

# Inexpensive synthesis of 1,4-bis(4-aminophenoxy)-2-(6-oxido-6H-dibenz <c,e> <1,2> oxaphosphorin-6-yl) phenylene and its oxygen-plasma resistant polyamides

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## ABSTRACT

Inexpensive synthesis of diamine, 1,4-bis(4-nitrophenoxy)-2-(6-oxido-6H-dibenz <c,e> <1,2> oxaphosphorin-6-yl) phenylene was revealed in this work. Based on the diamine, a series of organosoluble polyamides were prepared by direct polycondensation of the diamine with various aromatic diacids using triphenyl phosphite and pyridine as condensing agents. The number-average molecular weights of the resulting polyamides range from  $4.2 \times 10^4$  to  $10.5 \times 10^4$  g/mol, and the weight-average molecular weights are in the range of  $7.5$ – $28.2 \times 10^4$  g/mol. The  $T_g$ s of these polyamides range from 210 to 255 °C by dynamic mechanical analysis. The resulting polyamides are tough and flexible with tensile strength, elongation at break and moduli range from 84 to 101 MPa, 4.8–7.0%, and 2.36–3.22 GPa, respectively. The degradation temperatures ( $T_d$  5%) and char yields at 800 °C in nitrogen range from 460 to 486 °C and 59–68 wt%, respectively. The cutoff wavelength of these polyamides falls in the range of 345–366 nm, showing a very light color characteristic. In addition, these polyamides display good oxygen plasma resistance.

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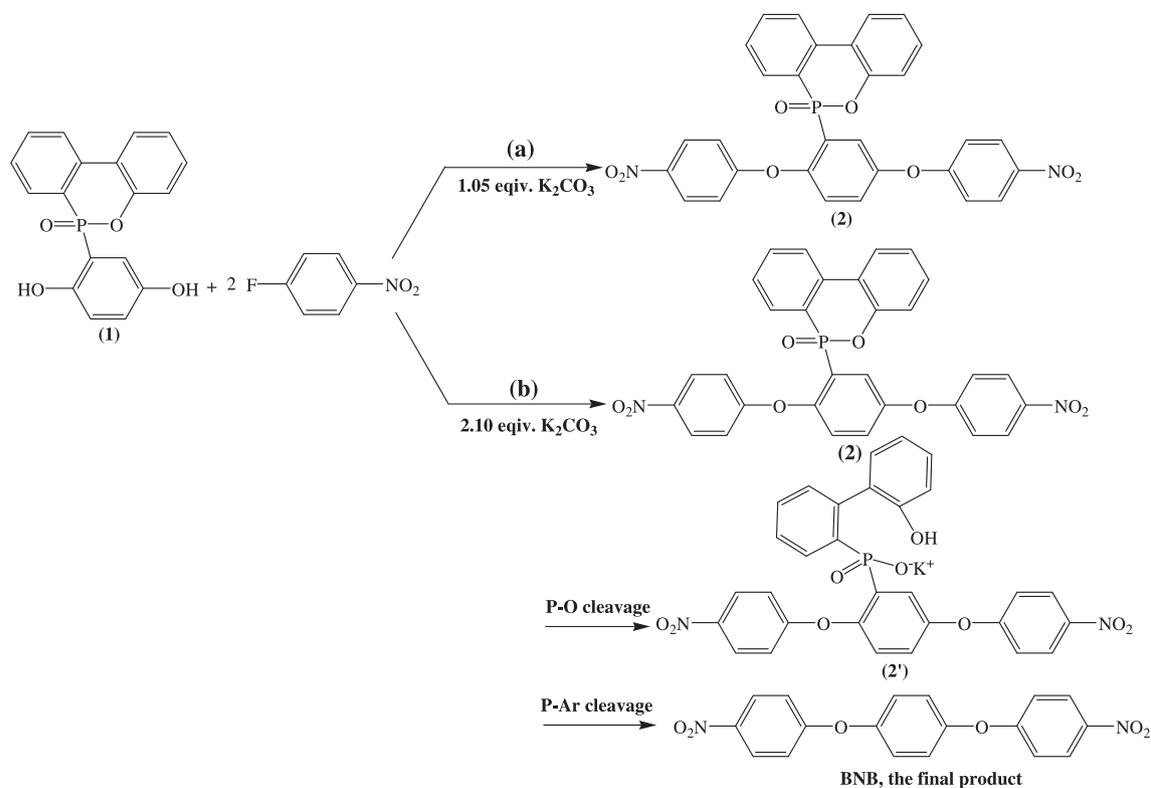
## 1. Introduction

Aromatic polyamides have many desirable physical properties such as high glass transition temperature, high thermal stability and good mechanical properties. Because of these characteristics, they are considered as one of the most important high-performance polymers [1–8]. However, polyamides often possess poor processability due to high softening or melting temperatures and limited solubility in organic solvents. One of the successful approaches to improve processability of polymers is incorporating bulky pendants into the polymer backbone [9–13]. The bulky pendant is expected to reduce packing efficiency and crystallinity, therefore, enhancing the solubility of polymers. It has also been reported phosphorus-functionalized polymers, whether in the phosphine oxide form [14–17], in the phosphonate [18,19] or in the phosphinate form [20–26], can improve organo-solubility, adhesion to metal and flame retardancy. Another attractive property of phosphorus-containing polymers is their atomic oxygen resistance. According to X-ray photoelectron spectroscopy (XPS) analysis [27],

when exposed to an oxygen plasma, the phosphorus element in polymers reacts with the atomic oxygen present in the plasma, forming a dense phosphate layer, which can inhibit further erosion of polymer chains and protect the underlying polymers. As a result, phosphorus-containing polymers, such as poly(arylene ether heterocycle) [28,29], polyimide [14,30–32], polybenzimidazoles [30], polyoxadiazoles [30], poly(ether ketone) [33], and per-fluorocyclobutyl aromatic ether [34] have been proved as potential polymers for low Earth orbit (LEO) applications.

