

# One-Pot Synthesis of Cyclomatrix-Type Polyphosphazene Microspheres and Their High Thermal Stability

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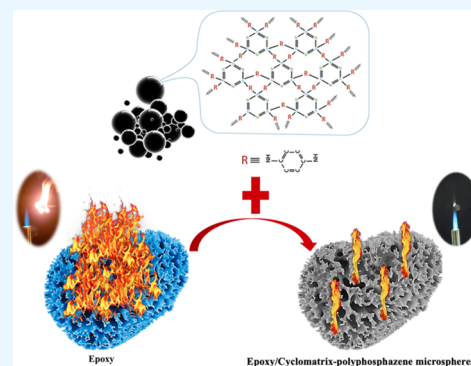


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**ABSTRACT:** Highly cross-linked inorganic and organic hybrid cyclomatrix-polyphosphazenes microspheres (C-PPZs) have been successfully synthesized by a one-pot polymerization technique between hexachlorocyclotriphosphazene and *p*-phenylenediamine in the presence of triethylamine (TEA), and they were used for enhancing the flame retardancy of epoxy resins (EPs). A thermoset EP was prepared by incorporating different percentages (2, 5, and 10%) of C-PPZs into diglycidyl ether of bisphenol A (DGEBA). The results reveal that the size and morphology of the microspheres can be tuned by varying the synthesis temperature. The average size of C-PPZs gradually increased from 3.1, 4.9, to 7.8  $\mu\text{m}$  as the temperature was increased from 100, 120, to 200  $^{\circ}\text{C}$ , respectively. The thermogravimetric analysis showed that the C-PPZ microspheres have good thermal stability up to 900  $^{\circ}\text{C}$  with about  $\sim 10$  wt % mass loss for C-PPZs formed at 200  $^{\circ}\text{C}$  compared to  $\sim 30$  wt % mass loss for those obtained at 100 and 120  $^{\circ}\text{C}$ . The 10% loss at 900  $^{\circ}\text{C}$  is much lower than the previous research concerning the thermal stability of cyclophosphazene, in which more weight losses were observed at lower temperatures. The resulting C-PPZ microspheres were characterized by spectroscopic and imaging techniques including Fourier transform infrared spectroscopy, Raman spectroscopy, X-ray diffraction, scanning electron microscopy, energy-dispersive X-ray spectroscopy, elemental mapping, and X-ray photoelectron spectroscopy.



## INTRODUCTION

Cyclomatrix-polyphosphazenes have attracted considerable interest in recent years.<sup>1,2</sup> Since their discovery, they have emerged as new inorganic materials for various applications. They have exceptional attributes in various fields of interdisciplinary science, such as metallo-organic and biomedical polymers, solid polyelectrolytes, and flame-retardant materials.<sup>3</sup> Their main starting material, hexachlorocyclotriphosphazene (HCCP), is an essential material for synthesizing a variety of functionalized organocyclotriphosphazenes,<sup>4,5</sup> as well as a versatile network of functionalized amorphous porous organic polymers (POPs)<sup>6</sup> and covalent organic frameworks (COFs).<sup>7,8</sup> HCCP has also been used in the preparation of functionalized dendrimers, which found various applications as catalysts and biosensors.<sup>9</sup>

It is known that the most efficient flame-retardant additives are the halogen-containing compounds, their use is limited and restricted because the combustion reaction products of halogenated additives exhibit higher toxicity. Another disadvantage is their harmful characteristics to the ozone layer of the atmosphere, which has a negative impact on climate change. The phosphazene unit could be a good alternative to use as a starting point for the synthesis of halogen-free phosphazenes derivatives aiming to introduce flame-retardant characteristics to organic polymers. Cyclomatrix-polyphosphazenes, one of the important classes of materials of phosphazene chemistry, whether in the crystalline or

amorphous phase, have shown increased thermal stability and flame-retardant characteristics.<sup>10–12</sup> Thermal stability of these polymers mainly depends on the linkages between phosphazene and other organic moieties, as well as the structure and particle size of the cyclomatrix itself.<sup>13</sup> Studies have shown that the coexistence of nitrogen (N) and phosphorus (P) compounds in an organic polymer can undoubtedly lead to the nonflammability and high thermal stability of the polymer.<sup>14,15</sup> More recent studies have shown that the inclusion of phosphorus and sulfur atoms as linkages to HCCP further increased their thermal stability.<sup>16,17</sup> For example, Xu et al. reported the synthesis of phosphorus–nitrogen–sulfur-containing microspheres using HCCP and sulfonyldiphenol as starting materials. The product obtained showed very good thermal stability, showing about 55% weight loss at the end of 800  $^{\circ}\text{C}$ .<sup>17</sup> Li and Ma et al. designed a microporous phosphazene-based covalent organic framework by reacting HCCP with *p*-phenylenediamine. The product had high thermal stability, with about 45% weight loss at 800  $^{\circ}\text{C}$ .<sup>7</sup>

