# Synthesis and Performance of Cyclomatrix Polyphosphazene Derived from Trispiro-Cyclotriphosphazene as a Halogen-Free Nonflammable Material

Jian Sun, Zhengyang Yu, Xiaodong Wang,* and Dezhen Wu

State Key Laboratory of Organic−Inorganic Composites, School of Materials Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, China

ABSTRACT: Novel cyclomatrix polyphosphazene was designed as a halogen-free nonflammable material and was successfully synthesized through ring-opening and ring expansion of trispiro-cyclotriphosphazene as a precursor. The chemical structure and composition of the synthesized trispiro-cyclotriphosphazene were characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy, Fourier transform infrared (FTIR) spectroscopy, mass spectroscopy, and elemental analysis. The polymerization of the cyclomatrix polyphosphazene was dynamically monitored by FTIR spectroscopy. The synthesized cyclomatrix polyphosphazene exhibits a highly rigid and brittle nature as well as a high decomposition temperature over 350 °C due to its densely cyclic structure. This polyphosphazene material also shows a high limiting oxygen index and a V-0 classification in a UL-94 burning experiment. Such an excellent flame-retardant property is attributed to the construction of trispiro-cyclotriphosphazene on the backbone of the cross-linking system, which can lead to a synergistically flame-retardant effect resulting from the unique combination of phosphorus and nitrogen. With the characteristics of more safety and excellent performance, the cyclomatrix polyphosphazene designed by this work exhibits a broad prospect for electronic and microelectronic applications as a sustainable nonflammable polymeric material.

KEYWORDS: Cyclomatrix polyphosphazene, Trispiro-cyclotriphosphazene, Synthesis, Characterization, Thermal stability, Flammability characteristics
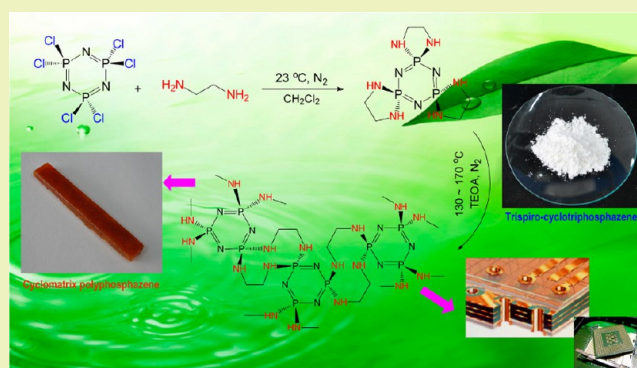
■ INTRODUCTION

The halogen-containing polymeric materials such as brominated epoxy resins have been widely exploited to meet the applications requiring flammability protection and safe reliability. Especially for the application in electronic and microelectronic areas, the brominated epoxy thermosetting systems have been particularly used for the printed circuit board manufactures and the encapsulation of semiconductor chips and devices, where a high degree of flame retardancy is absolutely mandated.[1,2] However, the use of halogenated polymeric materials has brought a lot of problems due to the generation of corrosive fumes and the emission of toxic gases during combustion.[3] Such a variety of halogen-containing polymeric materials move away from the trend of green chemistry and sustainable development. Moreover, the manufacturers also have to comply with governmental rules and laws in regard to environmental impact and sustainability. In this case, there is a strong interest in the development and utilization of more environmentally friendly polymeric materials with good flame retardancy and high performance.

In recent years, the design and synthesis of halogen-free functional polymers have received much attention for the aim of flame retardancy from academia as well as industrial communities. The scientific literature reported very diverse and efficient strategies for improving the fire resistance of polymeric materials in a halogen-free way.[4−6] There is no doubt that the synergistic effect of phosphorus and nitrogen can lead to nonflammability for polymeric materials when these two elements coextend in a molecule.[7,8] Cyclophosphazene derivatives and polyphosphazenes are inorganic polymeric materials containing alternate phosphorus and nitrogen atoms in their cyclic skeletons. Chemically linking cyclotriphosphazene with polymers can be considered as a very effective way to achieve a dramatically high efficiency in flame retardancy as well as an autoextinguishability due to the synergistic effect of the skeletal phosphorus and nitrogen elements in the phosphazene ring.[9,10] The use of cyclophosphazene derivatives as oligomers is an area of interest for the design and preparation of such phosphazene-based polymeric materials. Cyclotriphosphazenes having spirocyclic structures are particularly interesting systems.[11−13] A cyclotriphosphazene with spirocyclic or transannular side groups would have more phosphazene rings
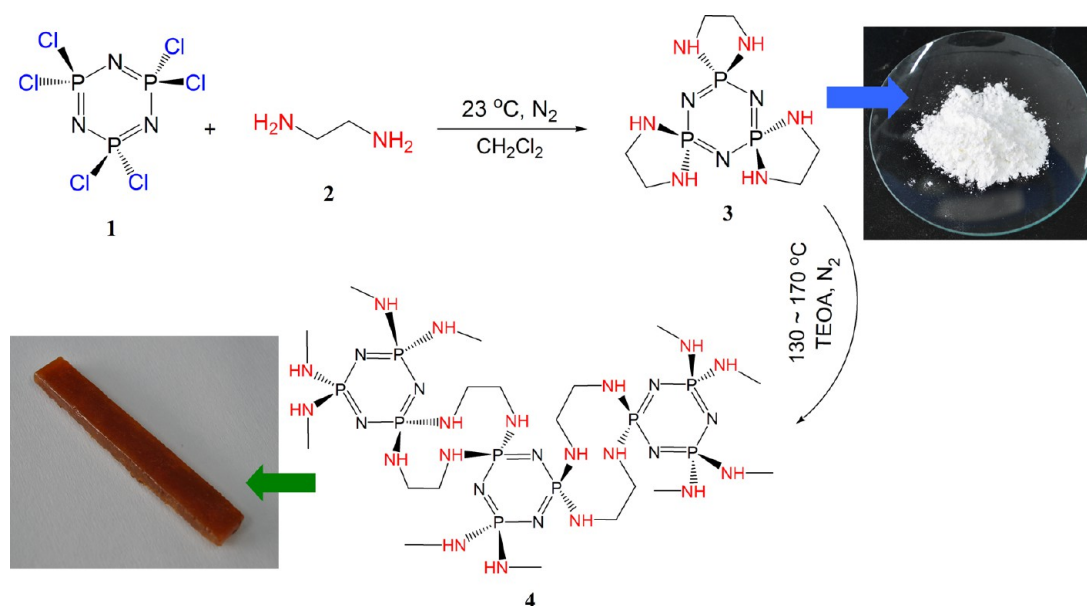
Figure 1. Scheme of synthetic route for cyclomatrix polyphosphazene.

