Synthesis and characterization of new diphenylfluorene-based aromatic polyamides derived from 9,9-bis[4-(4-carboxyphenoxy)phenyl]fluorene

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SUMMARY: A new bis(ether-carboxylic acid), 9,9-bis[4-(4-carboxyphenoxy)phenyl]fluorene (**3**), was synthesized from the nucleophilic fluorodisplacement of *p*-fluorobenzonitrile with the dipotassium bisphenolate of 9,9-bis(4-hydroxyphenyl)fluorene, followed by alkaline hydrolysis of the intermediate bis(ether nitrile). A novel series of aromatic polyamides containing ether and bulky fluorenylidene groups were prepared by the direct polycondensation of the diacid **3** with various aromatic diamines in *N*-methyl-2-pyrrolidone (NMP) solution containing dissolved $CaCl_2$ using triphenyl phosphite and pyridine as condensing agents. The obtained polyamides have inherent viscosities in the range of 0.50–1.75 dL/g. All the polymers are readily soluble in a variety of organic solvents, such as NMP, *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), and *m*-cresol, and afford transparent, flexible, and tough films by solvent casting. These polyamides have glass transition temperatures ranging from 200 to 303 °C and show no significant weight loss up to 450 °C, with 10% weight loss being recorded above 511 °C in nitrogen or air.

Introduction

Aromatic polyamides have found wide commercial acceptance due to their unique property combinations[1]. They can be fabricated into strong abrasion-resistant fibres and films with very high modulus, good thermal stability and high solvent resistance. However, most of the aromatic polyamides are insoluble in organic solvents; they are only soluble in concentrated mineral acids. The insolubility and also high transition temperatures make these polymers difficult to process. Therefore, much effort has been spent on synthesizing processable, tractable polyamides without compromising desired properties. To accomplish this goal, the incorporation of flexible bridging units and/or bulky groups into the polyamide backbone has been widely used[2–11]. Introduction of aryl ether linkages is known to impart processability to the polymer without significant reduction in thermal stability. Incorporation of bulky pendant groups can impart a significant increase in both glass transition temperature (T_g) and thermo-oxidative stability by restricting segmental mobility while providing good solubility due to decreasing packing density and crystallinity. Combining these two structural modifications minimizes the trade-off between processability and properties of aromatic polymers.

An impressive series of high T_g soluble polymers, referred as cardo polymers, was pioneered in the early 1960s and reviewed by Korshak et al.[12] Such polymers contain at least one element in the repeating unit that includes a cyclic side group such as 9,9-fluorenylidene which imparts a combination of enhanced thermal stability, high T_g, and improved solubility. It has been demonstrated in our previous articles[13–16] that incorporation of both ether and a fluorene group into the macromolecular backbone resulted in aromatic polyamides, polyimides, and poly(amide-imide)s with good thermal stability and high T_g. The polyamides and poly(amide-imide)s also showed excellent solubility; however, the polyimides showed some or limited enhancement in solubility. Recently, aromatic polyazomethines were reported from diphenylfluorene-based dialdehyde and aromatic diamines that showed excellent solubility, high T_g, and reasonable thermal stability[17].

In a continuation of the study on fluorene-based polymers, the present article describes a successful preparation of novel soluble and tractable aromatic polyamides without much sacrifice of thermal properties by incorporating bulky diphenylfluorene moiety into the polymer backbone. For this, a new aromatic dicarboxylic acid monomer having diphenylfluorene unit and ether-linked groups was synthesized, which was subjected to direct polycondensation with various aromatic diamines. It was hoped that incoporation of the bulky diacid would decrease hydrogen bonding between amide groups and generally disrupt the co-planarity of aromatic units to reduce packing efficiency and crystallinity. This should promote solubility while maintaining high T_g through controlled segmental mobility.