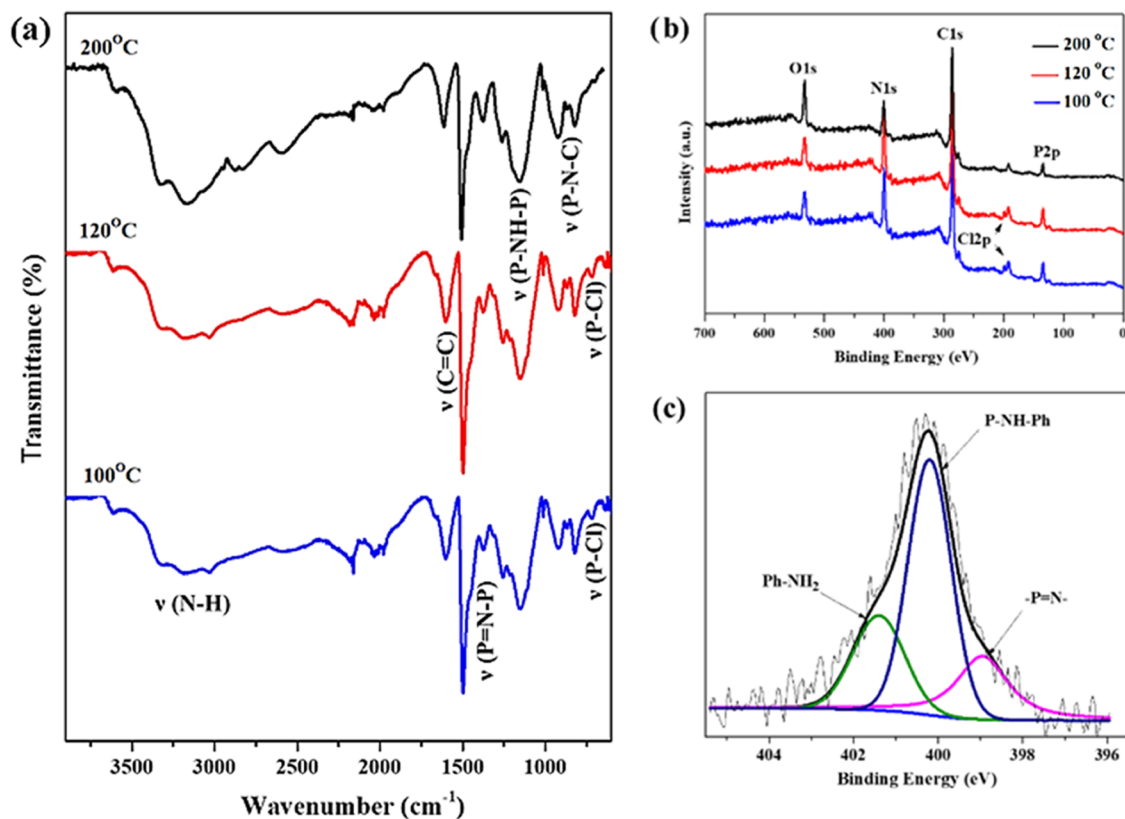
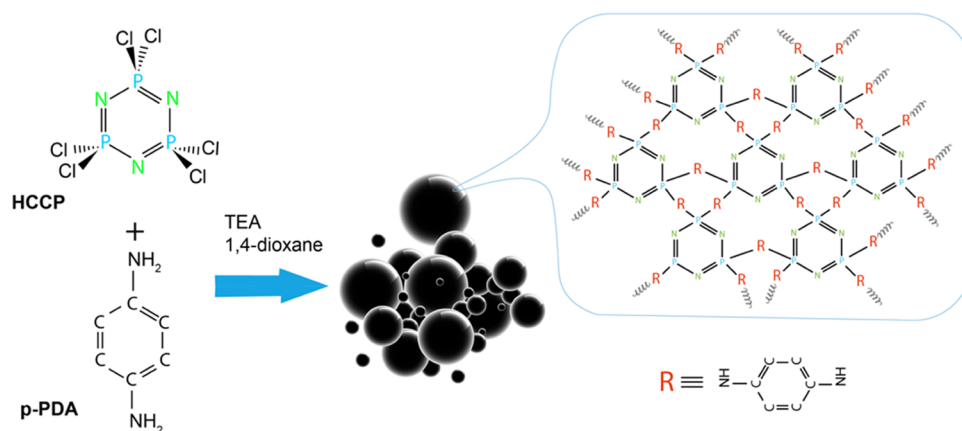
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## Scheme 1. Synthetic Route of C-PPZ Microspheres



**Figure 1.** (a) FTIR spectra of C-PPZ microspheres obtained at different temperatures. (b) XPS survey spectra for C-PPZ microspheres. (c) High-resolution spectrum of N 1s.

