Journal of Applied Polymer Science

Preparation and Properties of Three Novel Poly(phosphazene-aryl amide)s Containing Cyclotriphosphazene Structures

Zhengping Zhao,[1] Qiang Guo,[1] Xia Li,[1] Jinliang Sun,[1] Zhijun Nie,[1] Weili Luo[2]

[1]School of Materials Science and Engineering, Shanghai University, Shanghai 201800, China

[2]Shanghai Research Institute of Materials, Shanghai 200437, China

Correspondence to: Q. Guo (E-mail: guoq@shu.edu.cn)

ABSTRACT: 1,1,3,5-tetraphenoxy-3,5-bis(4-aminoanilino)cyclotriphosphazene, 1,1,3,5-tetraphenoxy-3,5-bis[4-(4-aminophenysulfone) anilino)]cyclotriphosphazene, and 1,1,3,5-tetraphenoxy-3,5-bis(*N*,*N*′-ethanediamine)cyclotriphosphazene were synthesized in two steps from the *p*-Phenylenediamine, 4,4′-diaminodiphenylsulfone, and ethylenediamine via nucleophilic substitution and catalytic reduction with hexachlorocyclotriphosphazene. Three novel aromatic polyamides such as poly(cyclotriphosphazene-p-phenylene amide), poly (cyclotriphosphazene-p-sulfuryl amide), and poly(cyclotriphosphazene-ethyl amide) were synthesized from these diamines by direct polycondensation reaction with terephthaloyl chloride and pyridine in *N*-methyl pyrrolidone, respectively. The chemical structures of the diamine monomers and three novel poly(cyclotriphosphazene-aryl amide)s were characterized by Fourier Transform Infrared, (^{1}H and ^{31}P) Nuclear Magnetic Resonance, and Elemental Analysis. The thermal properties of the polyamides were determined by Differential Scanning Calorimetry and Thermogravimetric Analysis (TGA). The crystallization behaviors of the polyamides were studied by Wide-ray X-ray diffraction, and the morphology of the pyrolysis residues were observed by Scanning Electron Microscope. The three poly(cyclotriphosphazene-aryl amide)s with amorphous structure would exhibit an enhanced solubility in polar aprotic solvents and a superior thermal stability with initial decomposition temperature being at about 198–259°C. TGA curves of the poly(cyclotriphosphazene-aryl amide)s exhibit mainly three thermal decomposition steps, and the poly(cyclotriphosphazene-p-phenylene amide) presents the highest solid residue rate 62.6% heated to 600°C. In the morphology analysis of the poly(cyclotriphosphazene-aryl amide) solid residues, organophosphorus gelatum forms in the surface layer were observed. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 128: 4368–4377, 2013

KEYWORDS: polyamides; synthesis and processing; thermal properties; degradation

Received 7 January 2012; accepted 28 September 2012; published online 27 October 2012
DOI: 10.1002/app.38650

INTRODUCTION

Aromatic polyamides are known to have excellent high-temperature resistance, mechanical strength, and superior insulating properties. These materials emerge of interest industrially with application 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 polyamides, which lie above their decomposition temperatures, and their poor solubility in common organic solvents give rise to processing difficulties and limit their applications. In addition, the properties can be easily tailored through changing their molecular chain structure.[5–7] Policy 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. 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] Considering the extraordinary characteristics of the chemically simplest aramids, the research efforts are twofold directed: (i) diminishing of the cohesive energy that causes intractable materials (due to their extremely low solubility and exceptionally high thermal transitions) with little change to their high-performance properties; and (ii) the expansion of their applications as high-performance materials in new and promising advanced fields, such as optically active, luminescent, ionic exchange, flame resistant, and fiber-forming materials.

Cyclophosphazenes are inorganic heterocyclic rings containing a $[N{=}PX_2]$ repeat unit. Among this family of compounds, the hexachlorocyclotriphosphazenes (HCCP) $N_3P_3Cl_6$ received

maximum attention. In the recent 10 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, very few literature references of poly(cyclotriphosphazene-aryl amide)s were provided.

Vapor phase lubrication has been proposed as a scheme for lubrication of high efficiency engines operating at temperature outside the range in which any fluid lubricants can be used.[16–22] These applications include gas-turbines which operate with bearing temperatures in excess of 500°C. The most commonly used vapor phase lubricants for these applications are the aryl phosphates and in particular tricresyl phosphate.[23]

In this article, three novel polyamides containing cyclotriphosphazene groups in the main chain were synthesized in order to investigate their properties. Also the polyamides can also be used as the addition-type monomers selected on the basis of the tribopolymerization concept in vapor phase lubrication study. The preparation and properties of the three novel poly(cyclotriphosphazene-aryl amide)s were reported in the present work. Their physical chemistry properties including solubility behavior, crystallization behavior, thermal properties, and degradation behavior were studied.

EXPERIMENTAL

Materials

HCCP (synthesized as described in the literature[24]) was recrystallized from dry hexane followed by sublimation (60°C, 0.05 mmHg) twice before use (mp = 112.5–113.0°C). *p*-Phenylenediamine (PPD), 4,4′-diaminodiphenylsulfone (DDS), ethylenediamine (EDA) were used as received from Sinopharm Chemical Regents Co. (99%, Shanghai, China). Phenol (Chengdu, China) was recrystallized from pentane. Tetrahydrofurane (THF) was dried over and distilled from sodium/benzophenone. Triethylamine (TEA) was distilled onto molecular sieves. *N*-methyl pyrrolidnone (NMP) was purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves. Terephthaloyl chloride (TPC) was purified by recrystallization form anhydrous hexane. Lithium chloride (LiCl) was dried for 8 h at 170°C under vacuum. All chemicals and solvents were provided commercially by Sinopharm Chemical Regents Co. (China) and used without further purification unless otherwise noted. All glassware was dried in an oven under vacuum before use.