In our previous work [22], we developed 1,4-bis(4-nitrophenoxy)-2-(6-oxido-6H-dibenz <c,e> <1,2> oxaphosphorin-6-yl) phenylene (**3**) by the nucleophilic aromatic substitution of 2-(6-oxido-6H-dibenz <c,e> <1,2> oxaphosphorin-6-yl)-1,4-dihydroxy phenylene (**1**) with 4-fluoronitrobenzene, followed by catalytic hydrogenation. However, the catalyst for the nucleophilic substitution is cesium fluoride, which is very expensive compared with common inorganic bases such as potassium carbonate. The expensive catalyst prohibits the application potential of (**3**). In this work, we reveal an inexpensive synthesis of (**3**). Based on (**3**), a series of novel polyamides (**5a–5d**) were prepared by Yamazaki reaction conditions [35]. The thermal properties, tensile properties, solubility, optical transparency, and oxygen plasma resistance of polyamides (**5**) were evaluated. Polyamides (**6**) based on

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**Scheme 1.** Products of the nucleophilic substitution under different molar ratios of potassium carbonate-to-(1).

1,4-bis(4-aminophenoxy)benzene (BAB) were also prepared for property comparison.

## 2. Experimental

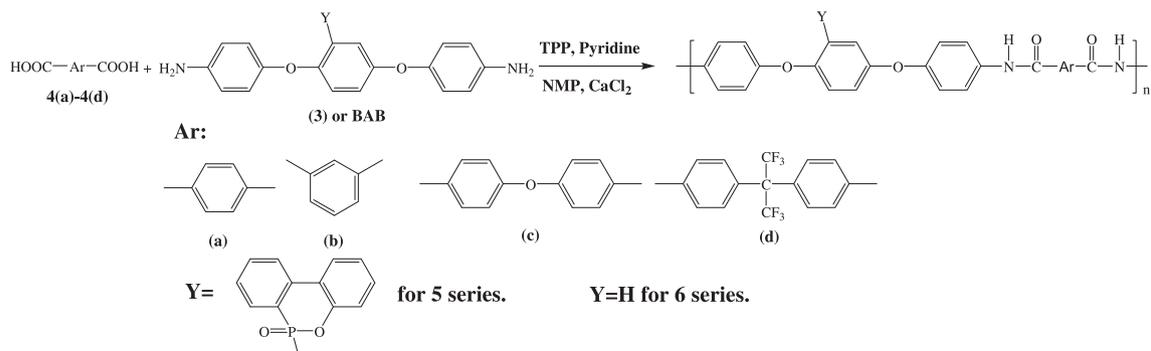
### 2.1. Materials

2-(6-oxido-6H-dibenz[1,2-c:1,2-c']oxaphosphorin-6-yl)-1,4-dihydroxybenzene (**1**) was synthesized from 9,10-dihydro-9-oxa-10-phosphaphenanthrene 10-oxide (DOPO, from TCI) and 1,4-benzoquinone (from Acros) according to a published procedure [36]. 1,4-Bis(4-nitrophenoxy)benzene (BNB) was prepared by the typical nucleophilic substitution of hydroquinone and 1-chloro-4-nitrobenzene catalyzed by  $K_2CO_3$ . 1,4-Bis(4-aminophenoxy)benzene (BAB, from ChrisKev) was used as received. Aromatic diacids, such as terephthalic acid (TPAc, from SHOWA), isophthalic acid (IPAc, from Acros), 4,4'-oxybis(benzoic acid) (ODAc, from Lancaster), and 2,2-bis(4-carboxyphenyl)-1,1,1,3,3,3-hexafluoropropane (6FAC, from

Aldrich) were used as received. *N*-Methyl-2-pyrrolidone (NMP), *N,N*-dimethylacetamide (DMAc) and *N,N*-dimethylformamide (DMF) were purchased from Acros and purified by distillation under reduced pressure over calcium hydride (from Acros) and stored over molecular sieves. Pyridine (from TEDIA), triphenyl phosphite (TPP, from TCI), calcium chloride ( $CaCl_2$ , from SHOWA) were used as received. Other solvents used for solubility tests were obtained from various commercial sources and used without further purification.

### 2.2. Inexpensive synthesis of (3)

(1) 5.0 g (15.42 mmol), 1-fluoro-4-nitrobenzene 4.7864 g (33.92 mmol),  $K_2CO_3$  2.2376 g (16.19 mmol) and DMAc 100 ml were introduced into a round-bottom 500 ml glass flask equipped with a nitrogen inlet, a condenser, and a mechanical stirrer (Scheme 1a). The reaction mixture was heated to 160 °C and maintained at that temperature for 12 h. Then, the reaction mixture was poured into an ethanol and water (1/1, V/V) solution. Then, solution sodium