Huang et al. showed that the inclusion of oxygen linkers, such as Phloroglucinol, in the cyclotriphosphazene polymer drastically increased thermal stability up to less than 30% weight loss at 800 °C.<sup>18</sup> Although the 800 °C threshold temperature attained by numerous cyclotriphosphazene frameworks is considered good, preparation of such a class of polymers reaching such a temperature with minimum weight loss remains a quest. A water-triggered polycondensation reaction of HCCP with amino acid esters reported by Lu et al. produced a mixture of cyclotriphosphazene nanoparticles bearing unsubstituted phosphorus–chlorine (P–Cl) moieties as proved by <sup>31</sup>P solid-state NMR studies.<sup>19</sup> Although SEM data showed aggregations of perfectly spherical particles with different diameters, complete polycondensation where the Cl atoms

were all substituted could not be obtained, and the thermal stability of the cyclotriphosphazene showed about 55% weight loss at only 600 °C.<sup>17</sup> In an attempt to further study the temperature effect on the structure and geometry of amorphous cyclotriphosphazene and further improve their thermal stability, we report a simple one-pot hydrothermal polymerization method for preparing cross-linked polyphosphazene microspheres with controllable particle size by tuning the synthesis temperature, using HCCP and *p*-phenylenediamine (*p*-PDA) as comonomers. We found that the temperature plays a determinant role to reach complete –NH<sub>2</sub>–Cl substitution. The resulting product exhibits a very high thermal stability, which could be used as a fire retardant and could find other electrochemical applications. To the best of our knowledge, the

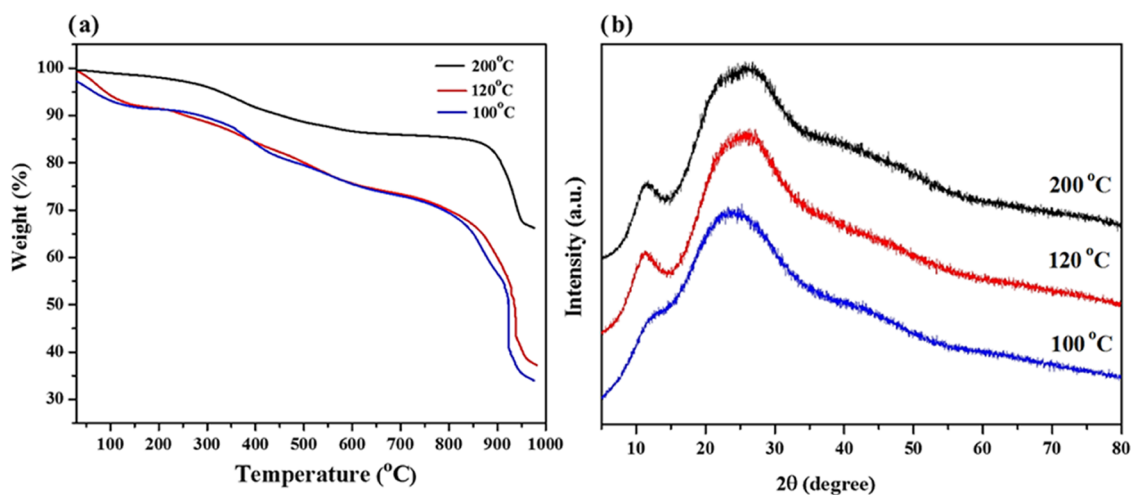


Figure 2. (a) TGA curves of C-PPZ microspheres under nitrogen. (b) X-ray diffractogram patterns of C-PPZ microspheres.

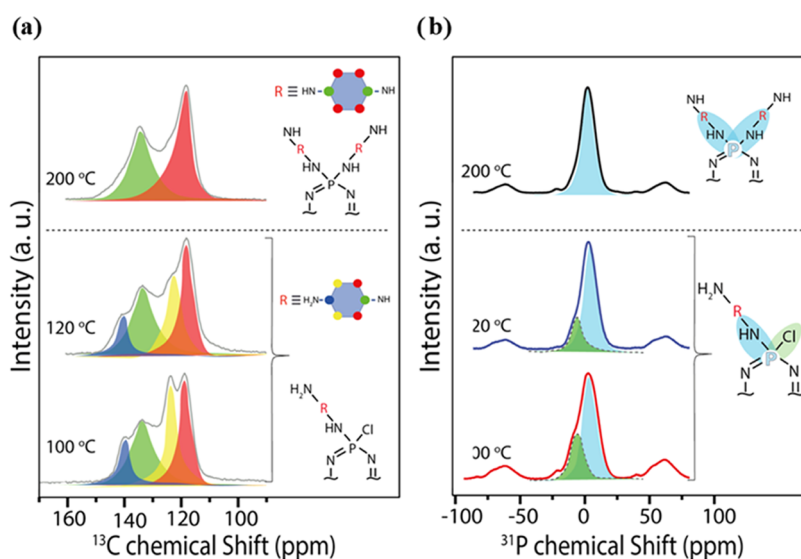


Figure 3. (a) Solid-state  $^{13}\text{C}$  CP/MAS NMR spectrum of C-PPZ microspheres. (b) Solid-state  $^{31}\text{P}$  CP/MAS NMR spectrum of C-PPZ microspheres.

