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Preparation of a halogen-free P/N/Si flame retardant monomer with reactive siloxy groups and its application in cotton fabrics☆

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ABSTRACT

A novel halogen-free phosphorus–nitrogen–silicon flame retardant monomer with reactive siloxy groups, *N*-(diphenylphosphino)-1,1-diphenyl-*N*-(3-(triethoxysilyl)propyl) phosphinamine (DPTA) has been synthesized and was applied to the fire-resistant finishing of cotton fabrics. The molecular structure of DPTA has been well characterized by elemental analysis, FTIR, ^1H NMR, and ^{31}P NMR spectroscopies. The chemically-grafted cotton fabrics, which were treated with 25 wt% DPTA, were obtained and confirmed by attenuated total reflectance Fourier infrared spectroscopy (ATR-FTIR). The flame retardancy and thermal property of the treated samples were investigated by limited oxygen index (LOI), vertical flammability test (VFT), thermogravimetric analysis (TGA) and microscale combustion calorimeter (MCC). It is noted that in vertical flammability test, the treated samples extinguished immediately upon removing the ignition source, whereas the untreated one was completely burned out. Furthermore, TGA and MCC tests revealed that the treated samples produced a high char formation and a low heated release during combustion. The surface morphology of the untreated and treated samples and the char residues after LOI tests were observed by scanning electron microscopy (SEM). Therefore, all the results showed that the treated cotton fabrics with 25 wt% DPTA apparently improved the fire-resistant and thermal performances.

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1. Introduction

Cotton fabrics are widely used in every aspect of our world, wherein they are versatile starting materials for development of new products [1]. However, cotton fabrics are very flammable [2]. Meanwhile, the demand for the flame-retardant cotton fabrics has a steady growth in the past decades [3,4].

To increase the flame retardancy of cotton fabrics, most researchers have focused on the development of the flame-retardant compound of cotton fabrics. In previous studies, phosphorus-containing compounds are well-known as novel flame retardants in providing the certain flame retardancy to cotton fabrics [5,6]. Afterwards, organophosphorus flame retardants that contain synergistically-active nitrogen can show the higher effectiveness in the flame-retardant treatment of cotton fabrics as compared with the phosphorus counterparts [7,8]. Most recently, silicon-containing compounds have been considered to be a kind of halogen-free flame retardants. This is because that (1) these compounds are harmless to the human and the eco-system [9]; (2) during the combustion, the produced thermal degradation products such as silicon dioxide, can form a protective silica layer that protects

polymer matrix from further thermal decomposition at high temperatures [10]; (3) during burning, the formation of inorganic barrier silica demonstrated self-extinguishing behavior in the flame-retardant treatment of cotton fabrics [11]. However, to the best of our knowledge, the application of the phosphorus–nitrogen–silicon reactive flame retardants to cotton fabrics is little reported.

This work is focused on the fire-resistant application of a halogen-free P/N/Si flame retardant monomer with reactive siloxy groups in cotton fabrics. This is mainly because that (1) the reactive siloxy moieties in the target flame retardant can be easily hydrolyzed and then well react with the hydroxyl groups of fabric matrix, which forms the chemically covalent bond; (2) the as-produced covalent bonds can strongly increase the attachment of flame retardant with fabric matrix, which further improves the flame retardancy of cotton fabrics [12]. So, in this paper, a novel P/N/Si flame retardant monomer with reactive siloxy groups, *N*-(diphenylphosphino)-1,1-diphenyl-*N*-(3-(triethoxysilyl)propyl)phosphinamine (DPTA) has been synthesized and was applied to the fire-resistant finishing of cotton fabrics. The molecular structure of DPTA was characterized by elemental analysis, FTIR, ^1H NMR, and ^{31}P NMR spectra. The cotton fabrics treated with 25 wt% DPTA were prepared and confirmed by attenuated total reflectance Fourier infrared spectroscopy (ATR-FTIR). The flame retardancy and the thermal property of the treated samples were investigated by limited oxygen index (LOI), vertical flammability test (VFT),

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thermogravimetric analysis (TGA) and microscale combustion calorimeter (MCC). The surface morphologies of the untreated and treated samples and the char residues after LOI tests were observed by scanning electron microscopy (SEM).

