

## Synthesis of a melamine-cyclotriphosphazene derivative and its application as flame retardant on cotton gauze

Meixiang Lv, Chunfeng Yao, Dingqiao Yang, Heping Zeng

Key Laboratory of Theoretical Chemistry of Environment, Ministry of Education, School of Chemistry and Environment, South China Normal University, Guangzhou, Guangdong 510006, People's Republic of China

Correspondence to: D. Q. Yang (E-mail: yangdq@scnu.edu.cn) and H. P. Zeng (E-mail: zenghp@scnu.edu.cn)

**ABSTRACT:** The halogen-free flame retardance of natural fiber is an everlasting challenge due to the well-known poor solubility of phosphazene in water. In this case, a new cyclotriphosphazene derivative (MCP) was synthesized. It was etherized hexamethylolmelamine (HMMM) and hexachloro-cyclotriphosphazene (HCCP) by one pot reaction. It was characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR,  $^{31}\text{P}$  NMR, FT-IR, TGA, SEM, limited oxygen index (LOI) and vertical flame testing. The MCP has good solubility in water and thermo-setting MCP has compact structure which can expand several times after burning. Cotton gauze was soaked in six different concentration of aqueous solutions of MCP (0 wt %, 5 wt %, 10 wt %, 15 wt %, 20 wt % and 25 wt %, respectively) to obtain the flame retardant cloth. The cloth was soaked in 20 wt % MCP solution had higher char yield and LOI. They had no any afterflame and afterglow, and gauze 2- gauze 5 cannot be burned out in 12s ignition time. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43555.

**KEYWORDS:** flame retardance; fibers; synthesis and processing; textiles; thermal properties

Received 16 April 2015; accepted 18 February 2016

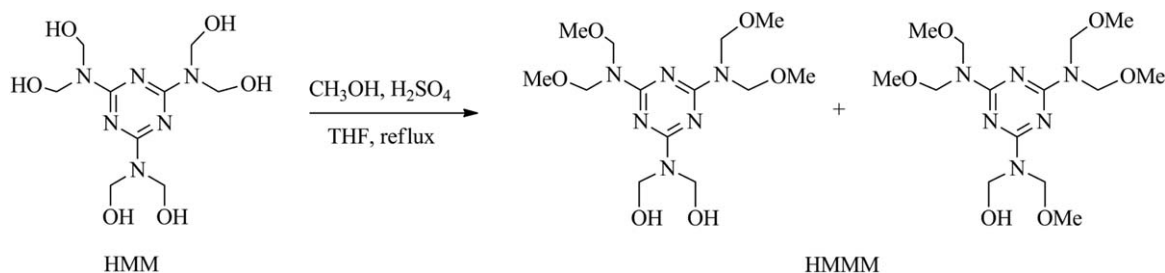
DOI: 10.1002/app.43555

### INTRODUCTION

Cotton cloth has become a necessity for daily life and is commonly used in cloth but they are easy to ignite. Flame-retardant treatments are routinely applied to cotton and polyester fabrics in order to prevent fires and reduce the casualties and property damage caused by fires. Basak *et al.* provided sodium metasilicate nonahydrate (SMSN) as a flame retardant and antimicrobial on jute fabrics. The LOI value was found to increase to 43 in the 8% SMSN treated sample.<sup>1,2</sup> However, many inorganic retardants have poor compatibility with resins and adversely affect the mechanical, electrical and processing properties of epoxy thermosets. Thus they as flame retardants are usually needed larger dosage that limits their application scope.<sup>3</sup> Phosphorus-containing compounds have also been recognized as one of the most efficient flame retardants,<sup>3,4</sup> which have excellent fire retardancy and low toxic gas evolution during combustion compared with halogen-containing ones. During the combustion process, phosphorus-based compounds work in either a vapor phase by diluting combustible gases or a condensed phase by synergistically promoting the phosphorylation on cotton fabrics and enhancing the formation of a protective char.<sup>5,6</sup>

Phosphazenes are a kind of hybrid organic-inorganic materials with alternating nitrogen and phosphorus atoms in the main

chains. Materials containing phosphazenes tend to be thermally- and chemically-stable and have been shown to provide improved flame-retardant and heat-resistant properties to reinforced polymers.<sup>7-9</sup> In addition to their flame-retardant behavior, they also exhibit unusual thermal properties such as self-extinguishability.<sup>10,11</sup> More importantly, phosphazene materials are halogen-free and environmentally-friendly, with some compounds even demonstrating biocompatibility.<sup>12-17</sup> In a previous study, a series of resins were prepared via reacting cyclotriphosphazene with organic amine,<sup>9</sup> monohydric alcohol,<sup>18</sup> and polyol.<sup>16,19</sup> However, most of phosphazene derivatives have poorly soluble in water, so that they are difficult to incorporate into the network of cotton fabric.<sup>5</sup> As a result, subsequent reports attempted to produce a fire-retardant product by using melt blending or padding processes to combine the polymer<sup>20</sup> and the textile.<sup>21-23</sup> Guo *et al.*<sup>24</sup> reported two additives of hexachlorocyclotriphosphazene that they were mixed with MMA at the ratio of 5-70%, the LOI increased from 20 to 28. As such, cyclotriphosphazene derivatives have not been extensively explored as flame retardants for cotton textiles. In order to make these materials to become widely and easily applicable, it is necessary to improve their water solubility in a most economically and environmentally friendly manner. Fortunately, triazine derivatives have aroused a great deal of attention due to their little water solubility<sup>25,26</sup> and outstanding charring performance.



**Scheme 1.** The synthesis route of HMMM.

They can be as efficient charring agents because of their thermostable triazine rings.<sup>6,14,27,28</sup> Lai *et al.* synthesized a triazine-based macromolecule (TBM) has little water solubility and superior char-forming capability.<sup>27</sup> In our previous work,<sup>6</sup> a triazine-based compound was synthesized via hexamethylol melamine (HMM) with hexachlorocyclotriphosphazene (HCCP). It possesses some water solubility but has good solubility in alcohol (95%). It has superior char-forming capability in flame retardant cloth but the yield is too low. So we want to further improve triazine-phosphazene in water solubility and product's yield. Herein, a new type of intumescent flame retardant (MCP) is presented which combines etherified hexamethylol melamine (HMMM) with hexachlorocyclotriphosphazene (HCCP) and overcomes the solubility barrier presented by cyclotriphosphazene derivatives. The fire retardant properties of the treated cotton gauze with different concentrations of MCP loading were further studied.

