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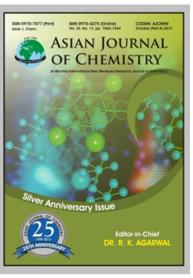

Synthesis and Properties of Novel Organic-Inorganic Hybrid Polyamides

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Four novel organic-inorganic hybrid polyamides containing cyclophosphazene groups in the main chain were synthesized and their properties had been characterized and compared with those of ordinary polyamides. The chemical structures of all samples were characterized by FT-IR technique and their thermal properties were determined by DSC and TGA. The four polyamides with amorphous structure exhibit an enhanced solubility in polar aprotic solvents and a superior thermal stability with initial decomposition temperature being at about 198-259 ºC. All polyamides exhibited two-step thermal decomposition behaviour and present a maximum char residue at 600 ºC in their thermal decomposition.

Key Words: Polyphosphazene, Polyamide, Synthesis, Properties.

INTRODUCTION

Polyamides are known to have excellent high-temperature resistance, mechanical strength and superior insulating properties. They 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[1-4]. However, the extremely high transition temperatures of the commercial amides, which lie above their decomposition temperatures and their poor solubility in common organic solvents give rise to processing difficulties and limit their applications. The properties can be easily tailored through changing their molecular chain structure[5-7]. Research efforts are therefore underway to take advantage of their properties, enhance their machinability, solubility and incorporate new chemical functionalities in the polyamide backbone or lateral structure, so that their applicability is expanded and remains on the forefront of scientific research[8-10].

Cyclophosphazenes are inorganic heterocyclic rings containing a [N = PX2] repeat unit. In the recent ten years, research about the functionality of polyphosphazene is very active which includes flame retardant, special rubber, high temperature resistant material, liquid crystal, photoelectricity materials, *etc*.[11-15]. However, to date, there have been few literature references of polyamides containing cyclotriphosphazene groups in the main chain.

In this paper, four novel organic-inorganic hybrid polyamides containing cyclotriphosphazene groups in the main chain were synthesized in order to investigate their properties. Their physical chemistry properties including solubility behaviour, crystallization behaviour and thermal properties were studied.

EXPERIMENTAL

Hexachlorocyclotriphosphazene (HCCP, self-made) was purified by recrystallization from dry *n*-heptane and subsequent sublimation twice. *p*-Phenylenediamine, 4,4-diaminodiphenyl ether, 4,4'-diaminodiphenylsulfone, ethylenediamine were used as received from Sinopharm Chemical Regents Corp. (Shanghai, China). Phenol (Chengdu, China) was recrystallized from pentane. Tetrahydrofuran was dried over and distilled from sodium/benzophenone. Triethylamine was distilled onto molecular sieves. *N*-methyl pyrrolidinone was purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves. Terephthaloyl chloride was purified by recrystallization form anhydrous hexane. Lithium chloride was dried for 8 h at 170 under vacuum. All glassware was dried in an oven under vacuum before use.

Synthesis of the diamine monomers: The synthesis of monomers **1**, **2**, **3** and **4** involved two nucleophilic substitution reaction steps with a certain mole ratios of hexachlorocyclotriphosphazene, phenol and *p*-phenylenediamine, 4,4-diaminodiphenyl ether, 4,4'-diaminodiphenylsulfone, ethylenediamine, respectively. The synthesis specific steps were listed in our previously work[16].

Synthesis of novel polyamides *via* solution polycondensation: In a typical experiment, polyamide PA-1, which derived from monomer **1** and terephthaloyl chloride, was prepared as follows: A two-necked flask equipped with a dropping funnel and gas inlet tube was charged with a solution of monomer **1** (7.21 g, 0.01 mol), LiCl (0.1 g) and pyridine (1.55 g) in 20 mL of N-methyl pyrrolidinone, to which terephthaloyl chloride (2.04 g, 0.01 mol) was added with stirring under N_2. The mixture was firstly stirred at 0 ºC for 0.5 h, then at room temperature for 7 h to yield a viscous polyamide solution. Then the solution was trickled into excess ethanol with stirring to afford a precipitate. The precipitate was collected, washed with hot ethanol for three times and dried at 150 ºC under vacuum for 6 h to give polyamide PA-1. The other polyamides PA-2, PA-3 and PA-4 were also prepared *via* a similar procedure as described for PA-1 by the polymerization of 1 equiv. of terephthaloyl chloride with 1 equiv. of the corresponding aromatic monomers.

Measurement: FT-IR spectra of all samples were recorded using polymer granule on a Perkin-Elmer Wellesley MA spectrophotometer. Thermogravimetric analysis (TGA) was performed on a TGA 7 instrument (PerkinElmer) thermal analysis system. Sample weight taken was 2-4 mg. DSC analysis was carried out on a Perkin-Elmer Pyris 2 DSC analyzer (Perkin Elmer), at a heating rate of 10 ºC/min in nitrogen atmosphere. Sample weight taken was 15-20 mg. Wide-angle X-ray scattering measurements were performed on a Bruker AXS-D_8 Avance X-ray diffractometer with a copper target (40 kV, 15 mA). Solubility of the polymers was tested in various organic solvents at 3 wt. % concentration.