2. Experimental

2.1. Materials

Ph_2PCl and Et_3N were purchased from Changgen Chemical Technology Co., Ltd. (Shanghai, China). 3-Triethoxysilylpropylamine was purchased from Tianda Chemical Reagent (Tianjin, China). All the chemicals were used without further purification. Plain woven cotton fabrics with density of $184 \text{ g} \cdot \text{m}^{-2}$ were supplied by Taiyuan Chunguang textile Co., Ltd.

2.2. Preparation of the target flame retardant (DPTA)

A stirred solution of 3-triethoxysilylpropylamine (4.46 ml, 19.0 mmol) in CH_2Cl_2 (20.0 ml) was added Et_3N (5.8 ml, 41.6 mmol). Ph_2PCl (7.7 ml, 42.9 mmol) was slowly added to the above solution, and the reaction mixture was stirred at room temperature overnight. After the reaction was completed, the $\text{Et}_3\text{N} \cdot \text{HCl}$ salt was filtered through a short activated alumina column. The filtrate was evaporated to give the desired product as a white solid (yield: 91%). Anal. Calcd for $\text{C}_{33}\text{H}_{41}\text{NO}_3\text{P}_2\text{Si}$ (found): C, 67.21 (67.06); H, 7.01 (7.28); N, 2.38 (2.59). IR (KBr disk): ν 735 (P–N), 1080 (Si–O–C), 1432 (P–Ar), and 1479 (Ph) cm^{-1} . ^1H NMR (400 MHz, CDCl_3 , TMS): δ 0.20 (t, J = 8.4 Hz, 2H, SiCH_2), 1.10 (t, J = 7.2 Hz, 9H, OCH_2CH_3), 1.16–1.26 (m, 2H, SiCH_2CH_2), 3.17–3.26 (m, 2H, CH_2N), 3.61 (q, J = 7.2 Hz, 6H, OCH_2CH_3), 7.28–7.42 (m, 20H, PhH). ^{31}P NMR (161.9 MHz, CDCl_3 , 85% H_3PO_4): δ 62.47 (s).

2.3. Procedure for the fire-resistant finishing of cotton fabrics

Firstly, the cotton fabrics were washed with 4 wt% aq NaOH solution, rinsed with distilled water for three times, and dried naturally. Then, the fabric samples were impregnated in a $\text{H}_2\text{O}/\text{EtOH}$ (v/v, 1:4) solution containing 25 wt% DPTA, 5 wt% sodium hypophosphite (SHP) and 5 wt% boric acid (BA) at 40 °C for 2 h, and passed through a laboratory-scale padder with two dips and nips to keep an approximately 80% of wet pick up. Finally, the impregnated samples were dried at 80 °C for 5 min and cured at 160 °C for 3 min.

2.4. Measurements

FTIR and ATR-FTIR spectra were recorded on Thermo Scientific Nicolet IS50 FT-IR spectrometer with an ATR attachment in the range of 500–4000 cm^{-1} . ^1H NMR and ^{31}P NMR spectra were recorded by a Bruker Avance III spectrometer (400 MHz) in CDCl_3 at room temperature using TMS and 85% H_3PO_4 as the internal standards, respectively. Elemental analyses were performed on a Perkin-Elmer 240C analyzer. Limiting oxygen index (LOI) test was measured on a HC-2 analyzer with strips of fabrics ($15.0 \times 5.0 \text{ cm}$) according to GB/T 5454-1997. The vertical flammability test (VFT) was measured on a CZF-5

horizontal vertical combustion apparatus referring to GB/T 5455-1997 textiles. Microcombustion calorimetry (MCC) was used to determine the flammability characteristics of treated cotton fabrics according to ASTM D 7309-07. Thermogravimetric analysis (TGA) was performed on ZCT-A thermal analyzer in a temperature range of 25–700 °C in air temperature at a heating rate of $10 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$ and sample mass was in the range of 5–10 mg. Scanning electron microscopy (SEM) was performed on a Hitachi X650 instrument at room temperature and all the samples were sputtered with platinum before SEM analysis.

3. Results and Discussion

3.1. Synthesis and characterization of DPTA

As shown in Fig. 1, the target flame retardant (DPTA) was easily prepared by treatment of 3-triethoxysilylpropylamine and 2.2 equivalent chlorodiphenylphosphine in the presence of triethylamine as acid-binding agent at room temperature in high yield.

