



Synthesis and Characterization of Novel Aromatic Polyamides Based on New Aromatic Poly(phosphazene-diamine) Monomer

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A new amino-terminated oligomer containing ether groups, 2,2-bis(4-amino-4,4-oxybisbenzene)tetraphenoxyoligocyclotriphosphazene (AOPP) was synthesized. 2,2-Bis(4-amino-4,4-oxybisbenzene)tetraphenoxyoligocyclotriphosphazene was characterized using FT-IR, ¹H NMR and thermal analyses. New aromatic phosphazene polyamides were prepared by polycondensation reaction of synthesized aromatic diamine with terephthaloyl dichloride. Polyamide properties were investigated by DSC, TGA, GPC (gel permeation chromatographic analysis) and wide-angle X-ray scattering, viscosity and solubility measurements. The polyamides show excellent thermal stability, low-temperature resistance and solubility in polar aprotic solvents.

Key Words: Polyamide, Polyphosphazene, Characterization.

INTRODUCTION

Aromatic polyamides are considered to be high-performance organic materials due to their outstanding chemical, physical and mechanical properties¹. Their properties arise from their aromatic structure and amide linkages. However, the poor solubility, high softening and melting temperatures caused by high crystallinity and high stiffness of polymer backbone leads to be hampered in processing of aromatic polyamides. The properties can be easily tailored through changing their molecular chain structure^{2,3}. The strategies which have been employed for solubility increase in aromatic polyamides are lateral substitution and the distortion of the rigid character introducing non-planar, kinked or flexible parts in the main chain. On the other hand, incorporation of bulky pendent groups can impart a significant increase in both T_g and thermo-oxidative stability by restricting segmental mobility, while providing good solubility due to decreased packing and crystallinity^{4,5}.

In present study, a new aromatic phosphazene diamine monomer *i.e.*, 2,2-bis(4-amino-4,4-oxybisbenzene)tetraphenoxyoligocyclotriphosphazene (AOPP) is prepared and use it for the synthesis of new phosphazene-containing polyamides. The monomers and polymers were synthesized and their physical properties including intrinsic viscosity, solubility behaviour, crystallization behaviour, thermal properties and stability are also studied.

EXPERIMENTAL

Hexachlorocyclotriphosphazene (HCCP, self-made) was purified by recrystallization from dry hexane and subsequent sublimation twice. 4,4-Diaminodiphenyl ether (ODA) was used as received from Sinopharm Chemicals (Shanghai, China). Phenol (Chengdu, China) was recrystallized from pentane. Tetrahydrofuran (THF) was distilled from sodium/benzophenone. Petroleum ether and triethylamine (TEA) were distilled onto molecular sieves. All reactions were carried out under a dry nitrogen atmosphere by using standard Schlenk line techniques.

The FT-IR spectra were recorded using polymer granule on a Perkin-Elmer Wellesley MA spectrophotometer. ¹H NMR spectra were recorded on a Varian DRX 400 NMR spectrometer with the operating frequency at 400 MHz using CDCl₃ as a solvent. Thermogravimetric analysis was performed on a TGA 7 instrument (Perkin-Elmer) thermal analysis system. DSC analysis was carried out on a Perkin-Elmer Pyris 2 DSC analyzer (Perkin-Elmer), at a heating rate of 20 °C/min in nitrogen atmosphere. Sample weight taken was 10-15 mg. The intrinsic viscosities of polyamides were measured in concentrated sulfuric acid. The numbers were counted by measured value from Ubbelohde viscometer. XRD patterns were recorded using an XRD-6000 X-ray diffractometer with a copper target (40 kV, 15 mA).