**Scheme 2.** Synthesis of polyamides **5** and **6**.

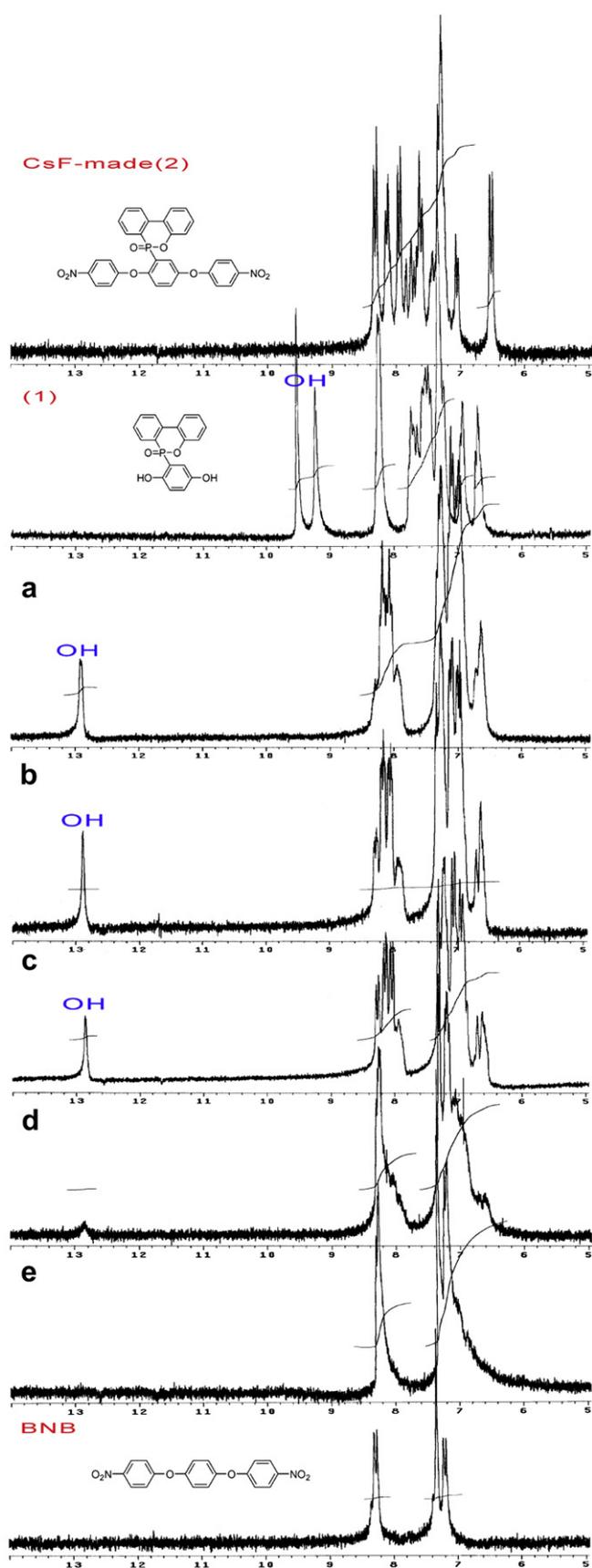


Fig. 1.  $^1\text{H}$  NMR spectra of the product of the nucleophilic substitution at various reaction times. (a) 2 h, (b) 4 h, (c) 6 h, (d) 8 h, (e) 10 h.

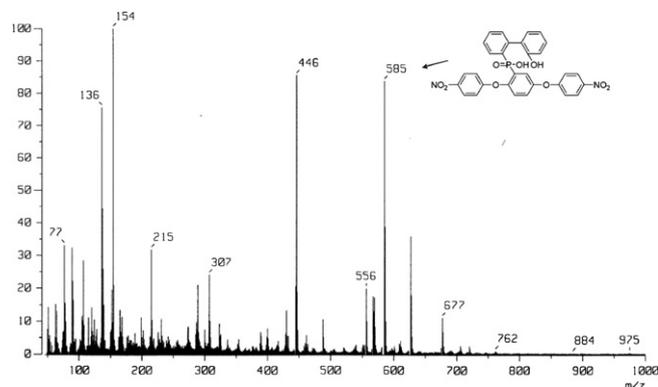


Fig. 2. Mass spectra of protonated (2').

chloride was added to prompt the formation of precipitate. The precipitate was filtered and recrystallized from acetic anhydride, and then dried in a  $120\text{ }^\circ\text{C}$  vacuum oven for 6 h. Light yellow crystals 67% yield with a DSC melting peak at  $251.5\text{ }^\circ\text{C}$  and enthalpy of  $89.5\text{ J/g}$  were obtained. Then, the  $\text{K}_2\text{CO}_3$ -made (2) was then reduced to (3) by the same procedure reported in our previous paper [22].

