

## SYNTHESIS OF NEW AROMATIC POLY(AMIDE IMIDE)S FROM UNSYMMETRICAL EXTENDED DIAMINE CONTAINING A PHTHALAZINONE MOIETY\*

Lin Cheng<sup>a\*\*</sup> and Xi-gao Jian<sup>b</sup>

<sup>a</sup> Department of Materials Science & Engineering, Huaqiao University, Quanzhou 362011, China

<sup>b</sup> Department of Polymer Science, Dalian University of Technology, Dalian 116012, China

**Abstract** The direct polymerization of an unsymmetrical kink non-coplanar heterocyclic diamine (**1**) with various aromatic bis(trimellitimide)s (**2a–e**) using triphenyl phosphite and pyridine as condensing agents could generate a series of new aromatic poly(amide imide)s (**3a–e**) containing the kink non-coplanar phthalazinone heterocyclic units in the polymer main chains with inherent viscosities of 0.58–0.66 dL/g. The polymers are readily soluble in a variety of solvents such as *N,N*-dimethylformamide, *N,N*-dimethylacetamide, dimethyl sulfoxide, *N*-methyl-2-pyrrolidinone, pyridine and *m*-cresol and can be cast to form flexible and tough films. The glass transition temperatures of polymers ( $T_g$ ) are in the range of 301–327°C, and the temperatures for 5% weight loss in nitrogen are in the range of 498–521°C.

**Keywords** Poly(arylene amide imide)s, Heterocyclic polymer, High-performance polymer, 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 rigidity of the backbone and strong hydrogen bonding in aromatic polyamides and charge transfer complex formation in aromatic polyimides result in their 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 linkages<sup>[1]</sup> and bulky lateral substituents<sup>[2]</sup>, kink noncoplanar biphenylene moieties<sup>[3, 4]</sup>, organometallic complexation<sup>[5]</sup> and hyperbranched or dendritic architectures<sup>[6]</sup> 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 using aromatic poly(amide imide)s (PAIs) for a variety of applications as they retain good mechanical properties at high temperatures and show easier processability as compared with aromatic polyamides and polyimides<sup>[7]</sup>. PAIs have been developed as engineering thermoplastic materials, *e.g.*, Torlon<sup>®</sup> (Amoco Chemical Co.), and used as electrical wire enamel, adhesives, and various injection-molding and extrusion products. They inherit some desirable characteristics from both polyamides and polyimides, and possess good thermal properties compared to polyamide, and better melt processability than polyimides. To further improve the solubility of PAIs in organic solvents, flexible linkages have been introduced into the polymer main chain. For example, soluble PAIs based on trimellitic anhydride (TMA) have been synthesized using diamines having isopropylidene<sup>[8]</sup>, biphenyl<sup>[9]</sup>, and naphthalene moieties<sup>[10]</sup>. Although being more soluble in organic solvents, the glass transition temperatures ( $T_g$ ) of the PAIs containing a flexible linkage often

\* This work was supported by the Key Natural Science Foundation of Fujian Province (E0320003).

\*\* Corresponding author: Lin Cheng (程琳), E-mail: cheng@hqu.edu.cn

Received June 2, 2003; Revised July 17, 2003; Accepted July 31, 2003

decreased.

In previous articles<sup>[11–16]</sup>, we have described the synthesis of poly(arylene ether amide)s bearing kink non-coplanar biphenyl phthalazinone groups. It was found that incorporation of kink non-coplanar biphenyl heterocyclic units into aromatic polymer backbone reduces the crystallinity and enhances the solubility as well as the thermo-oxidative stability of aromatic polymers. They have very high  $T_g$ s (up to 337°C) and excellent thermal stability together with good solubility. In order to develop easily processable high-performance polymers, we extend our investigation to the synthesis of a series of new poly(amide imide)s from direct polymerization of a new unsymmetrical kink non-coplanar heterocyclic diamine, 1,2-dihydro-2-(4-aminophenyl)-4-[4-(4-aminophenoxy)phenyl](2*H*)phthalazin-1-one (**1**) with various aromatic bis(trimellitimide)s (**2a–e**).

## EXPERIMENTAL

### Materials

Unless specified otherwise, reagent-grade chemicals and solvents were used as received. *N*-methyl-2-pyrrolidinone (NMP) and pyridine (Py) were purified by distillation under reduced pressure over calcium hydride and stored over molecular sieves (0.4 nm). 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. Diamine **1**<sup>[14]</sup> and aromatic bis(trimellitimide)s<sup>[17]</sup> **2a–e** were prepared according to the reported methods respectively.

