linkage is reversible.

Key Words: Aromatic polyamide; 4,5-bis[4-(4-Aminophenoxy)phenyl]-2-phenylimidazole; Thermal resistance; Solubility.

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INTRODUCTION

Recent advances in aerospace, automotive and electronics industries have produced continuing and growing needs for materials that will withstand exposures at elevated temperature. Above all, Kevlar™ aramide, the commercial all para-polyamide fiber from terephthalic acid and *p*-phenylenediamine, and Nomex™ aramide, the all meta-polyamide fiber from isophthalic acid and *m*-phenylenediamine, are known to be magnificent for their high thermal stability, chemical resistance and mechanical properties. However, they are only soluble in concentrate sulfuric acid and in the latter case, NMP or DMAc with added metal salts, such as LiCl or CaCl₂. And they are less processable due to their high *T_g*s (e.g., Kevlar™: 345°C, Nomex™: 280°C).^[1]

Previously, Connel et al.^[2] and Mikroyannidis^[3] reported that the polymers containing imidazole unit in the main chain improved the processabilities without losing thermal stabilities. Also, we described the synthesis and properties of polyamides having 4,5-imidazolediyl unit in the main chain. Polyamide derived from 4,4'-(2-phenyl-4,5-imidazole)dibenzoic acid with aromatic diamines, **IV**^[4] and polyamides derived from 4,5-bis(3-aminophenyl)-2-methylimidazole or 4,5-bis(3-aminophenyl)-2-phenylimidazole with several aromatic diacid chlorides,^[5,6] were highly soluble in aprotic polar solvents and displayed excellent thermal properties.

Furthermore, one of the approaches to increase processability or solubility is the introduction of flexible linkage into polymer backbone. It is reported that the incorporation of the ether linkages into the rigid polymer chains reduces the internal rotation energy and leads to lower *T_g*s and melting temperatures, as well as significant improvements in solubility without sacrificing their thermal stabilities.^[2,7-9]

In this report, we prepare aromatic polyamides **I**, **II** and **III** (Sch. 1), from the diamines, 4,5-bis(4-aminophenyl)-2-phenylimidazole **1**, 4,5-bis(4-aminophenyl)-2-(4-methylphenyl)imidazole **2** or 4,5-bis[4-(4-aminophenoxy)phenyl]-2-phenylimidazole **3**, with several aromatic diacid chlorides or aromatic dicarboxylic acids, respectively. In general, the introduction of alkyl or any substituents into the polymer chain increases the solubility of the polymer, the properties of polymer **I**s were compared with those of polymer **II**s. In addition, polymer **III**s were bulkier than polymer **I**s, the influence of the bulkiness due to phenoxy units upon the solubilities and thermal properties were investigated. Also, the effect of the order of aromatic nuclei and amide linkage on the thermal property and solubility is examined.