Synthesis of *i.e.*, 2,2-bis(4-amino-4,4-oxybisbenzene)-tetraphenoxyoligocyclotriphosphazene: The preparation of 2,2-bis(4-amino-4,4-oxybisbenzene)tetraphenoxyoligocyclotriphosphazene (AOPP) involved two steps: In the first step, A solution of sodium hydride (NaH) (4.8 g, 0.2 mol) and 20 mL of THF in glacial acetic acid (150 mL) was prepared under stirring and nitrogen atmosphere. To this, a solution of THF (50 mL) dissolving phenol (20 g, 0.204 mol) in glacial acetic acid was added dropwise. The temperature of reaction mixture was maintained at room temperature for 2 h and then added this solution dropwise to a solution of hexachlorocyclotriphosphazene (17.4 g, 0.05 mol) in 100 mL of THF at room temperature for 24 h. Then, the reaction mixture was to be purified by dimethyl sulfide and deionized water. Finally, the product I (*bis*-chlorinetetraphenoxycyclotriphosphazene) was dried under vacuum. In the second step, A solution of 4,4-diaminodiphenyl ether (10 g, 0.050 mol) and triethylamine (10.1 g, 0.10 mol) in 100 mL of THF was added dropwise to a solution of the product I (28.9 g, 0.050 mol) in 100 mL of THF at room temperature. After completion of the addition, the mixture was stirred and refluxed at 60 °C for 12 h. Then, the reaction mixture was cooled to room temperature. THF was removed by distillation under reduced pressure. The residue was dissolved in dichloromethane, washed three times with deionized water and dried over anhydrous magnesium sulfate. Finally, the product II (AOPP) was dried under vacuum.

Synthesis of PPT/AOPP/TDC composites: Aromatic polyamides were synthesized following a procedure described in the literature⁶. All composites described were synthesized by similar methods. The chemical compositions of the polyamides are listed in Table-1.

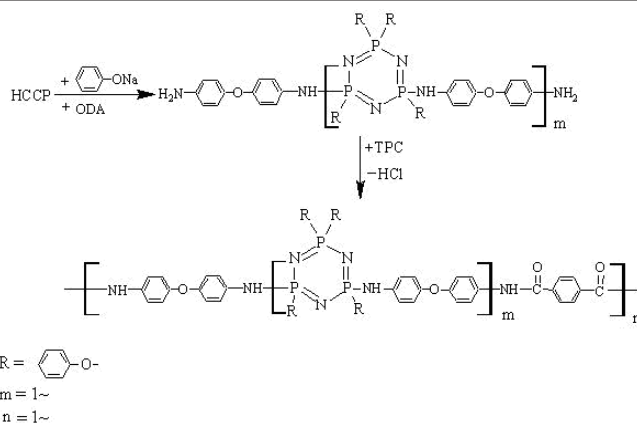
Code	PPT (molar %)	AOPP (molar %)	TDC (molar %)
PPTA	100	0	100
PA-10	70	30	100
PA-30	50	50	100
PA-50	30	70	100
PAA	0	100	100

RESULTS AND DISCUSSION

Synthesis and characterization of AOPP and the polyamides: Polyphosphazene was reacted with respective stoichiometric amounts of sodium phenoxide in the first and with a large excess of 4,4'-diaminodiphenyl ether in the second step (**Scheme-I**).

The chemical structures of the AOPP and synthesized polymers were confirmed by FT-IR and ¹H NMR spectroscopy and elemental analyses are given in Figs. 1-3, respectively.

The broad band at 1490 and 1580 cm⁻¹ corresponds to the benzene ring in AOPP. Moreover, the spectra exhibit characteristic bands of AOPP at 1230 cm⁻¹ (P=N stretch), 1250 cm⁻¹ (C-C stretch), 1160 cm⁻¹ (C-O-C stretch), 875 cm⁻¹ (P-N stretch) and 940 cm⁻¹ (P-O-Ar stretch). The structures of the new polyamide (PAA) were identified by FT-IR spectra are shown in Fig. 2. The diamine compounds showed typical N-H stretching bands at 3450 cm⁻¹, 1660 cm⁻¹ (C=O stretching) and 1500 cm⁻¹