### 2.3. Single crystal data of (3)

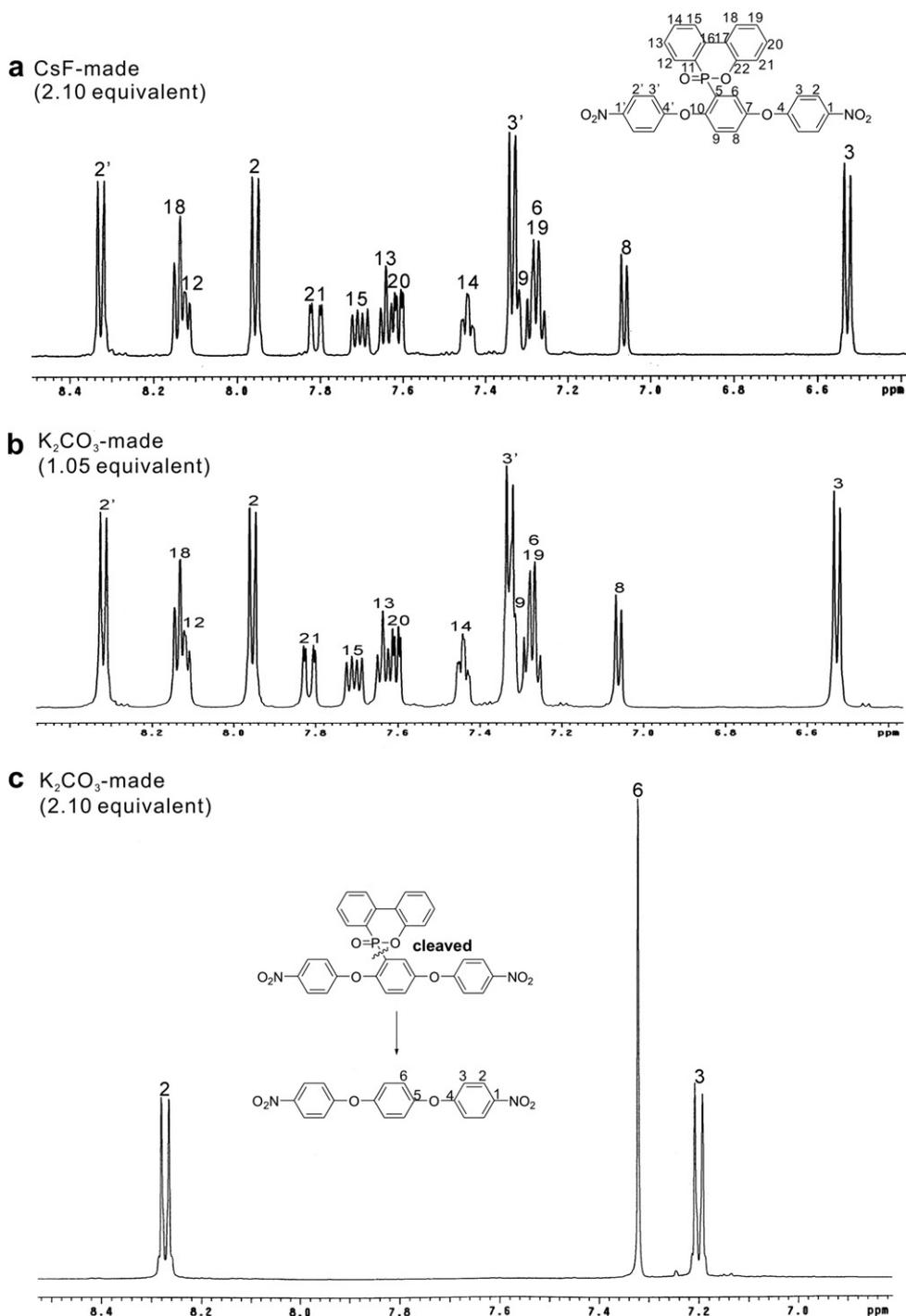
The single crystal of (3) was grown slowly in the dichloromethane/hexane solution. The crystal size for X-ray diffraction is  $0.41 \times 0.35 \times 0.34\text{ mm}^3$ . The crystal system is Monoclinic with P 21/c space group. The unit cell dimension is  $a = 7.0894(7)\text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $b = 20.535(2)\text{ \AA}$ ,  $\beta = 97.411(2)^\circ$ ,  $c = 17.4608(18)\text{ \AA}$ ,  $\gamma = 90^\circ$ . The calculated density is  $1.335\text{ g/cm}^3$ .

### 2.4. Synthesis of polyamides

Phosphorus-containing polyamides were prepared by reacting equal mole of (3) with various aromatic diacids. Polyamides syntheses are exemplified by specific synthesis of 5a from the condensation of (3) and TPAC. To a 100 ml three-neck round-bottom flask equipped with magnetic stirrer, and nitrogen inlet, diamine (3) 0.633 g (1.25 mmol), TPAC 0.208 g (1.25 mmol),  $\text{CaCl}_2$  0.3 g, TPP 0.9 ml, pyridine 1.2 ml and NMP 5 ml were added. The mixture was stirred at  $100\text{ }^\circ\text{C}$  for 4 h. After cooling to room temperature, the solution was poured into 300 ml of methanol. The fiber-like precipitate was filtered and washed with hot water, and then dried in a vacuum oven at  $150\text{ }^\circ\text{C}$ . The yield is quantitative. The precipitate was dissolved in DMF to afford an approximately 20 wt% solution. The clean and viscous solution was casted on glass by an automatic film applicator, and dried at  $80\text{ }^\circ\text{C}$  for overnight, then dried at  $100\text{ }^\circ\text{C}$  (1 h) and  $200\text{ }^\circ\text{C}$  (2 h). The other phosphorus-containing polyamides (5 series) were prepared in a similar procedure. The non-phosphorus containing polyamides (6 series) derived from BAB were also prepared in a similar procedure. The synthetic equations of polyamides 5 and 6 are shown in Scheme 2.

### 2.5. Characterization

Differential scanning calorimetry (DSC) scans were obtained from samples of about 10 mg in a nitrogen atmosphere at a heating rate of  $20\text{ }^\circ\text{C/min}$  by a Perkin–Elmer DSC 7. Dynamic mechanical analysis (DMA) was performed by a Perkin–Elmer Pyris Diamond DMA in a tension mode at a heating rate of  $5\text{ }^\circ\text{C/min}$ . Thermal gravimetric analysis (TGA) was performed with a Seiko Exatar 600 at a heating rate of  $20\text{ }^\circ\text{C/min}$  in a nitrogen atmosphere from  $60\text{ }^\circ\text{C}$



**Fig. 3.** NMR spectra of the product of the nucleophilic substitution (a) CsF-made (**2**), (b) 1.05 equivalent K<sub>2</sub>CO<sub>3</sub>-made (**2**) and (c) 2.10 equivalent K<sub>2</sub>CO<sub>3</sub>-made (**2**); the BNB.

to 800 °C. NMR measurements were performed using a Varian Inova 600 NMR in DMSO-*d*<sub>6</sub>, and the chemical shift was calibrated by setting the chemical shift of DMSO-*d*<sub>6</sub> as 2.49 ppm. Gel permeation chromatography (GPC) was carried out on a Hitachi L2130 with a UV detector (L2400) using *N,N*-dimethylformamide (DMF) as the eluent at 60 °C with a flow rate of 1.0 mL/min. The data were calibrated with polystyrene standard. The stress-strain behavior of the polyamides was characterized by an EZ tester at room temperature with film specimens 0.5 cm wide, 6 cm long and about 20 μm in thickness. The gauge length of the test specimens was 2 cm, and the crosshead speed for film testing was 5 mm/min.