than those with uncyclized side groups because the former just needs three substituents per cyclotriphosphazene group, but the latter requires six.[14] This may impart more efficient flame retardancy to the resulting polymers.[15]

The spiro-cyclotriphosphazenes are formed by the replacement of two geminal chlorine atoms in $N_3P_3Cl_6$ with difunctional substituents and can afford very interesting multiple reactive sites.[16,17] They have drawn considerable attention for further design of high performance and nonflammable thermosetting polymeric materials because the spiro rings provide a mechanism for polymerization. Some cyclotriphosphazenes with five-membered spiro rings, such as $N_3P_3(O_2C_6H_4)_3$, are known to form transparent cross-linked cyclomatrix polymers by opening of the spiro ring.[18−20] This polymerization takes place without a solvent and produces no byproducts. In the current work, we synthesized and characterized a trispiro-substituted cyclotriphosphazene and, furthermore, described the polymerization of a cyclomatrix phosphazene-based polymer derived from this species. The investigation of thermal stability and flame retardant performance were also performed for the resulting cyclomatrix polyphosphazene. Considering the trispiro-cyclotriphosphazene precursor is a dry white powder, the polymerization process should not produce any byproducts and can preferably be carried out without the use of solvents. The newly designed cyclomatrix polyphosphazene will not only be used as a halogen-free nonflammable material but also potentially for 3D printable applications.[21,22]

EXPERIMENTAL SECTION

Materials. Hexachlorocyclotriphosphazene (**1**) was commercially supplied by Shanghai Yagu Chemical Co., Ltd., China and was recrystallized in *n*-heptane before use. Ethylenediamine (**2**), dichloromethane (CH_2Cl_2), triethylamine (TEA), triethanolamine (TEOA), ethanol, and *n*-hexane were commercially provided by Beijing Chemical Reagent Co., Ltd., China. Some solvents like CH_2Cl_2 and *n*-hexane should be dried by Na_2SO_4 prior to use. Other chemical reagents were of chemical pure grade and were used as received without further purification.

Synthesis. *Synthesis of 1,1,3,3,5,5-Trispiro(ethylenediamino)-cyclotriphosphazene (3).* A 1000 mL three-necked round-bottomed flask was filled with nitrogen atmosphere, and then a solution of **1** (69.5 g, 0.2 mol) in CH_2Cl_2 (500 mL) was added into the flask. Sequentially, a mixture of **2** (40 mL, 0.6 mol) and TEA (167 mL, 1.2 mol) in CH_2Cl_2 (70 mL) was added dropwise into this flask during 4 h under vigorous agitation. A white solid formed immediately, and cooling of the reaction mixture was performed in an ice bath. After mechanical stirring for 72 h at room temperature, the reaction mixture was filtered and then was washed several times with hot ethanol. The primary product was purified by recrystallization in the mixture of ethanol and H_2O to achieve a white crystalline solid of **3** (48.4 g, yield 78.4%). ^1H NMR (D_2O): δ 3.15 (s, 2H). ^{13}C NMR (D_2O): δ 36.50 ppm (s, C). ^{31}P NMR (D_2O): 22.41 ppm (s, 1P). MS: m/z = 310.3 $[M + 1]^+$. Elemental analysis found: C, 22.82; H, 5.76; N, 39.84. Calculated for $C_6H_{12}N_5P_3$: C, 23.31; H, 5.87; N, 40.77. FTIR (KBr): ν (N−H): 3299 cm^{-1}, ν (C−H): 2959, and 2880 cm^{-1}, ν (P=N): 1237 cm^{-1}, (C−N): 1082 cm^{-1}, ν (P−N): 834 cm^{-1}.

Polymerization of Cyclomatrix Phosphazene-Based Polymer (4). A 1000-mL round-bottomed flask equipped with a nitrogen inlet, thermometer, and mechanical stirrer was charged with **3** (124 g, 0.4 mol) and TEOA (1.24 g, 8.3 mmol) as a catalyst. The reactant mixture was melted at 120 °C and then was vigorously agitated for 30 min to ensure the removal of volatile impurities. In succession, the reactant slurry was transferred to polyterafluoroethylene-coated copper molds, and a two-stage polymerization process was performed at 130 °C for 2 h under a nitrogen atmosphere followed by a post-polymerization at 170 °C for 3 h to achieve a variety of casting specimens for further testing. In order to avoid the stress crack, the casting specimens should be gradually cooled after the polymerization finished. Finally, the cyclomatrix polyphosphazene **4** was obtained as some of brown test bars with different shapes.