Instrumentation

Fourier Transform Infrared (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, New Jersey) thermal analysis system. Sample weight taken was 2–4 mg. The thermal stabilities of the monomers and poly(cyclotriphosphazene-aryl amide)s were evaluated by TGA at a heating rate of 10°C/min up to 600°C under nitrogen. Differential Scanning Calorimetry (DSC) analysis was carried out on a Perkin-Elmer Pyris 2 DSC analyzer (PerkinElmer, New Jersey), and the glass transition temperature of the polyamides is measured during the heating part of the second thermal cycle at a heating rate of 10°C/min in N_2 atmosphere. Sample weight taken was 15–20 mg. The (^{1}H and ^{31}P) NMR spectra were recorded on a Varian DRX 400 NMR spectrometer (Varian NMR Instruments, California) with the operating frequency at 400 MHz using dimethylsulfoxide (DMSO) as a solvent, using trimethylsiyl (TMS) as inner reference and H_3PO_4 (85%) as external reference. Elemental analysis was carried out using a Heraeus CHN-O rapid elemental analyzer with acetanilide as a standard. Gel Permeation Chromatographic analysis (GPC) was carried out on a PL GPC 50 plus evaporative mass detector instrument. DMSO was used as mobile phase after calibration with polystyrene standards of known molecular weights. Wide-ray X-ray diffraction (WARD) measurements were performed on a Bruker AXS-D8 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. The microstructures of solid residues were recorded using a Cambridge S250MK3 scanning electron microscope (U.K.). The pyrolysis process was conducted by a TG analyzer under nitrogen atmosphere from room temperature to 600°C with a heating rate of 10°C/min and then rapidly cooling to room temperature to obtain the solid residue of the samples.

The Synthetic Routes of Novel Diamine Monomers and Polyamides

In order to examine the presence of cyclotriphosphazene groups in the polyamides backbone, new aromatic diamines containing phosphazene groups and three novel poly(cyclotriphosphazene-aryl amide)s were synthesized to be compared with ordinary polyamides. These descriptions of synthetic routes are shown in Scheme 1.

The preparation of diamine monomers can be divided into two stages. Co-substituted monomers were accomplished by introduction of phenol first to synthesize product I (bis-chlorinetetrsphenoxycyclotriphosphazene), followed by excess PPD, DDS, and EDA in an attempt to generate a 2 : 1 ratio of substituent to give product II. Poly(cyclotriphosphazene-aryl amide)s were prepared by a direct polycondensation reaction of product II with TPC, with HCl as the only by-product adsorbed by pyridine during the reaction.

Synthesis of 1,1,3,5-tetraphenoxy-3,5-bis(4-aminoanilino)cyclotriphosphazene (TPAACP). The synthesis of monomer TPAACP involved two nucleophilic substitution reaction steps with a certain mole ratios of HCCP, phenol, and PPD. The synthesis specific steps were listed in our previous work.[25] A dark brown powder was obtained (yield: 87.5%).

^{1}H NMR (DMSO-d_6; δ, ppm): 6.40 (d, C_6H_4 in PPD), 7.18-7.30 (t, C_6H_5 in phenoxy), 6.18 (s, NH_2), 3.74 (s, NH).

^{31}P NMR (DMSO-d_6; δ, ppm): 20.68 (PPh(PPD)), 8.64 (PPh_2).

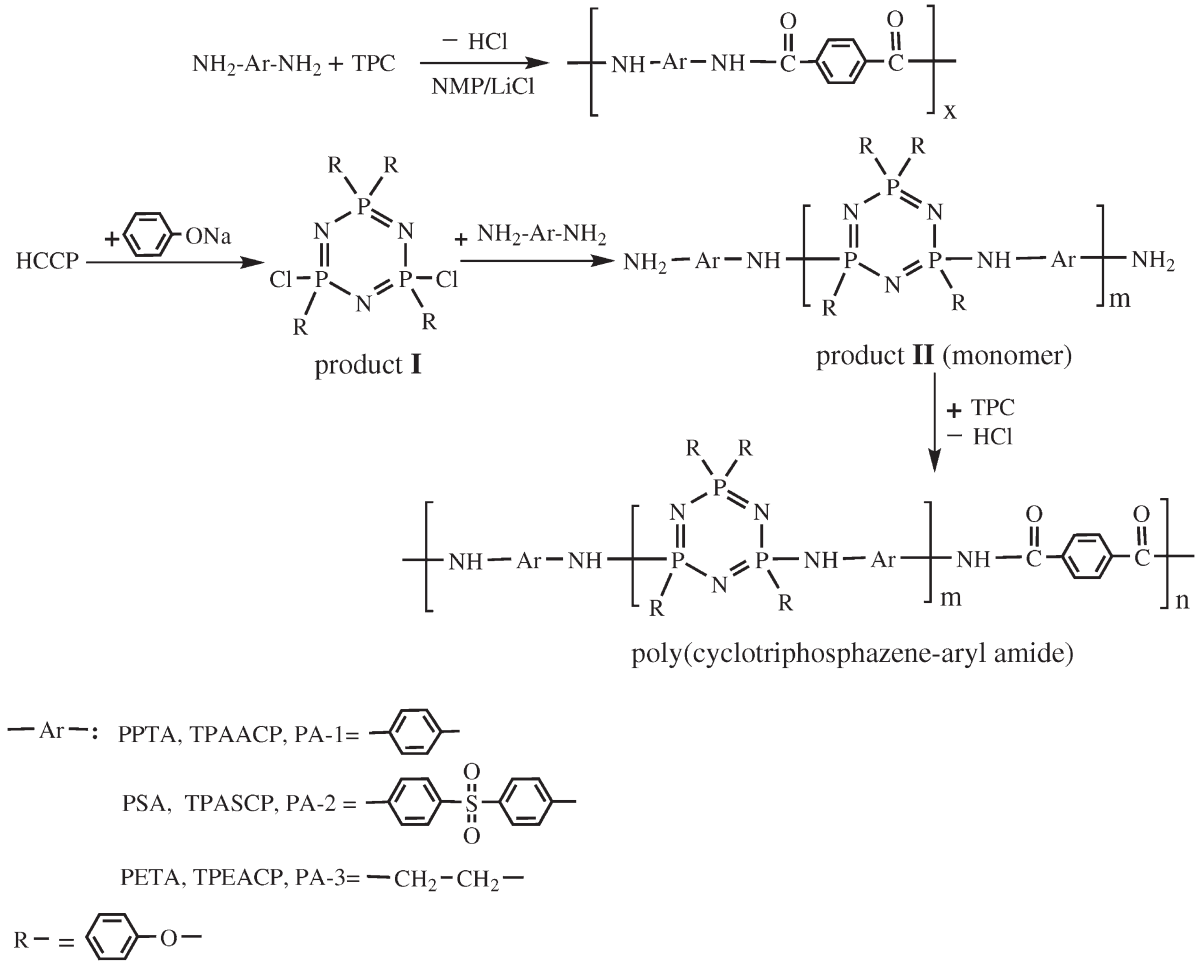
Elemental analysis:

Anal. calcd for $C_{36}H_{34}N_7O_4P_3$: C 59.92, H 4.72, N 13.59, O 8.88, P 12.89;

Found: C 59.83, H 4.81, N 13.47, O 8.96, P 12.75.

