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Synthesis and characterization of novel aromatic polyamides derived from 4-aryl-2,6-bis(4-aminophenyl) pyridines

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Abstract

In order to prepare new polyamides with enhanced thermal stability and high solubility in common organic solvents, new diamine monomers containing a pyridine ring bearing several kinds of aromatic type pendant groups on its 4-position were introduced and fully characterized by IR, NMR and mass spectroscopies. Optimal conditions for polyamidations were obtained via study of the model compounds. The polymers were fully characterized by IR, NMR spectroscopies and elemental analysis. The physical properties of the polymers were studied. All of these new polymers show excellent thermal stability and very good solubility in polar aprotic solvents. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Aromatic polyamides; Pyridine ring; Pendant groups

1. Introduction

Aromatic polyamides have been known for their commercial acceptance in the industry since the introduction of high-performance thermoplastic materials having high thermal stability, good chemical resistance and ultrahigh mechanical strength, e.g. poly(*p*-phenylene terphthalamide) (Kevlar) [1]. Despite having the usual characteristics, there are certain drawbacks associated with aromatic polyamides because of their infusible and insoluble nature in organic solvents, which restrict their processing. However, these inherent problems have been dealt with by many research efforts during the last decades by copolymerization [2,3], incorporation of alkyl or aryl substitution to reduce the hydrogen bonding at the amide linkage [3,4], symmetric/asymmetric bulky substitution in the aromatic rings [5–11], nature of parent chain [12–14], lateral substituents in the polymer forming monomeric units [15], noncoplanar biphenylene moieties [16,17], flexible alkyl spacers [18], and pendant phenyl group into the polyamide backbone [19,20]. It is well known that polyamides containing heterocyclic units in the main chain possess excellent thermal stabilities [21]. So in order to prepare novel processible polyamides with enhanced thermal stabilities, new diamine monomers containing pyridine heterocyclic group and bearing bulky aromatic pendant groups in the 4-position of the pyridine ring are introduced and used for preparation of polyamides. Physical properties of polymers including characterization, inherent viscosity, solubility behavior, thermal property, and thermal stability are also studied.

2. Experimental

Chemicals were either prepared in our laboratory or purchased from Fluka AG, Chemical Company. ^{1}H NMR spectra were recorded on a Bruker Avance DPX 250 MHz instrument, using DMSO-d_6 as solvent and tetramethylsilane as shift reference (tube diameter, 5 mm). Infrared spectra analyses were performed on a Perkin–Elmer IR 157G instrument, using KBr pellets. Mass spectra were recorded on Shimadzu GC-MS QP 1000 Ex. Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) analysis were performed on a Stanton STA-G25 with heating rate of 20°C/min under air. Elemental analysis was performed by the Research Center of the National Oil Company of Iran. Melting points were determined in open capillaries with a Buchi 535 instrument. Inherent viscosities of polymers were determined for a solution of 0.5 g/dl in DMAc at 30°C using an Ostwald viscometer.

2.1. Preparation of monomers

2.1.1. 4-Phenyl-2,6-bis(4-nitrophenyl) pyridine (DNM$_a$)

In a round-bottomed flask (150 ml) equipped with a reflux

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Table 1
Yield, melting point and spectroscopic data of monomers and model compounds