The molecular structure of DPTA was characterized by FTIR, ^1H NMR, and ^{31}P NMR spectroscopies. In the FTIR spectrum of DPTA, some characteristic absorption peaks were assigned in the following: 735 (P–N), 1080 (Si–O–C), 1432 (P–Ar), and 1479 (Ph) cm^{-1} . The appearance of these significant groups demonstrated that DPTA should be prepared.

NMR technique was used to further confirm the structure of DPTA. As shown in Fig. 2, the ^1H NMR spectrum of DPTA displayed the following proton signals: 0.20, 1.16–1.26, and 3.17–3.26 (6H of one $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{N}$ group, H-c, H-d and H-e); 1.10 and 3.61 (15H of three OCH_2CH_3 moieties, H-a and H-b); 7.28–7.42 (20H of four C_6H_5 groups, H-f). Meanwhile, there was only a sharp peak at 62.47 ppm in the ^{31}P NMR spectrum as displayed in Fig. 3. Thus, the IR and NMR assignments well indicated the successful obtainment of DPTA.

3.2. Fire-resistant finishing condition of cotton fabrics

To investigate the optimal finishing conditions, the fire-resistant finishing of cotton fabrics containing different DPTA concentrations with and without $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}/\text{H}_3\text{BO}_3$ (5 wt%/5 wt%) as catalyst has been evaluated and compared by LOI tests, the results of which are displayed in Tables 1 and 2, respectively.

As it is known that pure cotton fabrics easily burned, its LOI value is measured and being 18.4%. On the condition that the cotton fabrics are treated with the mixture solution containing DPTA and $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}/\text{H}_3\text{BO}_3$, the LOI values of treated samples with different concentrations of DPTA are measured as shown in Table 1. When the concentration of DPTA is only 10 wt%, the LOI value of treated samples sharply increases to 29.0%. The LOI value of treated samples steadily rises with the increasing of the DPTA concentration. The LOI value of treated samples with 25 wt% DPTA reaches 30.7%, which can achieve B1 grade ($\text{LOI} \geq 30\%$) according to the GB/T 5454-1997. However, it is seen from Table 2 that the LOI values of treated samples only containing DPTA are from 23.3% to 25.4%, which are much lower than those of treated samples containing DPTA and $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}/\text{H}_3\text{BO}_3$.