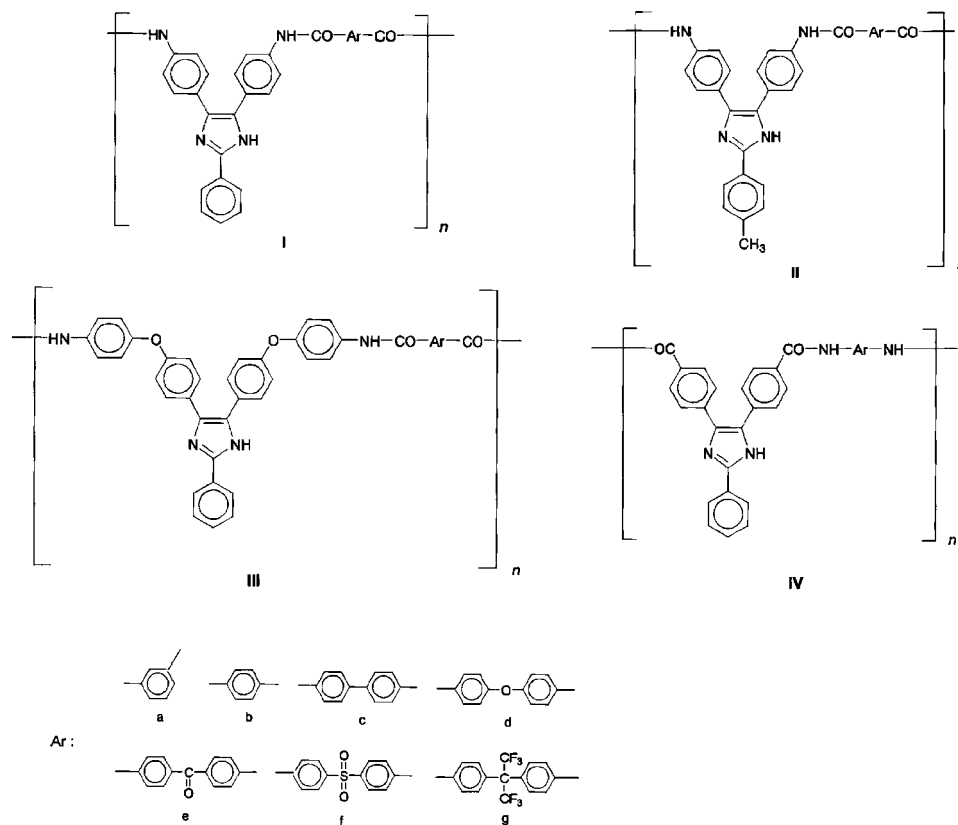
EXPERIMENTAL

Monomers

4,4'-Dimethoxybenzil, 4-fluoronitrobenzene, cesium fluoride, lithium chloride, palladium-carbon(Pd-C), hydrazine monohydrate, and propylene oxide were commercially available and used as received. Benzaldehyde (b.p. 44.0°C/5 mmHg) and other organic solvents were distilled before use. All the dicarboxylic chlorides and dicarboxylic acids were recrystallized before use. Diamine **1** and **2** were prepared according to the previously reported.^[10,11]

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Scheme 1.

4,5-bis(4-Hydroxyphenyl)-2-phenylimidazole **5**

5 was derived from 4,4'-dimethoxybenzil **4** as a starting material. **4** was reacted with ammonium acetate and benzaldehyde in acetic acid as a solvent, the subsequent demethylation using aqueous hydrobromic acid (HBr) afforded **5** according to the method Connell and Hergenrother reported.^[2] Yield: 95%. M.p. 333°C (*lit.* m.p. 327–330°C).

4,5-bis[4-(4-Nitrophenoxy)phenyl]-2-phenylimidazole **6**

6 was prepared in the way Imai et al. reported.^[12] In a 200 mL flask equipped with a reflux condenser and a nitrogen gas inlet, was placed dihydroxyphenyl compound **5** 9.9 g (30 mmol), 1-fluoro-4-nitrobenzene 10.6 g (75 mmol) and NMP 50 mL in the presence of cesium fluoride 13.8 g (91 mmol). The mixture was stirred at 160°C for 4 h and cooled to room temperature. The reaction mixture was poured into 900 mL of water and then the filtrate was washed with hot water and dried in vacuo. The crude product was recrystallized

from aqueous pyridine (pyridine: H₂O = 5:1) twice and dried at 190°C under reduced pressure for 12 h to present **6** as yellow powder. Yield: 9.5 g (56%). M.p. 279°C [differential thermal analysis (DTA)]. I.r. (KBr, cm⁻¹); 1504, 1342 (-NO₂) and 869 (Ar-N-). E.A. Calcd. for (C₃₃H₂₂N₄O₆ 570.57): C, 69.47%; H, 3.89%; N, 9.82%. Found: C, 69.21%; H, 4.21%; N, 9.86%. ¹H-NMR(DMSO-*d*₆): δ = 12.78(s, 1H, imidazole NH), 8.31-8.24(q, 4H, Ar-H), 8.09(d, 2H, Ar-H), 7.69-7.63(m, 4H, Ar-H), 7.48(t, 2H, Ar-H), 7.38(t, 1H, Ar-H), 7.30(d, H, Ar-H), 7.21-7.15(m, 6H, Ar-H).