Characterization. ^1H, ^{13}C, and ^{31}P NMR spectroscopies were performed on a Bruker AV-400 400 MHz spectrometer using deuteroxide (D_2O) solution. Mass spectra were obtained using a Waters Quattro XE mass spectrometer in a mass range of 10−1000 m/z, and electrospray ionization was performed at 25 EV to produce ions. Fourier transform infrared (FTIR) spectroscopy was performed using a Bruker Tensor-27 FTIR spectrometer with 32 scans. Elemental analysis was carried out on with a Vario-EL-cube CHNS elemental analyzer (Elementar Analysensysteme GmbH, Germany). Differential scanning calorimetry (DSC) measurements were carried out on a TA Instruments Q20 differential scanning calorimeter equipped with a thermal analysis data station, operating at heating rates of 10 °C/min under a nitrogen atmosphere. Thermogravimetric analysis (TGA) was performed in both air and nitrogen atmospheres using a TA
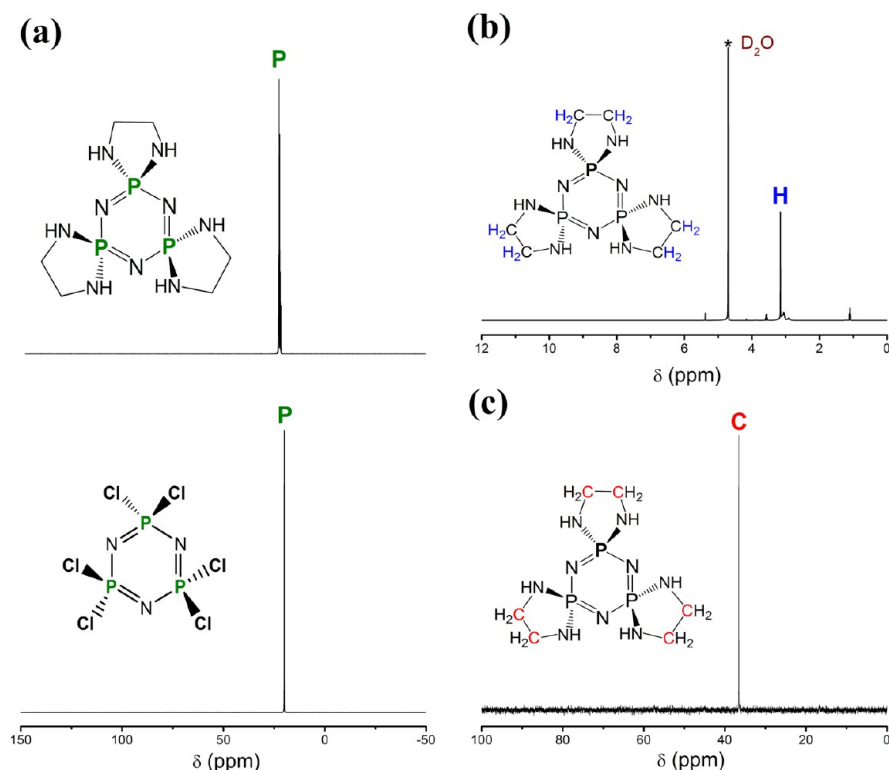
Figure 2. ^{31}P, ^{1}H, and ^{13}C NMR spectra of trispiro-cyclotriphosphazene precursor.

Instruments Q50 thermal gravimetric analyzer at a heating rate of 10 °C/min. TG–FTIR combined measurements were performed using a TGA/DSC 1 STAR^e System (Mettler Toledo Co., Ltd., Switzerland.) coupled with a Nicolet 6700 FTIR spectrometer (Thermo Scientific, Inc., U.S.A.) equipped with an IR gas cell. The limit oxygen index (LOI) was measured using a HD-2 oxygen index apparatus with a magneto-dynamic oxygen analyzer according to the ASTM D-2863 standard. The UL-94 vertical burning experiments were carried out based on the testing method proposed by Underwriter Laboratory and ASTM D-1356 standard. Scanning electron microscopy (SEM) observation was performed on a Hitachi S-4700 scanning electron microscope to investigate the morphology of char. The char sample for the SEM observation was obtained after combustion in the vertical burning experiment.

RESULTS AND DISCUSSION

Figure 1 shows the synthetic strategy of cyclomatrix polyphosphazene, which also reflects the structural features of the precursor and the final product. In order to obtain the cyclomatrix polyphosphazene, trispiro-cyclophosphazene **3** as a precursor was first synthesized through the reaction of **1** and **2**. TEA was added as the hydrochloride accelerator and also created a base medium to favor the geminal attack by primary amino groups. As a result, the two reactive functions of **2** as the nucleophile reacted geminally with the two chlorides of the same phosphorus in **1** to obtain **3**. The dilute solution of **2** should be added slowly and dropwise to the dilute solution of **1** so as to avoid the occurrence of side reactions. The ratios of **2** to **1** were more than 3:1 to force the system to complete substitution. For the same reason, the sufficient reaction time was adopted to allow the substitution reaction to complete. The reactivity of diamine may gradually decrease with an increasingly enlargement of the organic group; however, this reaction was finally completed after 72 h to give a good yield of **3** as determined by ^{31}P NMR spectroscopy.

The chemical structure of **3** was well confirmed by the ^{1}H, ^{13}C, and ^{31}P NMR spectra shown in Figure 2. The ^{31}P NMR spectrum of **3** distinctly reveals a singlet resonance signal at 22.41 ppm, which is attributed to the phosphorus atoms of cyclotriphosphazene bearing three spirocyclic groups. An intensive singlet signal is also observed on the ^{13}C NMR spectroscopy of **3**, which is assigned to the carbon atoms in diamino spirocyclic groups. It should be mentioned that the active hydrogen atoms of secondary amino groups on spirocyclic moieties are easily exchanged by deuterium atoms of D_2O. In this case, the ^{1}H NMR spectrum of **3** only shows a singlet resonance signal corresponding to the protons of methylene groups. Figure 3 shows the FTIR spectrum of **3**,
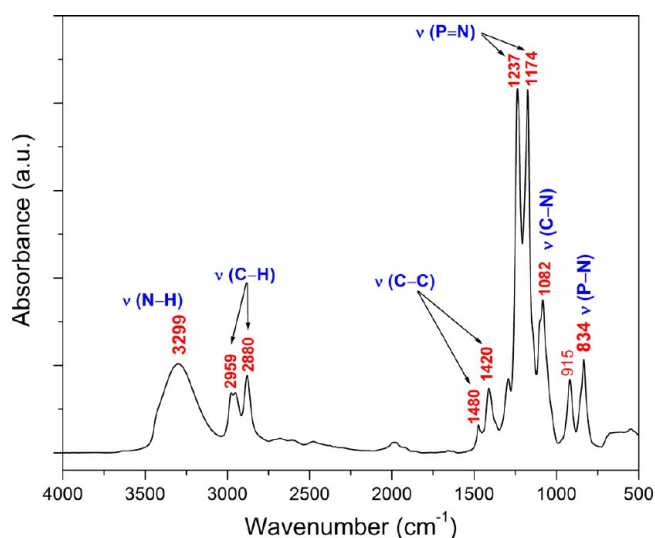

Figure 3. FTIR spectra of trispiro-cyclotriphosphazene precursor.

which also characterized the molecular structure of **3** by a series of characteristic absorption peaks indexed in the spectrum. Additionally, the mass spectrum shows $[M + 1]^+$ at m/z of 310.3 in good agreement with the structure of **3**, and the elemental analysis result is as well consistent with the calculated data from the molecular formula of **3**. The above characterization results further confirmed an achievement of the trispiro-substituted phosphazene precursor without any side products.

