

Synthesis of New Soluble Aromatic Poly(amide imide)s from Unsymmetrical Extended Diamine Containing Phthalazinone Moiety

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ABSTRACT: The preparation of a new unsymmetrical kink non-coplanar heterocyclic diamine, 1,2-dihydro-2-(4-aminophenyl)-4-[4-(3-phenyl-4-aminophenoxy)phenyl]-(2*H*)phthalazin-1-one (**3**), from a readily available unsymmetrical phthalazinone bisphenol-like (**1**) was described. The diamine can be directly polymerized with various aromatic bis(trimellitimide)s (**4a–e**) by using triphenyl phosphite and pyridine as condensing agents to give a series of new aromatic poly(amide imides) (**5a–e**) containing the kink non-coplanar phthalazinone heterocyclic units with inherent viscosities of 0.57–1.06 dL/g. The polymers were readily soluble in a variety of solvents such as *N,N*-dimethylform-

amide, *N,N*-dimethylacetamide, dimethylsulfoxide, *N*-methyl-2-pyrrolidinone, and even in pyridine and *m*-cresol and could be cast to form flexible and tough films. The glass transition temperatures were in the range of 315–340°C, and the temperatures for 5% weight loss in nitrogen were in the range of 487–512°C. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 1516–1520, 2004

Key words: poly(arylene amide imide)s; heterocyclic polymer; high-performance polymer; polycondensation; phthalazinone

INTRODUCTION

Aromatic polyamides and polyimides are important classes of high-performance polymers providing many useful applications for high technology as advanced materials. However, the rigid backbone and strong hydrogen bonding in aromatic polyamides and charge transfer complex formation in aromatic polyimides result in insolubility in most organic solvents and high softening temperatures. These characteristics make them generally difficult or too expensive to process. Therefore, much effort has been made to increase the solubility of aromatic polymers. Structural modifications of aromatic polymers, such as the introduction of flexible linkages¹ and bulky lateral substituents,² kink non-coplanar biphenylene moieties,^{3,4} organometallic complexation,⁵ and hyperbranched or dendritic architectures^{6–8} into the aromatic polymer main chains have been utilized to tune the polymer properties by the design and synthesis of new monomers.

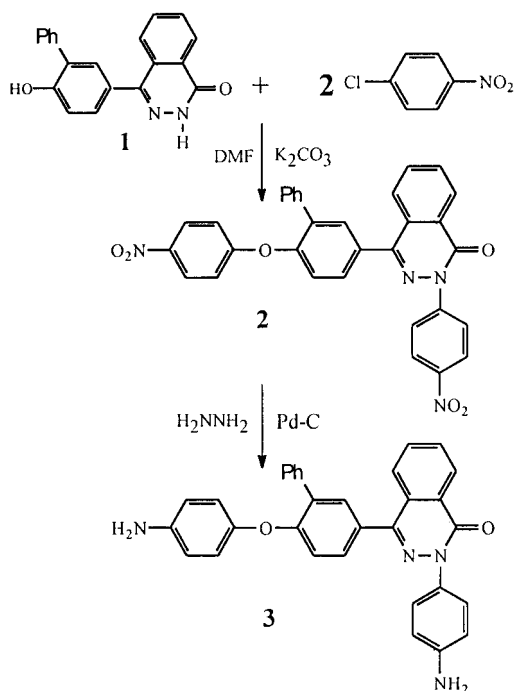
There is a growing interest in aromatic poly(amide imides) (PAIs) for a variety of applications as they

retain good mechanical properties at high temperatures and show easier processibility when compared with aromatic polyamides and polyimides.^{9,10} PAIs have been developed as engineering thermoplastic materials, for example, Torlon® (Amoco Chemical Co.), and used as electrical wire enamel, adhesives, and various injection-molding and extrusion products. They inherit desirable characteristics from both polyamides and polyimides and possess good thermal properties compared to polyamide, and better melt processibility than polyimides. To further improve solubility in organic solvents, flexible linkages have been introduced in the polymer main chain. For example, soluble PAIs based on trimellitic anhydride (TMA) have been synthesized by using diamines having isopropylidene,¹¹ biphenyl,^{12,13} and naphthalene moieties.¹⁴ Although being more soluble in organic solvents, the glass transition temperatures (T_g) of the PAIs containing a flexible linkage often decreased.