Synthesis of 1,1,3,5-tetraphenoxy-3,5-bis[4-(4-aminophenysulfone)anilino)] Cyclotriphosphazene (TPASCP). The synthesis of monomer TPASCP involved two steps like the synthesis above mentioned. The distinction is an act of replacing PPD by

Applied Polymer SCIENCE



Scheme 1. Synthesis of novel diamines and polyamides.

DDS and all other variables being unchanged. A rosy-red powder was obtained (yield: 88.6%).

^{1}H NMR (DMSO-d_6; δ, ppm): 6.50-7.58 (d, C_6H_4 in DDS), 7.18-7.28 (t, C_6H_5 in phenoxy), 6.18 (s, NH_2), 4.04 (s, NH).

^{31}P NMR (DMSO-d_6; δ, ppm): 19.30 (PPh(DDS)), 7.48 (PPh_2).

Elemental analysis:

Anal. calcd for $C_{48}H_{42}N_7O_8S_2P_3$: C 57.54, H 4.20, N 9.79, O 12.79, S 6.39, P 9.29;

Found: C 57.72, H 4.43, N 9.48, O 12.96, S 6.31, P 9.21.

Synthesis of 1,1,3,5-tetraphenoxy-3,5-bis(N,N′-ethanediamine)cyclotriphosphazene (TPEACP). The synthesis of monomer TPEACP involved two steps like the synthesis above mentioned. The distinction is an act of replacing PPD by EDA and all other variables being unchanged. A rosy-red colloid was obtained (yield: 81.2%).

^{1}H NMR (DMSO-d_6; δ, ppm): 2.71–3.02 (d, CH_2 in EDA), 7.10–7.30 (t, C_6H_5 in phenoxy), 5.12 (s, NH_2), 2.04 (s, NH).

^{31}P NMR (DMSO-d_6; δ, ppm): 17.57 (PPh(EDA)), 8.04 (PPh_2).

Elemental analysis:

Anal. calcd for $C_{28}H_{34}N_7O_4P_3$: C 53.76, H 5.44, N 15.68, O 10.24, P 14.88;

Found: C 53.58, H 5.62, N 15.52, O 10.47, P 14.76.

Synthesis of Poly(cyclotriphosphazene-Aryl Amide)s via Solution Polycondensation

In a typical experiment, poly(cyclotriphosphazene-*p*-phenylene amide) (PA-1), which derived from TPAACP and TPC, was prepared as follows: a two-necked flask equipped with a dropping funnel and gas inlet tube was charged with a solution of TPAACP (7.21 g, 0.01 mol), LiCl (0.1 g), and pyridine (1.55 g) in 20 mL of NMP, to which TPC (2.04 g, 0.01 mol) was added with stirring under N_2. The mixture was first stirred at 0°C for 0.5 h, then at room temperature for 7 h to yield a viscous polyamide solution. Then the solution was added dropwise into excess methanol with stirring to afford a precipitate. The precipitate was collected, repeatedly washed with hot methanol and deionized water for three times. Then, it was purificated by Soxhlet extracted method with acetone, eluted with deionized water, and dried at 80°C under vacuum for 6 h to give the polyamide (grey powder, yield: 87.5%). Other polyamides:

poly(cyclotriphosphazene-*p*-sulfuryl amide) (PA-2) (canary yellow powder, yield: 88.6%), poly(cyclotriphosphazene-ethyl amide) (PA-3) (brownish yellow powder, yield: 86.1%), poly (*p*-phenylene terephthamide) (PPTA) (golden yellow powder, yield: 93.4%), polysulfone amide (PSA) (white powder, yield: 91.7%) and poly-EDA amide (PETA) (yellow powder, yield: 90.4%) were also prepared via a similar procedure as described for PA-1 by the polymerization of 1 equiv. of TPC with 1 equiv. of the corresponding aromatic monomers.

RESULTS AND DISCUSSION

Synthesis and Characterization of the Monomers and Polyamides

We have previously reported the synthesis and characterization of the diamine monomer (1,1,3,5-tetraphenoxy-3,5-bis(4-aminophenoxy)oligocyclotriphosphazene), which involved two nucleophilic substitution reaction steps with a certain mole ratios of HCCP, phenol, and ODA. The values of M_w and PD of the monomer were determined by GPC analysis in *N,N'*-dimethyl formaide (DMF) (polystyrene was used as standard) to calculate the number of repeating units '*m*'. It equals to 1.02 by averages calculation. This has happened in our case, mainly as a result of a stepwise nucleophilic substitution reaction of HCCP and phenol would form a larger steric hindrance, then the ability of SN_2 reaction will weaken. In the presence of acid-captor and excessive ether amines, the reaction activity of cyclotriphosphazene and ether amines is a moderate synthesis reaction, so it is hard to form the oligomer ($m > 1$), but it is also not completely impossible. So that in our experiments, phosphazene diamine is calculated and deduced as the structure of monomer ($m = 1$), and the ^{31}P detection have also demonstrated the point. The rationale behind these studies was that cyclic phosphazenes are found with both planar and puckered phosphorus-nitrogen rings. σ and σ-π bonds are observed in the neutral system. It has polar groups, imparting an additional dipole moment to the molecule, and hence they can interact with each other. The nucleophile aromatic substitution for chlorine reaction is a moderate synthesis reaction. "Non-geminal" mixed-substituent will be preferential than "geminal". Theoretically speaking, when sodium phenolate engage in nucleophile substitution reaction with HCCP at the mole ratio 4 : 1, there will be almost entirely tetra substitution product, $N_3P_3Cl_2Ph_4$.[26]

The key structural features of diamine monomers were verified by FT-IR based on their characteristic absorption bands. The spectra are shown in Figure 1. The monomers show a strong absorption band at around 1230 cm^{-1} due to the P═N stretch, whereas the absorption band at around 875 cm^{-1} is 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. (^1H and ^{31}P) NMR spectra were also used to identify the structure of diamine monomers. Figure 2 illustrates the NMR spectra of monomers in DMSO-d_6. From the FT-IR spectra, it was observed clearly that P—Cl absorption peaks (at around 505 and 607 cm^{-1}) were disappeared. It is possible to prove that the chlorine atom nucleophilic substitution reactions occurred. The ^{31}P NMR spectra further evidence to support the claim. There are only two different substituents

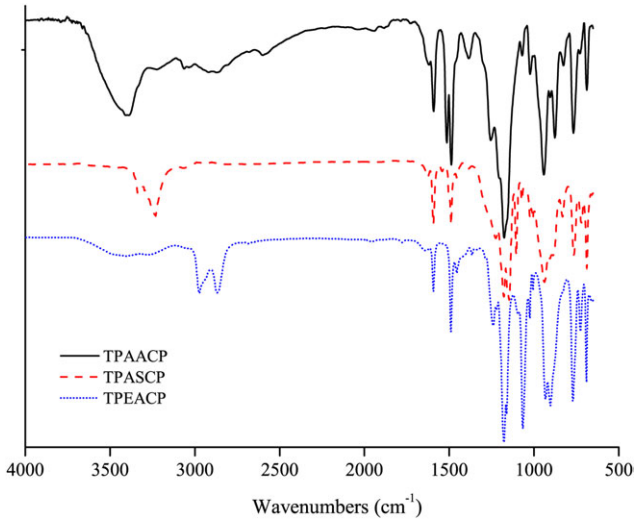


Figure 1. FT-IR spectra of the diamine monomers TPAACP, TPASCP, and TPEACP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

as phenoxy and amino groups on the phosphorus atom. And the ^1H NMR spectra concretely describe the corresponding location of the hydrogen atom in synthetic monomers. All these demonstrate the desired products and structures were successfully synthesized.