The behavior of the spirocyclic cyclophosphazene compounds in polymerization reactions and in clathration has been reported in the literature, and some studies indicate that some of these compounds participate in ring-expansion reactions when heated.[14,23] In the current work, a DSC−TGA heating scan was first run to investigate the thermal ring-opening and thermal stability of trispirocyclophosphazene so that an optimal polymerization condition could be determined. Figure 4 shows
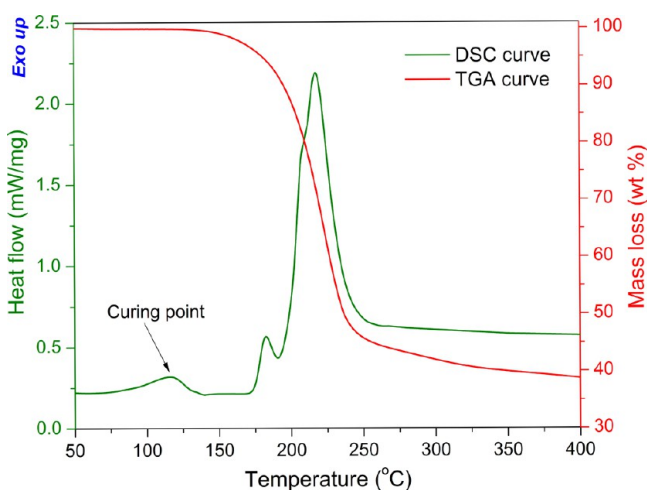

Figure 4. DSC and TGA combined thermograms of trispiro-cyclotriphosphazene.

the DSC−TGA thermograms of trispirocyclophosphazene on which three exothermic peaks could be noted. The broad peak at 130 °C may attributed to the ring-opening and ring-expansion reactions of trispirocyclophosphazene because the other two exothermic peaks appeared in the temperature region of occurrence of the mass loss as shown by the TGA thermogram and were relative to the thermal degradation of trispirocyclophosphazene. In this case, we designed a two-stage polymerization procedure for trispirocyclophosphazene, including an initial polymerization at 130 °C for 2 h followed by a post-polymerization at 170 °C for 3 h.

FTIR spectroscopy was employed to monitor the extent of reaction during the polymerization process of trispirocyclo-phosphazene because it allows us to obtain molecular level information and to quantify the concentration of the reaction groups such as amino groups. Figure 5 illustrates the FTIR spectra as a function of reaction time, in which the changes in absorbance of absorption bands at 3186, 3008, 1028, 871, and 756 cm^{-1} can be clearly distinguished during the polymerization of trispirocyclophosphazene. It has been acceptable that the involvement of amino groups to form the cyclomatrix polyphosphazene was assigned to the N−H stretching absorption bands around 3000−3300 cm^{-1}. As shown in Figure 5, such N−H stretching vibrations mainly include the free N−H band at 3186 cm^{-1} and hydrogen bonding at 3008 cm^{-1}. It should be noted that the N−H stretching peak at 3008
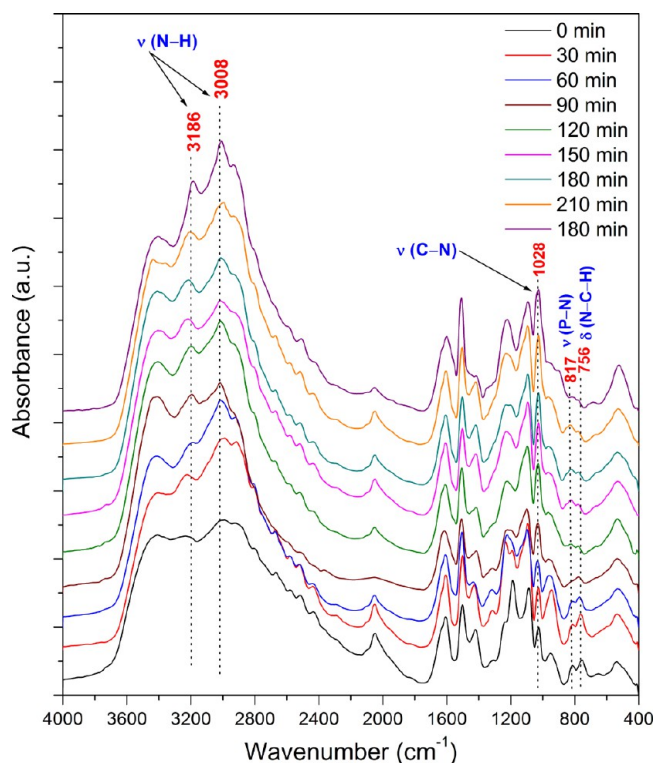

Figure 5. FTIR spectra of cyclomatrix polyphosphazene recorded at different temperatures during polymerization process.