## EXPERIMENTAL

### Chemicals

Hexachloro-cyclotriphosphazene (HCCP, 98%) was obtained from Zibo Lanyin Chemical Co., Ltd (China). HMM (98%) was purchased from Chongqing Jianfeng Haokang Chemical Co. Ltd (China). Tetrahydrofuran (THF), tetrabutylammonium bromide (TBAB), CH<sub>3</sub>OH, K<sub>2</sub>CO<sub>3</sub> and ethanol were purchased from Shanghai Aladdin Chemistry Co. Ltd. Medical absorbent gauze with 21s having 110 tex warp yarn count and 100 tex weft yarn counts per 10 cm<sup>2</sup> was from the drugstore (named the cotton gauze). It was pretreated in deionized water with detergent,

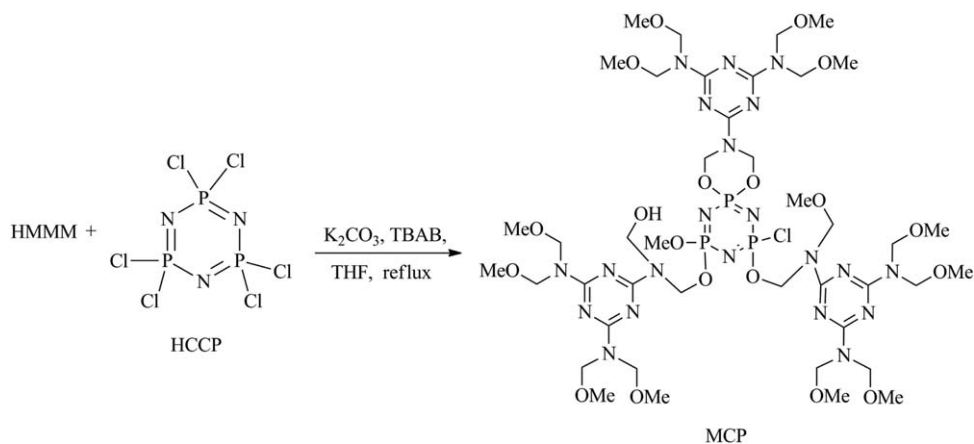
then, rinsed with distilled water, and finally air-dried at room temperature.

### Synthesis of HMMM

Water-soluble and etherized melamine formaldehyde resin (HMMM) was prepared as follows: HMM (12.24 g, 0.04 mol) was loaded into a 100 mL round-bottom flask. A mixture of THF and anhydrous CH<sub>3</sub>OH (12 mL, 0.28 mol) was subsequently added. H<sub>2</sub>SO<sub>4</sub> was used as a catalyst, and the pH value of the reaction system was adjusted to 3.5–4.5. The solution was maintained at room temperature for 1 h, and then refluxed until it was transparent. Then the solution was cooled to room temperature, and trimethylamine (used for neutralizing sulfuric acid) was added dropwise until the pH of the solution became 7–8. At last, it was filtered to remove insoluble salts and concentrated under reduced pressure to obtain the moderately etherized melamine formaldehyde resin mixture (HMMM). The mixture was water-soluble and used without purification.

### Synthesis of MCP

HMMM (12 g), K<sub>2</sub>CO<sub>3</sub> (8.28 g, 0.06 mol) and TBAB (1 mg) were added to flask in 50 mL THF at room temperature and stirred. HCCP (3.47 g, 0.01 mol) was dissolved in 50 mL of THF and then added dropwise to the solution of HMMM over the course of 2 h. The mixture was magnetic stirred with a N<sub>2</sub> inlet at room temperature for 12 h, and then refluxed for 24 h under N<sub>2</sub> atmosphere. At last, 6 mL methanol was added to this solution. The mixture was refluxed for 24 h under a nitrogen atmosphere. At timed intervals, the reaction progress was monitored by <sup>31</sup>P NMR [Figure 2(b)]. The solution was then filtered



**Scheme 2.** The synthesis route of MCP.

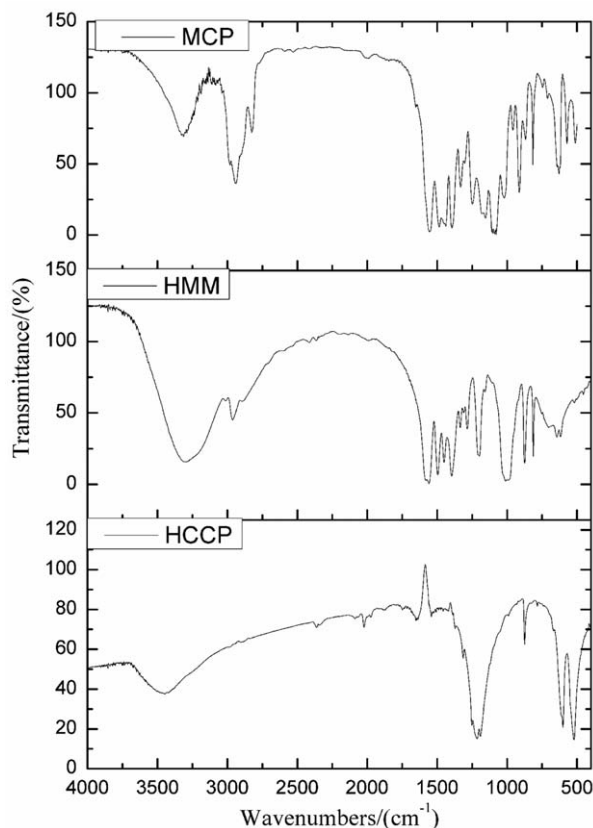


Figure 1. FT-IR spectra of HMM, HCCP and MCP.

to remove insoluble salts and concentrated under reduced pressure. A colorless liquid product MCP was obtained.

The MCP compound was dried for 72 h under vacuum at 40 °C to yield a transparent soft solid. The product was used without further purification. It could be easily dissolved in water, ethanol, etc., but insoluble in *n*-hexane. When it was dried at 80 °C under air, it was changed to hard and transparent solid that cannot be dissolved by any solvent.