All the poly(cyclotriphosphazene-aryl amide)s were characterized with FT-IR spectra to confirm their chemical structures (Figure 3). A broad and strong band in the range of 3200–3500 cm^{-1} was observed due to $\nu_{N—H}$ (amide A). Coupled vibrations (δ_{NH} and ν_{CO}, amide I) were distinctly apparent as two bands in the 1650–1680 cm^{-1} and 1700–1730 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 $\nu_{N=P}$ from introduced cyclotriphosphazene 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 1230 cm^{-1} and 890 cm^{-1}. The results further demonstrate that the poly(cyclotriphosphazene-aryl amide)s have the expected chemical structures.

Solubility of the Poly(cyclotriphosphazene-aryl amide)s

The solubility behavior of the poly(cyclotriphosphazene-aryl amide)s was tested qualitatively in various solvents at 3 wt % concentration and the data were summarized in Table I. It can be seen that all the poly(cyclotriphosphazene-aryl amide)s were readily soluble in polar aprotic solvents such as dimethyl sulfoxide, *N*-methyl pyrrolidone, *N,N'*-dimethyl acetamide (DMAc), and DMF at room temperature or upon heating compared to ordinary polyamide PPTA. In addition, when comparing the polyamides, it is found that polyamide PA-3 exhibited the best solubility because of the more flexible carbon-carbon bones of the polymer backbone. The high solubility of these poly(cyclotriphosphazene-aryl amide)s is apparently due to the presence of the cyclophosphazene groups and the non-planar diamine

Applied Polymer SCIENCE

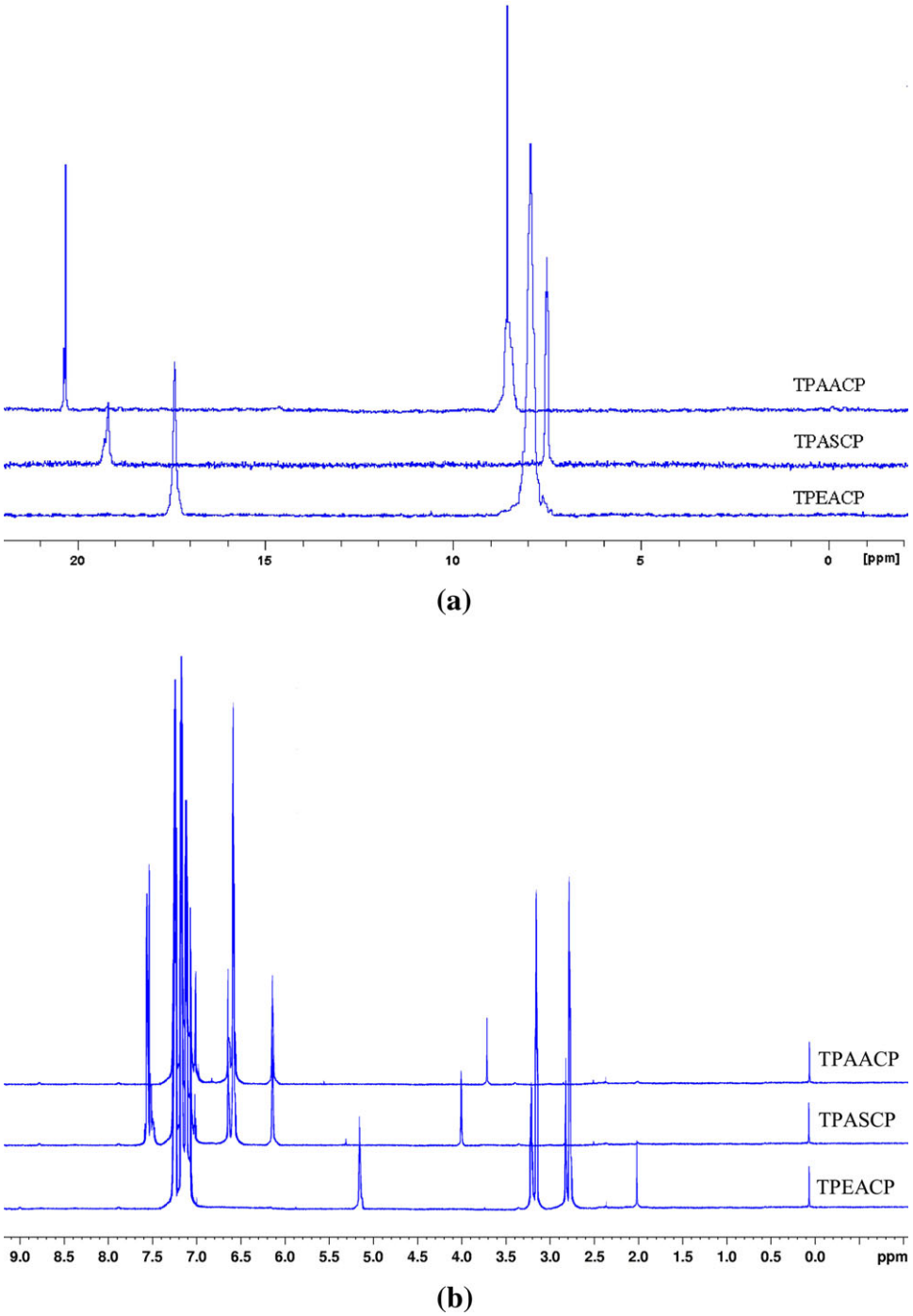


Figure 2. ^{31}P NMR and ^{1}H NMR spectra of the diamine monomers TPAACP, TPASCP, and TPEACP: (a) ^{31}P NMR and (b) ^{1}H NMR. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

monomers, which increased the disorder in the polymer chain and hindered chain packing, thereby reducing chain interactions.[27,28] In addition, the presence of cyclotriphosphazene 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. In other words, the increased solubility of these polyamides is due to their amorphous character.

