

# Synthesis and Characterization of Novel Aromatic Polyamides via Yamazaki–Higashi Phosphorylation Method

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Received 29 August 2011; accepted 19 January 2012

DOI 10.1002/app.36979

Published online in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** We synthesized four aromatic diacids: 1,3-bis(3-carboxyphenoxy)benzene, 1,4-bis(4-carboxyphenoxy)benzene, 1,4-bis(3-carboxyphenoxy)benzene, and 1,3-bis(4-carboxyphenoxy)benzene, following a procedure of a previously reported synthesis (Ueda and Komatsu, *J Polym Sci Part A: Polym Chem* 1989, 27, 1017). These diacids were condensed directly with aromatic diamines 4,4'-oxydianiline (ODA), via the Yamazaki–Higashi phosphorylation method in the presence of triphenylphosphite (TPP), pyridine (Py) and halide salts to give high molecular aromatic polyamides (PAs). The synthesized PAs were obtained in quantitative yields with inherent viscosities between 0.5 and 1.0 dL g<sup>-1</sup>. The structures and properties of the obtained PAs were characterized by Fourier transform infrared (FTIR) spectra, nuclear magnetic resonance (NMR), thermogravimetric analysis (TGA), polarizing

optical microscope (POM). Four PAs all showed good solubility in polar solvents, such as dimethylsulfoxide (DMSO), *N,N*-dimethylacetamide (DMAc), *N*-dimethylformamide (DMF), 1-methylpyrrolidone (NMP), and so on. The obtained polymers showed high thermal stability with decomposition temperature around 400°C. The polyamide membranes manifest excellent mechanical properties, with Young's modulus of 2.5–5.5 GPa. Interestingly, the film of PA-1, PA-2, and PA-3 is completely transparent in the visible range, while PA-4 film is opaque. Crystallization was observed in PA-4 film, although the molecular structure of PA-4 is not as symmetrical as PA-2. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

**Key words:** phosphorylation reaction; aromatic polyamide

## INTRODUCTION

Aromatic polyamides, such as poly(*p*-phenylene terephthalamide) developed by Du Pont (Wilmington, DE) in the early 1960s,<sup>1</sup> are well-known as high-performance polymers due to their excellent thermal, mechanical, and chemical properties.<sup>2–12</sup> Aromatic polyamides are finding increasing demand for use as advantageous replacements for metals or ceramics in currently used goods, or even as new materials in novel technological applications.<sup>5,13–24</sup>

There are two conventional methods for the synthesis of aromatic polyamides. One is a low-temperature solution polymerization, where diacid chlorides are reacted with aromatic diamines to form polyamides.<sup>25–27</sup> Kevlar (PPPT) and Nomex (PMPI) are prepared commercially by condensation of *p*-phenylenediamine (PPD) and terephthaloyl dichloride

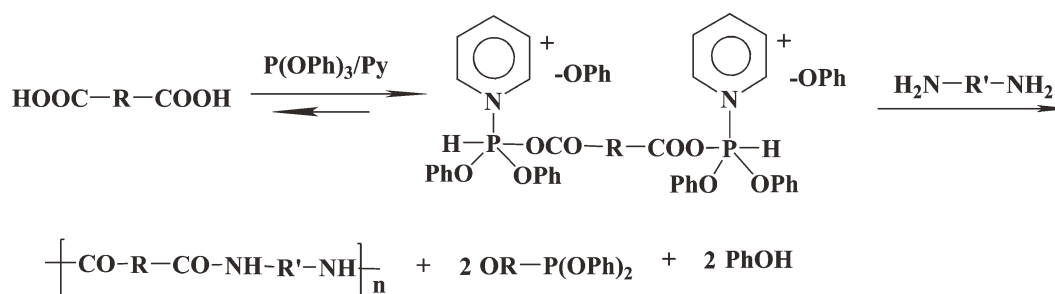
(TPC), or *m*-phenylenediamine (MPD) and isophthaloyl dichloride (IPC) by low temperature polymerization method. The solution method is generally preferred when the diacid chloride can be easily obtained from the corresponding aromatic diacid. Thermal polymerization is a well-known industrial process for aliphatic polyamides with a high molecular weight, but it is very difficult to obtain aromatic polyamides with a high molecular weight by the molten polycondensation method. This has been mainly explained by the lower reactivity of aromatic amines compared with that of aliphatic amines because of the resonance effect of phenyl groups. The high reaction temperature usually results in extensive side reactions that restrict polymer molecular weight.

The other method to synthesize aromatic polyamides is direct polycondensation, also known as Yamazaki–Higashi phosphorylation method, of aromatic diacids and diamines in the presence of condensing agents, such as triphenyl phosphite (TPP) and pyridine (Py). And salts, such as lithium chloride (LiCl), calcium chloride (CaCl<sub>2</sub>), or a mixture of both, are often used as solubility promoters because the cations interact with the amide groups, diminishing the strength of the interchain hydrogen

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Contract grant sponsor: National Nature Science Foundation of China; contract grant number: 50973062.