study of particle size and structure variation at variable phosphazene cyclomatrices at different temperatures is unprecedented. In addition, the exceptional thermal stability of the prepared cyclomatrices as well as their epoxy resin composites give additional value to the importance and applicability of such materials.

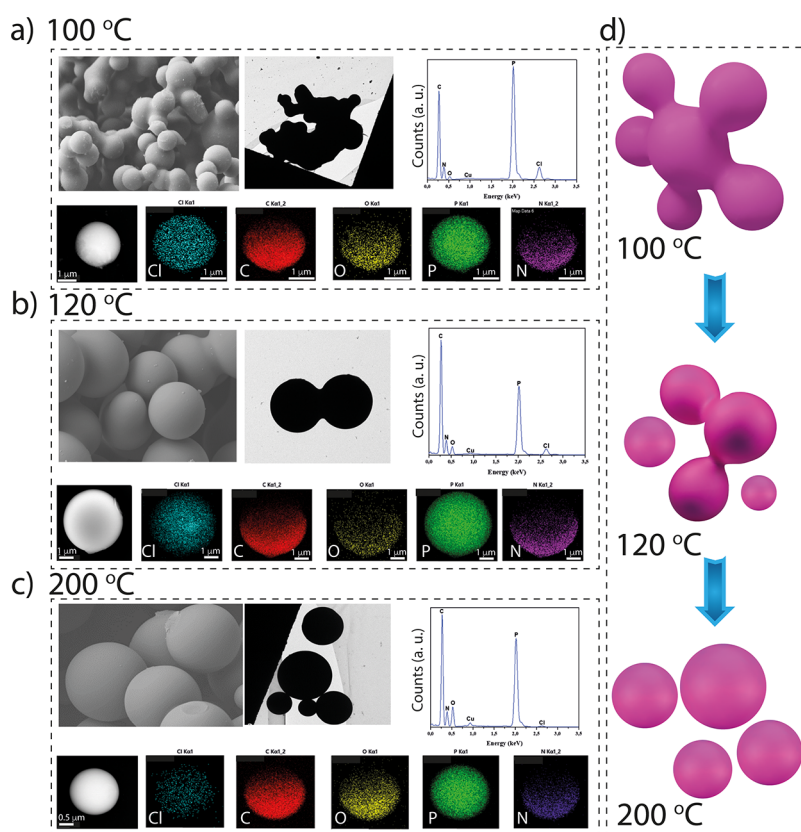
## RESULTS AND DISCUSSION

**Synthesis and Characterization of C-PPZs.** The synthesis of C-PPZs shown in Scheme 1, was prepared successfully via a one-pot and basic polymerization technique. HCCP is a cross-linker molecule having six reactive chlorine atoms. These features provide a high cross-linking ability to HCCP. TEA was used as a base just to consume the hydrogen chloride (HCl), which is released from the polymerization reaction of HCCP and *p*-PDA and forms triethylamine hydrochloride (TEA). The reaction was performed three times at three different temperatures with the same molar ratios of starting materials. The reaction was run at 100 and 120 °C, in which the analytical data showed an incomplete reaction, as reflected by NMR and IR studies. However, increasing the temperature

reaction to 200 °C resulted in a complete reaction, as illustrated in Scheme 1.

FTIR spectroscopy was used to identify the chemical structure of the obtained C-PPZs, as shown in Figure 1a. The peaks in the region of 3100–3400  $\text{cm}^{-1}$  correspond to the stretching vibrations of N–H.<sup>20</sup> The aromatic skeleton vibrations are observed between 1505 and 1604  $\text{cm}^{-1}$ .<sup>21</sup> The stretching band at 1170 and 834  $\text{cm}^{-1}$  are attributed to P=N and P–N characteristic absorption of the starting material (HCCP),<sup>22,23</sup> respectively, which indicated that C-PPZs kept the skeleton structure of phosphazene during the reaction. Meanwhile, another important peak appearing at 938  $\text{cm}^{-1}$  is associated to the stretching P–NH–Ph,<sup>24</sup> which obviously demonstrates the occurrence of copolymerization between HCCP and *p*-PDA. The P–Cl peak at 660  $\text{cm}^{-1}$  of HCCP<sup>25</sup> disappeared in the C-PPZs at 200 °C, suggesting the complete substitution reaction of P–Cl in HCCP by *p*-PDA.