Experimental part

Materials

9-Fluorenone (Fluka) and *p*-fluorobenzonitrile (Wako) were used as received. *p*-Phenylenediamine (**4a**; TCI) and benzidine (**4c**; TCI) were purified by vacuum sublimation. *m*-Phenylenediamine (**4b**; Janssen) was purified by vacuum distillation. 4,4′-Oxydianiline (**4d**; TCI), 3,4′-oxydianiline (**4e**; Mitsui Petrochemical Ind., Tokyo, Japan), 4,4′-methylenedianiline (**4f**; TCI), 1,4-bis(4-aminophenoxy)benzene (**4g**; TCI), and *a,a*′-bis(4-aminophenyl)-1,4-diisopropylbenzene (**4h**; Mitsui Petrochemical Ind.) were used without further purification. According to a reported procedure[18, 19], 4,4′-bis(4-aminophenoxy)biphenyl (**4i**; m.p. 198–199°C), 2,2-bis[4-(4-aminophenoxy)phenyl]propane (**4j**; m.p. 125–126°C), 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (**4k**; m.p. 162–163°C), 1,1-bis[4-(4-aminophenoxy)-phenyl]-1-phenylethane (**4l**; m.p. 67–68°C), bis[4-(4-aminophenoxy)phenyl] sulfone (**4m**; m.p. 228–230°C), and *a,a*′-bis[4-(4-aminophenoxy)phenyl]-1,4-diisopropylbenzene (**4n**; m.p. 187–189°C) were prepared by the chlorodisplacement reaction of *p*-chloronitrobenzene (TCI) with the corresponding bisphenols in the presence of potassium carbonate, giving the bis(4-nitrophenoxy) compounds, followed by catalytic hydrazine reduction. Calcium chloride ($CaCl_2$) was dried at 180°C under vacuum. Pyridine was purified by distillation after being refluxed with KOH. *N*-Methyl-2-pyrrolidone (NMP) was distilled over calcium hydride under reduced pressure and stored over 4 Å molecular sieves. Similarly, triphenyl phosphite (TPP; Fluka) was purified by distillation under reduced pressure.

Synthesis of 9,9-bis(4-hydroxyphenyl)fluorene (1)

In a 500-mL flask, 28.7 g (0.159 mol) of 9-fluorenone and 5 g of $ZnCl_2$ were dissolved in 60.0 g (0.637 mol) of molten phenol. The mixture was heated at about 60°C on an oil bath, and then dry hydrogen chloride was bubbled in for about 1 h. The reaction system became very dark and was quite viscous but in about 4 h it suddenly solidified. The resulting solid was dissolved with 100 mL of hot 2-propanol, and the mixture was diluted with 700 mL of water to give a lump of viscous, pale yellow product. After washing with hot water, the viscous mass solidified gradually. The pale yellow solid was collected, washed, and dried. The yield of the crude product was 55.1 g (99.1%). The crude product was purified by recrystallization from toluene to give white granular crystals with a yield of 26.6 g. The filtrate was concentrated to about 1/3 of its original volume, and another 11.7 g of the product was collected. Thus, the total yield was about 69% of theory. The melting point of bisphenol **1** was 220–222°C (224°C by DSC at a heating rate of 10°C/min) (lit.[20] 224°C).

Synthesis of 9,9-bis[4-(4-cyanophenoxy)phenyl]fluorene (2)

Fluorene-diphenol **1** (14.6 g, 0.042 mol) was dissolved in 70 mL of *N,N*-dimethylformamide (DMF) and 70 mL of toluene in a 250-mL round-bottomed flask equipped with a Dean-Stark trap. Anhydrous potassium carbonate (11.5 g, 0.08 mol) was added to this solution. The suspension solution was heated to reflux, and water was removed by azeotropic distillation with toluene. After water was removed completely, the residual toluene was distilled off. Then, the reaction mixture was cooled to about 60°C, *p*-fluorobenzonitrile (10.2 g, 0.084 mol) was added, and the reaction was continued at 150°C for 6 h. After cooling, the solution was precipitated into water to give a white powder. The product was isolated by filtration, washed repeatedly with water and methanol, and dried to give 22.3 g (96%) of dinitrile **2**, m.p. 278–280°C (282°C by DSC).

IR (KBr): 2222 (C≡N) and 1249 cm⁻¹ (C—O).