4,5-bis[4-(4-Aminophenoxy)phenyl]-2-phenylimidazole **3**

3 was obtained by reduction of the corresponding dinitro compound **6** 6.95 g (12 mmol) by refluxing for 6 h with Pd-C 0.15 g (12 mmol) and the hydrazine monohydrate 15.8 mL (325 mmol) in ethanol 63 mL under nitrogen atmosphere.^[12,13] The reaction mixture was filtered and dried in vacuo. Yield: 4.24 g (68%). M.p. 224°C (DTA). I.r. (KBr, cm⁻¹); 3428, 3384, 3348 (-NH) 1616 (-NH) and 1282 (Ar-N-). E.A. Calcd. for (C₃₃H₂₆N₄O₂ 510.60): C, 77.63%; H, 5.13%; N, 10.97%. Found: C, 77.32%; H, 5.22%; N, 10.90%. Mass (m/z) = 510.

Polymer Synthesis

Low-temperature solution polycondensation (LS); polymers were prepared by the typical procedure (**IIIaLS**) as follows.^[4] In a 50 mL four-necked flask equipped with a mechanical stirrer, a nitrogen gas inlet, a reflux condenser and a thermometer, 0.511 g (1.00 mmol) of **3** and LiCl 0.150 g were dissolved in 4 mL of NMP. The mixture was cooled to -18°C, then terephthalic chloride 0.203 g (1.00 mmol) and propylene oxide 0.78 mL (11 mmol) in NMP 2 mL was added and stirred for 2 h. The temperature was raised to room temperature and kept stirring for another 5 h. Additional NMP 8 mL was added until the reaction ended. The crude product was poured into aqueous methanol (MeOH: H₂O = 1:1). The precipitate was filtered and dried at 60°C under reduced pressure for 24 h. Yield: 0.56 g (89%). The inherent viscosity of the polymer **IIIa(LS)** was 0.39 dL/g (0.5 g/dL in H₂SO₄ at 30°C). I.r. (cast, cm⁻¹): 1664 (amide I), 1528 (amide II). E.A. Calcd. for **IIIa** (C₄₁H₂₈N₄O₄ 640.70): C, 76.86%; H, 4.41%; N, 8.74%. Found: C, 75.12%; H, 4.68%; N, 8.41%. **IIIb** (C₄₁H₂₈N₄O₄ 640.70): Calcd.: C, 76.86%; H, 4.41%; N, 8.74%. Found: C, 75.16%; H, 4.75%; N, 8.45%. **IIIc** (C₄₇H₃₂N₄O₄ 716.80): Calcd.: C, 78.76%; H, 4.50%; N, 7.82%. Found: C, 77.12%; H, 4.85%; N, 7.57%. **IIId** (C₄₈H₃₂N₄O₅ 732.80): Calcd.: C, 77.04%; H, 4.40%; N, 7.65%. Found: C, 75.54%; H, 4.71%; N, 7.49%. **IIIe** (C₄₇H₃₂N₄O₅ 744.81): Calcd.: C, 77.41%; H, 4.33%; N, 7.52%. Found: C, 76.52%; H, 4.72%; N, 7.41%. **IIIf** (C₄₇H₃₂N₄O₆S 780.87): Calcd.: C, 72.29%; H, 4.13%; N, 7.17%. Found: C, 70.77%; H, 4.52%; N, 6.88%. **IIIg** (C₅₀H₃₂F₆N₄O₄ 866.83): Calcd.: C, 69.28%; H, 3.72%; N, 6.46%. Found: C, 69.18%; H, 3.95%; N, 6.25%.

Direct polycondensation (DP); Direct polycondensations were carried out in traditional way (**IIIaDP**) as follows.^[14] In a 10 mL four-necked flask equipped with a mechanical stirrer, a nitrogen gas inlet, a reflux condenser and a thermometer, 0.200 g of CaCl₂ and 0.066 g of LiCl were dissolved in 2 mL of NMP at 80°C. After cooling down to

room temperature, isophthalic acid 0.166 g (1.00 mmol), pyridine 0.66 mL (8.2 mmol) and triphenyl phosphite 0.53 mL (2.00 mmol) were added, then 0.511 g (1.00 mmol) of **3** in NMP 4.0 mL was added and the temperature was raised to 115°C. After stirring for 5 h, the temperature was cooled to room temperature and 4.0 mL of NMP was added. The polymer was isolated as in a low temperature solution polycondensation. Yield was 0.62 g (97%). The inherent viscosity of the polymer **IIIa(DP)** was 0.16 dL/g (0.5 g/dL in H₂SO₄ at 30°C). E.A. for **IIIa(DP)** (C₄₁H₂₈N₄O₄ 640.70) was Calcd.: C, 76.86%; H, 4.41%; N, 8.74%. Found: C, 73.09%; H, 4.76%; N, 8.18%.