High-resolution XPS was employed to detect the surface composition and the chemical component of the C-PPZ microspheres. The survey XPS spectra of C-PPZs (Figure 1b) show three peaks attributed to C 1s, N 1s, and O 1s. A



**Figure 4.** SEM, TEM images, TEM EDS spectra, elemental mapping images of N, O, C, P, and Cl of C-PPZ microspheres at different temperatures: (a) 100 °C, (b) 120 °C, and (c) 200 °C. Explanatory sketch showing the morphology as a function of temperature and the formation of distinct spheres at 200 °C. (d) Growth kinetics of C-PPZ microspheres at different temperatures.

small amount of chlorine 1.7 and 1.9% was observed in C-CPPZs at 100 and 120 °C, respectively. Meanwhile, no Cl peaks in C-CPPZs appeared at 200 °C, confirming that the Cl atoms in HCCP were completely substituted by *p*-PDA.<sup>20</sup> The high-resolution spectra of N 1s for the C-CPPZ microspheres at different temperatures (Figure 1c) yield three peaks at about 397.5, 399.4, and 400.2 eV, corresponding to P=N, P-NH-Ph, and Ph-NH<sub>2</sub> bonds,<sup>7,26</sup> respectively. These results indicate the occurrence of polycondensation between HCCP and *p*-PDA.

The thermal stability of the C-PPZ microspheres was investigated by TGA as shown in Figure 2a. It shows that C-PPZs are more stable at 200 °C, having initial degradation at around 300 °C, while C-PPZs at 120 and 100 °C show similar behavior, having initial degradation at around 180 °C, which can be due to the incomplete reaction. C-PPZs at 200 °C showed excellent thermal stability, showing only 10% weight loss at 900 °C. Also, the improved thermal stability of the CPPZ microspheres compared with those of HCCP and *p*-PDA (Figure S2) is due to the formation of a highly cross-linked structure and the thermal stability of the cyclotriphosphazene rings.<sup>27</sup>

The phase structure of the C-PPZ microspheres was analyzed using powder X-ray diffraction (XRD), as shown in Figure 2b. Two broad diffraction peaks at  $2\theta$  values of around 12 and 26° were observed, which confirms the amorphous structure of the PZS microspheres without any crystallization.<sup>28</sup>

The chemical structures of C-PPZs are characterized by <sup>13</sup>C and <sup>31</sup>P CP/MAS NMR spectroscopy, as shown in Figure 3.

<sup>13</sup>C CP/MAS NMR spectra of C-PPZs obtained at 100 and 120 °C showed carbon chemical shifts as broad peaks at 118 ppm (C=C) and at 134 ppm (=C-N-P) in the aromatic region. Two smaller shoulders at 123 and 140 ppm were observed in the spectra, suggesting that more than one *p*-PDA moiety chemical environment exists in C-PPZs at 100 and 120 °C, which could be attributed to the presence of the unreacting NH<sub>2</sub> moieties in *p*-PDA (Figure 3a). The <sup>13</sup>C CP/MAS NMR spectrum of C-PPZs obtained at 200 °C clearly showed only two single peaks in the aromatic region at 118 ppm and 134 ppm, thus indicating that *p*-PDA had substituted all Cl atoms of HCCP.<sup>6</sup> As reflected by <sup>31</sup>P NMR (Figure 3a), the spectrum of C-PPZ microspheres showed major sharp phosphorous peaks at 3.1 and 2.6 ppm in C-PPZs at 100 and 120 °C, respectively, with an observed shoulder on the left of the peak in each spectrum, indicating the presence of structural units -N=P(-(NHPh))- and -N=P(-Cl)-, i.e., the existence of different chemical environments for phosphorus atoms in the cyclotriphosphazene moiety of the cyclomatrix, which can be attributed to the incomplete substitution of all of the Cl atoms by *p*-PDA.<sup>29</sup> In addition to the NMR data, the existence of unreacted chlorine is confirmed by EDS (Figure 4). However, C-PPZs obtained at 200 °C exhibit a single sharp phosphorous <sup>31</sup>P NMR peak at 2.8 ppm, indicating one phosphorous chemical environment and a complete substitution reaction.