The stress-strain data represent an average value of 5 time measurements. Wide-angle X-ray diffraction (WAXD) measurements were performed at room temperature using a MAC Science MXP3 X-ray diffractometer with monochromatized Cu *K*<sub>α</sub> radiation ( $\lambda = 1.5418$ , operating at 40 kV and 30 mA). The scanning rate was 3°/min over a range of  $2\theta = 5\text{--}45^\circ$ . Oxygen plasma exposures were performed on thin films (1 cm × 8 cm, ~20 μm thick). The plasma chamber was operated at 2 torr with a radio-frequency of 30 W and the ratio of flow rate of oxygen to argon was 1:4 at a total flow rate of 25 sccm. Since the power of the plasma was not calibrated, duplicate exposures of polyamides **6** and polyimide Kapton were

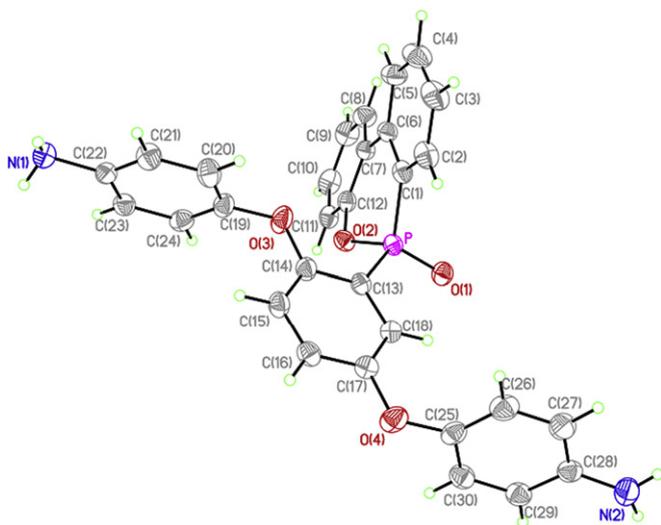


Fig. 4. Single crystal diffractogram of (3).

performed to compare with the polyamides **5**. The IR spectra were measured with a Perkin–Elmer spectrum RX1. Ultraviolet–visible (UV–vis) spectra of the polymer films were recorded by a Hitachi 320 spectrophotometer.

### 3. Results and discussion

#### 3.1. Inexpensive synthesis of (2)

According to the literature [37], when inexpensive potassium carbonate was used as a catalyst, the nucleophilic substitution of (1) and 1-chloro-4-nitrobenzene was not successful due to the cleavage of P–Ar bond. The cleavage of P–Ar bond was also observed in the nucleophilic aromatic substitution of (1) and 1-fluoro-4-benzonitrile using potassium carbonate as catalyst [38]. In our previous paper [22], we reported the successful synthesis of dinitro (2) using CsF as catalyst. However, CsF is very expensive compared with potassium carbonate, limiting the industrial application potential of (2). Recently, we retry the nucleophilic substitution. We sampled the solution of the nucleophilic substitution every 2 h and poured the sample into the ethanol/water solution with sodium chloride. Then, the precipitate was analyzed by  $^1\text{H}$  NMR (Fig. 1). A phenolic OH at 12.9 ppm appeared after reacting for 2 h (Fig. 1a). The phenolic OH reached a maximum at about 4 h (Fig. 1b), then decreased gradually (Fig. 1c) and disappeared completely after 10 h (Fig. 1e). Besides, the signals of Ar–H of biphenylene decrease gradually during reaction, and almost disappeared after 10 h. The chemical shift of the phenolic OH is 12.9 ppm, which is much downshift than

Table 1  
GPC<sup>a</sup> and organo-solubility<sup>b</sup> data of polyamides **5**.

Polyamide	$M_n^c$ ( $\times 10^4$ )	$M_w^d$ ( $\times 10^4$ )	Solvent				
			NMP	<i>m</i> -Cresol	DMAc	DMSO	DMF
<b>5a</b>	9.9	24.8	+ (–) <sup>f</sup>	+ (–)	+ (–)	+ (–)	+ (–)
<b>5b</b>	4.2	7.5	+ (+)	+ (–)	+ (+)	+ (–)	+ (–)
<b>5c</b>	6.7	12.7	+ (–)	+ (–)	+ (–)	+ (–)	+ (–)
<b>5d</b>	10.5	28.2	+ (+)	+ (+)	+ (+)	+ (+)	+ (+)

<sup>a</sup> Relative to polystyrene standard, using DMF as the eluent.

<sup>b</sup> Solubility was tested with a 5 mg sample in 0.5 mL of solvent.

<sup>c</sup> Number average molecular weight.

<sup>d</sup> Weight average molecular weight.

<sup>f</sup> The data in parenthesis is the solubility of **6** series. +: Soluble at room temperature. –: Insoluble at room temperature.

those of phenolic OH in (1), indicating the phenolic OH is hydrogen-bonded. According to Fig. 1, a two-stage cleavage of (2) under alkaline condition was proposed in Scheme 1(b). In the first stage, the ring-opening phosphinate occurred via the cleavage of P–O bond, forming (2') with a phenolic hydrogen-bonded OH (corresponding to signal at 12.9 ppm in Fig. 1). In the second stage, the bulky pendant was cleaved via the cleavage of P–Ar bond (corresponding the gradual disappearance of phenolic OH and Ar–H of biphenylene), forming the final product, 1,4-bis(4-nitrophenoxy)benzene (BNB). The ring opening of biphenylene phosphinate has also been observed by Liu et al. under alkaline condition [39], and the formation of BNB is consistent with the result observed by Liou and Hsiao [37]. That is, our result combines the observation reported by Liou and Hsiao [37] and Liu et al. [39]. The proposed mechanism can further be confirmed by the mass spectrum of protonated (2') (Fig. 2). An *m/e* value at 585 standing for the structure of (2') supports the existence of (2') proposed in Scheme 1b.