Contract grant sponsor: Shanghai Leading Academic Discipline Project; contract grant number: B202.



Scheme 1 The mechanism of phosphorylation method.

bonds.<sup>28–32</sup> The mechanism of Yamazaki–Higashi phosphorylation method is shown in Scheme 1. The direct polycondensation route is a very useful laboratory method and avoids using moisture-sensitive acid chlorides.<sup>33,34</sup>

However, despite their outstanding properties, most of them have some drawbacks associated with infusibility and insolubility, which were caused by the highly regular and rigid polymer backbones and the formation of intermolecular hydrogen bonding, resulting in their poor processability and limiting their applications.<sup>35–37</sup> As a consequence, to broaden the scope of the technological applications of these materials, recent basic and applied research has focused on enhancing their processability and solubility without a dramatic loss in the chemical, thermal, and mechanical properties. Therefore, diminishing the cohesive energy through lowering the interchain interactions is a way of improving the solubility. To achieve such a goal, much effort has been achieved in designing and synthesizing new diamines and/or dicarboxylic acids, which can fulfill this requirement, thus producing a great variety of soluble and processable polyamides for various purposes.<sup>38</sup> In addition to using meta substitution in the main chain phenylene residues, this can be achieved by reducing the hydrogen bond effectiveness through the introduction of bulky side groups to the main chain, by employing nonsymmetric monomers, or by introducing flexible linkages to the polymer backbone. Much work has been done in these areas, and most published papers claim polyamides with increasing solubility.<sup>39–47</sup> A critical evaluation of this property indicates that most of the polyamides are somewhat soluble in polar aprotic solvents such as NMP, DMA, DMF, and DMSO.

In this study, we designed and synthesized four kinds of new dicarboxylic acid containing flexible linkages, which successfully improved the solubility of aromatic polyamide. These diacids were condensed directly with aromatic diamines, 4,4'-oxydianiline (ODA), via the Yamazaki–Higashi phosphorylation method in the presence of triphenyl phosphate (TPP) and pyridine (Py). The structures and properties, such as solubility, thermal stability, mechanical prop-

erty, and crystallinity of obtained polyamides were investigated in detail.

## EXPERIMENT

### Materials

The 4,4'-oxydianiline (ODA), 4-fluorobenzonitrile, 3-fluorobenzonitrile, 1,4-dihydroxybenzene, 1,3-dihydroxybenzene were used as received from Acros. Methanesulfonic acid was purchased from Sino-pharm Chemical Reagent (SCRC) and used without further purification. Triphenyl phosphate (TPP), pyridine (Py), dimethylsulfoxide (DMSO), 1-methylpyrrolidone (NMP), *N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc) and ethylene glycol (EG) were purchased from Shanghai Chemical Reagents and dehydrated with 4 Å molecular sieves prior to use. Other materials were used as received. Commercially obtained anhydrous calcium chloride (CaCl<sub>2</sub>) and lithium chloride (LiCl) were dried under vacuum at 120°C for 6 h.

### Synthesis of aromatic diacids BCPOBCOOH-1,2,3,4

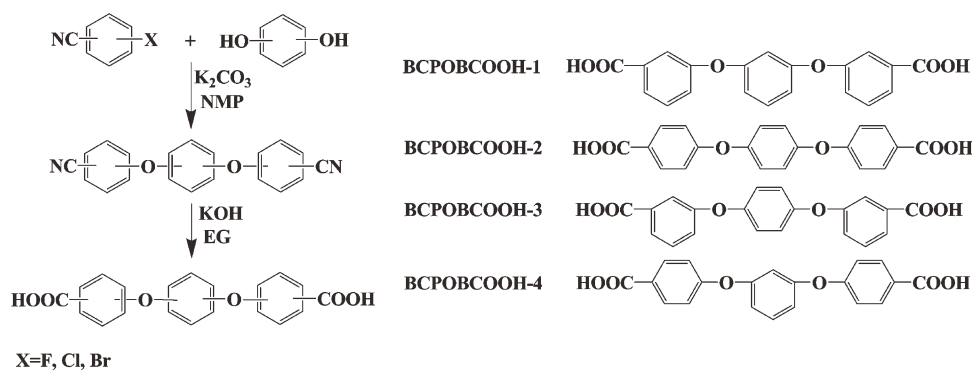
Here, four kinds of diacid BCPOBCOOH-1,2,3,4 are referred to as 1,3-bis(3-carboxyphenoxy)benzene, 1,4-bis(4-carboxyphenoxy)benzene, 1,4-bis(3-carboxyphenoxy)benzene, 1,3-bis(4-carboxyphenoxy)benzene, respectively. For the preparation of these diacids, we followed a procedure of previously reported synthesis.<sup>19–21,48</sup> The molecular structures of these aromatic diacids are shown below, and the synthetic route is shown in Scheme 2.