Compound code	Yield (%)	m.p. (°C)	IR (cm^{-1})	NMR (ppm)	Molecular ion (*m/z*)
DNM_a	65	320	3030, 1600, 1550, 1510, 1350, 1100, 1010, 850, 820, 750, 680, 620	6.8–8.2 (C–H arom., 15H)	397
DNM_b	65	316	3030, 2950, 2830, 1600, 1550, 1510, 1450, 1350, 1290, 1250, 1110, 1050, 860, 760, 700	6.8–8.0 (C–H arom., 14H), 3.8 (OCH_3, 3H)	427
DNM_c	64	312	3030, 2920, 1600, 1550, 1520, 1420, 1350, 1110, 1020, 860, 810, 760, 700	6.8– 8.1 (C–H.arom., 14H), 2.4 (CH_3, 3H)	411
DNM_d	63	305	3050, 2980, 2890, 1600, 1550, 1520, 1430, 1350, 1110, 860, 830, 760, 730, 700	6.8–8.1 (C–H arom., 14H), 3.15 (CH, 1H), 1.5 (CH_3, 6H)	439
DNM_e	60	301	3030, 1600, 1550, 1350, 1110, 860, 800, 780, 700	6.9–8.2 (C–H arom., 17H)	447
DAM_a	95	208	3400, 3340, 3200, 1620, 1600, 1540, 1510, 1450, 1400, 1290, 1250, 1180, 830, 760, 700	7–8.2 (C–H arom., 15H), 3.99 (NH_2, 4H)	337
DAM_b	94	197	3400, 3360, 3200, 3030, 2980, 2820, 1620, 1600, 1540, 1510, 1400, 1300, 1180, 1110, 1040, 820, 710	6.8–8 (C–H arom., 14H), 3.8 (OCH_3, 3H), 3.7 (NH_2, 4H)	367
DAM_c	92	195	3420, 3340, 3200, 1620, 1600, 1540, 1510, 1420, 1250, 1180, 820, 620	6.8–8 (C–H arom., 14H), 3.7 (NH_2), 2.4 (CH_3, 3H)	351
DAM_d	91	190	3440, 3380, 3200, 3030, 2980, 2890, 1620, 1600, 1540, 1400, 1300, 1250, 1180, 830	6.9–8.2 (C–H arom., 14H), 3.99 (NH_2, 4H), 3.15 (CH, 1H), 1.5 (CH_3, 6H)	370
DAM_e	90	185	3480, 3390, 3200, 3030, 1620, 1600, 1540, 1520, 1400, 1300, 1250, 1186, 840, 800, 750	6.8–8.1 (C–H arom., 17H), 3.7 (NH_2, 4H)	387
MDA	97	–	3400, 3330, 3040, 1660, 1600, 1520, 1490, 1430, 1300, 1190, 830, 710	10.3 (N–H amide, 2H), 7.1–8.1 (C–H arom., 25H)	575

condenser, a mixture of benzaldehyde (3.2 g, 0.03 mol), *p*-nitroacetophenone (10 g, 0.06 mol), ammonium acetate (30 g), and glacial acetic acid (75 ml) was refluxed for 2 h. Upon cooling, crystals separated, which were filtered and washed first with acetic acid (50%) and then with cold ethanol. These dark yellow crystals were recrystallized from absolute ethanol, and then dried at 60°C under vacuum.

The other dinitro compounds were prepared by the same procedure as above using the appropriate aldehyde. Yields and other data are shown in Table 1.

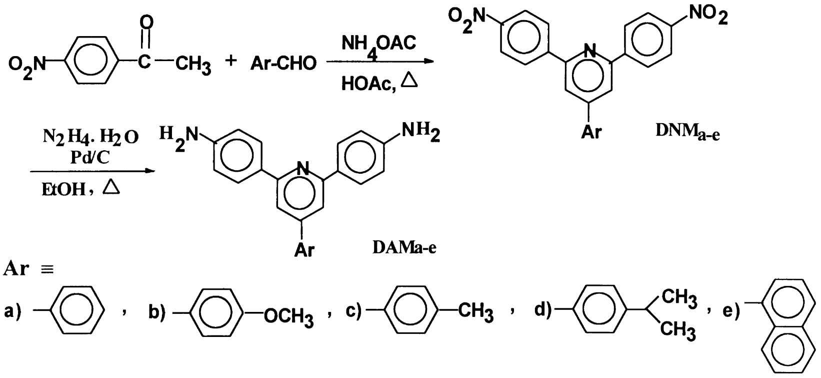
2.1.2. 4-Phenyl-2,6-bis(4-aminophenyl) pyridine (DAM_a)

In a two-necked round-bottomed flask (250 ml) equipped with a reflux condenser and a dropping funnel, a suspension of 4-phenyl-2,6-bis(4-nitrophenyl) pyridine (5 g, 0.012 mol),palladium on carbon 5% (0.4 g) and ethanol (200 ml) was prepared. The mixture was warmed and while being stirred magnetically, hydrazine hydrate 80% (10 ml) in ethanol (20 ml) was added dropwise over a 1.5 h period through the dropping funnel, while maintaining the temperature at about 50°C. The reaction mixture was then refluxed for 2 h and filtered while hot. On cooling, the filtrate gave white-cream colored crystals of the title diamine compound, which were recrystallized from ethanol and vacuum dried. The same procedure was repeated for reduction of other dinitro compounds. Yields and other data are shown in Table 1.