cm^{-1} shows a significant enhancement in absorbance intensity with increasing the reaction time, indicating an increase in the amount of intermolecular hydrogen bonded groups. It is known that the polymerization of trispirocyclophosphazene takes place by opening spiro rings and following with the ring expansion to form the cross-linked cyclomatrix polyphosphazene. The reorganization of the spiro rings make the intermolecular N−H groups increase and, thus, results in an enhancement of the intermolecular hydrogen bonding interaction. Meanwhile, the spectra also show a reduction in absorbance intensity of the peaks at 871 and 756 cm^{-1} corresponding to the P−N stretching vibration and H−C−N bending, respectively, while the absorption bands of C−N stretching vibration at 1028 cm^{-1} shows a considerable increase in absorbance intensity. These changes are ascribed to the rearrangement of the spiro rings and the formation of new ring skeletons. On the basis of the above results, it is deduced that the opening and expansion of the spiro rings are involved in the polymerization of trispirocyclophosphazene. Moreover, the evidence of polymerization and the information about the chemical structure of the cyclomatrix polyphosphazene could be obtained from mass spectroscopy. The mass spectrum presents successive major signals with an interval corresponding to $[M + 1]^+$ at m/z of 928.9, 1238.2, and 1547.5, indicating that the cyclomatrix polyphosphazene consists of trimers, tetramers, and pentamers of trispiro-cyclophosphazene, respectively, with one proton attached in the process of ionization. In addition, the signals corresponding to the molecular weights at higher m/z were also observed. This is consistent with the supposal that the cyclomatrix polyphosphazene was derived from the growth of trispirocyclophosphazene by ring-opening and ring expansion of the spiro rings. Nevertheless, small amount of monomers and dimers were also detected in the mass spectrum. This

implies that the ring-opening and ring expansion of the spiro rings are influenced by the steric hindrance, and thus, it is impossible to obtain 100% conversion from trispirocyclophosphazene to the cyclomatrix polymers.

The obtained cyclomatrix polyphosphazene presents a brown solid with different molded sharps. A mechanical investigation shows that the cyclomatrix polyphosphazene has tensile and flexible strength of 62.54 and 107.92 MPa, respectively. Meanwhile, the cyclomatrix polyphosphazene also exhibits high tensile and flexible moduli of 6526 and 11700 MPa, respectively. However, the notched Izod impact strength of this cross-linked polymer is as low as 34.62 J/m. The mechanical evaluation indicates the cyclomatrix polyphosphazene has high rigidity but some brittle nature due to its densely cyclic structure, which also causes a no glass transition region appearing on the DSC thermogram. These features suggest that the fabrication of cyclomatrix polyphosphazene composites with inorganic fabrics like glass or carbon fabric can achieve prominent mechanical performance and thermal resistance.

The thermal stability is considered as the essential performance to be intensively investigated because it establishes a service environment for the cyclomatrix polyphosphazene and its composites. Figure 6 demonstrates the TGA and DTG
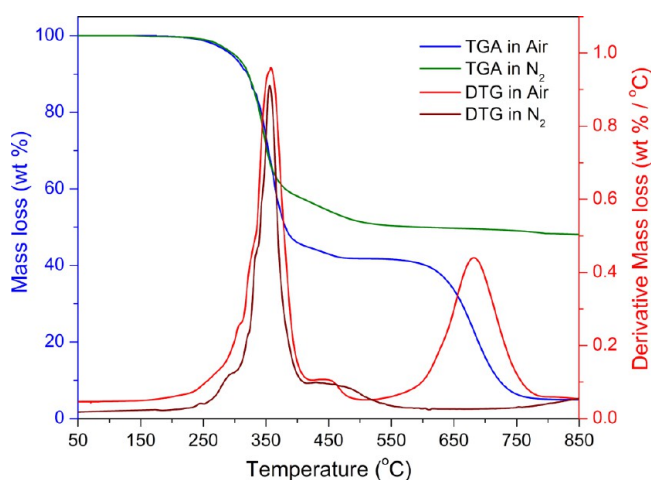

Figure 6. TGA and DTG thermograms of cyclomatrix polyphosphazene.

thermograms of the cyclomatrix polyphosphazene measured in air as well as in nitrogen atmospheres. As demonstrated in Figure 6, the TGA trace presents a typical two-step degradation in air when showing one-stage decomposition in nitrogen. The temperature in regard to 3 wt % weight loss is considered as a onset decomposition temperature (T_{onset}) as well as an index of thermal stability. The cyclomatrix polyphosphazene is found to present a T_{onset} in the range of 280−290 °C both in air and in nitrogen. It is noteworthy that the main degradation started at a maximum decomposition temperature (T_{max}) beyond 350 °C, at which the weight loss occurred at a maximum rate, and furthermore, these two characteristic decomposition temperatures show few differences in air and nitrogen. This indicated a good thermal stability in nature for the cyclomatrix polyphosphazene designed by this work. In addition, the two-step degradation behavior indicated the further thermooxidative decomposition of cyclomatrix polyphosphazene caused by the oxygen in air. This may result in the generation of the huge

amount of gaseous oxides as pyrolysis products and remaining little char.

To understand the pyrolysis mechanisms, the TG−FTIR spectroscopy was performed to determine the composition of the evolved gases during the dynamic pyrolysis process of the cyclomatrix polyphosphazene in air. Figure 7 illustrates the
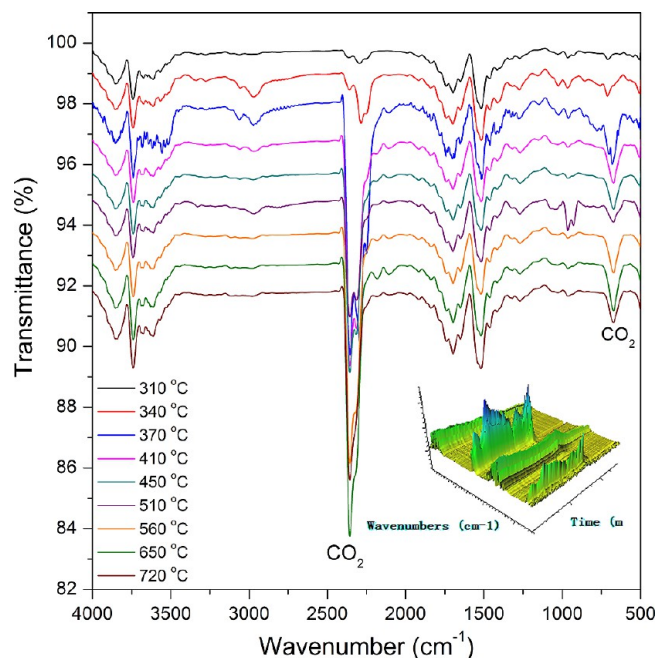

Figure 7. FTIR spectra of cyclomatrix polyphosphazene recorded at different temperatures from TG-FTIR measurement.