### Polymer synthesis

#### Preparation of PAs 1-4

The synthesis of PAs 1-4 are similar to each other, here a typical example of polymerization was illustrated.

*Synthesis of PA-1.* To a completely dried 100-mL, three-necked flask equipped with a mechanical stirring device were charged 1.7516 g (5 mmol) diacid BCPOBCOOH-1, 1.0012 g (5 mmol) 4,4'-oxydianiline



**Scheme 2** Synthesis and structures of four diacids.

(ODA), 1.2501 g calcium chloride ( $\text{CaCl}_2$ ), 2.8 mL (10 mmol) triphenylphosphite (TPP), 2.5 mL pyridine (Py), and 10.6 mL NMP under nitrogen flow. The mixture was mechanically stirred and heated to  $80^\circ\text{C}$ . After the mixture was completely dissolved, the mixture was heated with stirring at  $100^\circ\text{C}$  for 3 h and  $110^\circ\text{C}$  for 3 h under nitrogen, respectively. The resulting viscous polymer solution was poured slowly into 300 mL of stirring methanol giving rise to a stringy, fiberlike precipitate that was collected by filtration, washed thoroughly with methanol and hot water, and dried at  $120^\circ\text{C}$  for 24 h *in vacuo*.

#### Preparation of polymer membrane

A solution of polymer was made by dissolving about 0.50 g of the polyamide sample in 10 mL of NMP. For PA-2, the polymer can not dissolve completely in pure solvent, so pinch lithium chloride was added to prepare the homogeneous solution. The homogeneous solution was filtrated and poured onto a 11-cm glass Petri dish, which was placed in a  $80^\circ\text{C}$  oven overnight to remove most of the solvent. The cast membrane was then released from the glass substrate and further dried *in vacuo* at  $120^\circ\text{C}$  for 8 h. The obtained membranes were about 20–30  $\mu\text{m}$  in thickness and were used for tensile tests, solubility tests, thermal analyses, and optical property characterization.

#### Characterization

Fourier transform infrared (FTIR) spectra were recorded on a Perkin-Elmer Paragon 1000PC spectrometer.  $^1\text{H-NMR}$  spectra were measured on a Varian Mercury Plus 400 MHz instrument. The inherent viscosities were determined at  $0.5 \text{ g dL}^{-1}$  concentration using a Ubbelohde viscometer at  $30^\circ\text{C}$ . Thermogravimetric analysis (TGA) was performed in nitrogen with TGA 2050 instrument at a heating rate of  $20^\circ\text{C min}^{-1}$ . Tensile measurement was performed with an Instron-5567 instrument at  $22^\circ\text{C}$  and 50% relative humidity at a crosshead speed of 5 mm

$\text{min}^{-1}$  with a gauge length of 5 cm. The film specimens are 0.4-cm wide, 8-cm long, and an average of at least three replicates was used. The photo property of various polyamide membranes were analyzed by UV-2550 Spectrophotometer (SHIMADZU) and LEICA-DMLP polarizing optical microscope (POM).