Figure 4 shows the SEM and TEM images of C-PPZ microspheres at different temperatures. The morphology of microspheres gradually changed by changing the temperature to 100, 120, and 200 °C (Figure 4a). The morphology of C-PPZs at 100 °C adopts a deformed sphere-like structure, which

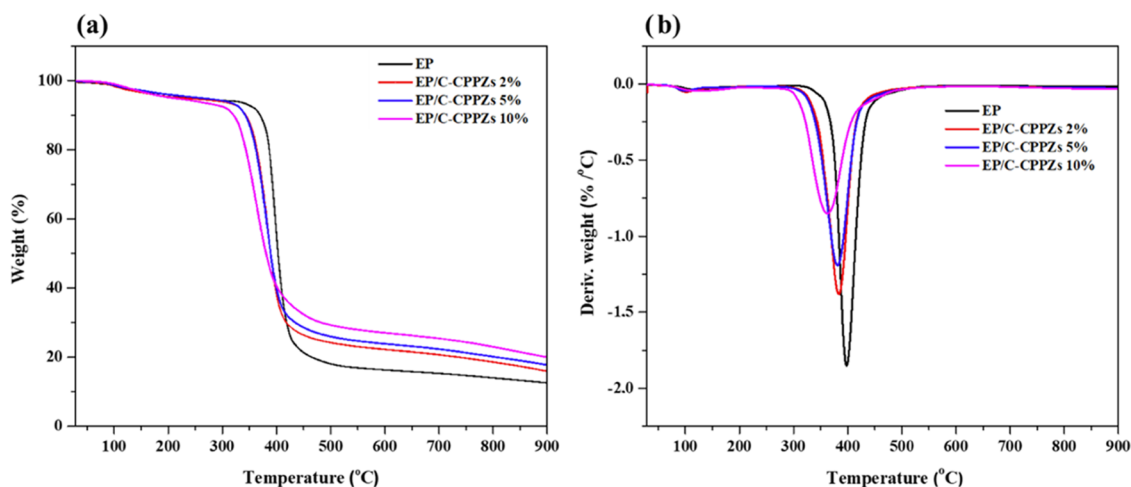
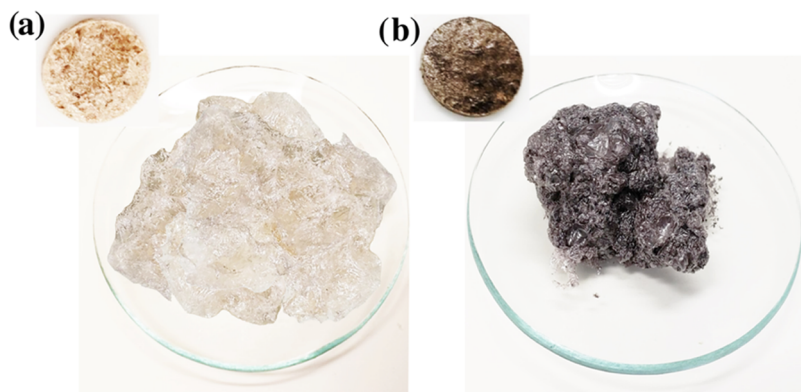


Figure 5. (a) TGA and (b) DTG thermograms of EP and its composites under nitrogen.

Scheme 2. Photographic Image of the Different Foams and Pellets: (a) EP and (b) EP/C-PPZs



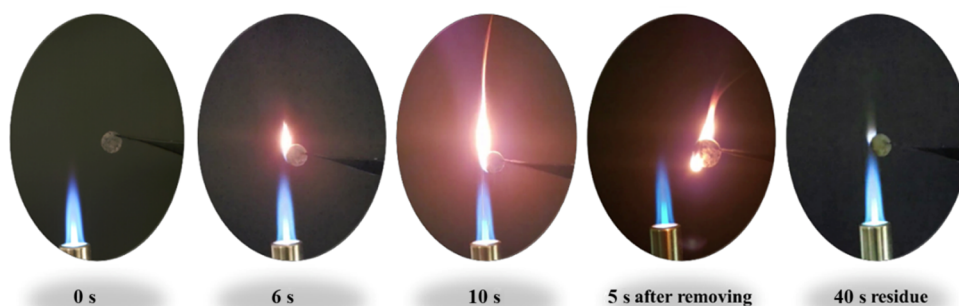
could be explained by the presence of unsubstituted Cl atoms on the cyclophosphazene moiety of the cyclomatrix. The same behavior is noted at 120 and 100 °C with a less deformed spherical C-PPZ structure. The obtained C-PPZs at 200 °C adopt a complete spherical structure with all spheres perfectly tangent to each other, and this is due to the completely symmetrical structure of the cyclomatrix, which contains almost no Cl atoms in the cyclophosphazene ring system according to energy-dispersive X-ray spectroscopy (EDX) and NMR data. EDX data show a relatively high percentage of Cl in C-PPZs at 100 °C (5.1%) compared to the obtained C-PPZs at 120 °C (2.9%) and 200 °C (0.2%). The gradually decreasing amount of Cl by 25 times from 100 to 200 °C confirms the proposed postulate that the resulting deformed spherical shape is related to the incomplete displacement of Cl atoms by *p*-PDA. In addition, the EDX mapping indicated a uniform distribution of nitrogen (N), oxygen (O), carbon (C), phosphorus (P), and unsubstituted Cl over the cyclomatrix microspheres.