2.2. Preparation of model compounds

2.2.1. Model diamide (MDA) from 4-(4-methoxyphenyl)2,6-bis(4-aminophenyl) pyridine and benzoyl chloride via solution condensation

A two-necked flask equipped with a dropping funnel and gas inlet tube was charged with a solution of 4-(4-methoxyphenyl)2,6-bis(4-aminophenyl) pyridine (1 g, 2.7 mmol)



Scheme 1.

in DMAc (10 ml). Propylene oxide (PO) (1 ml) was added to the solution. Benzoyl chloride (0.7587 g, 5.4 mmol) diluted with DMAc (5 ml) was added dropwise to the solution at 0°C under N_2. The mixture was then stirred at ambient temperature for 8 h under a stream of N_2. It was poured into methanol, and the light yellow solid obtained was filtered off, washed with methanol and dried to afford the diamide. Yields and other data are shown in Table 1.

2.2.2. MDA from 4-(4-methoxyphenyl)2,6-bis(4-aminophenyl) pyridine and benzoic acid via direct condensation (phosphorylation)

In a two-necked flask equipped with reflux condenser and gas inlet tube, a mixture consisting of NMP (30 ml), pyridine (6 ml), LiCl (0.6 g), and $CaCl_2$ (1.8 g) was prepared. Then 4-(4-methoxyphenyl)-2,6-bis(4-aminophenyl) pyridine (0.734 g, 2 mmol), benzoic acid (0.536 g, 4.4 mol) and triphenyl phosphite (1.27 g, 4.1 mmol) were added to the flask. The mixture was heated at 110°C for 7 h under a stream of N_2. The solution was then poured into methanol and the precipitate was filtered off and vacuum dried.

2.3. Preparation of polymers

2.3.1. Polyamide (PAMD$_b$) from 4-(4-methoxyphenyl)2,6-bis(4-aminophenyl) pyridine and terphthaloyl chloride via solution polycondensation

A two-necked flask equipped with a dropping funnel and gas inlet tube was charged with a solution of 4-(4-methoxyphenyl)2,6-bis(4-aminophenyl) pyridine (0.734 g, 2 mmol) in DMAc (10 ml). Propylene oxide (1 ml) was added to the solution. Terphthaloyl chloride (0.406 g, 2 mmol) diluted with DMAc (5 ml) was added dropwise to the solution at 0°C under a stream of N_2. The mixture was then stirred at ambient temperature for 8 h. It was poured into methanol and the light yellow solid obtained was filtered off, washed with methanol, redissolved in a minimum amount of DMAc and again precipitated in methanol, filtered and dried under vacuum at 120°C.

Solution polycondensation was chosen as a procedure for preparation of all polyamides using appropriate diamines and diacid chlorides. Yields and other data are shown in Table 2.

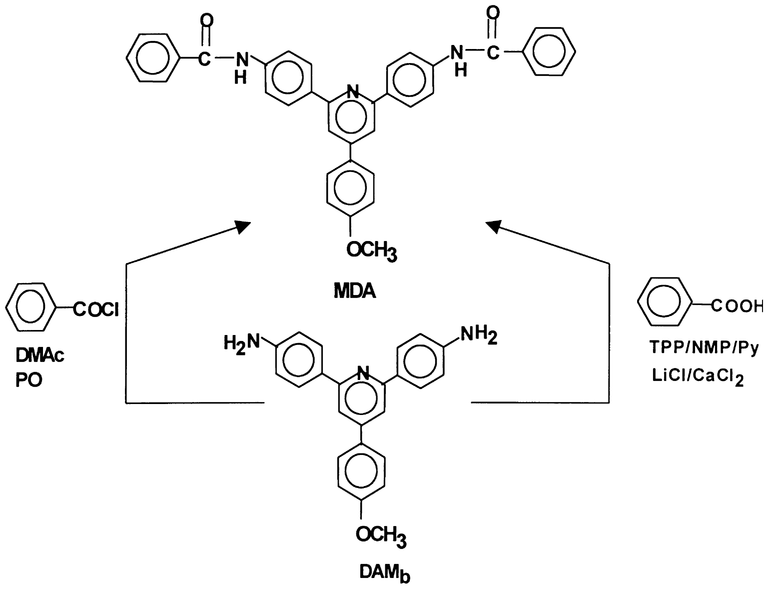
2.3.2. Polyamide (PAMD$_b$) from 4-(4-methoxyphenyl)2,6-bis(4-aminophenyl) pyridine and terphthalic acid via direct polycondensation