RESULTS AND DISCUSSION

Synthesis and characterization of the monomers and polyamides: Novel diamine monomers and four organic-inorganic hybrid polyamides containing cyclophosphazene groups in the main chain were synthesized. The key structural features of diamine monomers were verified by FT-IR. The spectrum is shown in Fig. 1. The monomers shows a strong absorption band at around 1230 cm^{-1} due to the P=N stretch, while the absorption band at around 875 cm^{-1} appeared due to the P-N stretch. It also shows strong absorption peaks at around 940 and 3250 cm^{-1} due to the P-O-Ar stretch and N-H stretch, respectively. These demonstrate the resulted diamine monomers maintaining the cyclophosphazene groups.

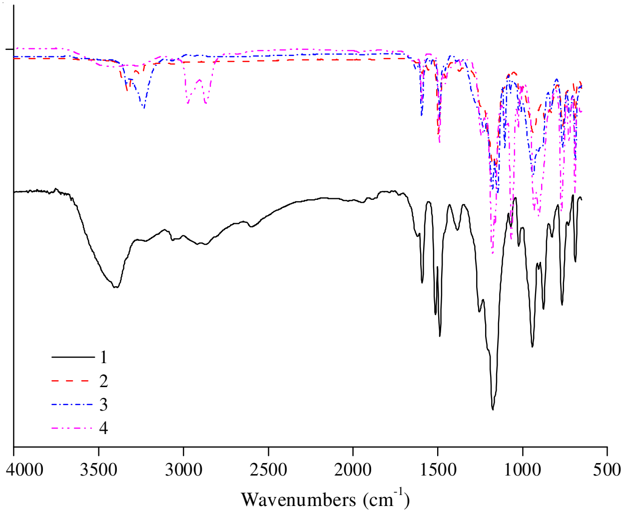

Fig. 1. FT-IR spectra of monomers

The four novel polyamides were characterized with FT-IR spectra to comfirm their chemical structures (Fig. 2). A broad and strong band in the range of 3500-3200 cm^{-1} was observed due to ν(N-H) (amide A). Coupled vibrations [δ(NH) and ν(CO), amide I] were distinctly apparents as two bands in the 1680-1650 cm^{-1} and 1730-1700 cm^{-1} range, respectively. In addition, mixed vibrations involving OCN and NH groups appeared as a strong band at around 1280 cm^{-1} (amide III) which was overlapped by ν(N=P) from introducted cyclophosphazene group. The amide II band arose from NH deformation mode and was situated at 1550 cm^{-1}. The presence of cyclophosphazene unit in polyamide structures was evidenced by the relevant bands centered at 1280 cm^{-1} and 890 cm^{-1}. The results further demonstrated that the novel polyamides have the expected chemical structures.

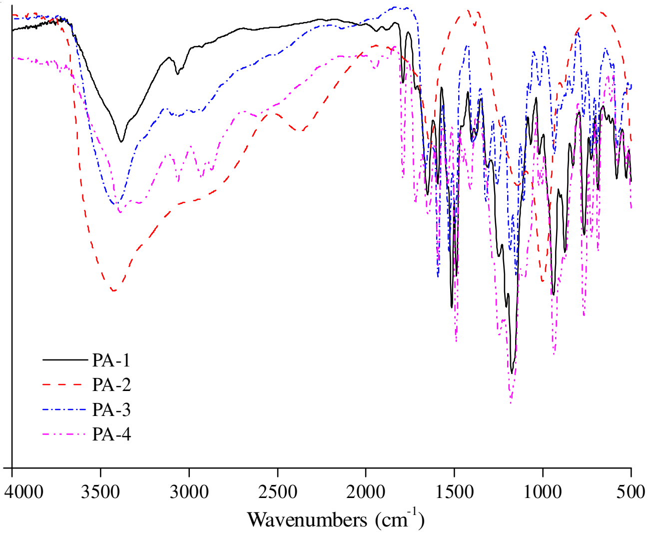

Fig. 2. FT-IR spectrum of the polyamides

Solubility of the novel polyamides: The solubility behaviour of the polyamides was tested qualitatively in various solvents at 3 wt. % concentration and data is summarized in Table-1. It can be seen that all the polyamides were readily soluble in polar aprotic solvents such as DMSO, *N*-methyl pyrrolidinone, dimethyl acetamide and DMF at room temperature or upon heating compared. The high solubility of these polyamides is apparently due to the presence of the cyclophosphazene groups and the non-planar diamine monomers, which increased the disorder in the polymer chain and hindered chain packing, thereby reducing chain interactions[17,18]. In addition, the presence of cyclophosphazene groups in the backbone further increased flexibility and also disturbed the planarity of aromatic units, resulting in reduction of the close packing and hence was found to be soluble in polar aprotic solvents at room temperature or upon heating.