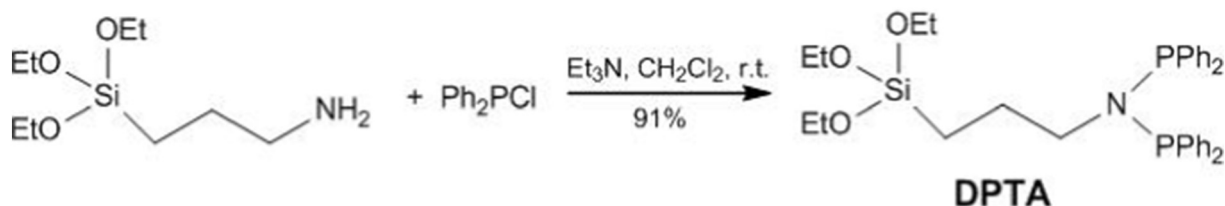
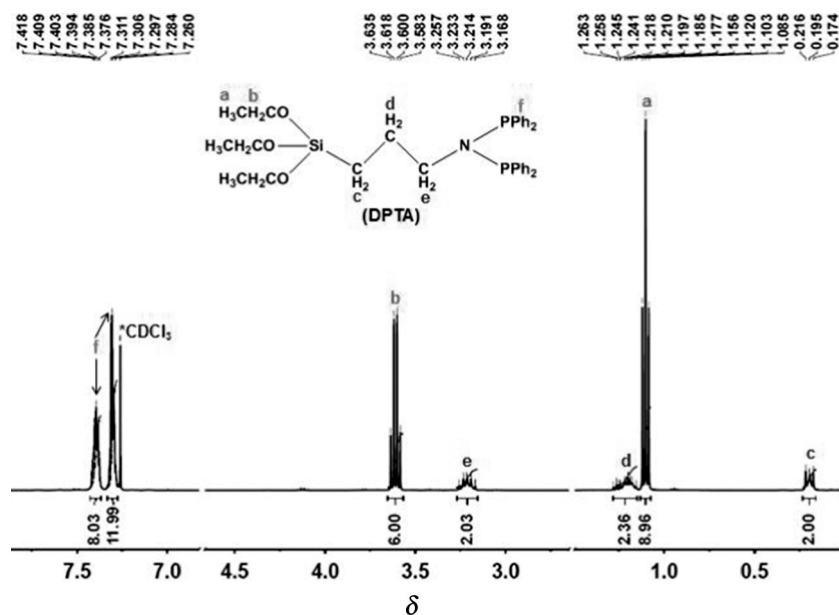
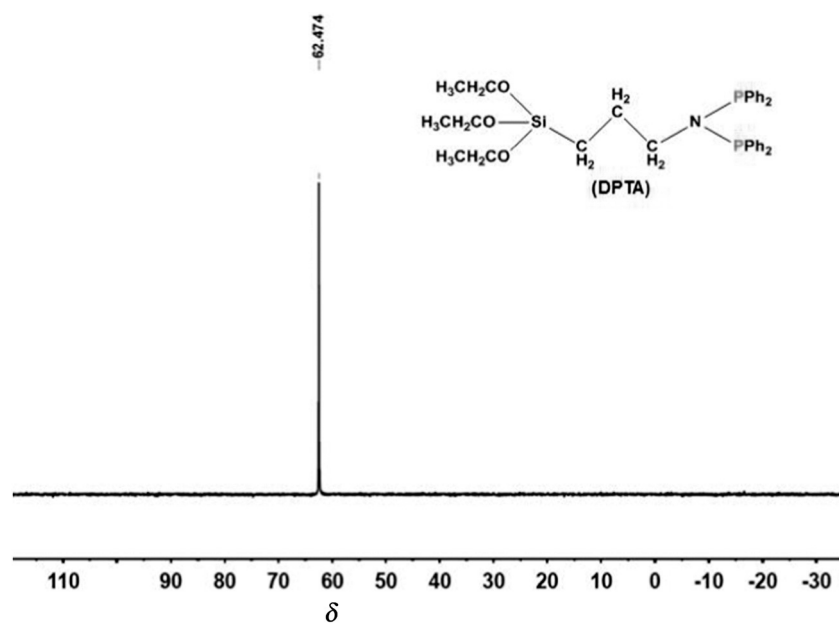


Fig. 1. Preparation of the target flame retardant (DPTA).

Fig. 2. ^1H NMR spectrum of the target flame retardant (DPTA).Fig. 3. ^{31}P NMR spectrum of the target flame retardant (DPTA).

Thus, these results indicated that DPTA as a good flame retardant is applied to cotton fabrics, and $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}/\text{H}_3\text{BO}_3$ as effective catalyst promotes the chemically-grafted reaction process [13]. And it can

be well deduced from the aforementioned information that the optimally-finishing condition of cotton fabrics is in the following of 25 wt% DPTA as flame retardant, the mixed 5 wt% $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ and

Table 1

The add-on and LOI data of untreated and treated cotton fabrics containing different DPTA concentrations with $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}/\text{H}_3\text{BO}_3$ (5 wt%/5 wt%)

Samples	Add-on/%	LOI/vol%
Untreated	–	18.4
10 wt% DPTA treated	14.9	29.0
15 wt% DPTA treated	19.2	29.1
20 wt% DPTA treated	39.0	29.6
25 wt% DPTA treated	39.4	30.7

Note: Add-on = $(W_t - W_o) / W_o \times 100\%$, W_o and W_t represent the masses of cotton fabrics before and after the treatment, respectively.

Table 2

The add-on and LOI data of untreated and treated cotton fabrics containing different DPTA concentrations without $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}/\text{H}_3\text{BO}_3$ (5 wt%/5 wt%)

Samples	Add-on/%	LOI/vol%
Untreated	–	18.4
10 wt% DPTA treated	18.3	23.3
15 wt% DPTA treated	20.6	23.9
20 wt% DPTA treated	27.7	25.0
25 wt% DPTA treated	29.3	25.4

Note: Add-on = $(W_t - W_o) / W_o \times 100\%$, W_o and W_t represent the masses of cotton fabrics before and after the treatment, respectively.