In previous articles,^{15,16} we have described the synthesis of poly(arylene ether amides) containing phthalazinone moieties from two unsymmetrical and kink non-coplanar heterocyclic diamines: 1,2-dihydro-2-(4-aminophenyl)-4-[4-(4-amino phenoxy)phenyl]-(2*H*)phthalazin-1-one and 1,2-dihydro-2-(4-aminophenyl)-4-[4-(4-aminophenoxy)-3,5-dimethylphenyl]-(2*H*)phthalazin-1-one. It was found that incorporation of kink non-coplanar phthalazinone heterocyclic units into aromatic polymer backbone reduces the crystal-

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Scheme 1 Synthesis of unsymmetrical heterocyclic diamines.

linity and enhances the solubility as well as thermooxidative stability of aromatic polymers. They have very high T_g 's (up to 329°C) together with good solubility. In our continuing effort to develop easily processible high-performance polymers, we extend our investigation to the synthesis of aromatic poly(amide imides) from direct polymerization of a new unsymmetrical kink non-coplanar heterocyclic diamine, 1,2-dihydro-2-(4-aminophenyl)-4-[4-(3-phenyl-4-aminophenoxy)phenyl](2*H*)phthalazin-1-one with various aromatic bis(trimellitimide)s (**4a–e**).

EXPERIMENTAL

Materials

Unless specified otherwise, reagent-grade reactants and solvents were used as supplied. Pd-C (5%) was obtained from Dalian Institute of Chemical Physics (Chinese Academy of Sciences). *N*-methyl-2-pyrrolidone (NMP) and pyridine (Py) were purified from distillation under reduced pressure over calcium hydride and stored over molecular sieves (4 Å). Reagent-grade calcium chloride was dried under vacuum at 180°C for 6 h prior to use. Triphenyl phosphite (TPP) was freshly vacuum-distilled before use. 1,2-Dihydro-4-(3-phenyl-4-hydroxyphenyl)(2*H*)phthalazin-1-one (**1**)¹⁷ and aromatic bis(trimellitimides)¹⁸ (**4a–e**) were prepared according to the reported methods, respectively.

Synthesis of monomer 3

Preparation of 2

A 500-mL three-necked flask containing 1,2-dihydro-4-(3-phenyl-4-hydroxyphenyl) (2*H*)phthalazin-1-one (**1**) (31.4 g, 0.1 mol), *p*-chloronitrobenzene (34.6 g, 0.22 mol), potassium carbonate (33 g, 0.24 mol), *N,N*-dimethylacetamide (DMAc; 200 mL), toluene (70 mL), was equipped with a mechanical stirrer, a Dean–Stark trap, a water condenser, a thermometer, and a nitrogen inlet. Under an atmosphere of nitrogen, the mixture was heated and maintained at 140°C for 5–6 h to remove all water by means of azeotropic distillation with toluene. The temperature was then increased to 150°C to remove toluene for 1 h and then cooled. The mixture was then poured into an ethanol–water mixture (1 : 1 v/v, 300 mL). The precipitate was collected on a filter and crystallized from *N,N*-dimethylformamide (DMF) to give a yellow solid (50.6 g, yield: 91%).

Melting point (mp): 204–205°C; IR (KBr): 1112 (w, N–N), 1262 (m, C–O–C), 1346, 1509 cm⁻¹ (s, –NO₂). Electronic impact–mass spectra (EI-MS) (m/z , relative intensity %): 556 (M⁺, 100%). ANAL. calcd for C₃₂H₂₀O₆N₄ (556.14): C, 69.00%; H, 3.62%. Found: C, 68.76%; H, 2.59%.

Preparation of 3

The dinitro compound **2** (38.92 g, 0.07 mol), Pd-C (5%, 0.8 g), and ethyl glycol monomethyl ether (500 mL) were introduced into a three-necked flask to which hydrazin monohydrate (175 mL) was added dropwise over 1 h at reflux temperature (about 105°C). After the addition was completed, the reaction was continued at reflux temperature for another 10 h. The mixture was then filtered and recrystallized from ethyl glycol monomethyl ether to remove Pd-C. After cooling, the product was obtained as pale yellow crystals (33 g, yield: 95%).