Crystallinity of the synthesized polyamides: Crystallinity of the polyamides was evaluated by WAXD measurements of powder samples at room temperature and the patterns are shown in Fig. 3. From the curves we can see that there are two dispersion peaks at 2θ = 20.5º and 23.5º for PPTA, which indicates PPTA has low crystallinity. But the polyamides showed broad halo at around 2θ = 20º indicating that the polyamides are amorphous in nature. This result can be attributable

TABLE-1
SOLUBILITY BEHAVIOUR[1] OF THE POLYAMIDES IN VARIOUS SOLVENTS[2]

Solvent	$CHCl_3$	THF	DMF	DMAc	NMP	DMSO	H_2SO_4
PA-1	–	–	±	±	±	+	+
PA-2	–	–	-	±	±	+	+
PA-3	–	–	±	±	±	+	+
PA-4	–	±	±	+	+	+	+

[1] Solubility: (+) soluble at room temperature; (±) soluble with worming or swollen; (–) insoluble; [2] THF: tetrahydrofuran; DMF: *N,N'*-dimethyl formaide; DMAc: *N,N'*-dimethyl acetamide; NMP: *N*-methyl pyrrolidone; DMSO: dimethyl sulfoxide

to the presence of the cyclophospazene groups in the polymer backbone which hindered packing of the polymer chains and decreased the inter-molecular force, subsequently causing a decrease in crystallinity.

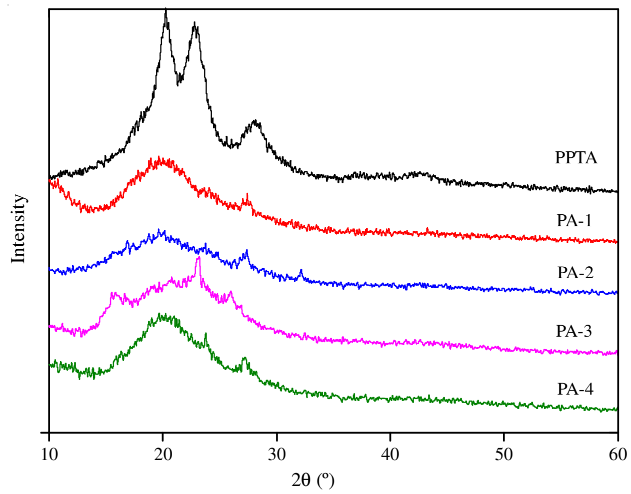

Fig. 3. X-ray diffraction patterns of the polyamides

Thermal characterization: The thermal properties and stability of the four novel polyamides were studied by DSC and TGA techniques (Table-2). The glass transition temperature (T_g) values of the polyamides are in the range of 112-169 °C. The polyamide PA-4 exhibited the lowest T_g value (112 °C) because of the effect of the flexible ethylenediamine polymer backbone, whereas, the highest T_g value (169 °C) was observed for polyamide PA-1 derived from the rigid phenyl diamine monomer **1**. This result is reasonable and can be attributed to the fact that phosphazene chains along the polymer backbone, which is acting as an internal plasticizer, increases free volume and thereby increase segmental mobility, thus resulting in a reduction in the T_g.

TABLE-2
THERMAL PROPERTIES OF THE POLYAMIDES

CODE	T_0 (°C)[1]	T_{10} (°C)[2]	Char yield[3] (%)	T_g (°C)[4]
PA-1	259.2	293.8	62.60	169
PA-2	198.6	263.4	55.23	143
PA-3	212.3	240.7	36.17	135
PA-4	214.5	300.1	42.69	112

[1] Initial decomposition temperature recorded by TGA at a heating rate of 10 °C/min in N_2; [2] Temp. at which a 10 % weight loss was recorded by TGA; [3] Anaerobic residual weight at 600 °C; [4] Glass transition temperature measured on DSC at a heating rate of 10 °C/min in N_2