According to above analysis, a higher reaction temperature, stronger base, longer reaction time, and a larger molar ratio of base-to-(1) are the wrong approaches to prepare (2). All led to severe cleavage of the phosphinate pendant. Typically, the molar ratio of potassium carbonate-to-(1) is chosen to be 2.0 or slightly higher for almost all the nucleophilic substitution of biphenol with 1-fluoro-4-nitrobenzene or 1-chloro-4-nitrobenzene. However, since 1 mol of potassium carbonate can react with 2 mol of acid (the first stage is  $\text{K}_2\text{CO}_3 + \text{HCl}$  result in  $\text{KHCO}_3 + \text{KCl}$ , and the second stage is  $\text{KHCO}_3 + \text{KCl}$  result in  $\text{K}_2\text{CO}_3 + \text{HCl}$ , so the overall reaction is  $\text{K}_2\text{CO}_3 + 2\text{HCl}$  result in  $2\text{KCl} + \text{H}_2\text{O} + \text{CO}_2$ ), the molar ratio of  $\text{K}_2\text{CO}_3$ -to-(1) was reduced from 2.1 to 1.05 in this work to prevent the alkaline hydrolysis resulting from the excess base. After the reactants were reacted at 160 °C for 12 h, the reaction solution was poured into the ethanol/water with sodium chloride. The precipitate was recrystallized by acetic anhydride. According to the melting point, FTIR and NMR analysis, (2) prepared by 1.05 equivalent  $\text{K}_2\text{CO}_3$  (Fig. 3b) has the same structure as that prepared by 2.10 equivalent CsF (Fig. 3a).

The  $\text{K}_2\text{CO}_3$ -made (2) can be reduced to diamine (3) according to our previous procedure. After growing the crystal of (3) in the dichloromethane/hexane solution, the structure of diamine (3) was confirmed by an X-ray single crystal crystallography (Fig. 4). As shown in Fig. 4, the conformation demonstrates the non-coplanar and bulky characteristics of the biphenylene phosphinate pendant. The biphenylene phosphinate pendant is nearly perpendicular to the phenylene, and does not cause steric hindrance to the amino groups. As a result, the reactivity of both amino groups is not affected by the steric hindrance of the biphenylene pendant.

#### 3.2. Synthesis and characterization of polyamides

Polyamides **5** and **6** were synthesized from the condensation of (3) or BAB with various aromatic diacids (4a–4d) by Yamazaki reaction conditions using TPP and pyridine as condensation agents (Scheme 2). A homogeneous solution was achieved during the polymerization, indicating that the polyamides possessed good solubility in the polymerization medium. Since the chemical shift of the amino group of (3) is 4.97 ppm, which is only slightly higher than that of BAB (4.92 ppm), it indicates that the electron density of the amino groups of (3) is almost the same as that of BAB. That is, the electron-withdrawing effect of O=P bond is negligible in (3). Since the reactivity of amino groups (3) is quite high, polyamides with high viscosity were easily prepared. Table 1 lists the GPC data of polyamides **5**. The number-average molecular weights of **5** ranges from  $4.2 \times 10^4$  to  $10.5 \times 10^4$  g/mol, and the weight-average molecular weight ranges from  $7.5 \times 10^4$  to  $28.2 \times 10^4$  g/mol. The high molecular weight reflects the high reactivity and purity of (3).

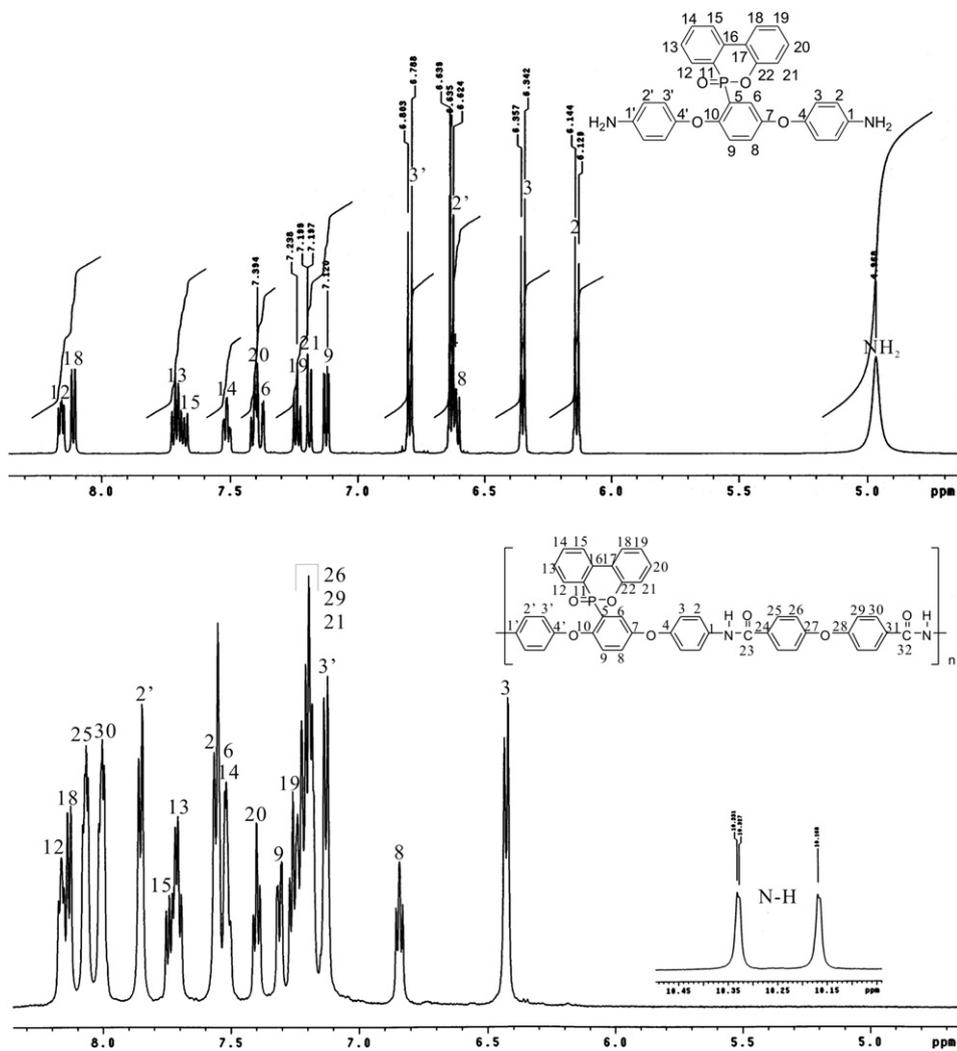


Fig. 5. <sup>1</sup>H NMR spectra of (3) and 5d.