Figure S3 shows the particle-size distribution of the C-PPZ microspheres at different temperatures. The average size of C-PPZs gradually increased from  $3.2 \pm 0.7$ ,  $4.9 \pm 0.7$ , to  $7.7 \pm 1.6$   $\mu\text{m}$  as the temperature increased from 100, 120, to 200 °C, respectively. Therefore, the increase in diameter is directly proportional to the increase in temperature.

**Thermal Properties of EP/C-PPZ Composites.** The degradation of epoxy resin (EP) and its composites have two mass-loss ranges. The first range is observed at 250–400 °C in

the TGA shown in Figure 5. It can be seen that the epoxy composites (EP/C-PPZs) display a first maximum degradation temperature lower than that of the EP, which shows that the phosphorus and nitrogen (P–N)-containing flame retardants (FRs) decompose preferentially at a relatively low temperature, promoting char formation and forming a protective layer that retards further degradation of the char at higher temperatures.<sup>30,31</sup> The second stage, which is the main mass-loss range, occurs between 400 and 500 °C. The EP/C-PPZ composites exhibit higher thermal stability than the EP in the second range because of the strong interfacial interactions between the polyphosphazene layers and the EP matrix.<sup>32</sup> As shown in Figure 5a, after pyrolysis at 900 °C, the char yield ratio of the EP/C-PPZ composites increases remarkably with the increasing phosphorus and nitrogen content. The char yield of EP/FC-PPZs 2% is progressively increased to 17.7%, higher than that of the EP, which demonstrates that C-PPZs can retard the decomposition of the composite. The main reason behind this retarded decomposition is that C-PPZ sheets are well-distributed in the EP matrix and form linkages with EP segments to effectively increase the intermolecular cross-linkage density.<sup>33</sup> From derivative thermogravimetry (DTG) curves (Figure 5b), it is apparent that maximum mass-loss rates of the composites are decreased by C-PPZs.<sup>34</sup>

**Flammability Tests.** We investigated the flame-retardant properties of epoxy resin (EP) and its composites EP/C-PPZs 10% by direct exposure to an acetylene flame. For this purpose, the different polymers have been modulated in the



**Figure 6.** Photographs of the burning behavior of EP/C-CPPZs 10% during a vertical burning experiment.

form of pellets for practical application (as shown in Scheme 2). Figure 6 demonstrates the typical burning procedures for the sample pellets. Compared to our previous published work,<sup>20</sup> in which we demonstrate that the pellets of EP immediately caught fire, showing a highly combustible behavior with almost no residue left after 10 s of combustion. However, in the case of the C-PPZs (Figure 6), composites only exhibited slight combustion and almost nonexistent propagation. One of the fascinating characteristics of their combustion is that they just burned lightly with a little flame even after repeated exposure to a high-temperature flame for 40 s while keeping their initial form. The excellent flame-retardant properties are mainly due to the formation of a high-quality barrier layer, which is based on the graphitic char from the HCCP-catalyzed char from the EP matrix.<sup>34</sup>

## EXPERIMENTAL SECTION

**Materials.** Hexachlorocyclotriphosphazene, *p*-phenylenediamine, 1,4-dioxane, ethanol, acetone, and triethylamine were purchased from Sigma-Aldrich (Oakville, ON, Canada). Deionized (DI) water was produced by a water purification machine (Milli-Q Reference). 1,4-Dioxane was dried using 4 Å molecular sieves before being used.

**Preparation of Cyclomatrix-Type Polyphosphazene Microspheres (C-PPZs).** HCCP (348 mg, 1 mmol) and (*p*-PDA) (486 mg, 4.5 mmol) were dissolved in 15 mL of 1,4-Dioxane to form a light purple suspension. Then, 1.74 mL of TEA was added. The suspension was transferred to an 80 mL Teflon-lined stainless steel autoclave, which was then sealed and heated in an oven, and the reaction was run separately at three different temperatures (100, 120, and 200 °C) each for 24 h to prepare C-PPZ microspheres, which were named C-PPZs-100, C-PPZs-120, and C-PPZs-200 °C, respectively. The products were left to gradually cool down to room temperature. The resulting powders were collected by centrifugation and washed with deionized water, ethanol, and acetone three times respectively. Then, they were dried under a vacuum at 80 °C overnight.