In order to estimate the molecular weights of the three synthetic poly(cyclotriphosphazene-aryl amide)s, their intrinsic viscosities (η_{inh}) were measured using an Ubbelohde viscometer with concentrated sulfuric acid at 30 ± 0.2°C. Meanwhile, the weight average molecular weight (M_w) and polydispersity index (PD = M_w/M_n) of the polyamide were estimated by GPC measurements in DMSO. The values are all listed in Table II. The testing data indicate that the polymers have quite a narrow molecular weight distribution and a low quantity of oligomers.

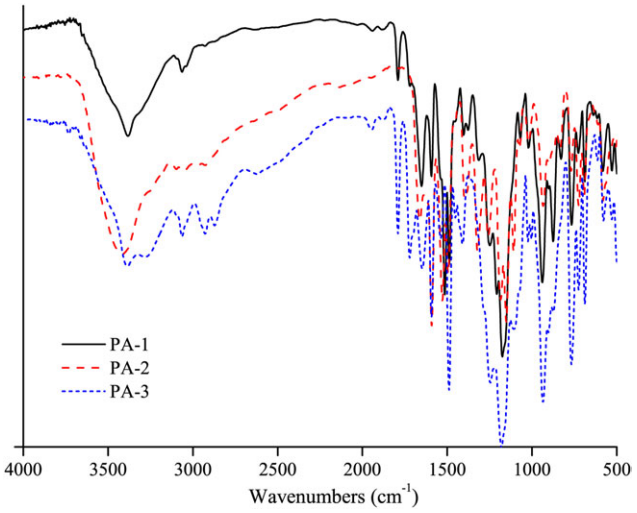


Figure 3. FT-IR spectra of the poly(cyclotriphosphazene-aryl amide)s. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Crystallinity of the Synthesized Poly(cyclotriphosphazene-aryl amide)s

Crystallinity of the synthesized polyamides was evaluated by WAXD measurements of powder samples at room temperature and the patterns are shown in Figure 4. From the curves, we can see that the poly(cyclotriphosphazene-aryl amide)s show broad halo at around $2\theta = 20°$ indicating that the polyamides are almost amorphous in nature. However, there is also a peak around 27 deg which is attributed to amidolink crystallite. This result can be attributable to the presence of the cyclotriphosphazene groups in the polymer backbone which hindered packing of the polymer chains and decreased the inter-molecular force, subsequently causing a decrease in crystallinity. X-ray diffractogram indicated a diffuse reflection for PA-2 in the small-angle region at $2\theta = \sim 17°$, which may be attributable to presence of the sulfone groups compared to the curve of PSA.[29] Thus, the amorphous structure of these polyamides also reflected in their excellent solubility as can be observed in Table I.

Thermal Characterization

The thermal properties and stability of all the monomers, ordinary polyamides, and poly(cyclotriphosphazene-aryl amide)s were studied by DSC and TGA techniques, respectively, and the date reported in Table III. The glass transition temperature (T_g) values of the polyamides are in the range of 112–169°C. The polyamide PA-3 exhibited the lowest T_g value (112°C) because

Table I. Solubility Behavior[a] of the Polyamides in Various Solvents

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

[a]Solubility: (+) soluble at room temperature; (±) soluble with worming or swollen; (–) insoluble.

Table II. Inherent Viscosity (η_{inh}) and GPC Measurements of the Polyamides

Polymer code	η_{inh}[a].(dLg^{1})	M_w[b].(gmol^{-1})	PD
PPTA	3.16	-	-
PA-1	0.66	46200	1.58
PA-2	0.61	42500	1.69
PA -3	0.58	38700	1.81

[a]Inherent viscosity measured at a concentration of 0.5 g/dL in concentrated sulfuric acid, at 30 ± 0.2°C.
[b]Measured by GPC in DMSO; polystyrene was used as standard.

of the effect of the flexible EDA polymer backbone, whereas, the highest T_g value (169°C) was observed for polyamide PA-1 derived from the rigid phenyl diamine monomer TPAACP. Comparatively speaking, the ordinary polyamide PPTA has a much more higher T_g value (341°C) than poly(cyclotriphosphazene-aryl amide)s. This result is very 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 glass transition temperature.

The thermal stabilities of the monomers and poly(cyclotriphosphazene-aryl amide)s were evaluated by TGA up to 600°C in Figures 5–7. It is noteworthy that all the poly(cyclotriphosphazene-aryl amide)s exhibited complicated thermal decomposition behavior. There is a small weight loss at the beginning of TG curves of the polyamides which is due to the moisture. The presence of moisture could be attributed to one or more of the following points. (i) Physical adsorption of moisture typically exist. (ii) The effect of attractions between the hydrogen bond of amide groups; Moreover, there is a way in which the water molecules are bonded to the P—N bone of phosphazene polymers backbone (due to the long-pair electrons on backbone nitrogens).[30] (iii) It could also mean that amide groups are involved in extensive hydrogen bonding with adsorbed water molecules.

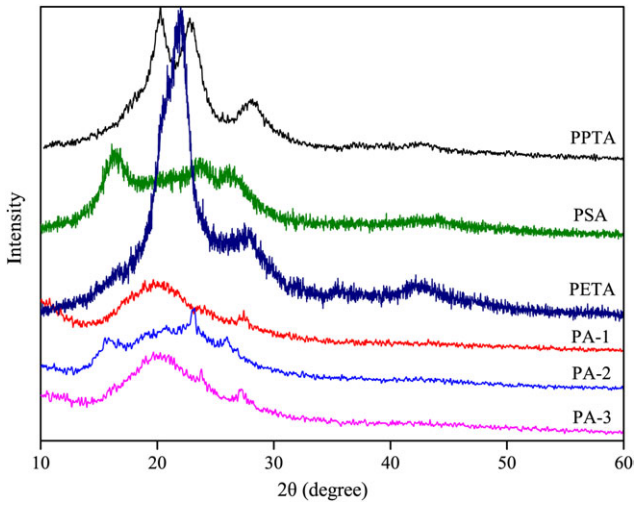


Figure 4. X-ray diffraction patterns of the polyamides. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Applied Polymer SCIENCE

Table III. Thermal Properties of the Ordinary Polyamides and Poly(cyclotriphosphazene-aryl amide)s

Code	T_0 (°C)[a]	T_{10} (°C)[b]	Char yield[c] (%)	T_g (°C)[d]
PPTA	455.3	482.8	58.68	341
PSA	430.7	434	42.12	306
PETA	283.0	306.8	30.12	184
PA-1	259.2	293.8	62.60	169
PA-2	212.3	240.7	55.23	135
PA-3	214.5	300.1	37.69	112

[a]Initial decomposition temperature recorded by TGA at a heating rate of 10°C/min in N_2.
[b]Temperature at which a 10% weight loss was recorded by TGA.
[c]Anaerobic residual weight at 600°C.
[d]Glass transition temperature measured on DSC at a heating rate of 10 C/min in N_2.