FTIR  $\text{cm}^{-1}$  (KBr): 3315(—O—H), 2936 ( $\nu$  C—H), 1220 ( $\nu$  P=N), 1148 ( $\nu$  C—O—C), 923 ( $\nu$  P—O—C), 735 w ( $\delta$  P—N).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 18.14(d, 2P),  $-2.40$ (t, 1P),  $^2J_{\text{P,P}} = 45.36\text{Hz}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 5.09(s, 2H, —N—CH<sub>2</sub>—O—CH<sub>3</sub>), 3.32(s, 3H, CH<sub>3</sub>—).  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO}-d_6$ ,  $\delta$ ): 82.34(—N—CH<sub>2</sub>—O—CH<sub>3</sub>), 84.38(—N—CH<sub>2</sub>—O—P), 68.91(—N—CH<sub>2</sub>—OH), 64.49(—N—CH<sub>2</sub>—O—CH<sub>3</sub>), 165.23–166.12 (C of melamine). MS-ESI ( $m/z$ ): calcd for  $\text{C}_{41}\text{H}_{78}\text{C}_{12}\text{N}_{21}\text{O}_{18}\text{P}_3$ , 1297, found, 391, 1298  $[\text{M} + \text{H}]^+$ .

#### Preparation of Flame Retardant Fabrics of MCP

In the first step, MCP was diluted with water to prepare the different concentration of solutions. Cotton gauze was soaked in the solution of MCP for 1 h at room temperature. The solutions containing 0% (gauze 0), 5 wt % (gauze 1), 10 wt % (gauze 2), 15 wt % (gauze 3), 20 wt % (gauze 4) or 25 wt % (gauze 5) of the flame retardant MCP were used. Then, these impregnated gauze samples were removed from the solution, placed onto the glass plates to dry at 60 °C for 1 h and cured at 80 °C for 15 min. After being cured, the fabrics were soaked in

deionized water for 10 h and then dried at 80 °C for 15 min. The process of washing and weighing of the fabric samples was repeated two or three times.<sup>3</sup>

#### Measurements

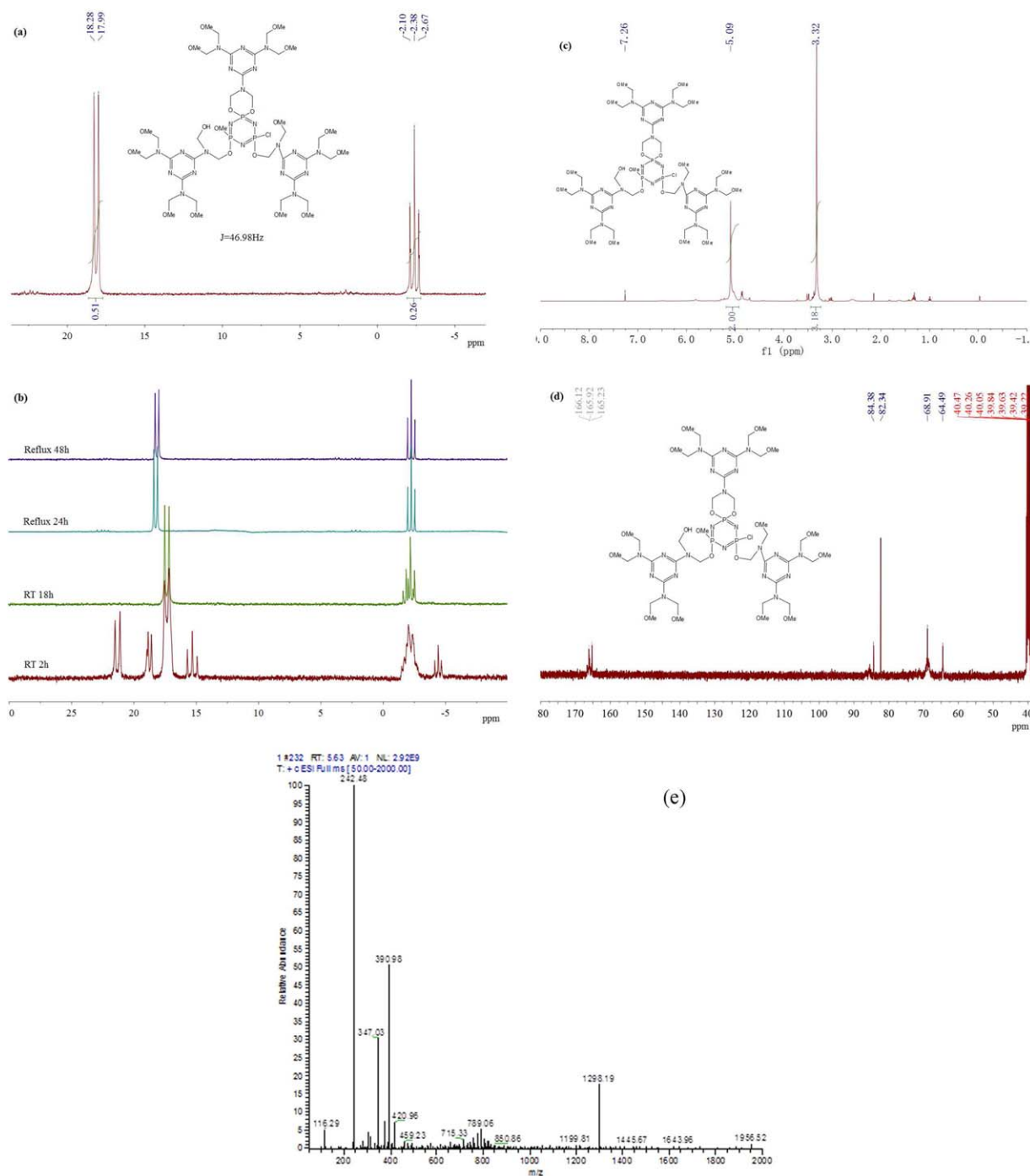
Fourier-transform infrared (FTIR) spectra was employed using a Shimadzu Fourier Transform Infrared Spectrophotometer (IR Prestige-21) to characterize the raw materials and products using thin KBr disk. The transmission mode was used and the range of wavenumber range was set from 4000 to 400  $\text{cm}^{-1}$ . The NMR measurements were conducted on a System 400 spectrometer (Varian, USA) at room temperature.  $^1\text{H}$  and  $^{31}\text{P}$  NMR were measured with  $\text{CDCl}_3$  as the solvent, and  $^{13}\text{C}$  NMR with DMSO as the solvent. The electrospray ionization mass spectra (ESI-MS) was recorded on LCQ DECA XP MAX mass spectrometer (Thermo, USA). Limiting oxygen index (LOI) was carried out in an JF-3 oxygen index meter (Jiangning Analysis Instrument Co., China) with sample measurement of 140 mm  $\times$  52 mm, following the procedure described in the GB/T 5454-1997 standard. The vertical burning test was performed on CZF-3 instrument (Jiangning Analysis Instrument Co., China) according to GB/T 5455-1997 standard testing procedure with sheet dimensions of 300 mm  $\times$  80 mm. Thermogravimetric analysis (TGA) was carried out (STA 409PC, NETZSCH) at a heating rate of 10 °C/min from room temperature to 800 °C with continuous high pure nitrogen and air atmosphere. The field-emission scanning electron microscopy (FESEM, ZEISS Ultra 55, 5 kV, Pt-spraying treatment) was employed collecting at different gauze samples.