FTIR spectra of evolved gases recorded at different times during the TGA experiment. A good evolution of gases over time was obtained as a correlation with the thermal decomposition processes. It is highly noted that the characteristic bands at 2240−2400 and 669 cm^{-1} evidently indicate the formation of CO_2 in the whole pyrolysis process. The release of CO_2 is mainly attributed to the scission and decomposition of expanded spiro ring moieties, which exhibits the most intense absorption peak during the whole pyrolysis process. A series of absorption bands appearing at 3400−3800 cm^{-1} were attributed to the N−H and O−H stretching vibrations, which also implies that the gases and supplementary fragments like water were released due to the pyrolysis of spiro ring moieties as well as cyclophosphazene ones. The characteristic band at 1520 cm^{-1} confirms the release of amine-containing gases, while absorption peak at 1698 cm^{-1} identifies the reformation of −C═O groups during the thermooxidative decomposition process. In the FTIR spectra registered at 340 and 370 °C, the presence of absorption peaks around 2963 and 3065 cm^{-1} suitable for the −CH$_3$ and ═CH$_2$ stretching vibrations indicates an reorganization of the methine groups in spiro rings at these temperature levels. Moreover, the bands at around 960 cm^{-1} were attributed to the formation of phosphate derivatives derived from the decomposition of cyclophosphazene moieties.

Flammability characteristics of the cyclomatrix polyphosphazene were evaluated by the LOI test and the UL-94 vertical burning experiment. The test result revealed that the cyclomatrix polyphosphazene had a high LOI of 37.4 vol %, implying that this material should almost be nonflammable in

air. The UL-94 vertical burning experiment determined a V-0 classification for the cyclomatrix polyphosphazene. During the vertical burning experiment, five test bars were observed to quench within 4−6 s when stopping ignition, indicating an auto-extinguishable feature. Moreover, there are no flaming drips observed in vertical burring test, indicating a good structural stability of this material and confirming the formation of char as a protective layer sticking to the surface of burning item. The residual char formed during combustion can give some important information regarding the inherent flammability characteristics of a material and can also reflect the flame-retardant mechanisms to some extent. Figure 8 illustrates the
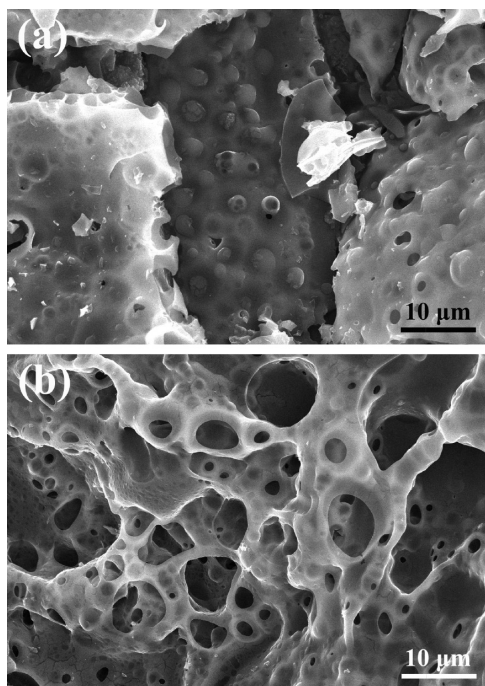

Figure 8. SEM micrographs of (a) outside aspect and (b) inside structure of the residual chars obtained from the vertical burning experiment for cyclomatrix polyphosphazene.

SEM micrographs of the outside aspect and the inside structure of the char obtained from UL-94 experiments. The outside aspect of the char is observed to present a very gassy surface with seldom pores breaking through, while the inside shows a multipurpose structure. This indicates a typical morphology associated with the intumescent char formation. It is well known that the charring structure is one of the most important factors determining flame retardancy. On the basis of the SEM observation, the char layer looks rigid and compact, and there are lots of integrated closed honeycomb pores inside. This structural feature could impart a temperature grad to char layer during combustion and, thus, protects the inside matrix.[24] Such a protective char layer can serve as a barrier against heat and oxygen diffusion to when forming on the surface of burning item, and thus, the cyclomatrix polyphosphazene achieves a remarkable improvement in flame retardancy.[25]

Figure 9 shows the FTIR spectrum of the residual char, which presented some information about the chemical structure of residual chars. The spectrum seems to present a pattern of highly phosphoro-carbonaceous compounds. As shown in Figure 9, a broad peak at 3400−3200 cm^{-1} can be attributed to the N−H and O−H stretching vibrations of thermal
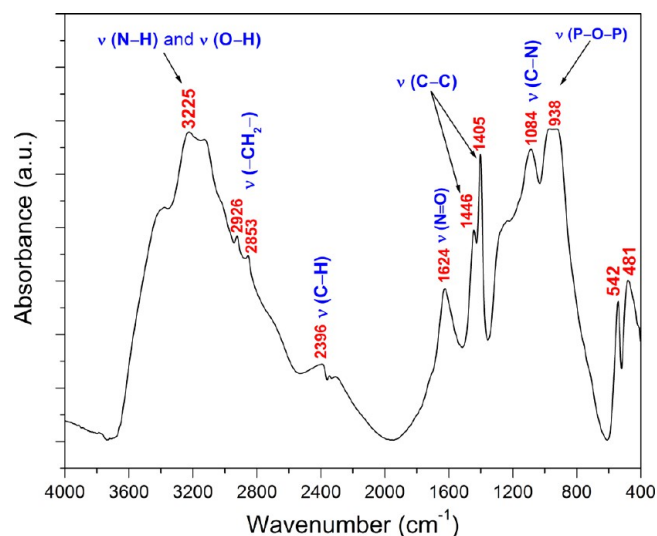

Figure 9. FTIR spectrum of the residual chars collected from the vertical burning experiment for cyclomatrix polyphosphazene.

decomposition products of cyclomatrix polyphosphazene such as phosphoric acid and amino compounds. An intensive absorption band could be observed at 938 cm^{-1} as a result of P−O−P stretching vibration, indicating that the char contains abundant phosphorus oxides. Two weak characteristic bands at 2926 and 2396 cm^{-1} are attributed to the organic moieties of the char. This may be ascribed to the pyrolysis products strongly absorbed by the carbonized phosphorus-rich char. Additionally, the absorption peaks at 1446 and 1405 cm^{-1} are due to the C−C stretching vibration of the carbonized products derived from the pyrolysis of cyclomatrix polyphosphazene. It is deduced from the FTIR spectrum that the residual char is composed of highly carbonized networks, and the major composition of char includes cross-linked phosphorocarbonaceous and phosphorooxidative substances.