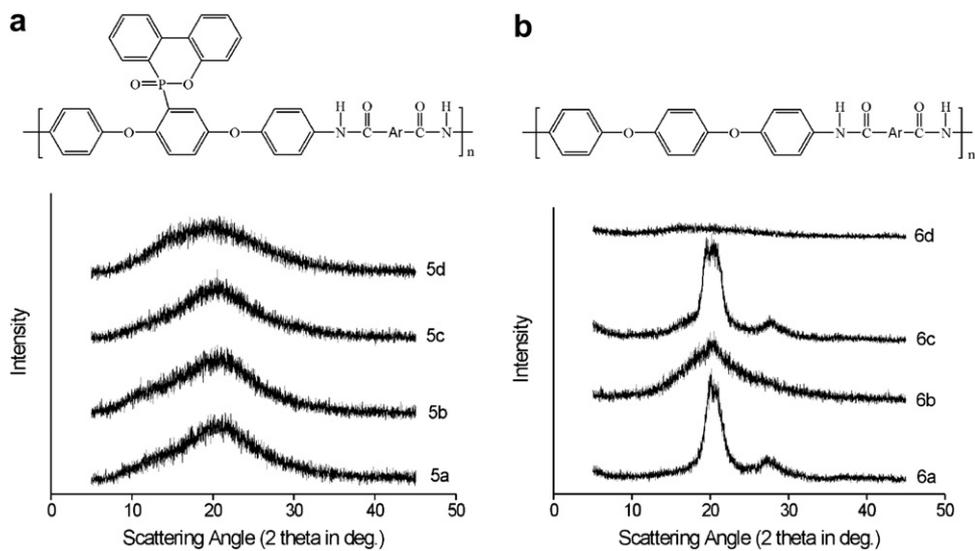


Fig. 6. Wide-angle X-ray diffractograms of polyamides (a) 5 and (b) 6.

**Table 2**  
Thermal, optical and mechanical properties of the polyamides **5**.

Polymer	$E'$ (GPa) <sup>a</sup>	$T_g$ (°C) <sup>b</sup>	Tensile strength (MPa)	Elongation at break (%)	Initial modulus (GPa)	Cutoff wavelength (nm)	$T_d$ 5% (°C) <sup>c</sup>	Char yield (%) <sup>d</sup>
<b>5a</b>	2.26	243	101	7.0	3.22	366	486	68
<b>5b</b>	2.02	210	95	6.5	3.13	345	460	63
<b>5c</b>	1.77	231	84	4.8	3.01	346	467	65
<b>5d</b>	1.62	255	86	6.8	2.36	358	478	59

<sup>a</sup> Storage modulus ( $E'$ ) at 50 °C, measured by DMA at a heating rate of 5 °C/min.

<sup>b</sup> Based on peak temperature of tangent delta in the DMA thermogram.

<sup>c</sup> Temperature corresponding to 5% weight loss by thermogravimetry at a heating rate of 20 °C/min in nitrogen.

<sup>d</sup> Residual weight % at 800 °C in nitrogen.

Fig. 5 shows the  $^1\text{H}$  NMR spectrum of (**3**) and **5e**. Comparing the peaks pattern of (**3**) with that of **5e**, a downshift phenomenon was observed. The downshift is very obvious for the peaks of  $\text{H}^2$  and  $\text{H}^2$  because the strong electron-donating amino groups are replaced by amide linkages, which exhibit less electron-donating ability. Two amide protons were observed at 10.5 and 10.3 ppm. This can be attributed to asymmetrical substitution of biphenylene pendant, one NH is closer to the biphenylene pendant than the other NH. The IR spectrum of the polymers exhibited characteristic absorptions of the amide group at around  $3300\text{ cm}^{-1}$  (N–H stretching) and  $1665\text{ cm}^{-1}$  (C=O stretching), further confirms the structure.

### 3.3. Organo-solubility and X-ray diffraction

The solubility of polyamides **5** and **6** in various solvents are summarized in Table 1. Polyamides **5a–5d** are readily soluble in DMF, DMAc, NMP, m-cresol and DMSO. In contrast, only polyamides **6b** and **6d** are soluble in the same solvents. Fig. 6 shows the wide-angle X-ray diffractograms of polyamides **5** and **6**. The results show that all the polyamides **5** are amorphous. In contrast, polyamides **6a** and **6c** are crystalline, consistent with the solubility data. According to the X-ray diffractograms and solubility data, the bulky phosphinate pendant, which prevents polymer chains from packing well, should be responsible for the amorphous and good solubility characteristics of polyamide **5**.

### 3.4. Tensile properties

All the polyamides **5** are tough, flexible and creasable. Their tensile properties are summarized in Table 2. The tensile strength, elongation at break and moduli range from 84 to 101 MPa, 4.8–7.0%,

and 2.36–3.22 GPa, respectively, demonstrating good mechanical properties.