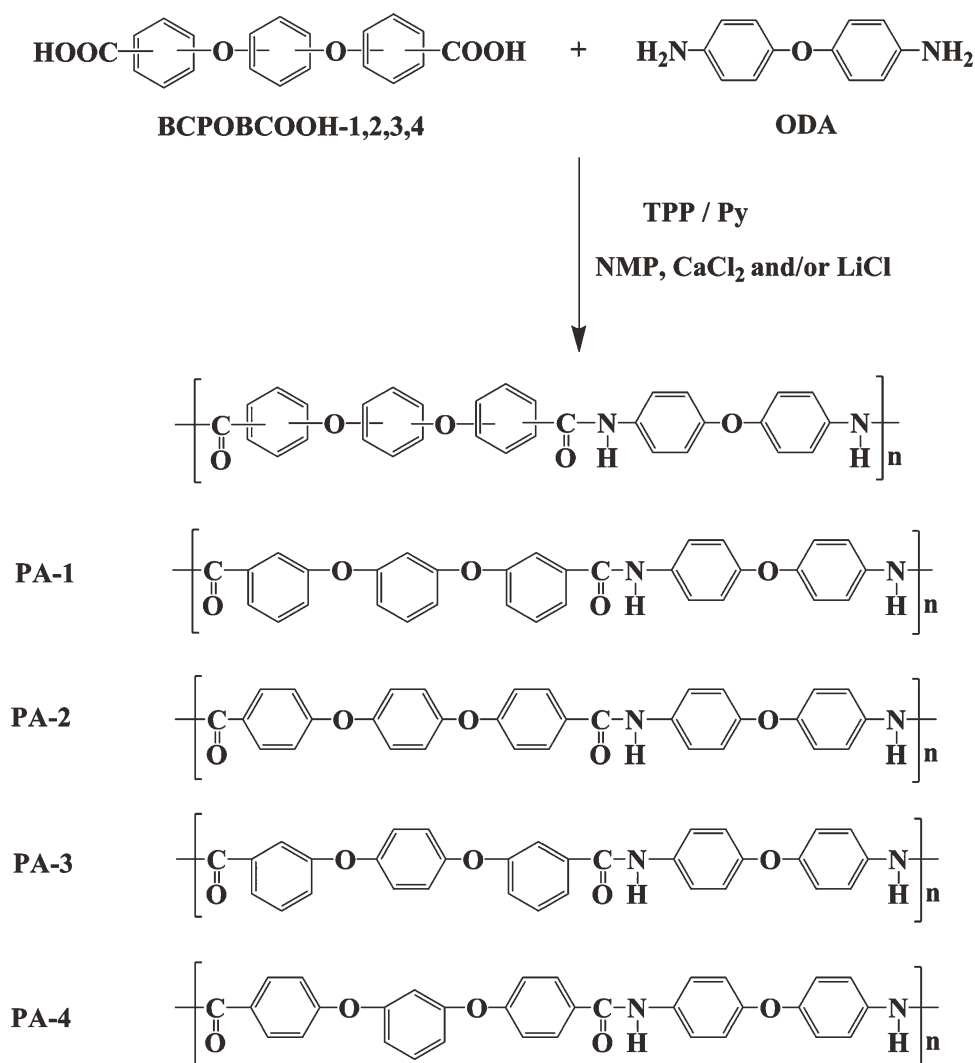
## RESULTS AND DISCUSSION

### Synthesis of polyamides 1-4

A series of new aromatic polyamides were prepared by the direct polycondensation reactions of the aromatic diamine 4,4'-oxydianiline (ODA) with various synthesized aromatic dicarboxylic acid monomers BCPOBCOOH-1, BCPOBCOOH-2, BCPOBCOOH-3, BCPOBCOOH-4 using triphenylphosphite (TPP) and pyridine (Py) as condensing agents. As the structures of the diacid monomers differs from each other, and the reaction conditions varies. Scheme 3 shows the synthetic partway of various polyamides.

Except polymerization of polyamide-2, other three polymerizations proceeded homogeneously throughout the reaction and afforded clear, highly viscous polymer solutions. For polyamide-2, the resulted high molecular polyamide-2 has a limited solubility in the reaction system, so the reaction system presented a turbid appearance. Nevertheless, all the polymers precipitated in a tough, fiberlike form when the resulting polymer solutions were slowly poured with stirring into methanol. These polyamides were obtained in almost quantitative yields, with inherent viscosity values in the range of  $0.53\text{--}0.91 \text{ dL g}^{-1}$  (Table I).

The obtained polyamides were characterized by FTIR and  $^1\text{H-NMR}$  analyses. Structural features of these polyamides were verified by FTIR spectra based on characteristic absorption bands, as shown in Figure 1. These spectra are quite similar to each other because of their structural similarity of the polymers. The analyses to the exhibited characteristic absorptions are as followings: The broad absorption bands



Scheme 3 Synthesis of polyamides 1–4.

in the range of 3500–3000  $\text{cm}^{-1}$  are assigned to the N–H stretching of amide band and the C–H stretching of benzene rings. The absorption band around 1667  $\text{cm}^{-1}$  is assigned to C=O stretching of amide I band. The absorption band around 1525  $\text{cm}^{-1}$  is assigned to C–N stretching and N–H bending vibration of amide II band. The absorption band around

1254  $\text{cm}^{-1}$  is assigned to C–C=O stretching and N–H bending vibration of amide III band. The absorption band around 706  $\text{cm}^{-1}$  is assigned to N–H out-of-plane formation vibration of amide IV band. The absorption band at 1230  $\text{cm}^{-1}$  is assigned to aryl–ether–aryl (C–O–C) symmetrical stretching in the polymer backbone.

**TABLE I**  
**Solubility and Reduced Viscosity of PAs**

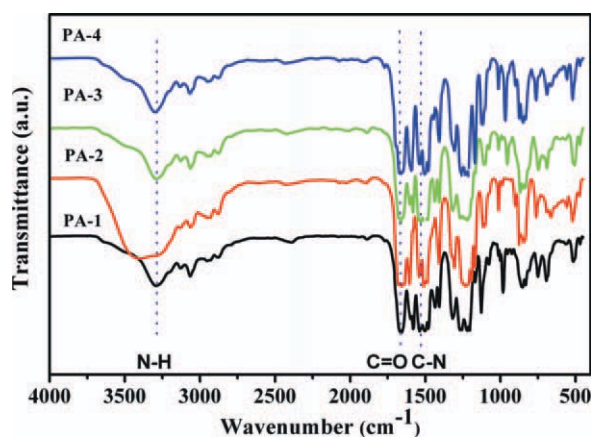
Pas	$\eta^a(\text{dL g}^{-1})$	Solubility <sup>b</sup>					
		DMSO	DMF	DMAc	NMP	H <sub>2</sub> SO <sub>4</sub>	MeSO <sub>3</sub> H
PA-1	0.64	++	++	++	++	++	++
PA-2	0.53	+-	+-	+-	+-	++	++
PA-3	0.57	++	++	++	++	++	++
PA-4	0.91	++	+-	++	++	++	++

++: soluble in 30 min; +-: partially soluble in pure solvent even at a long time, soluble in the presence of pinch LiCl.