Measurements

T_g s were measured by differential scanning calorimetry (DSC) on a MAC Science DSC 3100 with heating rate of 10°C min⁻¹ and were determined by second scanings. Thermoanalytical measurements were obtained by thermogravimetry (TG) on a MAC Science TG-DTA 2000 with heating rate of 5°C min⁻¹. All the above measurements were carried out in a nitrogen atmosphere. Dynamic mechanical analysis (DMA) were performed on an Iwamoto Seisakusho VED-F dynamic viscoelastometer, heating rate of 3°C min⁻¹ in air. I.r. spectra were recorded on a Hitachi 270-30 spectrophotometer. NMR spectra were obtained with FT-NMR spectrometer (JEOL JNM-LA400 and JNM-LA500). X-ray diffraction patterns were obtained on a Rigakudenki RAD-B at room temperature (operating at 40 kV, 300 mA). The scanning rate was 2 deg min⁻¹. Mass spectra were recorded on a JEOL JMS-AM^{II}15.

RESULTS AND DISCUSSION

Monomer

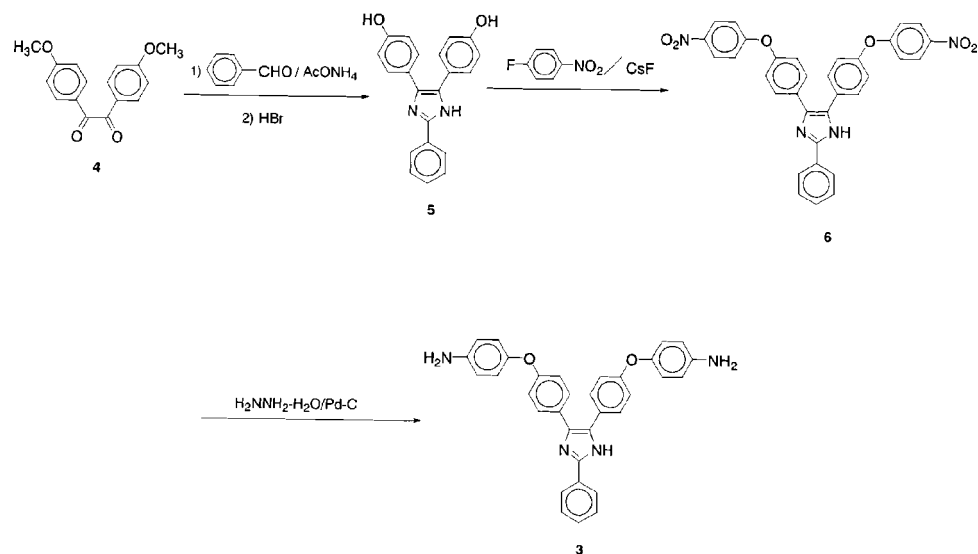
A novel diamine monomer, 4,5-bis[4-(4-aminophenoxy)phenyl]-2-phenylimidazole **3** was prepared from 4,4'-dimethoxybenzil **4** as a starting material as shown in Sch. 2. **4** was reacted with benzaldehyde and ammonium acetate in acetic acid, and then treated with HBr to produce 4,4'-bis(4-hydroxyphenyl)-2-phenylimidazole **5**. The precursor of diamine, 4,4'-bis(4-nitrophenoxy)-2-phenylimidazole **6** was prepared by the nucleophilic aromatic substitution reaction of **5** with 1-fluoro-4-nitrobenzen using cesium fluoride. Diamine **3** was obtained by the reduction of **6** using Pd-C and hydrazine monohydrate in ethanol. **3** was confirmed by E.A., I.r., ¹H-NMR spectra and mass spectrum. The elemental composition of it was almost in good agreement with the calculated values of proposed one.