$C_{39}H_{24}N_2O_2$ (552.63)	Calc.	C 84.76	H 4.38	N 5.07
	Found	C 84.36	H 4.72	N 4.98

Synthesis of 9,9-bis[4-(4-carboxyphenoxy)phenyl]fluorene (3)

Into a 1-L round-bottomed flask were placed 22.2 g (0.04 mol) of fluorene-dinitrile **2**, 45 g (0.8 mol) of potassium hydroxide, 300 mL of ethanol, and 200 mL of distilled water. The suspension was refluxed for 8 days to form a clear solution. The resulting solution was filtered hot to remove any possible impurities. After cooling, the filtrate was acidified by concentrated HCl to pH = 2–3, and the precipitated white powder was isolated by filtration, washed thoroughly with water, and dried *in vacuo*, to give 22.8 g (96%) of the fluorene-based dicarboxylic acid **3**; m.p. 286–288°C (293°C by DSC).

IR (KBr): 2500–3500 (broad, O—H), 1691 (C═O), and 1243 cm⁻¹ (C—O).

$C_{39}H_{26}O_6$ (590.63)	Calc.	C 79.31	H 4.43
	Found	C 79.13	H 4.29

General polyamide synthesis

Synthesis of polyamide **5a** is described as a typical procedure. A mixture of fluorene-diacid **3** (0.7383 g, 1.25 mmol), *p*-phenylenediamine (0.1315 g, 1.25 mmol), $CaCl_2$ (0.3 g), TPP (0.9 mL), and pyridine (1 mL) in NMP (3 mL) was heated to 120°C with stirring. After 3 h of stirring at this temperature, it was cooled to room temperature and precipitated into methanol. The polymer (**5a**) was isolated as a white fiber which was washed thoroughly with methanol and hot water, collected by filtration, and dried; yield, 0.85 g (97%); inherent viscosity 1.08 dL/g in DMAc containing 5 wt.-% LiCl at a concentration of 0.5 g/dL at 30°C.
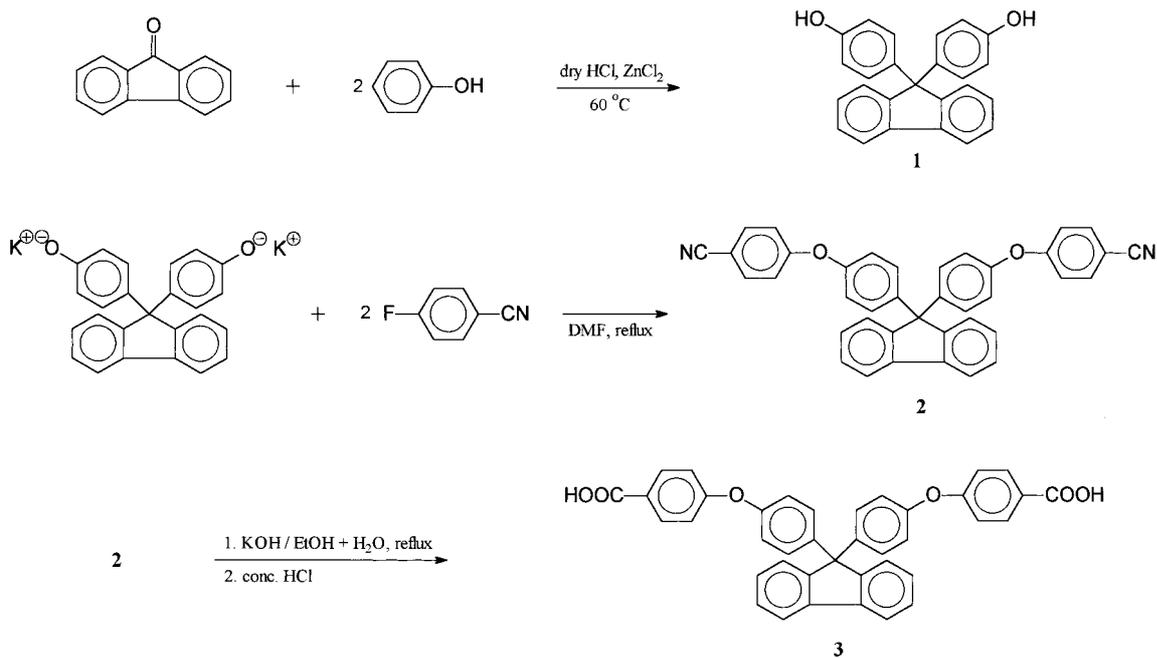
IR (film): 3324 (N—H), 1656 (C═O), and 1241 cm⁻¹ (C—O).