Initial decomposition temperatures of the monomers were in the range 201–245°C, of the poly(cyclotriphosphazene-aryl amide)s were in the range 214–259°C. The temperature at 10 wt % loss of the monomers and polyamides were in the range 270–300 and 240–300°C, respectively. The monomer samples present a maximum char residue on 50% at 600°C in their thermal decomposition. It can be readily attributed to the inherent thermal-stability properties of the cyclotriphosphazene and aryl rings. With the presence of cyclotriphosphazene, cross-linking and gelation occurs in the thermal decomposition. As the network structure and gelatin can inhibit the production of small molecules, the higher char yield is due to the synergistic effect between the individual units.[31] Comparing the curves in Figures 6 and 7, it emerges that the first decomposition step of the poly(cyclotriphosphazene-aryl amide)s 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 cyclotriphosphazene groups.[32,33] It also determines the lower thermal stability of the fully aromatic cyclotriphosphazene polyamides with respect to their non-phosphazene samples. At the second decomposition step, the cyclotriphosphazene rings processes ultimately yield phosphoric acid and ammonia at the presence of H_2O.[26] The obtained structure could act as an acid catalyst, accelerating the cleavage of side groups in poly (cyclotriphosphazene-aryl amide)s. Then, the polyamides react to form more stable structures. The appearance of P—O—P group is considered as cross-linking to different species, resulting in the formation of complex phosphorus structures. This is why the poly(cyclotriphosphazene-aryl amide)s have a higher char residue than ordinary polyamides, especially the PA-1 and PA-2. Therefore, it can be found that the introduction of cyclotriphosphazene groups into the main chain of polyamides could significantly decrease the thermal decomposition temperature but delaying the subsequent thermal decomposition temperature and increasing the char yield.

The solid residues of the polyamides samples after the TGA from room temperature to 600°C were analyzed by FT-IR and

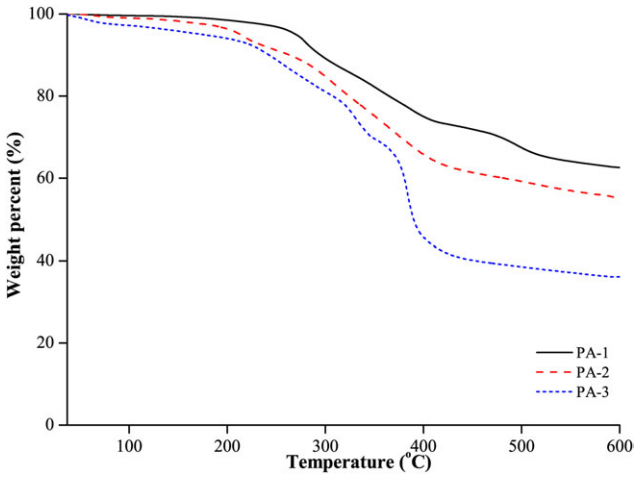


Figure 6. TGA curves of the poly(cyclotriphosphazene-aryl amide)s. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

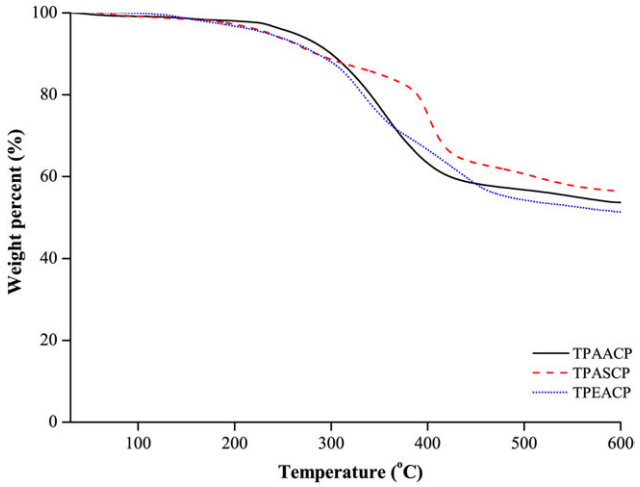


Figure 5. TGA curves of the diamine monomers TPAACP, TPASCP, and TPEACP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

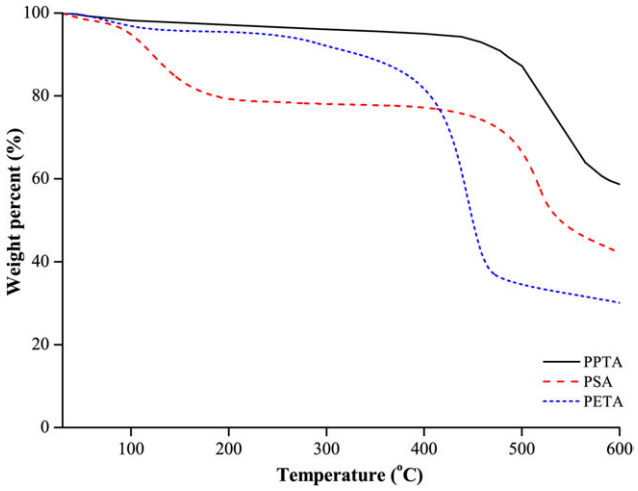


Figure 7. TGA curves of the ordinary polyamides. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

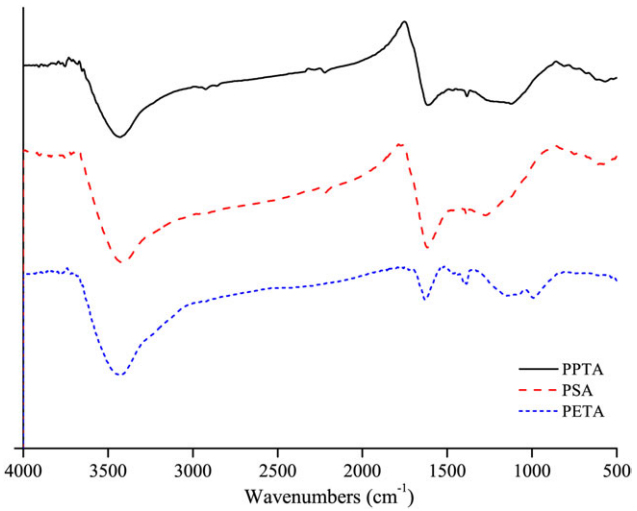


Figure 8. FT-IR spectra of the residues of the ordinary polyamides after pyrolysis. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