## RESULTS AND DISCUSSION

### Structural Characterization

To obtain the cyclotriphosphazene derivative with etherized hexamethylmelamine substituents (MCP), two step reactions have been performed as shown in Schemes 1 and 2, where the synthetic pathway and the structural features of precursors and final products are clearly illustrated. In Scheme 1, HMMM was a mixture, we knew that the etherification is a complex process, product is varied. But according to the structural characterization of MCP, we determined HMMM is the two main structure in scheme 1.

The FTIR data (Figure 1) suggest that MCP was successfully synthesized. According to the reference,<sup>9,10,25,27,28</sup> 3315  $\text{cm}^{-1}$  is the —OH of characteristic absorption peak but it is weaker than in the HMM. It proved hydroxyl content is less. But alkyl is more in MCP. The absorption bands at 1441–1438  $\text{cm}^{-1}$  and 2936  $\text{cm}^{-1}$  [Figure 1(a)] were assigned to the flexural vibrations and stretching vibration of C—H bonds, respectively. 1545  $\text{cm}^{-1}$  and 1468  $\text{cm}^{-1}$  (triazine ring), and 1392  $\text{cm}^{-1}$  (C—N). The characteristic absorption peaks of C—O—C groups were detected at approximately 1148  $\text{cm}^{-1}$ . Peaks at 1220  $\text{cm}^{-1}$  and 735  $\text{cm}^{-1}$  were assigned to the vibrations of P=N and P—N bonds. Only weak absorption band characteristic of P—Cl bond was detected, indicating that the chlorine atoms were almost completely substituted. Meanwhile, the presence of a band at 923  $\text{cm}^{-1}$  is an indication that P—O—C bonds were formed. Peaks at 1545  $\text{cm}^{-1}$ , 859  $\text{cm}^{-1}$  and 626  $\text{cm}^{-1}$  represent the melamine backbone. By contrast, we found that P—N—P infrared absorption area of

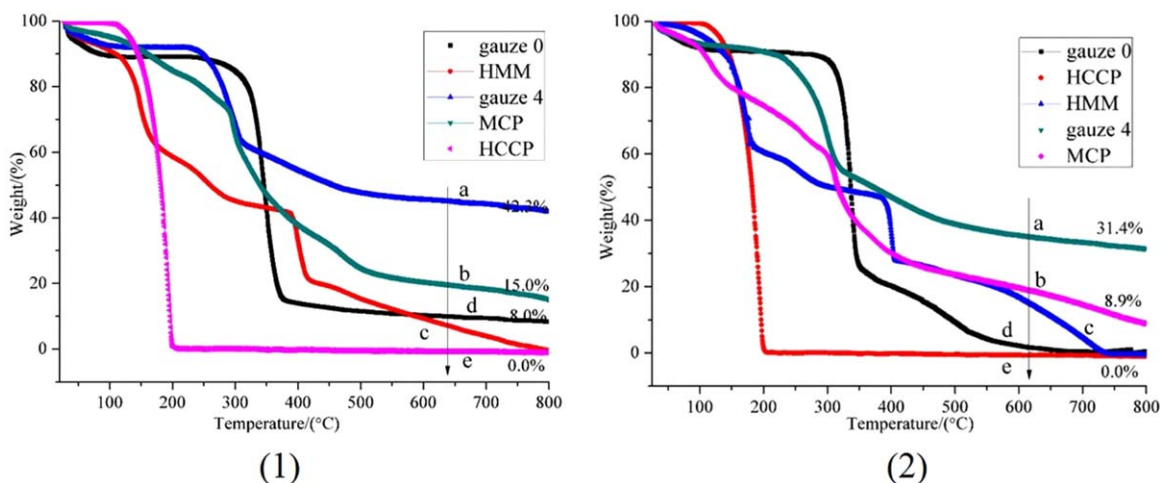


**Figure 2.**  $^{31}\text{P}$  NMR spectra of MCP (a),  $^{31}\text{P}$  NMR spectra of reaction liquid of different reaction time (b). RT = room temperature,  $^1\text{H}$  NMR spectra of MCP (c),  $^{13}\text{C}$  NMR spectra of MCP (d), ESI-MS spectra of MCP (e). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

HCCP is covered by the triazine ring of HMM. So, many peak of MCP looks similar with HMM.

$^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR spectra were operated at 400, 100 and 162 MHz for the different nuclei, respectively.  $^1\text{H}$  [Figure 2(c)] and  $^{13}\text{C}$  NMR [Figure 2(d)] spectra were referenced to tetramethylsilane signals,  $\text{CDCl}_3$  and  $\text{DMSO}-d_6$  was used as the solvent respectively. While  $^{31}\text{P}$  NMR [Figure 2(a)] chemical shifts were referenced to 85% phosphoric acid, which was used as an external standard.  $^{13}\text{C}$  NMR and  $^{31}\text{P}$  NMR data were proton

decoupled. Stepwise substitution reactions were monitored by  $^{31}\text{P}$ -NMR spectroscopy [Figure 2(b)]. Figure 2(a) shows that the  $^{31}\text{P}$  NMR spectrum clearly displays a typical  $\text{AB}_2$  spin pattern with two sets of resonance signals appearing<sup>29,30</sup> as a triplet at 18.14 ppm and as a doublet at  $-2.40$  ppm respectively, and with a phosphorus-phosphorus coupling constants ( $J_{\text{PNP}}$ ) of 45.36 Hz, corresponding to the phosphorus atom of cyclotriphosphazene bearing a monospiro group and the other two bearing methoxy groups, respectively. These two different



**Figure 3.** TGA scans for gauze 4 (a); cured MCP (b); HMM (c); gauze0 (d) and HCCP (e) at 10°C/min in (1) N<sub>2</sub>, (2) air atmosphere. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

environmental phosphorus atoms give an integration ratio of 2:1. Meanwhile, the spectrum of HCCP as a reference shows only an intensive singlet signal at 19.97 ppm. In Figure 2(e), the  $m/z1298$  is  $[M + H]^+$  that consistency to the MCP of scheme 2.