$(C_{45}H_{30}N_2O_4)_n$ (662.74)$_n$	Calc.	C 81.55	H 4.56	N 4.23
	Found	C 80.70	H 4.60	N 4.02

Measurements

Elemental analyses were run in a Perkin-Elmer 2400 C, H, N analyzer at the National Taiwan University (Taipei). Inherent viscosities of the polymers were measured using a Cannon-

Scheme 1:

1

2

3

Fenske viscometer at 30 °C. IR spectra were obtained on a JASCO FT/IR-7000 Fourier transform spectrophotometer on KBr pellets or solution cast films. Solution ^1H and ^{13}C NMR spectra were recorded on a JEOL EX-400 NMR spectrometer. Differential scanning calorimetry (DSC) analyses were performed on a Perkin Elmer DSC 7 at a scan rate of 20 °C/min in flowing nitrogen. Glass transition temperatures (T_g's) were read at the middle of the change in the heat capacity, and were taken from the second heating scan after quick cooling from 400 °C. Thermogravimetry (TG) experiments were performed with 10 ± 1 mg samples heated in flowing nitrogen and air (50 cm³/min) at a scan rate of 20 °C/min with a Rigaku Thermoflex TG 8110. The measurements were taken after an initial 250 °C/10 min drying step. Wide angle X-ray diffraction patterns were recorded at room temperaure on a Rigaku Geiger Flex D-Max IIIa X-ray diffractometer, using Ni-filtered Cu-K_α radiation (1.5418 Å). The scanning rate was 2 °/min over a 2θ range of 5–40 °. Tensile properties of solution cast films were determined from stress-strain curves obtained with an Instron Universal Tester model 1130 with a load cell of 5 kg. A gauge length of 2 cm and an extension rate of 5 cm/min were used for this study. Measurements were performed with film specimens (length 6 cm, width 0.5 cm, and thickness about 0.1 mm), and an average of at least five individual determinations was used.

Results and discussion

Monomer synthesis

Fluorene-bisphenol **1** was prepared by a HCl-catalyzed condensation reaction of excess phenol with 9-fluorenone[20]. The new dicarboxylic acid monomer **3** having diphenylfluorene unit and two ether linkages was synthe-

sized according to a well-developed method[21–24] as shown in Scheme 1. The intermediate dinitrile **2** was obtained from the nucleophilic fluorodisplacement of p-fluorobenzonitrile with the potassium phenolate of fluorene-bisphenol **1** in DMF. The dinitrile was then readily converted into diacid **3** in high purity and high yield by alkaline hydrolysis. The structures of dinitrile **2** and diacid **3** were confirmed by elemental analysis and IR spectroscopy.
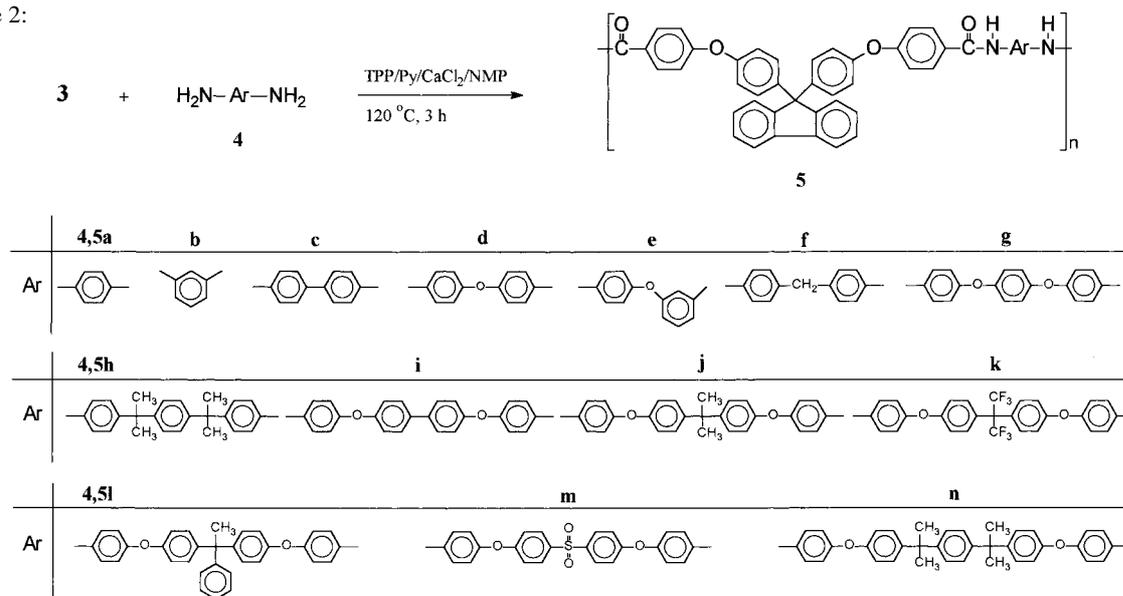
Polymer synthesis