In a two-necked round-bottomed flask equipped with a reflux condenser and a gas inlet tube, 4-(4-methoxyphenyl)2,6-bis(4-aminophenyl) pyridine (0.743 g, 2 mmol) and terphthalic acid (0.332 g, 2 mmol) were mixed with triphenylphosphite (TPP) (1.27 g, 4.1 mmol) in a solvent mixture of NMP (30 ml), and pyridine (6 ml), containing LiCl (0.6 g) and $CaCl_2$ (1.8 g). The reaction mixture was heated at 110°C for 7 h under N_2. The solution then was poured into methanol, the precipitate filtered, washed with methanol, refluxed for 1 h in methanol, filtered and vacuum dried at 120°C.

3. Results and discussion

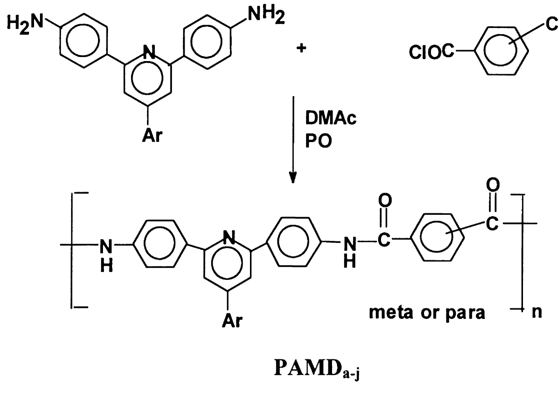
A comprehensive literature survey shows that there are several methods for preparation of the pyridine ring [22]. The modified Chichibabin method [23] is one of the best, which offers advantages such as good yield, available starting material and potential for introducing different substituents in the pyridine ring. Scheme 1 shows the synthetic route used for the preparation of diamino monomers. First, 4-aryl-2,6-bis(4-nitrophenyl) pyridines (DNM$_{a-e}$) were prepared with the use of several aryl aldehydes and 4-nitroacetophenone.

IR spectra of DNM$_{a-e}$ showed characteristic bands of nitro groups at 1350 and 1550 cm^{-1}. In addition, C=C and C=N bands of phenyl and pyridine rings at 1600 cm^{-1} were present. NMR spectra of DNM$_{a-e}$ showed the characteristic aromatic C–H peak of phenyl and pyridine rings at 8.2–6.8 ppm, which confirmed the formation of pyridine rings. Also, mass spectra of all these compounds showed the appropriate molecular ion peaks. A representative elemental analysis of DNM$_a$ was as follows: C, 69.0% (69.5%, calculated); H, 3.9% (3.8%); and N, 10.7% (10.6%). These



Scheme 2.

dinitro compounds were subjected to reduction, using hydrazine hydrate as the source of hydrogen and palladium on charcoal (5%) as the catalyst. Ir spectra of DAM_{a-e} showed characteristic bands of amino group at ca. 3400–3300 cm^{-1} (N–H stretching) and 1620 cm^{-1} (N–H out-of-plane bending). NMR spectra of DAM_{a-e} showed NH_2 protons at ca. 3.7 ppm. Also, all of these compounds showed molecular ion peak in their mass spectra. A representative elemental analysis of DAM_a was as follows: C, 81.0% (81.9%, calculated); H, 5.7% (5.6%); and N, 12.6% (12.5%). MDA was prepared via either low-temperature solution condensation or Higashi direct polycondensation [24], using DAM_b as a typical candidate of diamine monomers according to Scheme 2. Both of these methods were successful for preparation of MDA. The IR spectrum of MDA showed amide bands at 3350 cm^{-1} (N–H stretching), 1660 cm^{-1} (C=O stretching) and 1550 cm^{-1} (combined N–H bending and C–N stretching). In the NMR spectra an amidic proton was observed at ca.10.5 ppm. Also, in the mass spectra the molecular ion peak at 575 was observed. Elemental analysis of MDA was as follows: C, 78.5% (79.3%, calculated); H, 5.1% (5.0%); N, 7.4% (7.3%). Spectroscopic and physical data of all monomers and model compounds are collected in Table 1.