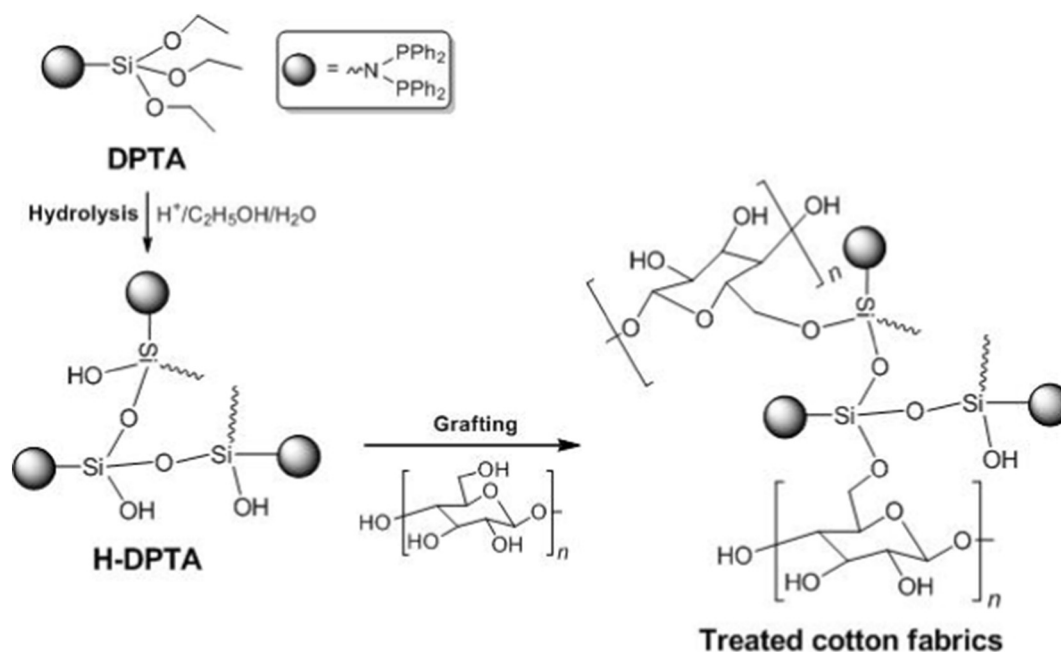


Fig. 4. Possible process of chemically-grafted reaction between DPTA and cotton fabrics.

5 wt% H_3BO_3 as catalyst, drying temperature of $80^\circ C$ for 5 min, as well as curing temperature of $160^\circ C$ for 3 min, where the corresponding treated cotton fabrics with B1 grade can be regarded as a kind of the good fire-resistant material.

3.3. ATR-FTIR study of untreated and treated cotton fabrics

To confirm the existence of the chemically-grafted reaction between DPTA and fabric matrix as shown in Fig. 4, the ATR-FTIR spectra of

cotton fabrics untreated and treated with 25 wt% DPTA are studied as displayed in Fig. 5.

It can be seen from Fig. 5 that such the following characteristic absorption bands as O–H stretching vibrations (cellulose) in the range of $3500\text{--}3200\text{ cm}^{-1}$, P–Ar stretching vibration (DPTA) at 1438 cm^{-1} , and P–N stretching vibration (DPTA) at 754 cm^{-1} are observed in the IR spectrum of treated samples [14,15]. Especially, it is noted that compared to that of untreated cotton fabrics, the new Si–O–C stretching absorption band at 963 cm^{-1} appears in the IR spectrum of treated samples. Therefore, the chemically-grafted