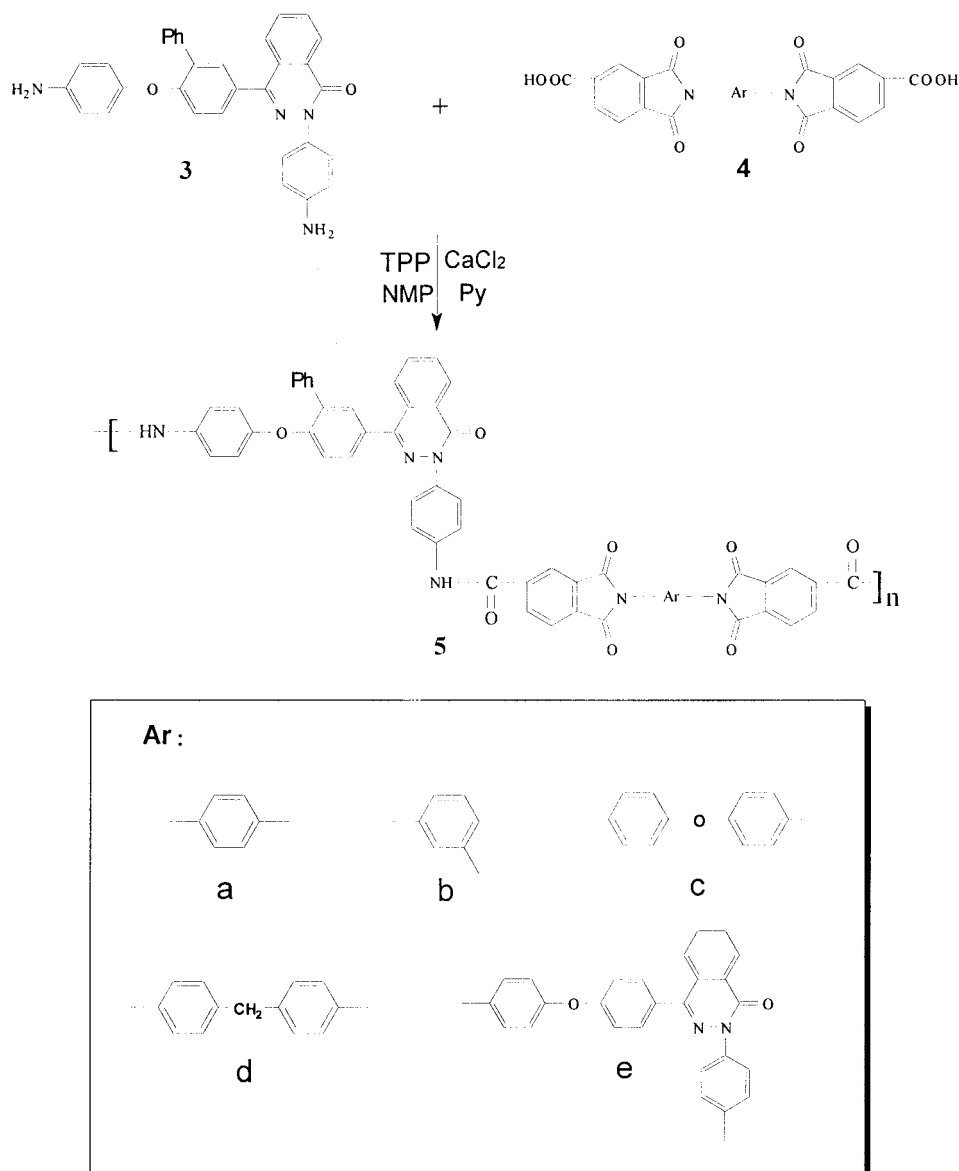
mp: 252–253°C. ¹H-NMR (DMSO-*d*₆), δ (ppm), 8.4 (m, 1H), 7.9–6.6 (m, 19H), 4.9–5.2 (brs, 4H, NH₂). IR (KBr): 1104 (w, N–N), 1244 (m, C–O–C), 1606 (m, C=N), 1656 (s, C=O), 3336, 3363, 3403, 3432 cm⁻¹ (m, N–H). EI-MS (m/z , relative intensity %): 496 (M⁺, 100%). ANAL. calcd for C₃₂H₂₄O₂N₄ (496.2): C, 77.39%; H, 4.88%. Found: C, 77.13%; H, 4.86%.

Polymerization

A typical example of direct polycondensation is shown as follows:

Polymer 5a from 3 and 4a

A mixture of **3** (2.48 g, 5 mmol), **4a** (5 mmol), calcium chloride (0.9 g), NMP (15 mL), pyridine (2.8 mL), and triphenyl phosphite (2.8 mL) was heated with stirring at 100°C for 3 h under nitrogen. The obtained polymer



Scheme 2 Synthesis of poly(amide imides) containing phthalazinone moiety.

solution was slowly poured into methanol (500 mL) with constant stirring, producing fibrous precipitate after being washed thoroughly with methanol and hot water, collected on a filter, and dried at 100°C under vacuum. The yield was 98%.