PAMD$_{a\text{-}j}$

Scheme 3.

Optimized conditions obtained from the study of model compounds were applied for the preparation of polyamides. Considering inherent viscosity (η_{inh}) of polymer solutions as a measure of the molecular weight, solution polycondensation offered polymers with higher molecular weight than Higashi's direct polycondensation method. So this method was chosen for preparation of polyamides (Scheme 3; $PAMD_a$ = phenyl, *para*; $PAMD_b$ = anisyl, *para*; $PAMD_c$ = tolyl, *para*; $PAMD_d$ = cumyl, *para*; $PAMD_e$ = naphthyl, *para*; $PAMD_f$ = phenyl, *meta*; $PAMD_g$ = anisyl, *meta*; $PAMD_h$ = tolyl, *meta*; $PAMD_i$ = cumyl, *meta*; $PAMD_j$ = naphthyl, *meta*).

The polyamides ($PAMD_{a-j}$) were characterized by IR and NMR spectroscopies. The presence of amidic bands at ca. 3350 cm^{-1} (N–H stretching), 1660 cm^{-1} (C=O stretching) and ca. 1530 cm^{-1} (N–H bending and C–N stretching) in the IR spectra and amidic proton at ca. 10.6 ppm in the NMR spectra of polymers confirmed the amidic structure of polymers. Spectroscopic data of all polyamides are collected in Table 2. Also as a representative example, the elemental analysis of $PAMD_b$ was as follows: C, 74.3% (75.3%, calculated); H, 4.7% (4.8%); and N, 8.4% (8.5%).

The inherent viscosities of polymers were in the range of 0.5–1.2 dl/g, which showed relatively high molecular weight of polymers (Table 2). All of these polymers produced clear, flexible and tough films, which could be cast from solution of polymers in DMAc solvent. This showed good mechanical strength of the films, which indirectly confirmed the high molecular weight of polymers.

Table 2
Yield, inherent viscosity and spectroscopic data of polyamides

Polymer code	Yield (%)	η_{inh} (dl/g)	IR (cm^{-1})	NMR (ppm)
$PAMD_a$	95	1.2	3350, 3030, 1660, 1600, 1520, 1320, 1250, 1130, 1030, 840, 760, 700	10.6 (N–H amide, 2H), 7–8.2 (C–H arom., 19H)
$PAMD_b$	94	0.8	3400, 3030, 2980, 2820, 1660, 1520, 1320, 1230, 1020, 830	10.6 (N–H amide, 2H), 7–8.2 (C–H arom., 14H), 3.7 (OCH_3, 3H)
$PAMD_c$	94	0.7	3350, 3030, 2930, 1660, 1600, 1520, 1320, 1250, 1020, 820, 730	10.6 (N–H amide, 2H), 7–8.2 (C–H arom., 18H), 2.4 (CH_3, 3H)
$PAMD_d$	92	0.6	3350, 3030, 2960, 1665, 1600, 1520, 1320, 1240, 1020, 840, 730	10.6 (N–H amide, 2H), 7–8.2 (C–H arom., 18H), 3.15 (CH, 1H), 1.5 (CH_3, 6H)
$PAMD_e$	90	0.6	3350, 3030, 1660, 1600, 1520, 1330, 1250, 1020, 840, 720	10.6 (N–H amide, 2H), 7–8.2 (C–H arom., 21H)
$PAMD_f$	94	1.0	3350, 3030, 1660, 1600, 1520, 1320, 1250, 1130, 1030, 840, 760, 700	10.6 (N–H amide, 2H), 7–8.2 (C–H arom., 19H)
$PAMD_g$	93	0.7	3350, 3030, 2950, 2830, 1660, 1600, 1520, 1320, 1250, 1130, 1030, 840, 760, 700	10.6 (N–H amide, 2H), 7–8.2 (C–H arom., 18H), 3.7 (OCH_3, 3H)
$PAMD_h$	93	0.6	3350, 3030, 2930, 1660, 1600, 1520, 1320, 1250, 1020, 820, 720	10.6 (N–H amide, 2H), 7–8.2 (C–H arom., 18H), 2.4 (CH_3, 3H)
$PAMD_i$	91	0.5	3350, 3030, 2960, 1665, 1600, 1520, 1320, 1240, 1020, 840, 730	10.6 (N–H amide, 2H), 7–8.2 (C–H arom., 18H), 3.15 (CH, 1H), 1.5 (CH_3, 6H)
$PAMD_j$	91	0.5	3350, 3030, 1660, 1520, 1330, 1250, 1020, 840, 720	10.6 (N–H amide, 2H), 7–8.2 (C–H arom., 21H)