### 3.5. Thermal properties

The dynamic mechanical property of polyamides **5** are evaluated by DMA, and the results are listed in Table 2. The  $T_g$ s of these polyamides range from 210 °C to 255 °C. **5b**, containing the meta-substituted structure shows the lowest  $T_g$ . **5d**, with bulky trifluoromethyl groups which will hinder the rotation of polyamide chains, displays the highest  $T_g$ . Fig. 7 shows the dynamic mechanical analysis of **5d** and **6d** at a heating rate of 5 °C/min. The storage moduli of **5d** and **6d** are maintained at about  $2 \times 10^9$  Pa before 230 °C. A transition at 255 and 263 °C corresponding to the glass transition was observed for **5d** and **6d**, respectively. As in Fig. 7, the difference in  $T_g$  values between polyamides **5d** and **6d** is relatively small, indicating that introducing the bulky biphenylene phosphinate pendant does not sacrifice the glass transition even though the free volume of **5d** is much larger than that of **6d**. The other polyamides show similar mechanical properties ( $E' \sim 10^9$  Pa up to 200 °C) in dynamic mechanical analyses (Table 2), demonstrating medium to high  $T_g$  characteristic. The thermal stability of the resulting polyamides was evaluated by TGA in a nitrogen atmosphere, and the TGA data is listed in Table 2. Depending on the structure of diacid used, the 5% decomposition temperatures ranged from 460 to 486 °C, and the char yields ranged from 59 to 68 wt%, demonstrating medium to high thermal stability.

### 3.6. Optical transparency

The transparency and cutoff wavelength of all polyamides were evaluated by UV–vis spectroscopy, and the results are listed

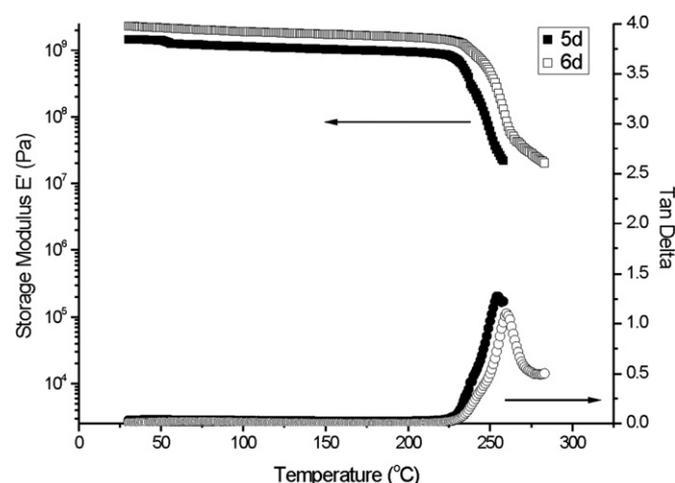


Fig. 7. DMA curves of **5d** and **6d**.

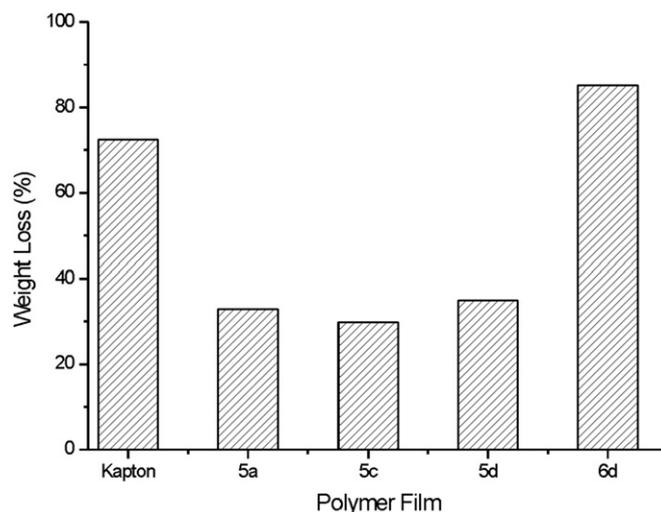


Fig. 8. The weight loss of polyamides **5**, **6d**, and Kapton under oxygen plasma.

in Table 2. The cutoff wavelength of these polyamides falls in the range of 345–366 nm, showing a very light color characteristic. The bulky biphenylene phosphinate pendant, which separated the chromophoric groups and interrupted the intramolecular conjugation, provided a highly irregular structure for the resulting polyamides, and might be responsible for the light color characteristic [40–42].

### 3.7. Oxygen resistance

The results of atomic oxygen resistance of polyamides **5** are shown in Fig. 8. The weight loss of polyamides **5** under oxygen plasma was compared with that of polyimide Kapton and polyamide **6**. To distinguish the effect between thermal-induced and oxygen plasma-induced decomposition, the plasma chamber was initially operated under a pure argon atmosphere at a flow rate of 20 sccm. Less than 1 wt% loss was observed for all polymers after 6 min exposure, indicating that the thermal-induced decomposition is negligible. When oxygen at a flow rate of 5 sccm was introduced, Kapton and polyamides **6** decomposed rapidly and severely within 6 min, indicating an atom oxygen-induced decomposition occurred. In contrast, polyamides **5** displayed lower weight loss, and thus much better oxygen plasma resistance than Kapton and polyamide **6**. Besides, the low-color characteristic of polyamide **5** resulted in low solar absorptivity in the low Earth orbital. The preliminary results demonstrate that polyamides **5** are promising materials for potential space applications.

## 4. Conclusions

An inexpensive route to prepare (**1**)-derivative via nucleophilic substitution was revealed. It is found that the molar ratio of potassium carbonate-to-(**1**) is crucial to the product of the nucleophilic substitution. When the molar ratio of is 2.10 (typical value of nucleophilic substitution), according to <sup>1</sup>H and Mass spectra, a two-stage cleavage of (**2**) was observed, and the 1,4-bis(4-nitrophenoxy) benzene is the final product. When the molar ratio was reduced to 1.05, the nucleophilic substitution can be carried out successfully without alkaline hydrolysis. This finding will provide an economic route for a successful synthesis of (**1**)-derivatives via nucleophilic substitution. The bulky biphenylene phosphinate pendant in polyamide **5** is responsible not only for the improved solubility, the low-color characteristic, but also for the good oxygen plasma resistance. The combination of light color, flexibility, high molecular weight, high glass transition temperature, high thermal stability, improved organo-solubility, and good oxygen plasma resistance makes polyamides **5** promising polymers.

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