Polymer Synthesis

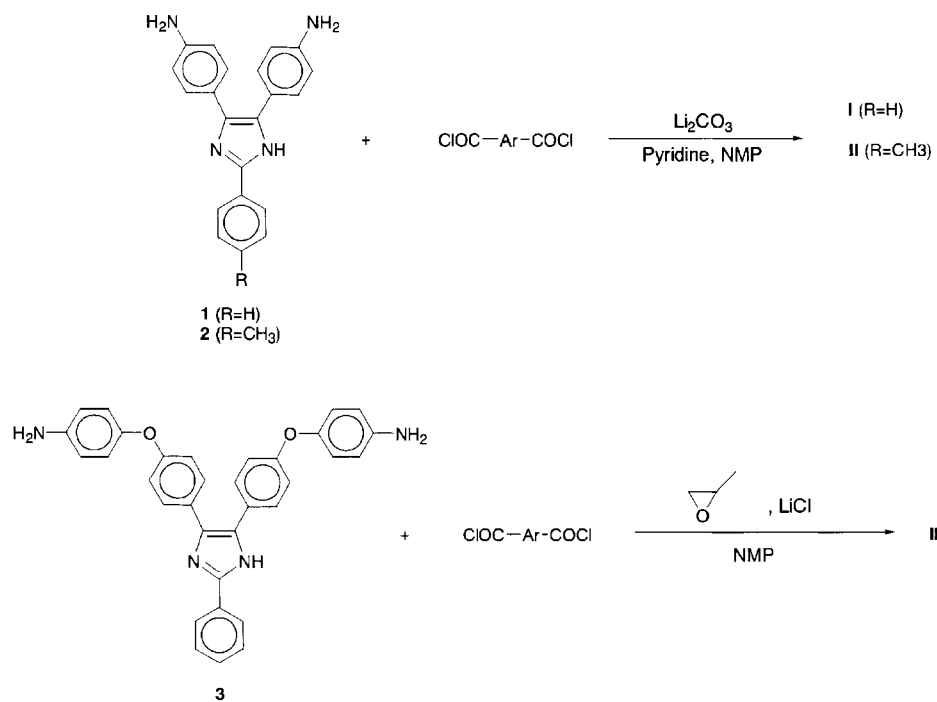
Aromatic polyamides **I**s, **II**s and **III**s were derived from diamine **1**, **2** and **3**, respectively, with several aromatic diacid chlorides (ClCO-Ar-COCl, Ar = **a** - **g**) by conventional low temperature solution polycondensation as shown in Sch. 3, or with

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Scheme 2.



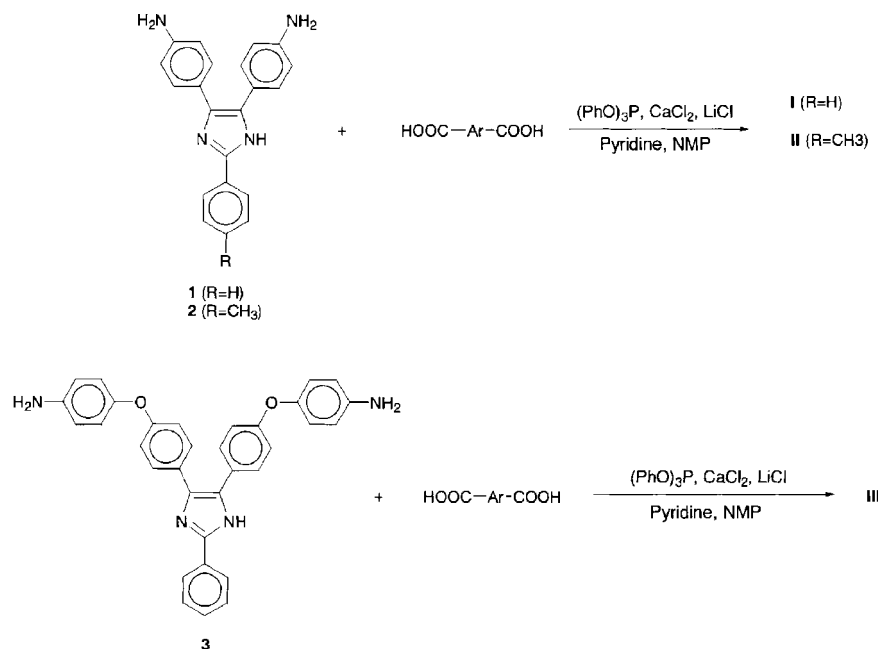
Scheme 3.

aromatic diacids (HOOC-Ar-COOH, Ar = **a** – **c**) by direct polycondensation as shown in Sch. 4.