#### Thermal Stability of Cyclotriphosphazene Derivatives

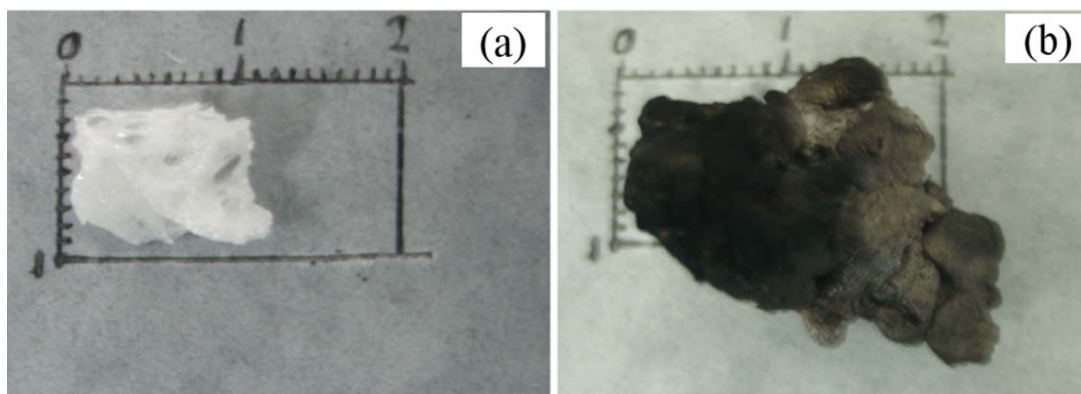
The thermal stability was tested under nitrogen gas [Figure 3(1)] and air [Figure 3(2)] using a thermogravimetric analyzer. Gauze 4 was compared with HMM, HCCP, MCP and gauze 0. In N<sub>2</sub> atmosphere, the onset temperature of gauze 4 is approximately 261.7°C, which is much lower than that of the decomposition of gauze 0 (324.7°C). Under air atmosphere, the onset temperature of gauze 4 is approximately 222.3°C, which is much lower than the onset temperature of the decomposition of gauze 0 (297.4°C). When MCP is incorporated into the network of cotton gauze (for example: gauze 4), the decomposition temperature of MCP is lower than naked cotton gauze (gauze 0), then the formation of the gas and the produce of phosphate protective the gauze to slow decomposition. This phenomenon is consistent with flame retardant plastics containing cyclotriphosphazenes in a lot of literature.<sup>6–8,10,13,14,16,18,19</sup> So the MCP can enhance the thermal properties of the gauze due to the synergistic effects of flame-retardant phosphorous and nitrogen content. Because the thermal decomposition of phosphazene-based

polymers is an endothermic process, and the phosphate, metaphosphate, and polyphosphate generated during the thermal decomposition form a nonvolatile protective film on the surface of the polymer which has the effect of isolating it from the air. Meanwhile, the gases released, including CO<sub>2</sub>, NH<sub>3</sub> and N<sub>2</sub>, are not flammable and also serve to cut off the supply of oxygen, leading to a synergistic increase in flame retardancy.<sup>7,9</sup> Moreover, the increase of the residue was found when MCP was loaded in the cotton gauze. For example, the residue of gauze 4 was 42.3% [Figure 3(1) a] in N<sub>2</sub> and 31.4% [Figure 3(2)a] in air. The residue of MCP was 15.0% [Figure 3(1) b] in N<sub>2</sub> and 8.9% [Figure 3(2) b] in air indicate MCP decomposed not only gas but also nonvolatile matter. The raw materials (HMM, HCCP and gauze 0) were almost no residue after heated to 800°C.

The TGA experiments showed that the MCP can protect molecular chain of the cotton gauze from fully decomposition.

#### Burning Behaviors of MCP and Flame Retardant Gauze in Air

A sample of 5 mm cured MCP lump of mass 0.1387 g was ignited with a lighter to test the combustion behavior of MCP in air. The lump became intumescent and black, increasing in



**Figure 4.** Photographs of MCP (a) and intumescent char of cured MCP (b). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**Table I.** Combustion Data of the Flame Retardant Cotton Gauze Soaking 1 h in Air

Sample	Afterflame Time(s)	Afterglow Time(s)	Residual carbon (%)	LOI (%)
Gauze 0	0	0	0	16.9
Gauze 1	0	0	25.6	23.5
Gauze 2	0	0	35.4	24.6
Gauze 3	0	0	42.3	25.4
Gauze 4	0	0	47.6	26.5
Gauze 5	0	0	46.6	25.8

The residual carbon data was obtained by weighing black part of sample through repeated lit unburned part.

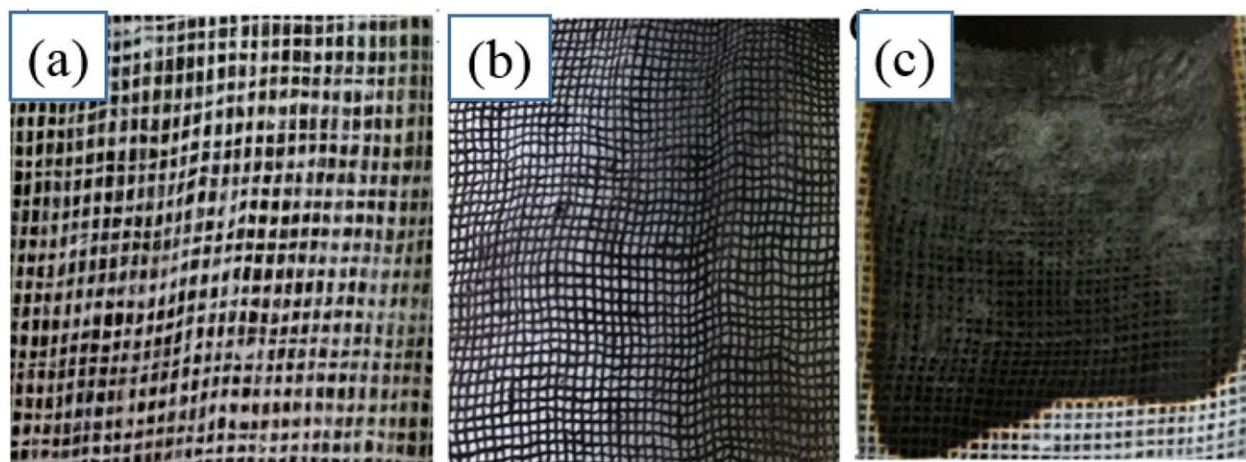
size by a factor of at least 2, a char-like foam was formed (Figure 4), resulting in black lump (char residue) weighing approximately 0.0762 g. The char yields of the cured MCP samples reached values of up to 54.9%. Figure 6(a) shows SEM microphotographs of surface morphology of char residue of MCP. This effect was ascribed to porous, cellular structure of the samples. Foam-like structure implies that MCP follows intumescent mechanism that have been reported by some researchers.<sup>31</sup> As MCP is a typical monomeric IFR, it is expected to demonstrate excellent fire retardant properties. Figure 6(b–d) presents SEM images of different gauze samples before and after combustion. Before burning, the naked cotton gauze (gauze0) can see rod-shaped fiber, but the fiber of treated cotton gauze (gauze 4) were wrapped in a smooth layer. After combustion, the gauze0 has no residue, but the comminuted residue of gauze 4 was smooth and rugged. We think that the MCP of gauze priority combustion and generate gas and phosphate to form the morphology when it was burned.