The thermal stabilities of the monomers and polyamides were evaluated by TGA at a heating rate of 10 °C/min up to 600 °C under nitrogen. TG curves of the monomers and polyamides are shown in Figs. 4 and 5. It is noteworthy that all polyamides exhibited two-step thermal decomposition behaviour. There is a small weight loss at the beginning of TG curves of the polyamides which is due to the hygroscopic moisture released. It could also mean that amide groups are involved in extensive hydrogen bonding with adsorbed water molecules. Initial decomposition temperatures of the monomers were in the range 201-245 °C, of the polyamides were in the range 198-259 °C. The temperature at 10 wt. % loss of the monomers and polyamides were in the range 270-300 °C and 240-300 °C, respectively. The monomer samples present a maximum char residue upon 50 % at 600 °C in their thermal decomposition. It can be readily attributed to the inherent thermal-stability properties of the cyclopolyphosphazene cores. With the presence of cyclophosphazene, cross-linking and gelation occurs in the decomposition. As the network structure and gelatin can inhibit the production of small molecules, the higher char yield is an effect of achieving synergy between the individual units. It emerges that the first decomposition step of the polyamides occurs around 150-300 °C. This is attributed to the less stable of the P-O-C bone linkage, as reported for other polymeric systems containing similar cyclophosphazne groups[19,20]. At the second decomposition step of the pyrolysis process, the cyclophosphazene rings processes ultimately yield phosphoric acid and ammonia with the presence of H_2O[21]. The obtained structure could act as an acid catalyst, accelerating the cleavage of side groups in polyamides. Then, the polyamides react to form more stable structures. The appearance of P-O-P group is considered as crosslinking to different species, resulting in the formation of complex phosphorus structures.

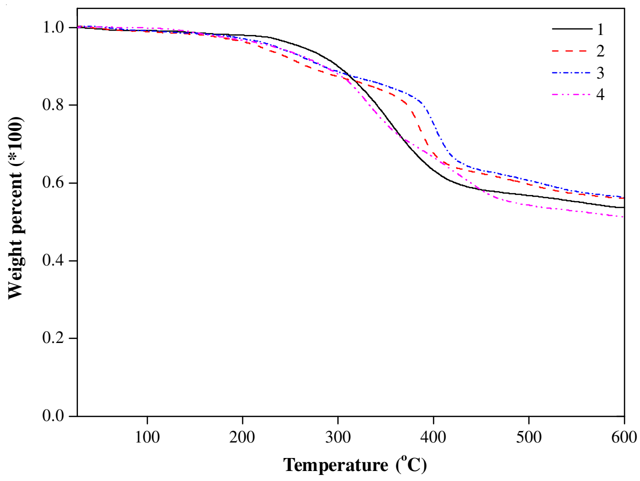

Fig. 4. TGA curves of the monomers

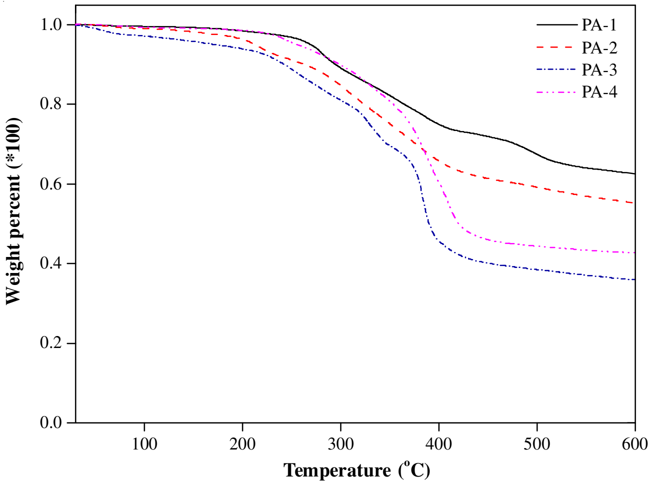

Fig. 5. TGA curves of the polyamides

Conclusion

The synthesis of four new aromatic diamine monomers, monomer 1, 2, 3 and 4, containing phosphazene as flexible units were successfully accomplished in high yields starting from hexachlorocyclotriphosphazene and diamines (*p*-phenylenediamine, 4,4-diaminodiphenyl ether, 4,4'-diaminodiphenylsulfone and ethylenediamine). The low temperature solution polycondensation of diamine monomers with terephthaloyl chloride resulted in a series of moderate to polyamides in good yields.

These polyamides' solubility in organo-solvents was significantly improved with incorporation of bulk, coplanar and polar cyclophosphazene groups into the polymers as backbone structure. The glass transition temperature (T_g) values of the polyamides are in the range of 112-169 ºC, probably due to the presence of phosphazene chains along the polymer backbone, which is acting as an internal plasticizer, increases free volume and thereby increase segmental mobility, thus resulting in a reduction in the T_g. TGA date of these polyamides indicated that all the polyamides exhibited comparable thermal stability to the ordinary aromatic polyamide and presented a maximum char residue at 600 ºC in their thermal decomposition. X-ray diffraction patterns indicated that the polyamides were amorphous in nature.

The presence of the cyclophosphazene groups increased the disorder in the polymer chain, hindered chain packing and disturbed the planarity of aromatic units, thereby reducing chain interactions and increasing the solubility. There is also a direct correlation of the increase in thermal stability and residual rate with the rigidity of diamines in the polymers.

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