**Preparation of Polymer Composites EP/C-PPZs.** A flammable epoxy resin was mixed with C-PPZs (Supporting Information), which was described in our prior publication (Figure S1).<sup>20</sup> Various amounts of C-PPZs were added to acetone and stirred until C-PPZs had completely dispersed to form a solution. Then, the C-PPZ solutions were separately added to the epoxy resin and stirred until homogeneous mixtures were obtained. The contents of C-PPZs were 0, 2, 5, and 10 wt %, and the resultant samples were marked as EP, EP/C-PPZs 2%, EP/C-PPZs 5%, and EP/C-PPZs 10%, respectively. To remove the solvent, the reaction mixture was

stirred at 40 °C in a water bath. Finally, the mixture was put in a vacuum oven at 70 °C. We investigated the flame-retardant properties of EP and its composites EP/C-CPPZs 10% by direct exposure to an acetylene flame. For this purpose, different polymers have been modulated in the form of pellets for practical application (as shown in Scheme 2). Figure 6 demonstrates the typical burning procedures for the sample pellets. It is clearly observed from these photographs that the pellets of EP immediately caught fire, exhibiting a highly combustible behavior, and left almost no residue after 10 s of combustion. However, in the case of the C-PPZs, composites only exhibited slight combustion and almost nonexistent propagation. One of the fascinating characteristics of their combustion is that they just burned lightly with a little flame even after repeated exposure to a high-temperature flame for 40 s while keeping their initial form. The excellent flame-retardant properties are mainly due to the formation of a high-quality barrier layer, which is based on the graphitic char from the HCCP-catalyzed char from the EP matrix or 40 min until the polymers (foams) were completely dry (Scheme 2).

**Characterization Methods.** Fourier transform infrared (FTIR) spectroscopy was acquired on a Nicolet smart iTR 6700 spectrometer in the wavenumber range of 4000–500  $\text{cm}^{-1}$  (Thermo-Nicolet, Madison, WI). The data were analyzed using OMNIC software (Thermo-Nicolet, Madison, WI). X-ray diffraction (XRD) was performed using a diffractometer (Bruker D8 Advance) with Cu  $K\alpha$  radiation ( $\lambda = 1.54182 \text{ \AA}$ ) in an angular interval from 5 to 80° at room temperature. X-ray photoelectron spectroscopy (XPS) data for elemental composition and valence information was collected with XPS PHI 5600-ci (Physical Electronics, Eden Prairie, MN). The morphology of materials was obtained with a scanning electron microscope (SEM) by utilizing a JEOL (JSM7600F) operated at 10 kV accelerating voltage and a working distance of 14 mm using secondary electron imaging mode. Transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDX) was performed on a JEOL JEM-2100F. The size and distribution of all as-prepared nanoparticles were determined from SEM micrographs using ImageJ (V1.41, NIH) for image analysis. A thermal gravimetric analysis (TGA Q500/Discovery MS) meter was used to measure the thermal stability under nitrogen ( $\text{N}_2$ ) with a heat ramp of 5 °C/min between 30 and 1000 °C.  $^{13}\text{C}$  and  $^{31}\text{P}$  MAS NMR spectra were recorded using a 400 MHz solid-state Bruker Avance III HD spectrometer (Milton, ON, Canada), operating at frequencies of 150.874 MHz for  $^{13}\text{C}$  and 162 MHz for  $^{31}\text{P}$ . Cross-polarization with the magic angle spinning (CP/MAS) technique was adopted.

## CONCLUSIONS

A simple and efficient method for the synthesis of highly cross-linked cyclomatrix-polyphosphazenes from HCCP and *p*-PDA is disclosed. The study showed that morphology and reactivity of HCCP with *p*-PDA were highly temperature dependent. Solid-state  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR data showed that complete displacement of the Cl atoms in HCCP by *p*-PDA molecules took place at 200 °C, proving a complete reaction, whereas an incomplete reaction was observed at 100 and 120 °C. SEM and TEM analysis revealed that the average particle size of the cyclomatrices increased with temperature, and TGA reflected excellent thermal stability for all cyclomatrices obtained, the highest being to the cyclomatrices obtained at 200 °C in which only 25% weight loss took place at 800 °C. In addition, EP composites of the obtained C-PPZs showed excellent flame-retardant properties. Studies on applications of these polyphosphazene cyclomatrices as well as other polyphosphazene materials in electrochemistry and other related fields are currently underway in our laboratories.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.2c06394>.

Illustration of TGA curves of *p*-phenylenediamine (*p*-PDA) and hexachlorocyclotriphosphazene (HCCP) and particle-size distributions of the C-PPZ microspheres at different temperatures (PDF)

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<https://pubs.acs.org/10.1021/acsomega.2c06394>

### Author Contributions

K.R., A.S.E., and M.S. conceptualized the study. K.R., S.C., and A.S.E. were responsible for the methodology. K.R., S.C., and A.S.E. validated the study. K.R. performed the formal analysis. M.S. managed the resources. K.R., S.C., A.S.E., and A.M. curated the data. K.R. prepared the original draft. K.R., S.C., A.S.E., A.M., and M.S. wrote, reviewed, and edited the manuscript. M.S. supervised the study. M.S. acquired funding. All authors have read and agreed to the published version of the manuscript.

### Notes

The authors declare no competing financial interest.

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