To investigate the combustion behaviors of cotton gauze with various amounts of MCP, gauze 1–gauze 5 were tailored to pieces of 3 cm<sup>2</sup>, then they were ignited from bottom, but the flames were anemic and soon died out. Some samples required 5–6 ignitions to form a complete char layer. The combustion data (afterflame time, smolder and residual carbon) of cotton gauze with different loadings of MCP is summarized in Table I.

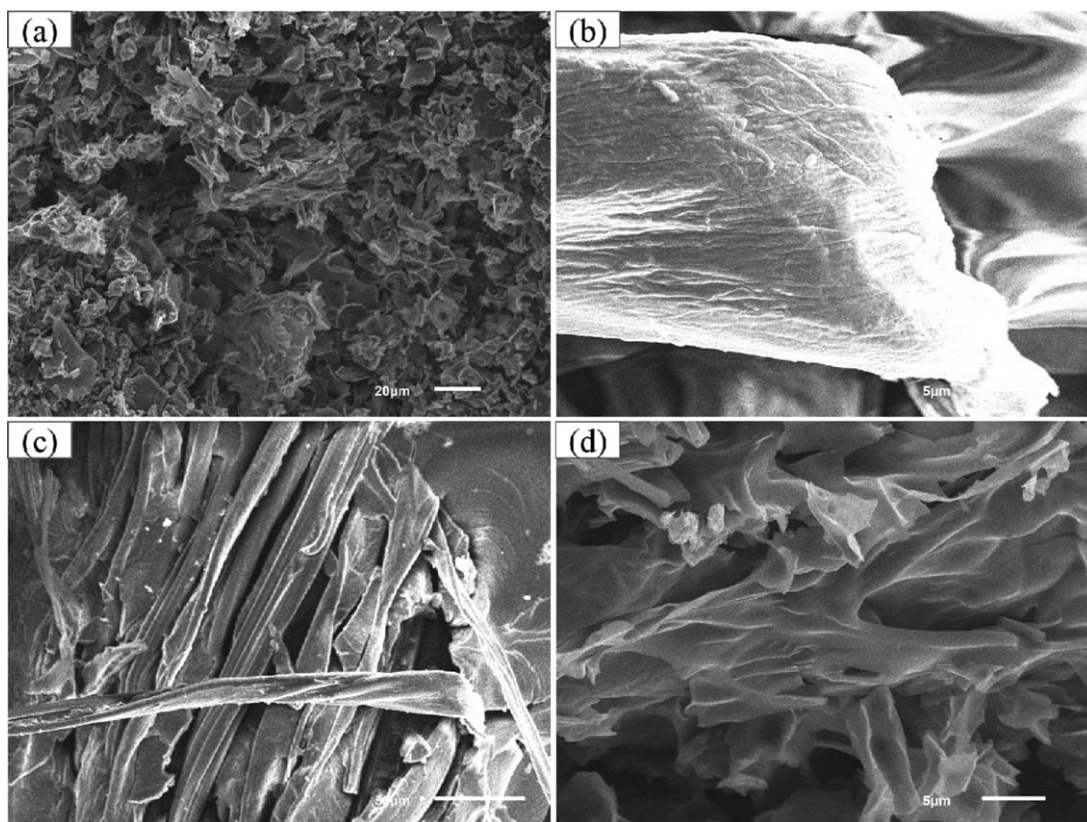
The MCP is thermosetting and irreversible. After thermosetting, the product become a transparent and hard solid, and it does not dissolve in any organic solvent and water.

Neat cotton gauze was ignited by a flame one time in air and burned out quickly without leaving a measurable residue. By contrast, gauze 4 withstood multiple direct, vertical ignitions in air until self-quenching [Figure 5(c)], with char yields of up to 47.6%. The higher residue represents the better flame retardancy. Samples also exhibited intumescent behavior, producing a foamed protective char on the surface of the cotton gauze at elevated temperatures.

Expansion type flame retardant of MCP earlier than fabrics preferred decomposition, phosphoric acid or poly phosphate, etc., these generated acids can be carbonized, catalytic dehydration of organic matter in the unspoil form a protective layer on the surface of matrix carbon layer, then part of nitrogen decomposed to produce flame retardant gas, The gas makes oxygen concentration is diluted near flammable fiber in combustion zone, at the same time promote the carbon layer foaming, inflating carbon layer. Inflating the formation of the carbon layer on the one hand, to prevent the outside of the oxygen and heat into the substrate part undisturbed, to protect the internal structure, on the other hand, the carbon layer and avoid the combustible gas escape, reduce the possibility of a combustion.