The results of these polycondensations are summarized in Table 1. The polymerizations of polymer **III** series were carried out in rather dilute solution, because the system appeared to gel as the reaction proceeded, resulting from polymer precipitation. In the listed concentrations, all of the reactions were proceeded homogeneously. The values for inherent viscosities of polymers obtained were moderate to high, ranging from 0.36–1.27 dL g⁻¹. By direct polycondensation, polymer **III** series having high inherent viscosity was not obtained, they were constantly as low as 0.16 dL g⁻¹. Although polymer **III** series have rather lower values than **I** or **II** series, they were high enough to develop the flexible, transparent and tough films, which could be cast from 10% solution of polymers in DMSO solvent.

Solubilities

The solubilities of obtained polymers in several organic solvents at 2.0% (w/v) are summarized in Table 2. Also the results of polyamides **IV** are listed for the comparison. The solubilities for polyamide **Ia-c** were very similar to those for corresponding polyamide **IIa-c**. This means that the methyl substitute in polyamide **II**s has little effect upon the solubilities. Comparison of polyamide **I**s and **IV**s shows that polyamide **IV**s were somewhat better solubilities in pyridine, DMAc, DMF and



Scheme 4.

Table 1. Results of polycondensation.

Polymer	Method ^a	[M] (mol l ⁻¹)	Yield (%)	η_{inh}^b (dL g ⁻¹)	Color
Ia	LS	0.33	quant.	0.37	yellow
	DP	0.33	quant.	0.58	pale yellow
Ib	LS	0.33	quant.	0.70	pale yellow
	DP	0.33	quant.	0.65	yellow
Ic	LS	0.33	99	0.74	yellow
	DP	0.33	quant.	1.22	yellow
IIa	LS	0.33	quant.	0.79	yellow
	DP	0.33	quant.	0.36	pale yellow
IIb	LS	0.33	98	0.54	pale yellow
	DP	0.33	quant.	0.68	yellow
IIc	LS	0.33	quant.	0.50	yellow
	DP	0.33	quant.	1.27	yellow
IIIa	LS	0.33	89	0.39	white
	DP	0.33	97	0.16	white
IIIb	LS	0.10	81	0.63	pale brown
IIIc	LS	0.17	86	0.54	white
IIId	LS	0.083	84	0.78	white
IIIe	LS	0.17	92	0.70	yellow
IIIf	LS	0.07	93	0.60	pale yellow
IIIg	LS	0.07	81	0.61	white

^a Method LS; low temperature solution polycondensation. Method DP; direct polycondensation.

^b Measured at a concentration of 0.5 g/dL in conc. H₂SO₄ at 30°C.

quant.; quantitative

formic acid. And the results for **IIIa-g** exhibited that the presence of the phenoxy groups in the main chain improve the solubilities in amide-type solvents such as DMAc, DMF and formic acid. Especially the polyamide **IIIa**, which was derived from *m*-phenylenediamine, **IIId**, containing ether linkage also in the unit of diacid chlorides, and **IIIg** having hexafluoroisopropylidene group in the main chain revealed higher solubilities in the solvents tested. Apparently the flexible ether linkage reduces the rigidity of the polymers. Since two phenyl groups bound to imidazole ring at 4- and 5-position are not coplanar to imidazole ring, this structure becomes bulky, which presumably inhibit close packing of the polymer chains.

The increased solubility of these polyamides is mainly due to their amorphous character. All the X-ray diffraction diagrams of polyamide **III**s gave amorphous patterns. These amorphous nature corresponds to their high solubilities and formation of creasable films.

Thermal Properties

T_g , thermal decomposition temperature (T_d) and Residual weight at 600°C values of polyamides **Ia-c**, **IIa-c** and **IIIa-g** were evaluated by DSC, DMA and TG under a nitrogen



Table 2. Solubility of polyamides.