A series of aromatic polyamides, **5a–n**, were synthesized using the Yamazaki-Higashi[25] phosphorylation polycondensation procedure from dicarboxylic acid **3** and various aromatic diamines (Scheme 2). All polyamidations proceeded in homogeneous, transparent and viscous solutions throughout the reaction, and the polyamides were isolated as tough fibers in quantitative yields. Inherent viscosities for **5a–n** ranged from 0.50 to 1.75 dL/g (Tab. 1), indicating moderate to high molecular weight polyamides. The molecular structures of the polyamides were verified by FTIR based on characteristic absorption bands observed around 3300 (N—H stretch), 1650 (C=O stretch), 1510 (N—H bending), and 1230 cm⁻¹ (C—O stretch).

Polymer properties

The crystallinity of the prepared polyamides was evaluated by wide-angle X-ray diffraction measurements. All

Scheme 2:

$$3 \quad + \quad H_2N-Ar-NH_2 \xrightarrow[120\,°C,\ 3\ h]{TPP/Py/CaCl_2/NMP}$$

4

5

Tab. 1. Synthesis conditions and inherent viscosities of polyamides[a]

Polymer	Amounts of reagents used[b]				η_{inh}[c] dL/g
	NMP in mL	Py in mL	TPP in mL	CaCl$_2$ in g	
5a	3	1	0.9	0.3	1.08
5b	3	1	0.9	0.3	0.73
5c	3	1	0.9	0.4	0.92
5d	2.5	1	0.9	0.3	0.92
5e	2.5	1	0.9	0.3	0.69
5f	2.5	1	0.9	0.3	0.67
5g	2.5	1	0.9	0.3	0.53
5h	3	1	0.9	0.4	0.58
5i	3 + 2[d]	1	0.9	0.4	1.13
5j	3.5 + 4	1	0.9	0.4	0.83
5k	3.5 + 3	1	0.9	0.4	1.75
5l	4	1	0.9	0.5	0.78
5m	4	1	0.9	0.5	1.42
5n	3.5	1	0.9	0.4	0.50

[a] 1.25 mmol each of the diacid **3** and diamine monomer were used.
[b] NMP: *N*-methyl-2-pyrrolidone; Py: pyridine; TPP: triphenyl phosphite.
[c] Measured in DMAc-5wt.-% LiCl at 30 °C at a concentration of 0.5 g/dL.
[d] "3 + 2" means that an initial amount of 3 mL of NMP was used and an additional 2 mL of NMP was added when the reaction solution was too viscous to stir.