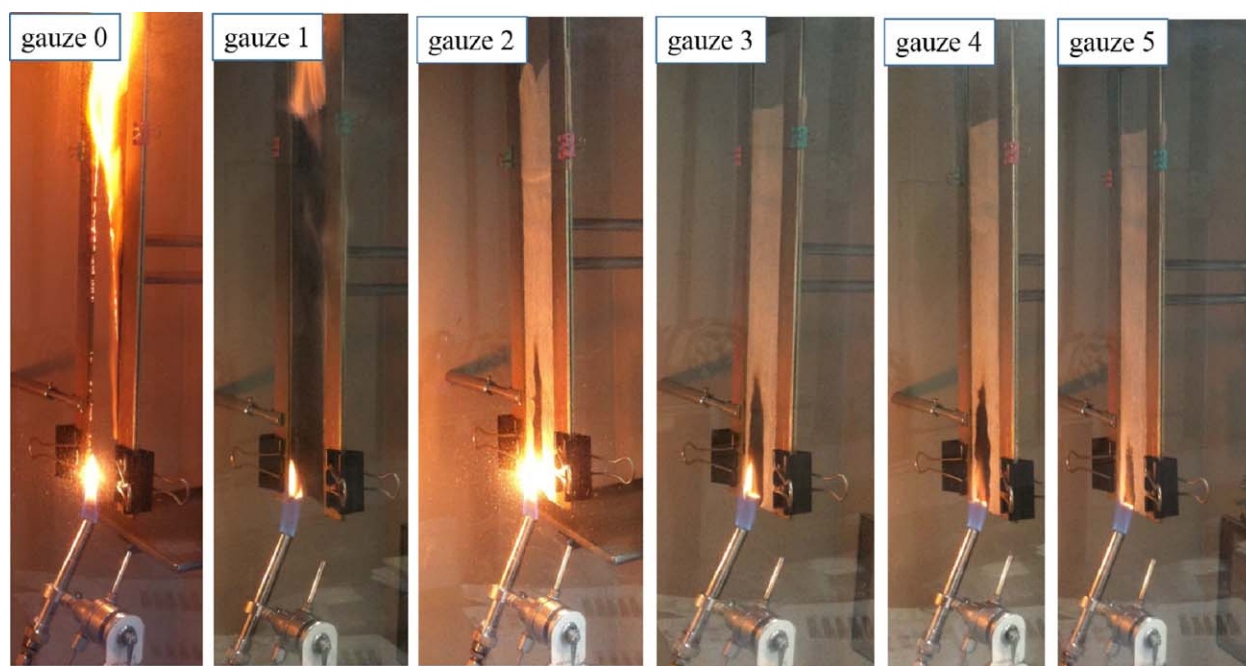
**Figure 5.** Photographs of pure cotton (a), the char residues of gauze 2 (b) and the char residues of gauze 4 (c) after LOI test. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



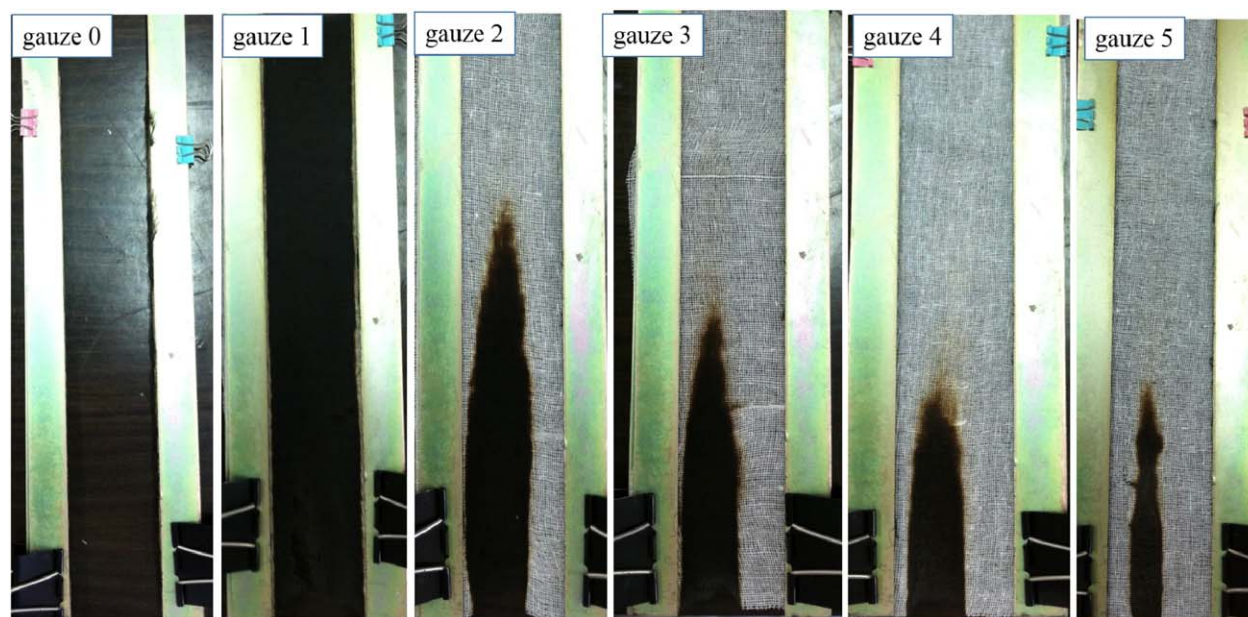
**Figure 6.** SEM micrograph of the surface morphology the char residues of MCP (a), gauze 0 (b), gauze 4 (c) and the char residues of gauze 4 (d).

The gauze 0-gauze 5 had been tested limited oxygen index (LOI). Neat cotton gauze is flammable and very easy to burn in air with a LOI of 16.9. But the gauze was flame retarded by 20

wt % MCP, LOI values increased to 26.5, indicating the increase of LOI by MCP additives. The LOI data is also summarized in Table I. The residual carbon and the LOI of gauze 5 is lower



**Figure 7.** Images of vertical flame testing of gauze 0 to gauze 5 after ignition. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 8.** Images of gauze 0 to gauze 5 during the vertical flame test. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

than that of gauze 4 in air, which consistent with the test results of TGA in  $N_2$ , the uptake of gauze is related to the solution of solubility, too much concentration is not conducive to the absorption of gauze.

The gauze 0 to gauze 5 had been tested vertical burning referring to the method of Li *et al.*<sup>32</sup> According to the GB/T 5455-1997 standard, the lighting time of all the samples are 5 s. The flame of gauze 0 and gauze 1 reached the top of sample, but the gauze 0 was brighter, more vigorous and without leaving any ashes at the instant of the light. The flames of gauze 2 to gauze 5 were not vigorous during continuous lighting of 12 s, they were quickly extinguished, fire does not burn up (Figure 7). Additionally, no any after flame and afterglow was seen after the flame was removed. After burning, no gauze 0 was left on the sample holder, but for gauze 1 to gauze 5, residues were significant for all the samples as shown in Figure 8. It showed their flame retardant effect is very good.

#### Adhesion Behaviors of MCP and Flame Retardant Gauze in Air

Thermosetted gauze, no matter how long soaked in water and how many times washing, when drying again, remained almost the same weight as before, indicating MCP's good adhesion.