### Polymerization

A typical procedure of direct polycondensation is described as follows.

Polymer **3a** from **1** and **2a**: A mixture of **1** (2.108 g, 5 mmol), **2a** (5 mmol), calcium chloride (0.9 g), NMP (15 mL), Py (2.8 mL), and triphenyl phosphite (2.8 mL), was heated with stirring at 100°C for 3 h under nitrogen. The obtained polymer solution was slowly poured into methanol (500 mL) with constant stirring to produce a 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%.

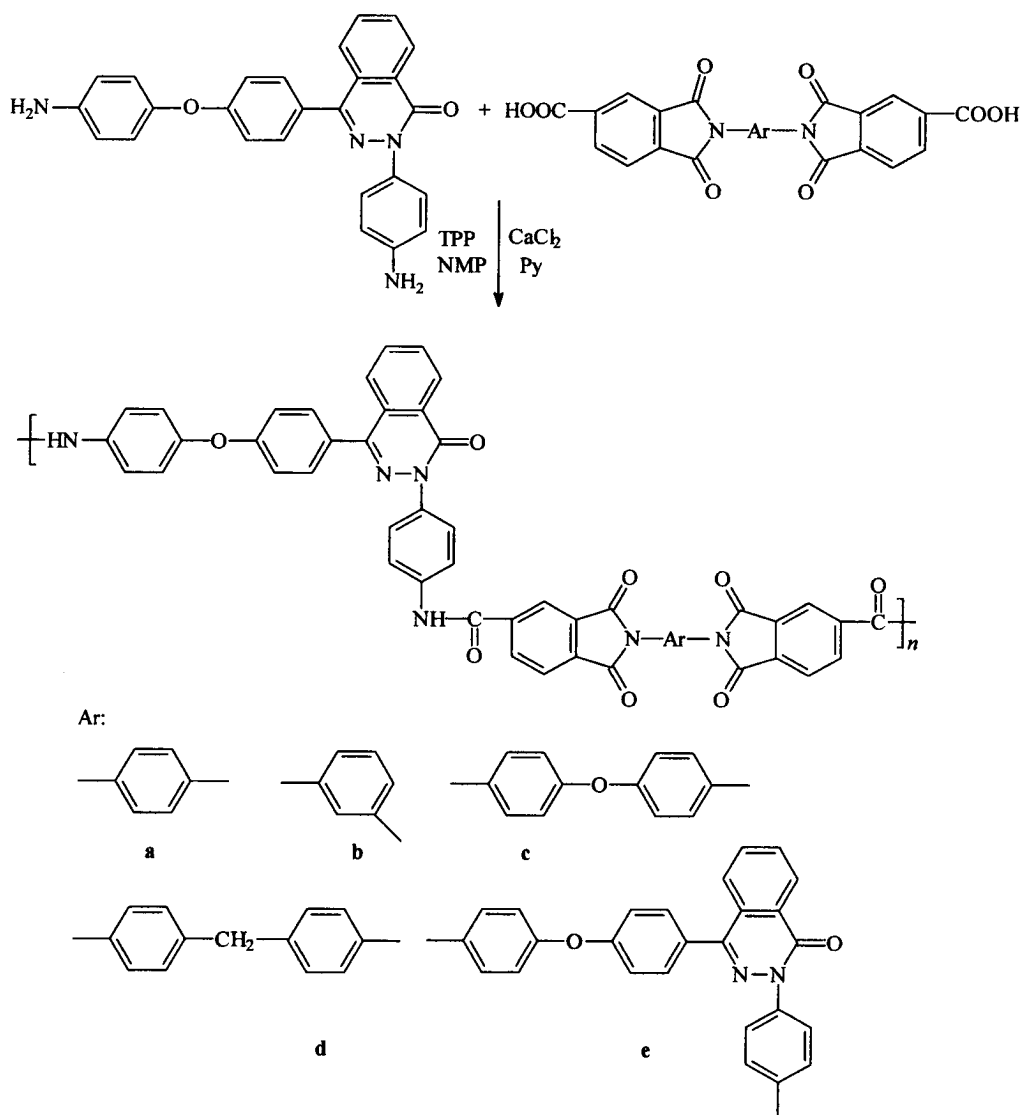
### Measurements

<sup>1</sup>H-NMR spectra were obtained on a Jeol FX 90Q spectrometer with dimethyl-*d*<sub>6</sub>-sulfoxide (DMSO-*d*<sub>6</sub>) as the solvent and chemical shifts were given relative to tetramethylsilane (TMS). IR measurements were performed on a Nicolet-20DXB spectrometer. Differential scanning calorimetry (DSC) was performed at a heating rate of 10 K/min under nitrogen on a TA 2200 thermal analyzer system. Thermal stability of the polymer samples was determined using a TA 2200 thermal analyzer from 25 to 800°C at a heating rate 20 K/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 using an Ubbelohde dilution viscometer.