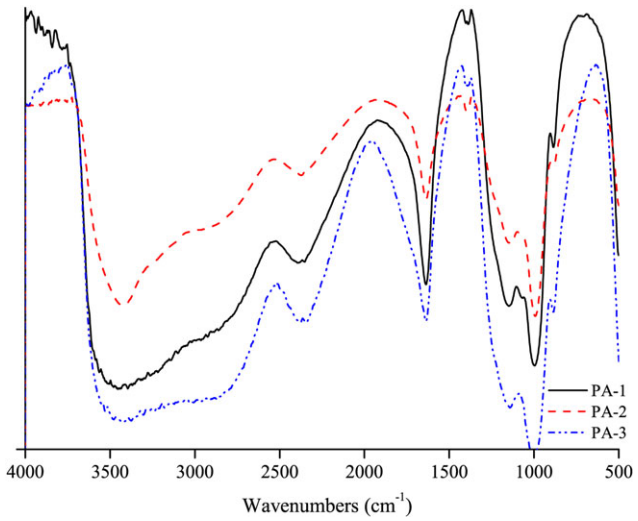


Figure 9. FT-IR spectra of the residues of the poly(cyclotriphosphazene-aryl amide)s after pyrolysis. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

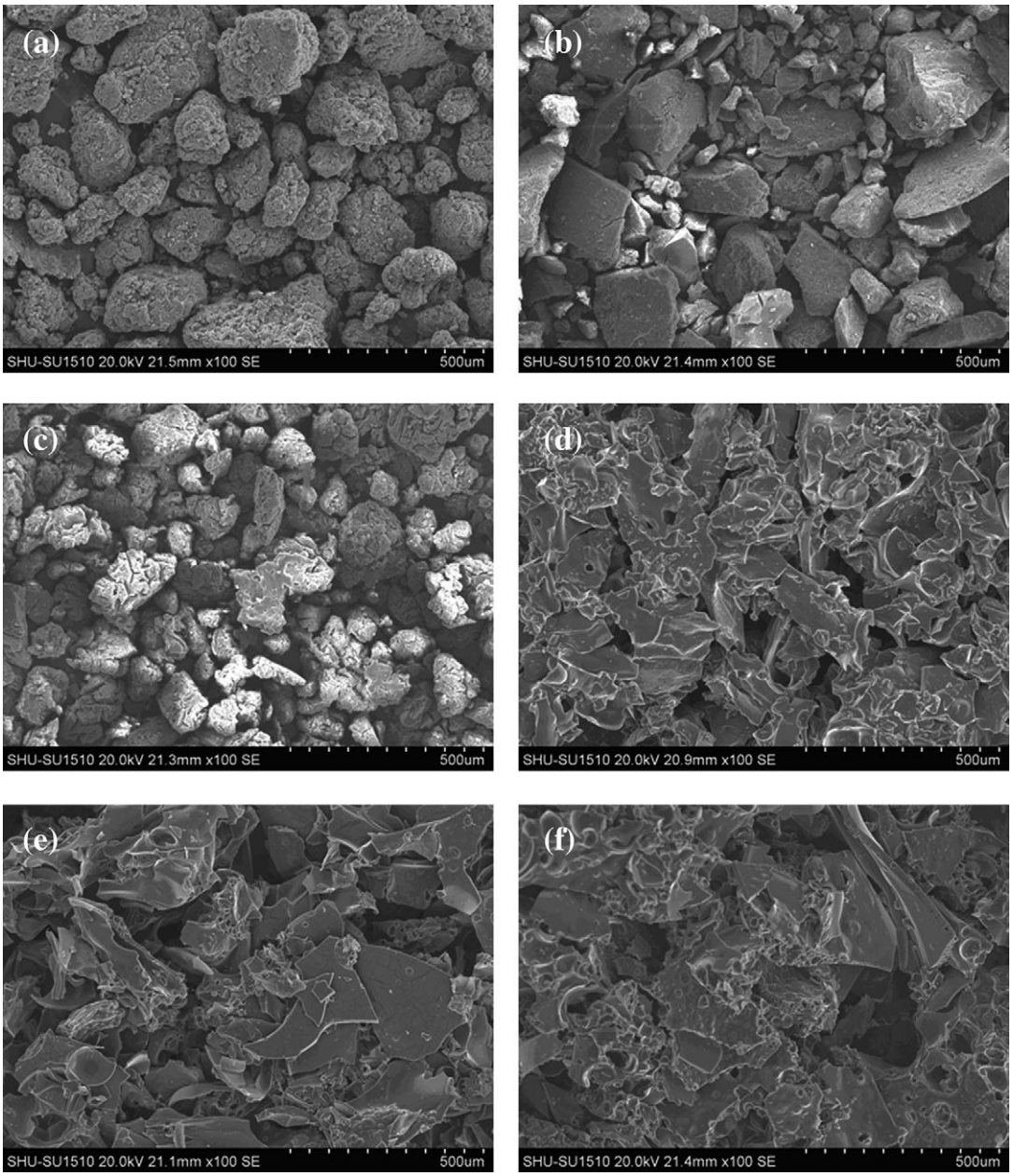


Figure 10. Morphology of the solid residues of the polyamides after pyrolysis: (a) PPTA, (b) PSA, (c) PETA, (d) PA-1, (e) PA-2, and (f) PA-3.

SEM. The FT-IR spectra of the residuals of the polyamides are shown in Figures 8 and 9, respectively. In the FT-IR spectra of poly(cyclotriphosphazene-aryl amide) samples, the absorption peak at 940 cm^{-1} due to P—O—C bone and the absorption peak at 1500 cm^{-1} due to N—H bending and C—N stretching disappear. The distinct absorption bands in the range of 3200—3500 cm^{-1} assigned to the stretching vibrations of N—H becomes broadened. The characteristic absorption peaks for P=N at about 1230 cm^{-1}, P—N at 875 cm^{-1} and for ether group at 1180 also disappear. However, a few new peaks appear at 1056 cm^{-1}, 1320 cm^{-1}, which might be ascribed to the generation of P—O—P and P=O, respectively. The obtained structure could act as an acid catalyst, accelerating the cleavage of side groups and the breaking of ether groups in poly(cyclotriphosphazene-aryl amide)s. Then, the polyamides react to form more stable cross-linked structures. The appearance of P—O—P group is considered resulting in the formation of complex phosphorus structures. This is why the thermal degradation of the poly(cyclotriphosphazene-aryl amide)s is much slower than PPTA at above 500°C. The formation of cross-linked structures also led to the increase in solid residues rate.