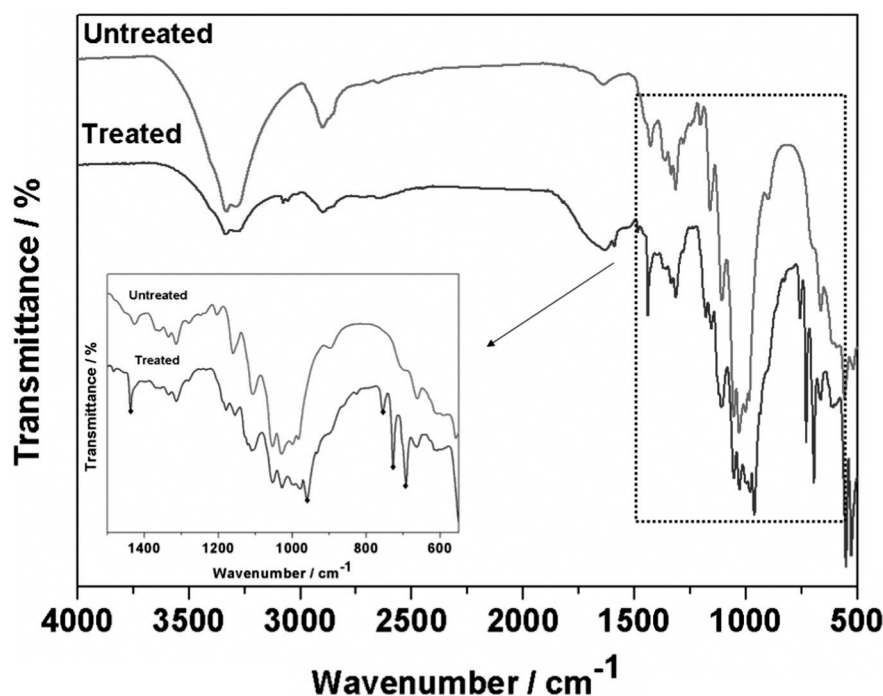


Fig. 5. ATR-FTIR spectra of untreated and treated cotton fabrics.

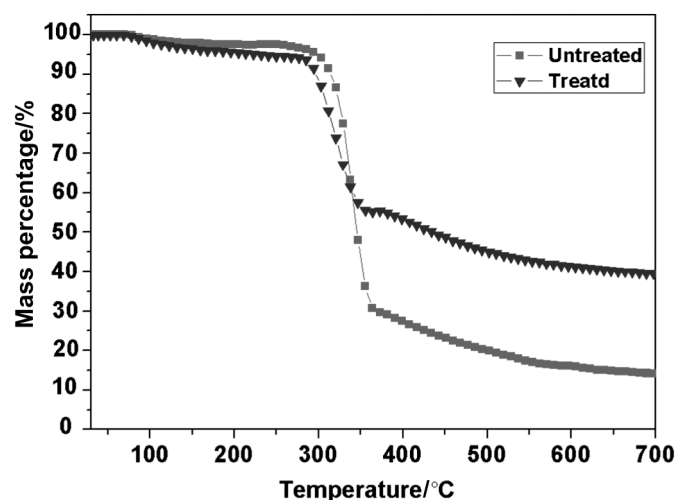


Fig. 6. TGA curves of untreated and treated cotton fabrics in nitrogen atmosphere.

reaction between DPTA and fabric matrix can occur through treating cotton fabrics with 25 wt% DPTA.

3.4. Thermal behaviors of untreated and treated cotton fabrics

The thermal degradation behaviors of untreated and treated cotton fabrics with 25 wt% DPTA have been investigated by thermogravimetric analysis (TGA). Fig. 6 shows the thermal degradation curves of samples while Table 3 lists the data of the following parameters in nitrogen.

It can be seen from Fig. 6 and Table 3 that TGA curves of untreated and treated samples mainly display one apparent decomposing process. For untreated sample, its initial degradation temperature is 297 °C. Furthermore, it gives the maximum mass loss rate at ca. 338 °C and loses ca. 70% mass. As the temperature increases, only 14% char residue was left at 700 °C. Thus, the large mass loss and the low char residue occurred in the decomposition process. This is possibly because that (1) the thermal decomposition of the cellulose cleavage occurred in the temperature range of 300–350 °C; (2) the further decomposition of char residue is produced in the weight loss stage after 350 °C [13].

For treated sample with 25 wt% DPTA, the onset decomposition temperature (232 °C) and the maximum mass loss temperature (320 °C) are lower than those of untreated sample (297 °C as well as 338 °C), respectively. This is possibly attributed to the presences of the phosphoric acid formed by the decomposition of DPTA [16]. Especially, it is noted that the char residue of treated sample reaches up to 40.1% at 700 °C, which is much more than that of untreated sample (14%). Therefore, the flame retardancy of treated cotton fabrics is apparently improved by the grafting of DPTA to the fiber matrix, possibly due to the following fact that (1) the phosphorus and nitrogen parts of DPTA can catalyze the dehydration and carbonization of matrix and reduce the amount of combustible gases and promote char formation [17]; (2) the silicon part of DPTA can form a protective silica layer during combustion, in which the silica layer may protect polymer residues from further thermal decomposition at high temperatures [11].