Scheme-I: Synthesis of AOPP and aromatic polyamides

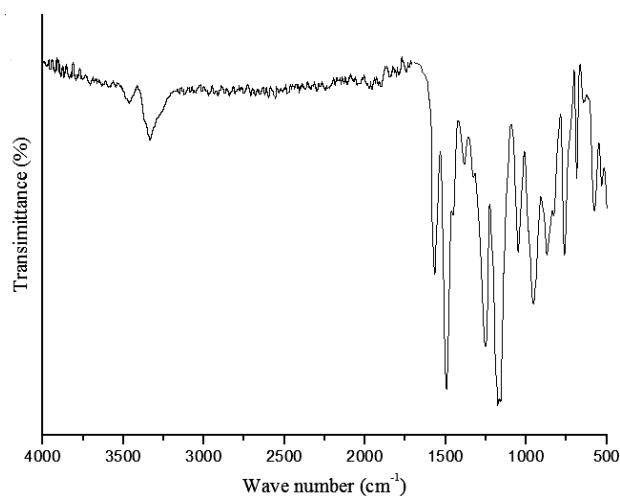


Fig. 1. FT-IR spectrum of AOPP

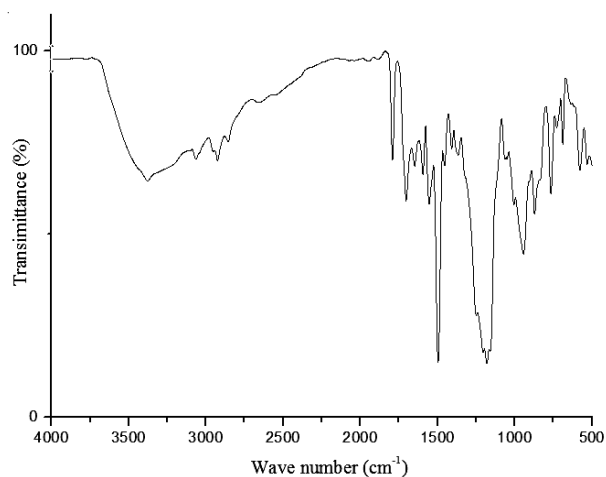


Fig. 2. FT-IR spectrum of PAA

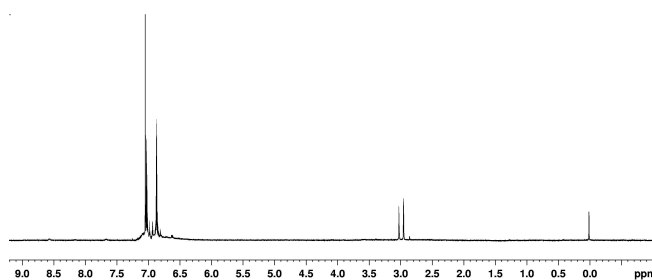


Fig. 3. ¹H NMR spectrum of the AOPP

(N-H bending and C-N stretching) which indicating that AOPP has been introduced into the backbone of polyamide.

In ^1H NMR spectra of AOPP the signal at 2.94 and 3.00 ppm in Fig. 2 is unique to amine protons. The peak at 7.10 and 7.24 ppm corresponds to the proton of phenyl groups. The ^1H NMR spectrum shows that AOPP was a mix-substituted product. By calculating integral area of the peaks, the ratios of substituents could be indicated as 2:1, consistent to the dosage of phenoxy. Furthermore, different substituted polyphosphazene could be obtained by changing the mol ratio of phenol to hexachlorocyclotriphosphazene.

Solubility of the polyamides: Solubility of the polyamides was tested in various organic solvents at 3 wt. % concentration and data is summarized in Table-2.

Polymer	Solvent								
	CHCl_3	DCM	THF	DMF	DMAc	NMP	Pyridine	DMSO	DOV
PPTA	-	-	-	-	-	-	-	-	+
PA-30	-	-	-	-	+	+	-	-	+
PAA	-	-	-	+	+	+	-	+	+

+ = soluble; - = insoluble

The new polyamide (PAA) was readily soluble in polar aprotic solvents such as dimethyl formamide, dimethyl acetamide and N-methyl pyrrolidine at room temperature or upon heating. It may be attributed to the increase of the disorder in the polymer chain and hindered chain packing, thereby reducing chain interactions.

Intrinsic viscosity of the polyamides: In order to estimate the molecular weights of the polyamide products, their intrinsic viscosities (η) were measured using an Ubbelohde viscometer with concentrated sulfuric acid at 30 ± 0.2 °C. Table-3 shows a plot of the resulting intrinsic viscosities (η_{inh}) about the reaction systems.

Code	PPTA	PA-10	PA-30	PA-50	PAA
η_{inh}	3.16	2.87	1.91	1.62	0.75

Meanwhile, the weight-average molecular weights (M_w) and polydispersities $P_d (=M_w/M_n)$ of the polyamide products are listed in Table-4, which were estimated by GPC measurements in dimethylformamide. The testing data indicate that the polymers have quite a narrow molecular weight distribution and a low quantity of oligomers.

Code	M_w	M_n	P_d
PPTA	38700	15400	2.66
PA-10	69300	32800	2.11
PA-30	57200	24700	2.31
PA-50	51600	19300	2.67
PAA	48400	16800	2.88

Thermal characterization of the polyamides: The thermal properties and the thermal stability of all the polyamides were studied by DSC and TGA techniques, respectively. The curves are shown in Fig. 4 and the data are reported in Table-5.