Tab. 2. Solubility behavior[a] of polyamides

Polymer	Solvent[b]					
	DMAc	NMP	DMF	DMSO	*m*-Cresol	THF
5a	+	+	+	+h	+	–
5b	+	+	+	+	+	s
5c	+	+	+	+	+	–
5d	+	+	+	+	+	s
5e	+	+	+	+	+	s
5f	+	+	+	+	+	s
5g	+	+	+	+	+	+
5h	+	+	+	+h	+	+
5i	+	+	+	+h	+	–
5j	+	+	+	+	+	+
5k	+	+	+	s	+	+
5l	+	+	+	+	+	s
5m	+	+	+	+	+	+
5n	+	+	+	+h	+	+h

[a] +: soluble at room temperature, +h: soluble on heating, s: swelling, –: insoluble even on heating.
[b] DMAc: *N,N*-dimethylacetamide, NMP: *N*-methyl-2-pyrrolidone, DMF: *N,N*-dimethylformamide, DMSO: dimethyl sulfoxide, THF: tetrahydrofuran.

the polyamides showed an almost completely amorphous nature. It appears that the presence of diaryl ether kinks, together with the bulky non-coplanar diphenylfluorene unit in the diacid moiety, leads to loose chain packing. Due to a similar reason, all of these polyamides possess excellent solubility in organic solvents, in spite of the fact that some of them were derived from diamines with a rather rigid structure such as *p*-phenylenediamine and benzidine. All the polyamides are readily soluble in DMAc, NMP, DMF, and *m*-cressol, and most of them also in DMSO and THF (Tab. 2). In addition, the present polymers displayed a comparable solubility with those of the structurally related polyamides from 9,9-bis[4-(4-aminophenoxy)phenyl]fluorene and aromatic dicarboxylic acids reported previously[14], thus supporting that the presence of diphenylfluorene in either diamine or dicarboxylic acid moiety did not affect noticeably the polymer solubility.

All of these polyamides gave good-quality creasable films suitable for the measurement of tensile properties.

Tab. 3. Tensile properties of polyamides[a]

Polymer	Strength to break in MPa	Elongation to break in %	Initial modulus in GPa
5a	76	27	1.7
5b	70	11	1.7
5c	80	9	2.2
5d	115	11	1.8
5e	110	10	1.8
5f	104	7	2.0
5g	88	83	1.4
5h	63	73	1.6
5i	70	14	1.9
5j	94	63	1.8
5k	60	51	1.4
5l	59	33	1.6
5m	75	69	1.5
5n	77	61	1.5

[a]   Films were cast from polymer solutions of DMAc.

The results are summarized in Tab. 3. These polyamide films had tensile strengths of 59–115 MPa, elongations to break of 7–83%, and initial moduli of 1.4–2.2 GPa. The polymers derived from flexible group-linked long-chain diamines revealed higher extensibility. It may be attributed to the fact that these diamine residues adopt a conformation that causes the polymer chain to coil strongly, through the disposition of the aromatic rings adjacent to the ether linkages, but that under stress these conformations are modified to give a more linear unit. The effective uncoiling of the diamine residues about their ether linkages could provide a mechanism for considerable chain extension.

The thermal properties of the polymers were evaluated by means of TG and DSC. Fig. 1 illustrates typical TG curves for the representative polyamide **5a** in both air and nitrogen atmospheres. All the polymers did not show significant weight loss below 450 °C either in air or nitrogen. The temperatures at 10% weight loss were recorded in the range of 521–560 °C in air and 511–565 °C in nitrogen, as shown in Tab. 4. They left a high char yield ranged from 52.2% to 71.6% due to high aromaticity.