Measurements

$^1\text{H-NMR}$ spectra were obtained on a JEOL FX 90Q spectrometer with DMSO-d_6 as the solvent and chemical shifts were given in parts per million relative to tetramethylsilane (TMS). IR measurements were performed on Nicolet-20DXB spectrometer. Mass spectra were obtained by using Finnigan MAT/SS220. Differential scanning calorimetry (DSC) was performed at a heating rate of 10°C/min under nitrogen on a TA 2200

thermal analyzer system. Thermal stability of the polymers samples was determined by using a TA 2200 thermal analyzer from 25 to 800°C at a heating rate of 20°C/min in nitrogen. X-ray diffractograms were recorded with an X-ray diffractometer (Philips Model PW 1710); measurements were performed on powdered samples of the prepared polymers. Intrinsic viscosities of all polymers were measured by using an Ubbelohde D viscometer.

RESULTS AND DISCUSSION

Monomer synthesis

The aromatic unsymmetrical extended phthalazinone-containing diamine monomer **3** was prepared accord-

TABLE I
Synthesis and Characterization Data of Polymers (5a–e)

Polymer	$[\eta]^a$	Yield (%)	$^1\text{H-NMR } \delta$ (ppm, 90 MHz)	IR (cm^{-1})	T_g^b ($^\circ\text{C}$)	T_d^c ($^\circ\text{C}$)
5a	0.57	98.1	10.4 (d, 2H, CONH-H) 8.6–6.7 (m, 30H, Ar-H)	3356 (w, N—H), 1778 (w, C=O), 1723 (s, C=O), 1665 (m, amide I), 1228 (s, C—O—C)	340	512
5b	0.61	98.2	10.4 (d, 2H, CONH-H) 8.6–6.7 (m, 30H, Ar-H)	3360 (w, N—H), 1779 (w, C=O), 1722 (s, C=O), 1665 (m, amide I), 1228 (s, C—O—C)	337	509
5c	0.74	98.5	10.6–10.5 (d, 2H, CONH-H), 8.5–6.7 (m, 34H, Ar-H)	3369 (N—H), 1778 (w, C=O), 1723 (s, C=O), 1665 (m, amide I), 1239 (s, C—O—C)	319	493
5d	0.85	98.3	10.5–10.6 (d, 2H, CONH-H), 8.5–7.0 (m, 34H, Ar-H), 4.1–4.0 (d-brs, 2H, CH_2 -H)	3376 (N—H), 1778 (w, C=O), 1723 (s, C=O), 1666 (m, amide I), 1228 (s, C—O—C)	315	487
5e	1.06	98.5	10.6–10.5 (d, 2H, CONH-H), 8.6–7.0 (m, 42H, Ar-H)	3369 (N—H), 1778 (w, C=O), 1723 (s, C=O), 1665 (m, amide I), 1239 (s, C—O—C)	326	496

^a Measured at a concentration of 0.5 g/dL in NMP at 25 $^\circ\text{C}$.

^b From DSC measurements conducted at a rate of 10 $^\circ\text{C}/\text{min}$ in nitrogen.

^c Temperature for 5% weight loss in nitrogen, heating rate of 20 $^\circ\text{C}/\text{min}$.

ing to the reaction sequence of Scheme 1. The key starting compound for the synthesis of new monomer **3** is 1,2-dihydro-4-(3-phenyl-4-hydroxyphenyl) (2H)phthalazin-1-one (**1**). The most frequently traveled synthetic route leading to phthalazines involves the Friedel–Crafts acylation reaction in the first step and the conversion of the acids upon reaction with hydrazine monohydrate in the next. There are two kinds of active hydrogens: an active O—H and an active N—H, in unsymmetrical bisphenol-like compound 2-dihydro-4-(3-phenyl-4-hydroxyphenyl) (2H)phthalazin-1-one **1**.^{19–22} The acidity of the N—H group is higher than that of O—H group on the basis of their different chemical shifts in the $^1\text{H-NMR}$ spectra. The phenolate anion and the aza-nitrogen anion, formed *in situ* by reaction with potassium carbonate under nitrogen, underwent a nucleophilic displacement reaction with *p*-chloronitrobenzene to yield the dinitro compound **2**. Subsequent hydrogenation with hydrazine monohydrate/Pd-C in refluxing ethyl glycol monomethyl ether gave a new diamine monomer **3** in high yield. Mathias et al. reported that there was 4,4'-oxydianiline in the analogous system.¹ In our procedures, there is no 4,4'-oxydianiline found in the nucleophilic displacement reaction system according to the thin-layer chromatograph monitoring. The resulting diamine could be simply purified by recrystallization from ethyl glycol monomethyl ether. The monomer obtained as such is in high purity and can be stored in a general container over months without any deterioration. Unlike commonly used diamines,

monomer **3** is quite stable on exposure to light and air. The structure of new monomer **3** was confirmed by FTIR, $^1\text{H-NMR}$, EI-MS, and elemental analysis.