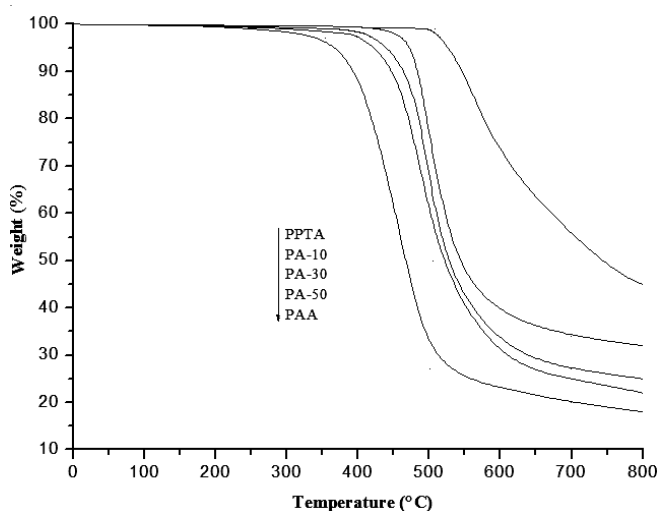


Fig. 4. TGA curves for the polyamides

Code	T_0 (°C) ¹	T_{10} (°C) ²	Char yield ³ (%)	T_g (°C) ⁴
PPTA	509	551	72	345
PA-10	467	498	38	251
PA-30	416	482	31	226
PA-50	383	467	28	217
PAA	355	409	23	183

¹Initial decomposition temperature; ²Temperature at which 10% weight loss is observed; ³Aerobic residual weight at 600 °C; ⁴Glass transition temperature measured on DSC at a heating rate of 20 °C/min in N_2 .

According to Table-5, the polyamides started to lose weight between 355-509 °C. In nitrogen, the 10 % weight-loss temperatures are about 409-551 °C, respectively. The polyamides showed slightly lower stability than PPTA, possibly due to the structural differences. The TGA curves for these polymers indicated that the polyamides bearing phosphazene-diamine groups were less thermally stable in comparison with conventional polyamides. These are probably due to the incorporation of AOPP segments that make the polyamides molecular chains more flexible. Therefore, it is not unexpected that the T_g values of the polyamides decrease.

Crystallinity of present synthesized polyamides: The results of XRD characterization of the polyamides are presented in Fig. 5. From the curves it is observed that there are two dispersion peaks at $2\theta = 20.5^\circ$ and 23.5° for PPTA, which indicates PPTA has low crystallinity. But, there are no peaks in the PA-X ($x = 10, 30, 50, 100$). It proves that PA-Xs are amorphous. This is because the introduction of AOPP weakens the regular structure of molecular chains, reduces the rigidity and therefore disrupts the crystallization capacity of the polyamides. These results are in agreement with those of the DSC analysis.

Conclusion

New kinds of aromatic polyamides were prepared by polycondensation in solution of the synthesized monomer AOPP

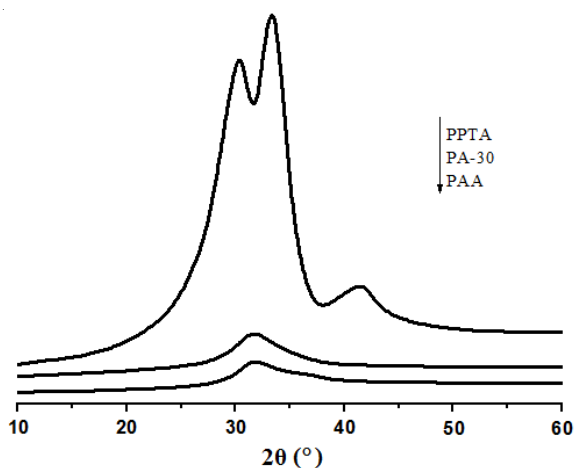


Fig. 5. XRD patterns of the polyamides

with *p*-phthaloyl chloride. The chemical compositions of present polymers were confirmed by FT-IR, DSC, TGA, GPC and XRD techniques. These polymers showed high thermal stability compared to conventional PPTA. It exhibited the

ability to redissolve in polar aprotic solvents. The XRD analyses showed that the crystallinity of present synthesized polyamides is reduced by the presence of the polyphosphazene groups along the polymer chains.

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