Polymer	Cy	Py	<i>m</i> -Cr	DMAc	NMP	DMF	HCOOH	DMSO	H ₂ SO ₄
Ia	±	±	±	±	+	±	±	+	+
Ib	±	±	+	±	+	±	±	+	+
Ic	±	+	+	+	+	+	±	+	+
IIa	±	±	±	±	+	±	±	+	+
IIb	±	±	+	±	+	±	±	+	+
IIc	±	+	+	+	+	+	±	+	+
IIIa	(±)	+	(+)	+	+	+	+	+	+
IIIb	(±)	–	(±)	+	(+)	+	(+)	+	+
IIIc	–	–	±	+	–	+	(+)	(+)	+
IIId	(+)	+	(+)	+	+	+	+	+	+
IIIe	(±)	+	(+)	+	+	+	+	+	+
IIIf	(+)	+	(+)	+	+	+	+	+	+
IIIg	+	+	+	+	+	+	+	+	+
IVa ^a	±	+	+	+	+	+	+	+	+
IVb ^a	±	+	+	+	+	+	+	+	+
IVc ^a	±	+	+	+	+	+	+	±	+

Cy, cyclohexanone; Py, pyridine; *m*-Cr, *m*-cresol; DMAc, *N,N*-dimethylacetamide; NMP, 1-methyl-2-pyrrolidone; DMF, *N,N*-dimethylformamide; DMSO, dimethyl sulfoxide; H₂SO₄, sulfuric acid.

+, soluble; –, insoluble; ±, partially soluble; (), on heating.

^aData of polyamide IVa–IVc are quoted from Ref.^[4].

atmosphere, and they are shown in Table 3. The results of polyamide IVa–c are listed, too. **Ia–c** and **IIa–c** exhibited T_g s ranged between 361 and 401°C. But T_g s for polyamides **IIIa–g** were ranged from 243–275°C at the highest and it shows that the introduction of flexible phenoxy groups caused a significant lowering of the values of T_g s by 120–160°C than analogue polyamide **Is**.

All the synthesized aromatic polyamides showed excellent resistance to thermal degradation. T_d s of polymer **IIIs** were ranging 456–482°C and exceeded those of **I** and **II** series. Residual weights at 600°C of **Is** and **IIIs** reached in the range of 71–88%, and those of **IIIa–g** were 57–72%. Commonly, the T_g s of the polyamides were relatively high according to the strong intermolecular association through hydrogen bonding via amide groups, whereas polyamides **IIIa–g** may be too sterically bulky that the amide units were hindered to associate with the intermolecular hydrogen.

To compare the results of polyamide **Is** with **IVs**, T_d values of polyamide **Is** were lower than **IVs**, however the T_g and Residual weight at 600°C values were higher than **IVs**. The preference for thermal resistance relative to these orders is unknown.

All the polyamides determined here showed no major weight loss below 422°C. And even at 800°C, the residual weights of the polyamides **Is**, **IIIs** and **IIIIs** were still in excess of 50%.

Table 3. Thermal properties of polyamides.

Polymer	T_g (°C) ^a	T_d (°C) ^b	Residual weight at 600°C(%) ^b
Ia	365	422	86
Ib	401	440	87
Ic	363	453	81
Iia	363	427	88
Iib	361	439	80
Iic	370	464	71
IIIa	248	467	59
IIIb	243	473	59
IIIc	249	482	61
IIId	272	473	57
IIIe	259	462	72
IIIf	275	456	68
IIIg	263	465	69
IVa ^c	361	487	80
IVb ^c	343	483	84
IVc ^c	> 370 ^d	487	81

^a Determined by DSC in nitrogen atmosphere with heating rate of 10°C min⁻¹.

^b Temperature of which 5% weight loss was observed, determined by TG in a nitrogen atmosphere with heating rate of 10°C min⁻¹.

^c Data of polyamide IVa–IVc are quoted from Ref.^[4].

^d Determined by DMA, heating rate 3°C min⁻¹ in air, because T_g of IVc was not detected by DSC.

CONCLUSION

The novel diamine **3** was successfully prepared in high purity and novel polyamides were produced from diamines, **1**, **2** and **3** with several aromatic diacid chlorides or aromatic dicarboxylic acids. They had moderate to high inherent viscosities. Aromatic polyamide **III** series, having bulkier and more flexible phenoxy unit, showed good solubilities and provided transparent, flexible and tough films. T_g s of polyamide **III**s were in the range of 243–275°C, and lower than corresponding polyamide **I**s or **II**s by 120–160°C. These polyamides are showing considerable promise for the processable and thermal resistant materials.

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