<sup>a</sup> Measured in NMP at 0.5 g dL<sup>-1</sup> and 30°C.

<sup>b</sup> Qualitative solubility was determined using about 0.2 g of polymer in 2 mL of solvent.





**Figure 1** FTIR spectra of PAs. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

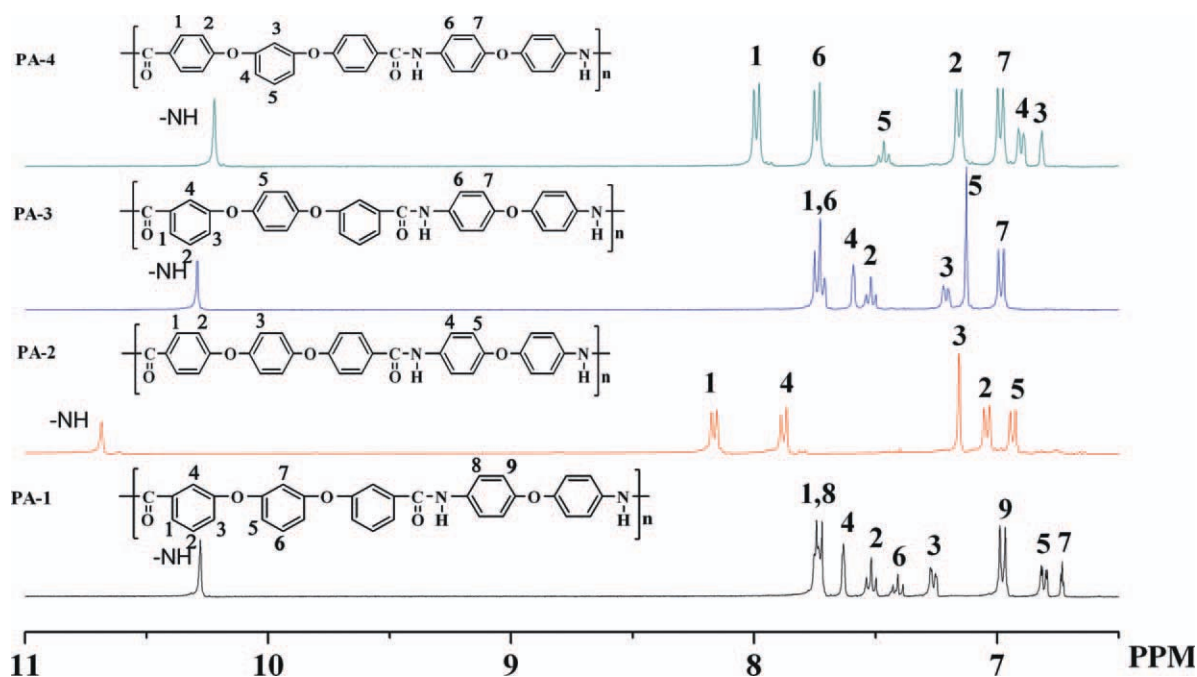
Figure 2 shows the  $^1\text{H-NMR}$  spectra of the obtained PAs.  $^1\text{H-NMR}$  spectra confirmed the chemical structures of the prepared polyamides. The peak assignments are in good agreement with the proposed chemical structures, for all polymers, amide proton chemical shifts were observed in the down-field regions of 10.2–10.7 ppm, as shown in Figure 2. The assignments of other peaks for each polymer have also been given in this figure.

### Solubility and thermal stability

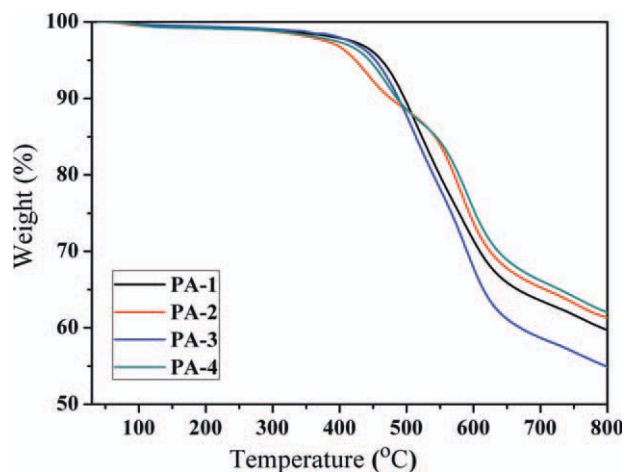
The solubility behavior of polyamides was tested qualitatively, and the results are summarized in