#### CONCLUSIONS

In conclusion, this work presents the successful development of a facile and effective approach for the synthesis of a cyclotriphosphazene derivative (MCP) with etherized hexamethylolmelamine substituents. MCP is a novel water-soluble compound that can act as a flame retardant by dipping when applied to cotton gauze. The thermosetting MCP is able to promote char formation in the early stages of degradation. MCP can also effectively prevent full combustion of the fabric. The char yields of cotton gauze treated with a 20% solution of MCP were up to

47.6%, and furthermore these samples required 5 ignitions with a flame before full combustion was achieved. The LOI value of the material was also increased from 16.9% to 26.5%. What is more, this new flame retardant can firmly attached on the cotton fiber.

#### ACKNOWLEDGMENTS

This study was supported by the Natural Science Foundation of Guangdong Province (No. S2013020013091).

#### REFERENCES

- Basak, S.; Samanta, K. K.; Chattopadhyay, S. K.; Das, S.; Narkar, R.; Dsouza, C.; Shaikh, A. H. *Pol. J. Chem. Technol.* **2014**, *16*, 106.
- Basak, S.; Samanta, K. K.; Chattopadhyay, S. K.; Das, S.; Narkar, R.; Dsouza, C.; Shaikh, A. H. *J. Sci. Ind. Res. India* **2014**, *73*, 601.
- You, G.; Cheng, Z.; Peng, H.; He, H. *J. Appl. Polym. Sci.* **2015**, *132*, 41859.
- Lai, X.; Yin, C.; Li, H.; Zeng, X. *J. Appl. Polym. Sci.* **2015**, *132*, 41580.
- Yoshioka-Tarver, M.; Condon, B. D.; Cintron, M. S.; Chang, S.; Easson, M. W.; Fortier, C. A.; Madison, C. A.; Bland, J. M.; Nguyen, T. M. D. *Ind. Eng. Chem. Res.* **2012**, *51*, 11031.
- Lv, M. X.; Liao, T.; Song, T.; Zeng, J.; Zeng, H. P. *J. South China Normal Univ. (Nat. Sci. Ed.)* **2015**, *47*, 78.
- Kaebisch, B.; Fehrenbacher, U.; Kroke, E. *Fire Mater.* **2014**, *38*, 462.
- Liu, H.; Wang, X.; Wu, D. *Polym. Degrad. Stabil.* **2014**, *103*, 96.



9. Sun, J.; Yu, Z.; Wang, X.; Wu, D. *ACS Sustain. Chem. Eng.* **2014**, *2*, 231.
10. Liu, R.; Wang, X. *Polym. Degrad. Stabil.* **2009**, *94*, 617.
11. Toldy, A.; Szabo, A.; Novak, C.; Madarasz, J.; Toth, A.; Marosi, G. *Polym. Degrad. Stabil.* **2008**, *93*, 2007.
12. Carriedo, G. A.; Valenzuela, M. L. *Eur. Polym. J.* **2011**, *47*, 338.
13. Chen, C.; Liu, X.; Tian, Z.; Allcock, H. R. *Macromolecules* **2012**, *45*, 9085.
14. Mathew, D.; Nair, C. P. R.; Ninan, K. N. *Polym. Int.* **2000**, *49*, 48.
15. Morozowich, N. L.; Weikel, A. L.; Nichol, J. L.; Chen, C.; Nair, L. S.; Laurencin, C. T.; Allcock, H. R. *Macromolecules* **2011**, *44*, 1355.
16. Tao, K.; Li, J.; Xu, L.; Zhao, X.; Xue, L.; Fan, X.; Yan, Q. *Polym. Degrad. Stabil.* **2011**, *96*, 1248.
17. Un, I.; Ibisoglu, H.; Un, S. S.; Cosut, B.; Kilic, A. *Inorg. Chim. Acta* **2013**, *399*, 219.
18. Bai, Y.; Wang, X.; Wu, D. *Ind. Eng. Chem. Res.* **2012**, *51*, 15064.
19. Jin, W.; Yuan, L.; Liang, G.; Gu, A. *ACS Appl. Mater. Interfaces* **2014**, *6*, 14931.
20. Li, Q.; Chen, Y. Q.; Song, X. P.; Xie, Y. P.; Hou, Q.; Shi, G. *J. Appl. Polym. Sci.* **2015**, *132*, 41677.
21. Wang, J.; Su, X.; Mao, Z. *Polym. Degrad. Stab.* **2014**, *109*, 154.
22. Wang, J. S.; Zhao, H. B.; Ge, X. G.; Liu, Y.; Chen, L.; Wang, D. Y.; Wang, Y. Z. *Ind. Eng. Chem. Res.* **2010**, *49*, 4190.
23. Zhang, X.; Zhang, L.; Wu, Q.; Mao, Z. *J. Ind. Eng. Chem.* **2013**, *19*, 993.
24. Guo, Y.-N.; Zhao, C.; Liu, S.-Z.; Li, D.; Wang, S.-J.; Qiu, J.-J.; Liu, C.-M. *Polym. Bull.* **2009**, *62*, 421.
25. Pathak, S. S.; Khanna, A. S.; Sinha, T. J. M. *Prog. Org. Coat.* **2007**, *60*, 211.
26. Kroger, A.; Hiltrop, K.; Bremser, W. *Prog. Org. Coat.* **2013**, *76*, 335.
27. Lai, X. J.; Zeng, X. R.; Li, H. Q.; Liao, F.; Yin, C. Y.; Zhang, H. L. *Polym. Compos.* **2012**, *33*, 35.
28. Xu, M.; Chen, Y.; Qian, L.; Wang, J.; Tang, S. *J. Appl. Polym. Sci.* **2014**, *131*, 41006.
29. Sun, J.; Wang, X.; Wu, D. *ACS Appl. Mater. Interfaces* **2012**, *4*, 4047.
30. Asmafiliz, N.; Ilter, E. E.; Isiklan, M.; Kilic, Z.; Tercan, B.; Caylak, N.; Hokelek, T.; Buyukgungor, O. *J. Mol. Struct.* **2007**, *832*, 172.
31. Aslzadeh, M. M.; Abdouss, M.; Sadeghi, G. M. M. *J. Appl. Polym. Sci.* **2013**, *127*, 1683.
32. Li, Y. C.; Schulz, J.; Mannen, S.; Delhom, C.; Condon, B.; Chang, S.; Zammarano, M.; Grunlan, J. C. *ACS Nano* **2010**, *4*, 3325.