The morphology of the solid residues was observed by Scanning Electron Microscope (Figure 10). Comparing the pictures, we can see that the granular of the solid residues of the ordinary polyamides disappeared in the poly(cyclotriphosphazene-aryl amide)s. The surface layer of poly(cyclotriphosphazene-aryl amide)s solid residues was grumous, for the syneresis of P—O—P took place. It proves that the cyclotriphosphazene moieties produce phosphoric acid, metaphosphoric acid, or orthophosphorous acid during pyrolysis which acts in the condensed phase promoting char formation on the surface. The formation of cross-linked structures effectively suppresses the spillover of the small molecules and provides a support network for the deposition of carbon layer. That is what effectively prevents the heat transfer in the gas and condensed phases and impedes substances continuing to decompose. These results further evidence of the late thermal decomposition rates of the poly(cyclotriphosphazene-aryl amide)s are more slowly than the ordinary polyamides, and the solid residue rate of thermal decomposition are also higher.

CONCLUSIONS

(1) The synthesis of three new aromatic diamine monomers and poly(cyclotriphosphazene-aryl amide)s, containing cyclophosphazene as flexible units, were successfully accomplished in high yields starting from HCCP, diamines (PPD, DDS, and EDA), and TPC.

(2) The solubility of these polyamides in organic solvents was significantly improved with incorporation of cyclotriphosphazene groups into the polymers as backbone structure. TGA curves of the poly(cyclotriphosphazene-aryl amide)s exhibit mainly three thermal decomposition steps, and the poly(cyclotriphosphazene-p-phenylene amide) presents the highest solid residue rate 62.6% heated to 600°C. X-ray diffraction patterns indicated that the polyamides (PA-1, PA-2, PA-3) were amorphous in nature. Cyclotriphosphazene moieties not only produced phosphoric acid or metaphosphoric acid which acts in the condensed phase promoting char formation on the surface but also promoted gelation to restrain pyrolysis on degradation behavior of polymers.

These poly(cyclotriphosphazene-aryl amide)s are showing considerable promise for processable and thermal resistant materials and can be regarded as engineering plastics and the addition-type materials selected in vapor phase lubrication study.

This work was supported by the National Nature Science Foundation of China (50975167) and Research Fund for the Doctoral Program of Higher Education of China (20113108110015).

REFERENCES

1. Gupata, K. C. J. *Appl. Polym. Sci.* **1998**, *66*, 643.
2. Bottino, F. A.; Pasquale, G. D.; Scalia, L.; Pollicino, A. *Polymer* **2011**, *42*, 3323.
3. Abraham, J. K.; Srinivasan, M. *Polym. Int.* **1993**, *30*, 327.
4. Scholl, M.; Kadlecova, Z.; Kolk, H. A. *Prog. Polym. Sci.* **2009**, *34*, 24.
5. Oshinski, A. J.; Keskkula, H.; Paul, D. R. J. *Appl. Polym. Sci.* **1998**, *61*, 623.
6. Sava, I.; Iosip, M. D. *Eur. Polym. J.* **2003**, *39*, 725.
7. Tamami, B.; Yeganeh, H. *Eur. Polym. J.* **2002**, *38*, 933.
8. Gill, R.; Mazhar, M.; Siddiq, M. *Polym. Int.* **2010**, *59*, 1598.
9. Rao, Y.; Waddon, A. J.; Farris, R. J. *Polymer* **2001**, *42*, 5937.
10. Aly, K. I.; Wahdan, M. H.; Hussein, M. A. J. *Appl. Polym. Sci.* **2009**, *112*, 513.
11. Allcock, H. R.; Steely, L. B.; Singh, A. *Polym. Int.* **2006**, *55*, 621.
12. Allcock, H. R.; Cameron, C. G.; Skloss, T. W.; Meyers, T. S.; Haw, J. F. *Macromolecules* **1996**, *29*, 233.
13. Li, Z.; Huang, C.; Hua, J. L. *Macromolecules* **2004**, *37*, 371.
14. Allcock, H. R.; Coley, S. M.; Manners, I. *Macromolecules* **1991**, *24*, 2024.
15. Lee, S. B.; Song, S. C. *Polym. Int.* **2005**, *54*, 1225.
16. Rao, A. *Lubr. Eng.* **1996**, *52*, 856.
17. Graham, E. E.; Klaus, E. E. *ASLE Trans.* **1985**, *29*, 229.
18. Lauer, J. L.; Bunting, B. *Tribol. Trans.* **1988**, *34*, 338.
19. Abdelmaksoud, M.; Bende, J. W.; Krim, J. *Tribol. Lett.* **2002**, *13*, 179.
20. Jin, Y. S.; Zhou, C. H. *Wear* **1997**, *205*, 71.
21. Michael, J. S.; Samuel, J. F. *Tribol. Lett.* **2000**, *8*, 171.
22. Christopher, S. J.; Michael, J. F.; Czeslaw, K. *Wear* **1995**, *181*, 581.
23. Ren, D. X.; Andrew, J. G. *Tribol. Lett.* **1999**, *6*, 191.
24. Krystyna, B.; Andries, P. J.; Auke, M.; Johan, C. G. *Inorg. Chim. Acta* **1989**, *157*, 251.

25. Zhao, Z. P.; Guo, Q.; Li, X.; Sun, J. L.; Nie, Z. J. *Express Polym. Lett.* **2012**, *6*, 308.
26. Allcock, H. R. *Chem. Rev.* **1972**, *72*, 315.
27. Mario, G.; Roger, D. J. *Top Curr. Chem.* **2005**, *250*, 165.
28. Kute, V.; Banerjee, S. J. *Appl. Polym. Sci.* **2007**, *103*, 3025.
29. Bellomo, M. R.; Pasquale, G. D.; Rosa, A. L.; Pollicino, A.; Siracusa, G. *Polymer* **1996**, *37*, 2877.
30. Guo, Q. H.; Pintauro, P. N.; Tang, H.; Sally, O. C. J. *Membr. Sci.* **1999**, *154*, 175.
31. Bosscher, G.; Wieringa, R. H.; Jekel, A. P.; Grampel, J. C. J. *Inorg. Organomet. Polym.* **1996**, *6*, 255.
32. Mustapha, E. G.; Abderrahim, E. B. *Polym. Degrad. Stab.* **2009**, *94*, 2011.
33. Wu, H. S.; Ke, D. Y. J. *Polym. Res.* **1998**, *5*, 95.