Table I. Except polyamide-2, other three polyamides were highly soluble in polar solvents such as NMP, DMSO, DMAc, and so on. The high solubility of polyamide-1, 3, 4 can be attributed in part to the introduction of flexible linkages, ether linkages, in the repeat unit, and the meta orientation of the phenylene moieties of the main chain is the other aspect. For polyamide-2, although flexible linkages, ether linkages, are also introduced in the repeat unit of the polymer, the rigid rod all-para orientations of the polymer make it difficult to dissolve in pure polar solvents. And the solubility can be improved when pinch lithium chloride is added in the solvent. Lithium chloride, known as solubility promoters, can interact with the amide groups, diminishing the strength of the intramolecular and intermolecular hydrogen bondings and making the solvent easy to diffuse into the polymers. Thus, all these polymers can be readily processed from solution. Flexible and tough films can be obtained via solvent casting.

Thermal properties of the resulting polyamides were determined by means of thermogravimetric analysis (TGA). TGA was measured in a nitrogen atmosphere at a heating rate of  $20^\circ\text{C min}^{-1}$ . As displayed in Figure 3, there are not great differences for the thermal stability of the resulting polyamides. The decomposition temperature of obtained polymers was higher than  $400^\circ\text{C}$ . The amount of carbonized residue of these polymers in nitrogen atmosphere was more than 55% at  $800^\circ\text{C}$ , which might be ascribed to their high aromatic content. The characterization result of thermal properties indicated that polyamides



**Figure 2**  $^1\text{H-NMR}$  spectra of PAs ( $\text{DMSO-}d_6$ ). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 3** TGA curves of the PAs in  $N_2$  from room temperature to  $800^\circ\text{C}$  (Heating rate was  $20^\circ\text{C min}^{-1}$ ). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

with good thermo stability were obtained in this study.

### Mechanical properties

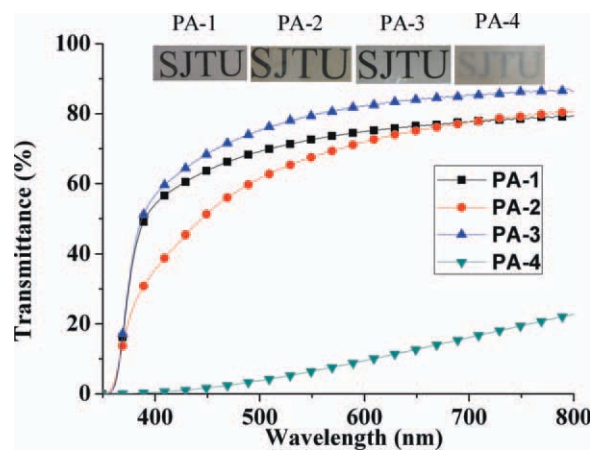
It is well known that aromatic polyamides generally have poor film forming ability because of the poor solubility of the polymers in common solvents which is caused by rigid polymer backbone.<sup>49</sup> However, in this study, flexible and tough films can be obtained via solvent casting. For this purpose, pinch lithium chloride was necessary for the preparation of polyamide-2 film.

The mechanical properties of these polyamides have been investigated, and the results were summarized in Table II. The cast films exhibited tensile strengths, Young's modulus and elongations at break, in the ranges of 87–147 MPa, 2.6–5.5 GPa, and 4.4–8.7%, respectively. The results indicated that polyamide-1 showed the best mechanical properties, with the max stress up to 147 MPa and a modulus of 5.5 GPa. Polyamide-2 was an exception, with a lower max stress and larger elongation at break. This was attributed to the addition of lithium chloride. Lithium chloride acted as the solubility pro-

**TABLE II**  
The Max Stress, Elongation at Break, and Young's Modulus of Various Polymer Membranes

Polymers	Max stress <sup>a</sup> (MPa)	Elongation at break <sup>a</sup> (%)	Young's modulus (GPa)
PA-1	147	4.4	5.5
PA-2	87	8.1	2.6
PA-3	129	8.0	3.4
PA-4	132	8.7	4.3

<sup>a</sup> Measured at  $22^\circ\text{C}$  and 50% relative humidity.