It is believable that the nonflammability of cyclomatrix polyphosphazene is derived from the inherent flame retardancy resulting from the synergistic effect of phosphorus−nitrogen combination upon spiro-cyclotriphosphazene moieties. As the backbone of cyclomatrix polyphosphazene, these spiro-cyclotriphosphazene moieties act in both condensed and gaseous phases during combustion to enhance the flame retardancy of cyclomatrix polyphosphazene.[26−28] The phosphorus-rich char is easily formed due to the thermooxidative reaction of spiro-cyclotriphosphazene moieties and then acts as an insulation layer of heat transfer to shield the materials from oxygen and heat during combustion as well as to prohibit the diffusion of gaseous products to fire. Meanwhile, the pyrolysis of spiro-cyclotriphosphazene moieties also generates phosphoric or polyphosphoric acid, which could enhance the char formation in condensed phase. Furthermore, the thermal degradation of cyclotriphosphazene moieties releases some gaseous products such as CO_2, NH_3, and N_2. These nonflammable gases could cool the hot surface of burning items and dilute the oxygen in air. As a result, the cyclomatrix polyphosphazene achieved an autoextinguishability.

In summary, the design of the particular cyclomatrix structure based on spiro-cyclotriphosphazene imparts several advantages to the resulting polymers with not only excellent flame retardancy but also high performance. First, compared to general cyclotriphosphazene-containing polymers, the amino-

spirocyclic cyclotriphosphazene moiety comprises much higher weight percent of inert nitrogen, resulting in a better flame-retardant effect on the resulting polymers.[29] Second, the cyclotriphosphazene structure has a good thermal stability and, thus, can make the cyclotriphosphazene-based cross-linking system more thermally stable. A ring-opening reaction to yield the cyclomatrix polyphosphazene or a further ring expansion to higher cyclic species can result in a highly cross-linking system. Such a ring-expansion/polymerization reaction can impart a much better thermal stability as well as a higher fire-resistance to the resulting polymers. Lastly, the cyclomatrix polyphosphazene was obtained directly from the ring-expansion reaction of trispiro-cyclotriphosphazene without using any solvents and leaving any byproducts. Such a facile process is preferably used for the new fabrication technologies of materials like 3D-printable applications.

CONCLUSIONS

Novel cyclomatrix polyphosphazene was synthesized through ring-opening and ring expansion of trispiro-cyclotriphosphazene. The chemical structure and composition of trispiro-cyclotriphosphazene as a precursor were confirmed by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy, elemental analysis, mass spectroscopy, and FTIR spectroscopy. The dynamical FTIR spectroscopy indicated that the polymerization of cyclomatrix polyphosphazene was well performed. The densely cyclic structure of cyclomatrix polyphosphazene causes its highly rigid and brittle nature, and meanwhile, this material shows good thermal stability and excellent flame-retardant performance. The construction of trispiro-cyclotriphosphazene on the backbone of a cross-linking system can lead to nonflammability of the resulting polymer due to the synergistically flame-retardant effect resulting from the unique combination of phosphorus and nitrogen. The thermooxidative decomposition of phosphazene rings enhances the char formation on the surface of burning items by acting in both condensed and gaseous phases. Such a phosphorus-rich char acts as an insulation layer of heat transfer to shield the materials from oxygen and heat during combustion as well as to prohibit the diffusion of gaseous products to fire. With the characteristics of more safety and excellent performance, cyclomatrix polyphosphazene designed by this work could be considered as a sustainable nonflammable polymer for electronic and microelectronic applications.

AUTHOR INFORMATION

Corresponding Author
*Tel: +86 10 6441 0145. Fax: +86 10 6442 1693. E-mail: wangxdfox@aliyun.com.

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

REFERENCES

(1) Pecht, M.; Deng, Y. Electronic device encapsulation using red phosphorus flame retardants. *Microelectron. Reliab.* **2006**, *46*, 53−62.

(2) Chen-Yang, Y. W.; Lee, H. F. A flame-retardant phosphate and cyclotriphosphazene-containing epoxy resin: synthesis and properties. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 972−981.

(3) Sun, D.; Yao, Y. Synthesis of three novel phosphorus-containing flame retardants and their application in epoxy resins. *Polym. Degrad. Stab.* **2011**, *96*, 1720−1724.

(4) Wang, X.; Song, Lei.; Xing, W.-Y.; Lu, H.-D.; Hu, Y. An effective flame retardant for epoxy resins based on poly (DOPO substituted dihydroxyl phenyl pentaerythritol diphosphonate). *Mater. Chem. Phys.* **2011**, *125*, 536−541.

(5) Allauddin, S.; Narayan, R.; Raju, K. V. S. N. Synthesis and properties of alkoxysilane castor oil and their polyurethane/urea−silica hybrid coating films. *ACS Sustainable Chem. Eng.* **2013**, *1* (8), 910−918.

(6) Gao, F.; Tong, L.; Fang, Z. Effect of a novel phosphorous−nitrogen containing intumescent flame retardant on the fire retardancy and the thermal behavior of poly(butylene terephthalate). *Polym. Degrad. Stab.* **2006**, *91*, 1295−1299.