## RESULTS AND DISCUSSION

### Monomer Diamine

Aromatic unsymmetrical extended phthalazinone-containing diamine monomer **1** was prepared according to the reported method<sup>[14]</sup>. The unique structural feature of the diamines lies in the unsymmetrical and kink non-coplanar conformation. It is of particular interest to investigate the effect of unsymmetrical and non-coplanar but still rigid diamine functionality on the properties of the aromatic polymers. The monomer diamine could be simply purified by recrystallization from ethylene glycol monomethyl ether and can be stored in an ordinary container over months without any deterioration. Unlike commonly used diamines, diamine monomer **1** is quite stable on exposure to light and air the reason for this behavior still remains unknown. Further investigation is under way.



**Scheme 1** Synthesis of poly(amide imide)s containing phthalazinone moiety

### Polymer Synthesis and Characterization

Direct polycondensation of aromatic diamines with dicarboxylic acids by using triphenyl phosphite and pyridine 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 ranging from 0.58 to 0.66 dL/g (Scheme 1). 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 1 do not inhibit polymerization, and large viscosity increases occur in very short reaction times during polymerization. The polymers obtained were identified with IR and NMR spectra. The IR spectra show the characteristic amide absorptions at 3356–3376 cm<sup>-1</sup> and 1665 cm<sup>-1</sup>, corresponding to amino (N–H stretch) and carbonyl (C=O stretch) groups, respectively. The absorption peaks at 1778 cm<sup>-1</sup> (weak) and 1723 cm<sup>-1</sup> (strong) corresponding to the imide carbonyl verify the presence of imide functional groups in the polymer backbone.

Solution <sup>1</sup>H-NMR spectra in DMSO-*d*<sub>6</sub> confirm the chemical structures of **3a–e** with amide proton chemical shifts observed at *ca.* 10.5 and downfield shifts of the unique protons of the imide-ring benzenes (*ca.* 8.60). Disappearance of chemical shifts corresponding to different amine groups of monomer **1** at *ca.* 5.1 indicates the complete conversion of amine groups into amides. Spectroscopic data, together with intrinsic viscosity and *T*<sub>g</sub> and *T*<sub>d</sub> measurements, are tabulated in Table 1. 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.

Table 1. Synthesis and characterization results of polymer (**3a–e**)

| Polymer | [η] <sup>a</sup> | Yield (%) | <sup>1</sup> H-NMR (δ)                                                                           | IR (cm <sup>-1</sup> )                                                                | <i>T</i> <sub>g</sub> <sup>b</sup> (°C) | <i>T</i> <sub>c</sub> <sup>d</sup> (°C) |
|---------|------------------|-----------|--------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|-----------------------------------------|-----------------------------------------|
| 3a      | 0.58             | 98        | 10.4 (d, 2H, CONH–H)<br>8.6–6.7 (m, 26 H, Ar–H)                                                  | 3356 (w, N–H), 1778 (w, C=O),<br>1723 (s, C=O), 1665 (m, amide I),<br>1228 (s, C–O–C) | 315                                     | 521                                     |
| 3b      | 0.60             | 98        | 10.4 (d, 2H, CONH–H)<br>8.6–6.7 (m, 26H, Ar–H)                                                   | 3360 (w, N–H), 1779 (w, C=O),<br>1722 (s, C=O), 1665 (m, amide I),<br>1228 (s, C–O–C) | 311                                     | 516                                     |
| 3c      | 0.65             | 99        | 10.6–10.5 (d, 2H, CONH–H),<br>8.5–6.7 (m, 30H, Ar–H)                                             | 3369 (N–H), 1778 (w, C=O),<br>1723 (s, C=O), 1665 (m, amide I),<br>1239 (s, C–O–C)    | 301                                     | 504                                     |
| 3d      | 0.66             | 98        | 10.5–10.6 (d, 2H, CONH–H),<br>8.5–7.0 (m, 30H, Ar–H),<br>4.1–4.0 (d-brs, 2H, CH <sub>2</sub> –H) | 3376 (N–H), 1778 (w, C=O),<br>1723 (s, C=O), 1666 (m, amide I),<br>1228 (s, C–O–C)    | 306                                     | 498                                     |
| 3e      | 0.61             | 99        | 10.6–10.5 (d, 2H, CONH–H),<br>8.6–7.0 (m, 38H, Ar–H)                                             | 3369 (N–H), 1778 (w, C=O),<br>1723 (s, C=O), 1665 (m, amide I),<br>1239 (s, C–O–C)    | 327                                     | 512                                     |