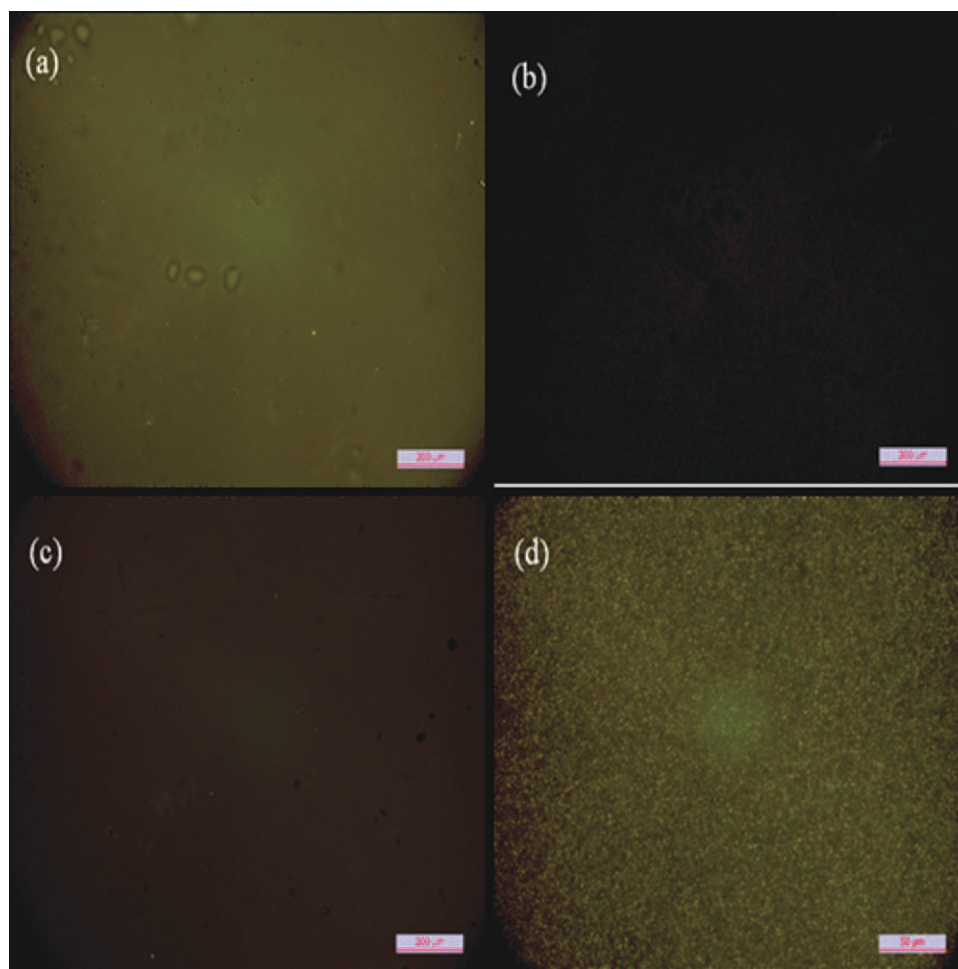
**Figure 4** UV-vis spectrum in transmittance mode of various polyamide membranes. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

moter in the preparation of the polymer solution, and it was as well as the plasticizer to the prepared film. Then it made the max stress decrease and the elongation at break increase.

### Optical property

Of these four kinds of polyamides, PA-2 has the most regular molecular structure, in which all phenylene moieties in the main chain have paraorientations. Compared with PA-2, other three kinds of polyamide have less regular molecular structures. As known to all, molecules with relative regular molecular structure is apt to crystallize, and form ordered crystal. So from theoretical analysis, PA-2 should be crystalline polymer. Figure 4 presents photographs of membranes of various polyamides. Membranes of PA-1, PA-2, PA-3 are transparent, while PA-4 is opaque, which is also supported by the transmittance of each membrane measured by UV-vis spectra (Fig. 4). The optical property of four kinds of polyamide membranes did not accord with the theoretical analysis above.