Polyamides **5a**–**n** showed T_g values between 303 and 200 °C, following the decreasing order of rigidity, steric hindrance, and symmetry of the polymer backbone. In general, the introduction of flexible ether linkages or less symmetrical *m*-phenylene unit leads to a decreased T_g. For example, *p*-phenylenediamine-based polyamide **5a** exhibited the highest T_g of 303 °C in this series polymers, while the *m*-phenylenediamine-, 4,4′-oxydianiline-, 3,4′-oxydianiline-, and 1,4-bis(4-aminophenoxy)benzene-derived polymers **5b**, **5d**, **5e**, and **5g** showed a decreasing T_g of 277, 259, 254, and 231 °C, respectively. It can also be noted that there is a large window between the T_g and the decomposition temperature, which could be advantageous in the processing of these polymers.
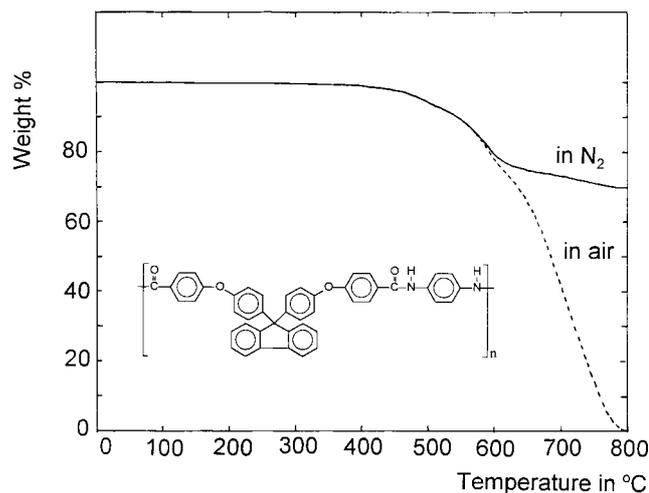

Fig. 1.   TG curves for polyamide **5a** at a heating rate of 20 °C/min

Tab. 4.   Thermal properties of polyamides

Polymer	T_g[a] °C	Decomposition temperature[b]/°C		Char yield[c] in %
		in N$_2$	in air	
5a	303	542	543	69.8
5b	277	535	543	71.6
5c	302	542	545	66.8
5d	259	538	535	68.4
5e	254	557	551	70.2
5f	268	522	540	71.1
5g	231	528	536	64.5
5h	240	511	521	53.2
5i	236	565	560	69.8
5j	219	528	533	63.4
5k	208	526	533	62.6
5l	241	524	530	65.5
5m	224	532	531	59.6
5n	200	528	528	55.2

[a]   Baseline shift in the second heating DSC trace, with a heating rate of 10 °C/min in nitrogen.
[b]   Temperature at which 10% weight loss was recorded by TG at a heating rate of 20 °C/min.
[c]   Residual wt.-% at 800 °C in nitrogen.

The thermal properties of the new aromatic polyamides were compared with those of the polyamides with isomeric repeating unit (for brevity, referred to as the isomeric polyamides) derived from 9,9-bis[4-(4-aminophenoxy)phenyl]fluorene and various dicarboxylic acids reported previously[14]. Tab. 5 compares the thermal properties of two sets of isomeric polyamides. The lower T_g of **5b** than of **5b′** suggests that the attachment of *m*-phenylene in the diamine moiety reduced the chain rigidity. However, the T_g's of **5a** and **5c** were comparable to those of the isomeric pairs of **5a′** and **5c′**. In addition, the present polyamides showed an almost comparable thermal stability with their isomeric counterparts.

Tab. 5. Comparison of thermal properties of polyamides having the isomeric repeating unit

$$\left[\begin{array}{c} \underset{\parallel}{\overset{O}{C}}-Ar-\underset{\parallel}{\overset{O}{C}}-\underset{\mid}{\overset{H}{N}}-Ar'-\underset{\mid}{\overset{H}{N}} \end{array}\right]_n$$

Polymer code	Ar	Ar'	T_g /°C	T_{10} [a] /°C
5a	(diphenylfluorene ether-linked unit)	(phenylene)	303	542
5b		(phenylene)	277	535
5c		(biphenylene)	302	542
5a′	(phenylene)	(diphenylfluorene ether-linked unit)	300	521
5b′	(phenylene)		290	545
5c′	(biphenylene)		309	548

[a] T_{10}: 10% weight loss temperature in nitrogen.

Conclusions

The ether-linked extended dicarboxylic acid **3**, containing the diphenylfluorene unit, was successfully synthesized in high purity and high yield. High-molecular-weight polyamides were synthesized in good yields by the direct polycondensation of the dicarboxylic acid with aromatic diamines by means of triphenyl phosphite and pyridine. These polymers are amorphous and readily soluble in various organic solvents. Flexible and tough films have been obtained by solvent casting. They show good thermal stability, moderate to high T_g's, and a large window between decomposition and glass transition temperatures. All these properties make the diphenylfluorene-based polyamides potential candidates for high-performance thermoplastic materials.

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