One of the major objectives of this study was producing modified polyamides with improved solubility. As is shown in Table 3, the polyamides were readily soluble in common polar aprotic solvents without need for heating. Also, by heating they were soluble in a less efficient solvent such as *m*-cresol. Among these polymers, $PAMD_i$ and $PAMD_j$, which contain cumyl and naphthyl groups on pyridine rings and also meta diacid moieties, were more soluble, and

Table 3
Solubility of polyamides (+: soluble at room temperature; ±: soluble with heating; DMAc: *N*,*N*-dimethyl acetamide; DMF: *N*,*N′*-dimethyl formamide; NMP: *N*-methyl pyrrolidone; HMPTA: hexamethyl phosphoric triamide; DMSO: dimethyl sulfoxide)

Polymer code	DMAc	DMF	NMP	HMPTA	DMSO	*m*-Cresol	H_2SO_4
$PAMD_a$	+	+	+	+	+	±	+
$PAMD_b$	+	+	+	+	+	±	+
$PAMD_c$	+	+	+	+	+	±	+
$PAMD_d$	+	+	+	+	+	±	+
$PAMD_e$	+	+	+	+	+	±	+
$PAMD_f$	+	+	+	+	+	±	+
$PAMD_g$	+	+	+	+	+	±	+
$PAMD_h$	+	+	+	+	+	±	+
$PAMD_i$	+	+	+	+	+	±	+
$PAMD_j$	+	+	+	+	+	±	+

Table 4
Thermal properties of polyamides

Polymer code	$T_{10\%}$ (°C)[a]	Ch. Y.[b]	Polymer code	$T_{10\%}$ (°C)[a]	Ch. Y.[b]
$\mathrm{PAMD_a}$	490	38	$\mathrm{PAMD_f}$	475	42
$\mathrm{PAMD_b}$	410	25	$\mathrm{PAMD_g}$	475	30
$\mathrm{PAMD_c}$	420	35	$\mathrm{PAMD_h}$	540	36
$\mathrm{PAMD_d}$	408	25	$\mathrm{PAMD_i}$	418	29
$\mathrm{PAMD_e}$	400	30	$\mathrm{PAMD_j}$	412	32

[a] Temperature of 10% weight loss, obtained from TGA.
[b] Char yield percent at 600°C, obtained from TGA.

shorter time was needed for their complete dissolution in solvents.

The thermal behavior of polyamides were studied by DSC. No exotherms associated with softening were observed in DSC traces of polyamides. Also, a glass transition temperature (T_g) could not be detected by DSC up to 400°C. All polyamides showed exotherms starting from about 400°C assigned to their thermal degradation. The thermal stability of polyamides were evaluated by TGA (Table 4). The polyamides started to lose weight, because of thermal degradation, around 400°C. The 10% weight loss of polymers as a standard indication for thermal stability of polymers were in the range of 400–490°C, which indicates excellent thermal stability of polymers. Also, char yields of polymers at 600°C were in the range of 25–42%, which was good for polyamides. Among polyamides, $\mathrm{PAMD_a}$ containing phenyl group as substituent in the pyridine ring and also *para*-substituent in diacid moiety had maximum thermal stability. It seems that using a bulkier substituent in the 4-position of the pyridine ring of diamine monomers causes improvement of solubility of resulting polyamides. However, a slight decrease in thermal stability also can be observed with this modification.

Synthesis and study of the corresponding polyimides derived from the 4-aryl-2-6-bis(4-amminophenyl) pyridines are underway and the results will be reported soon.

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