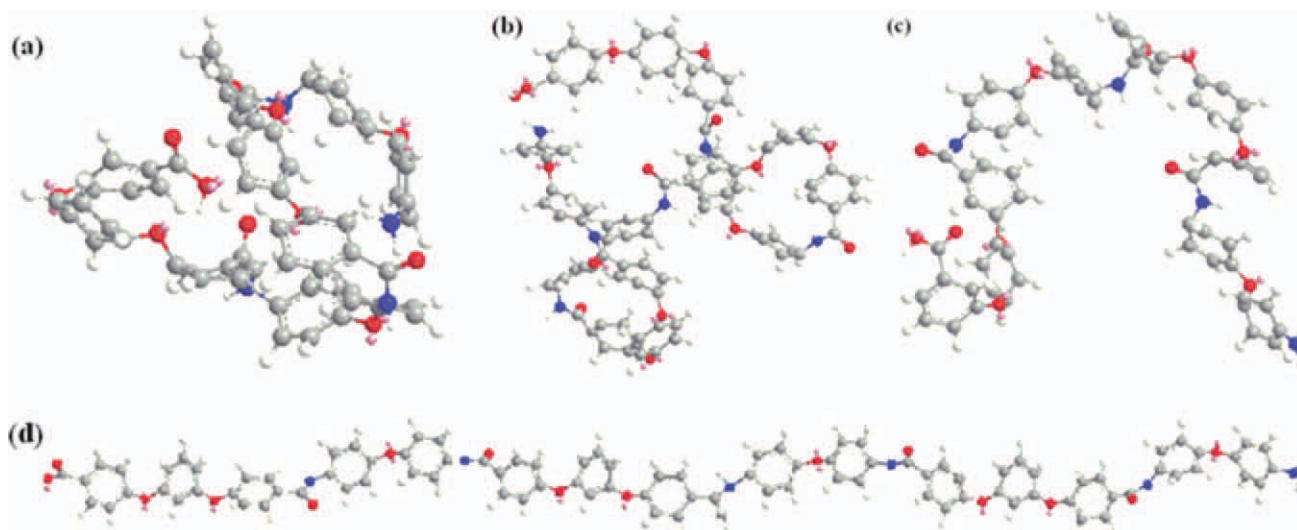
Optical property of polymer film is related to crystallization. To study the optical property of these four kinds of polyamide in depth, the crystallinity of these polyamides was investigated by the microscope with parallel and crossed polarizers. Figure 5 shows crystal morphology of PAs by polarizing optical microscope (POM). In the heating process, PA-4 began to melt at  $380^\circ\text{C}$ , while other three polyamides melt at lower temperature below  $300^\circ\text{C}$ . For (a) PA-1, (b) PA-2, (d) PA-3, they just showed a bright-field at some extent, of which PA-2 is the least bright, while obvious crystallinity could easily be seen in (d) PA-4. The POM result indicated that PA-1, PA-2, PA-3 were hard to crystalline, while PA-



**Figure 5** Crystal morphology of PAs by polarizing optical microscope (a. PA-1; b. PA-2; c. PA-3; d. PA-4). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

4 was highly crystalline. So we can see that the result of POM seems contrary to the theoretical analysis above.

To investigate the optical property in depth, we investigated the conformational characteristics of various polyamide molecules. For this purpose, we



**Figure 6** Molecular models of PAs optimized by Chem 3D Ultra 11.0. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



utilized Chem 3D to simulate the conformational behaviors and packing structures of four kinds of polyamide chains. Figure 6 shows the simulation result: three-dimensional conformation of the minimum energy of various polyamides. Different conformations can be observed in the figure. Of the four kinds of polyamides, PA-4 presents a relative outstretched conformation, and PA-3 shows the second outstretched conformation, while PA-2 shows the most entangled conformation. Polymers with different conformational structures will pack into aggregation structure with different ordered degree. For example, polymers with more outstretched main chain structure can easily form ordered packing structure and form more perfect crystals; while polymers with entangled main chain structure can hardly form order packing structure, so they are generally amorphous. On the other hand, flexibility or rigidity difference of polymer main chain will also affect the ability of crystallinity. Flexible polymers can easily adjust the chain conformation and pack into ordered structure, while rigid polymer can hardly change its conformation and cannot form ordered packing structure. From this point, PA-2, with all para orientation of the phenylene moieties in its main chain, can hardly be crystalline. And polymers with meta orientation of phenylene moieties in the main chain may be highly crystalline. The simulation results are in good agreement with the result of POM and the appearance of various membranes.

## CONCLUSIONS

Novel aromatic polyamides with high molecular weight could easily and successfully prepared via Yamazaki-Higashi phosphorylation method of 4,4'-oxydianiline (ODA) and various aromatic diacids designed in this work, i.e., 1,3-bis (3-carboxyphenoxy) benzene, 1,4-bis (4-carboxyphenoxy) benzene, 1,4-bis (3-carboxyphenoxy) benzene, 1,3-bis (4-carboxyphenoxy) benzene, by means of triphenylphosphite (TPP) in NMP-pyridine solution in the presence of metal salts such as calcium chloride, lithium chloride, or a mixture of both. The introduction of flexible linkages, ether linkages, into the aromatic polyamide backbone resulted in novel soluble polyamides, which showed good solubility in polar solvents, such as DMSO, DMAc, DMF, NMP, etc, and obtained polymers showed high thermal stability and they can withstand high temperature, e.g., 400°C. In addition, the polyamide membranes manifest excellent mechanical properties, with Young's modulus of 2.5–5.5 GPa. Therefore, the designation of the polymers succeeded in improving the solubility of aromatic polyamides without the loss of thermal stability and mechanical property of the polymers. Thus, these polyamides are considered to be

new promising processable high performance polymer materials. Finally, optical property of obtained polyamide membranes was investigated and analyzed. PA-2 has the most regular molecular structure, but it can hardly crystallize, and the corresponding membrane is transparent. On the contrary, PA-4, whose molecular structure is less regular, is a kind of typical crystalline polymer and its membrane is opaque. Molecular structure designation is becoming more and more important in developing materials with improved or new properties. However, molecular structure designation should not only concentrate on the molecular structure, some other aspects should also be taken into consideration, for example, the corresponding conformation of the designed structure, so that materials with expected properties can be obtained.

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