Polymer synthesis and characterization

Direct polycondensation of aromatic diamines with dicarboxylic acids with TPP and Py as condensation agents is well known to be a convenient method to prepare aromatic polyamides due to phosphorylation of the diacid and the phosphorylated acid is more reactive than the diacid. We used this method to prepare a series of new aromatic poly(amide imide)s containing the phthalazinone units with inherent viscosities from 0.57 up to 1.06 dL/g (Scheme 2). All polyamidations proceeded in homogeneous, transparent, and viscous solutions throughout the reaction, and the polymers were isolated as fibers or powders in quantitative yields. These observations suggest that phthalazinone groups in the unsymmetrical extended diamine monomer **3** did not inhibit polymerization, and large viscosity increases occurred in very short reaction times during polymerization. The polymers obtained were identified with IR and NMR spectra. The IR spectra showed characteristic amide absorptions at ~ 3356 – 3376 and 1665 cm^{-1} , corresponding to amino (N—H stretch) and carbonyl (C=O stretch) groups, respectively. The absorption peaks at 1778 (weak) and 1723 cm^{-1} (strong) corresponding to the imide carbonyl verified the imide functional groups present in polymer backbone. Solution $^1\text{H-NMR}$ spec-

TABLE II
The Solubility of Polymers in Various Solvents^a

Polymer	DMAc	NMP	DMF	DMSO	<i>m</i> -Cresol	Py	THF	CHCl ₃	Acetone
5a	++	++	++	++	+–	+–	+–	–	–
5b	++	++	++	++	+–	+–	+–	–	–
5c	++	++	++	++	+–	+–	+–	–	–
5d	++	++	++	++	+–	+–	+–	–	–
5e	++	++	++	++	+–	+–	+–	–	–

^a (++): soluble at room temperature; (+–): partially soluble at room temperature; –: insoluble.

tra in DMSO-*d*₆ confirmed the chemical structures of 5a–e with amide proton chemical shifts observed at ~10.5 ppm and downfield shifts of the unique protons of the imide-ring benzenes (~8.60 ppm). Disappearance of the different amine groups of monomer 1 at ~5.1 ppm indicates complete conversion of the amine groups into amides. Spectroscopic data, together with intrinsic viscosity and *T*_g and *T*_d measurements, confirming the structures of polymers, is given in Table I. The wide-angle X-ray scattering of the prepared aromatic polymers was investigated and only a very broad diffraction trace was observed and no sharp peak was found. This demonstrates that all obtained polymers are amorphous due to incorporation of unsymmetrical and kink non-coplanar phthalazinone heterocyclic structure.

Polymer properties

The thermal behavior and glass transition temperatures (*T*_g) of the polymers were evaluated with thermogravimetric (TGA) and DSC means, respectively. The phthalazinone-containing polymers showed very high *T*_g's up to 340°C. The *T*_g of the polymers was in the range of 315–340°C, all over 310°C. The temperatures for 5% weight loss in nitrogen were above 487°C, some above 500°C, indicating their excellent thermal stabilities, which may be due to the presence of very rigid aromatic heterocyclic backbone.

The solubility of the prepared aromatic polymers (5a–e) was determined at concentrations of 10% (w/v) in a number of solvents and the results are listed in Table II. Almost all prepared polymers were generally observed to be readily soluble in polar aprotic solvents such as NMP, DMF, DMAc, DMSO, and even in pyridine, *m*-cresol, and THF, but insoluble in chloroform and acetone. Transparent and flexible films were easily prepared by solution casting from DMAc solution of all polymers. Their high solubility with excellent thermal stability nature is attributed to the introduction of unsymmetrical and kink non-coplanar heterocyclic units along polymer backbone.

CONCLUSION

Wholly aromatic poly(amide imide)s containing the phthalazinone moiety was synthesized from direct po-

lymerization of a new unsymmetrical extended phthalazinone-containing diamine monomer with various aromatic bis(trimellitimide)s. The introduction of unsymmetrical and kink non-coplanar heterocyclic units into aromatic polymer backbone resulted in polymers with very high thermal stability (up to 340°C) as well as excellent solubility in common organic solvents. As to the aromatic polymers with both good solution processibility and excellent thermal stability, the present polymers are considered new candidates for processible high-performance polymeric materials.

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