(7) Shieh, J.; Wang, C. Effect of the organophosphate structure on the physical and flame-retardant properties of an epoxy resin. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 369−378.

(8) Gao, L.; Wang, D.; Wang, Y.; Wang, J.; Yang, B. A flame-retardant epoxy resin based on a reactive phosphorus-containing monomer of DODPP and its thermal and flame-retardant properties. *Polym. Degrad. Stab.* **2008**, *93*, 1308−1315.

(9) Allcock, H. R. A perspective of polyphosphazene research. *J. Inorg. Organomet. Polym. Mater.* **2006**, *16*, 277−294.

(10) Allcock, H. R. New approaches to hybrid polymers that contain phosphazene rings. *J. Inorg. Organomet. Polym. Mater.* **2007**, *17*, 349−360.

(11) Krishunamushy, S. S.; Ramachandran, K.; Murthy, A. R.; Shaw, R. A.; Woods, M. Studies of phosphazenes. Part 10. Spirocyclic derivatives of cyclotriphosphazatrienes. *J. Chem. Soc., Dalton Trans.* **1980**, 840−844.

(12) Kumaraswamy, S.; Vijjulatha, M.; Muthiah, C.; Kumara Swamy, K. C.; Engelhardt, U. Synthesis, reactivity and structures of spirocyclic products derived from octachlorocyclotetraphosphazene: comparison with spirocyclic cyclotriphosphazenes and linear phosphazenes. *J. Chem. Soc., Dalton Trans.* **1999**, 891−900.

(13) Coles, S. J.; Davies, D. B.; Eaton, R. J.; Hursthouse, M. B.; Kılıç, A.; Shaw, R. A.; Uslu, A. The structural and stereogenic properties of pentaerythritoxybridged cyclotriphosphazene derivatives: Spiro-spiro, spiro-ansa and ansa-ansa isomers. *Dalton Trans.* **2006**, 1302−1312.

(14) Fushimi, T.; Allcock, H. R. Synthesis and optical properties of sulfur-containing monomers and cyclomatrix polyphosphazenes. *Dalton Trans.* **2010**, *39*, 5349−5355.

(15) Zhang, J.; Zheng, H.; Bi, Y. High energy density compounds from cyclophosphazene. II. The preparation, structural characterization, and theoretical studies of 1,1-spiro(ethylenediamino)-3,3,5,5-tetrachlorocyclotriphosphazene and its nitration product. *Struct. Chem.* **2008**, *19*, 297−305.

(16) Bhuvan Kumar, N. N.; Kumara Swamy, K. C. Single diastereomers of unsymmetrical tris-spirocyclic cyclotriphosphazenes based on 1,10-bi-2-naphthol: Synthesis and structures. *Chirality* **2008**, *20*, 781−789.

(17) Allcock, H. R.; Diefenbach, U.; Pucher, S. R. New mono- and trispirocyclotriphosphazenes from the reactions of $(NPCl_2)_3$ with aromatic ortho dinucleophiles. *Inorg. Chem.* **1994**, *33*, 3091−3095.

(18) Allcock, H. R. Phosphonitrilic compounds. II. Reactions of phosphonitrilic chlorides with cathechol and triethylamine. *J. Am. Chem. Soc.* **1964**, *86*, 2591−2595.

(19) Allcock, H. R.; Kugel, R. L. Phosphonitrilic compounds. V. Cyclized products from the reactions of hexachlorocyclotriphosphazene (phosphonitrilic chloride trimer) with aromatic dihydroxy, dithiol, and diamino compounds. *Inorg. Chem.* **1966**, *5*, 1016−1020.

(20) Allcock, H. R.; Brennan, D. J.; Allen, R. W. Reactions between hexachlorocyclotriphosphazene and hexamethylcyclotrisiloxane: polymerization, ring cleavage, and cross-linking. *Macromolecules* **1985**, *18*, 139−144.

(21) Campbell, T. A.; Ivanova, O. S. 3D printing of multifunctional nanocomposites. *Nano Today* **2013**, *8*, 119−120.

(22) Gbureck, U.; Hölzel, T.; Klammert, U.; Würzler, K.; Müller, F. A.; Barrale, J. E. Resorbable dicalcium phosphate bone substitutes prepared by 3D powder printing. *Adv. Funct. Mater.* **2007**, *17*, 3940−3945.

(23) Allcock, H. R. Recent developments in polyphosphazene materials science. *Curr. Opin. Solid State Mater. Sci.* **2006**, *10*, 231−240.

(24) Liu, J.; Wang, X.; Wu, D. Synthesis, characterization and curing properties of a novel cyclolinear phosphazene-based epoxy resin for halogen-free flame retardancy and high performance. *RSC Adv.* **2012**, *2*, 5789−5799.

(25) Bai, Y.; Wang, X.; Wu, D. Novel cyclolinear cyclotriphospha-zene-linked epoxy resin for halogen-free fire resistance: synthesis, characterization, and flammability characteristics. *Ind. Eng. Chem. Res.* **2012**, *51*, 15064−15074.

(26) Nie, S.; Hu, Y.; Song, L.; He, Q.; Yang, D.; Chen, H. Synergistic effect between a char forming agent (CFA) and microencapsulated ammonium polyphosphate on the thermal and flame retardant properties of polypropylene. *Polym. Adv. Technol.* **2008**, *19*, 1077−1083.

(27) Levchik, S. V.; Weil, E. D. A review of recent progress in phosphorus-based flame retardants. *J. Fire Sci.* **2006**, *24*, 345−364.

(28) Allcock, H. R.; Taylor, J. P. Phosphorylation of phosphazenes and its effects on thermal properties and fire retardant behavior. *Polym. Eng. Sci.* **2000**, *40*, 1177−1189.

(29) Sun, J.; Wang, X.; Wu, D. Novel spirocyclic phosphazene-based epoxy resin for halogen-free fire resistance: synthesis, curing behaviors, and flammability Characteristics. *Appl. Mater. Interfaces* **2012**, *4*, 4047−4061.

238

dx.doi.org/10.1021/sc400283d | *ACS Sustainable Chem. Eng.* 2014, 2, 231−238