<sup>a</sup> Measured at a concentration of 0.5 g/dL in NMP at 25°C; <sup>b</sup> From DSC measurements conducted at a rate of 10 K/min in nitrogen; <sup>c</sup> Temperature for 5% weight loss in nitrogen, heating rate of 20 K/min

Properties of Polymer

The thermal behavior and glass transition temperatures (*T*<sub>g</sub>) of the polymers were evaluated by thermogravimetric (TGA) and differential scanning calorimetric (DSC) means, respectively. The phthalazinone-containing polymers show very high *T*<sub>g</sub>s ranging from 301–327°C. The temperatures for 5% weight loss in nitrogen are above 498°C, almost all above 500°C, indicating their excellent thermal stabilities, due to the presence of a very rigid aromatic heterocyclic backbone.

The solubility of prepared aromatic polymers (**3a–e**) was determined at concentrations of 10% (*W/V*) in a number of solvents and the results are listed in Table 2. Almost all polymers are readily soluble in polar aprotic solvents such as NMP, *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), DMSO, and even in pyridine, *m*-cresol and THF, but insoluble in chloroform and acetone. Transparent and flexible films can be easily prepared by solution casting from DMAc solution of all polymers. Their high solubility and excellent thermal stability are attributed to the introduction of unsymmetrical and kink non-coplanar heterocyclic units along polymer backbone.

Table 2. Solubility of polyamides in various solvents<sup>a</sup>

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

<sup>a</sup> (+ +): Soluble at room temperature; (+ -): Partially soluble at room temperature; (-): Insoluble

## CONCLUSIONS

Wholly aromatic poly(amide imide)s containing a phthalazinone moiety were synthesized from direct polymerization 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 an aromatic polymer backbone results in polymers with very high thermal stability (up to 327°C) as well as excellent solubility in common organic solvents. The present polymers are considered to be new candidates for processable high-performance polymeric materials.

## REFERENCES

- 1 Yagci, H. and Mathias, L., *J. Polym.*, 1998, 39: 3779
- 2 Spiliopoulos, I.K. and Mkroyannidis, J.K., *Macromolecules*, 1998, 31: 1236
- 3 Johnson, R.A. and Mathias, L.J., *Macromolecules*, 1995, 38: 79
- 4 Walsh, C.J. and Mandal, B.K., *Chem. Mater.*, 2001, 13: 2472
- 5 Dembek, A.A., Burch, R.R. and Feiring, A.E., *J. Am. Chem. Soc.*, 1993, 115: 2087
- 6 Kim, Y.H. and Webster, O.W., *J. Am. Chem. Soc.*, 1990, 112: 4592
- 7 Beltramo, M., *Eng. Plastics*, 1993, 6: 40
- 8 Yang, C.P., Hsiao, S.H. and Hsiao, H.C., *J. Polym. Sci. Polym. Chem.*, 1999, 37: 69
- 9 Yang, C.P., Hsiao, S.H. and Liou, G.H., *J. Polym. Sci. Polym. Chem.*, 1998, 36: 1169
- 10 Yang, C.P. and Chen, W.T., *J. Polym. Sci. Polym. Chem.*, 1994, 32: 435
- 11 Jian, X. and Cheng, L., *J. Polym. Sci. Polym. Chem.*, 1999, 37: 1565
- 12 Jian, X., Cheng, L., Zheng, H.B. and Wang, Z.Y., *Chin. Chem. Lett.*, 1999, 10: 371
- 13 Cheng, L. and Jian, X., *Chin. Chem. Lett.*, 2000, 11: 307
- 14 Cheng, L. and Jian, X., *J. Polym. Sci. Polym. Chem.*, 2002, 40: 3489
- 15 Zhu, X., Jian, X. and Wang, R., *Acta Polymer Sinica (in Chinese)*, 2002, (4): 544
- 16 Lu, Z. and Cheng, L. *J. Polym. Sci. Polym. Chem.*, 2004, 42: 925
- 17 Lin, J.H. and Yang, C.P., *J. Polym. Sci. Polym. Chem.*, 1996, 34: 747