Table 3

Data of TGA test for untreated and treated cotton fabrics in nitrogen atmosphere

Samples	Initial decomposed temperature $T_{on-set}/^{\circ}\text{C}$	Maximum weight loss temperature $T_{max}/^{\circ}\text{C}$	Char residue at 700 °C/%
Untreated	297	338	14.0
25 wt% DPTA treated	232	320	40.1

Table 4

Data of LOI and vertical flammability tests for untreated and treated cotton fabrics

Samples	After-flame time/s	After-glow time/s	Char length/cm	LOI/vol.%
Untreated	8.3	0	null	18.4
25 wt% DPTA treated	0	0	8.1	30.7

3.5. Flame retardancy of untreated and treated cotton fabrics

3.5.1. Limited oxygen index (LOI) and vertical flammability test (VFT)

To evaluate the flame-retardant performances of untreated and treated cotton fabrics with 25 wt% DPTA, the flame retardancy of these samples is studied using limited oxygen index (LOI) and vertical flammability test. The LOI data and the VFT values of after-flame time, after-glow time as well as char length are given in Table 4. The apparatus and char residue after the vertical flammability test are shown in Fig. 7.

It can be seen from Table 4 that the LOI value of untreated cotton fabrics is only 18.4% whereas that of treated sample with 25 wt% DPTA reaches to 30.7%, in which the latter is regarded as non-flammable material according to the GB/T 5454–1997. From Fig. 7 and Table 4, for the pure cotton fabrics, the whole sample is completely damaged and no char residue is formed during burning. However, for the treated sample with 25 wt% DPTA, it can be quickly self-extinguished and produce the compact char residue in combustion process. Meanwhile, there is 8.1 cm damaged char length and 0 s after-flame time as well as 0 s after-glow time, indicating that the treated cotton fabrics can achieve B1 rating according to GB/T 5455–1997.

On the basis of these results, it is deduced that DPTA as a phosphorus–nitrogen–silicon reactive flame retardant can well improve the flame-retardant ability of cotton fabrics. This is possibly attributed to the following facts that (1) the phosphorus-containing group in DPTA as acid source can form phosphoric acid and further promote the formation of char layer [16]; (2) the nitrogen-containing moiety in DPTA as blowing agent can release inert gases, which foam the char formation

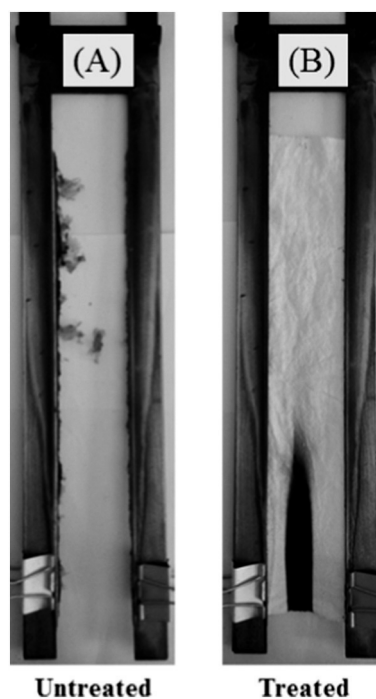


Fig. 7. Char residues of untreated (A) and treated (B) cotton fabrics after vertical flammability test.

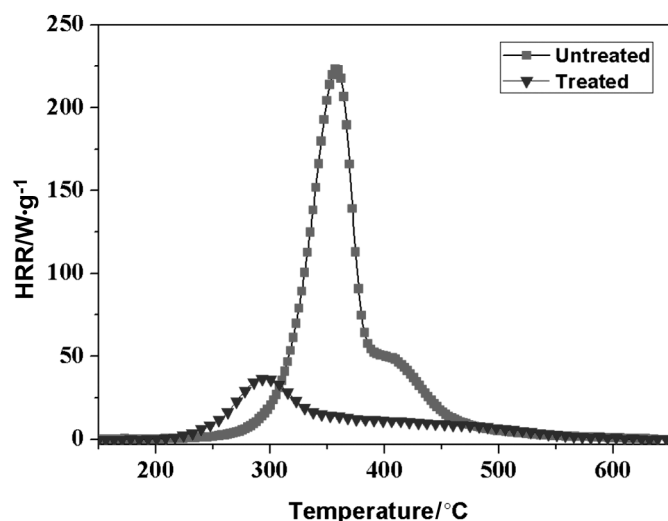


Fig. 8. MCC curves of untreated and treated cotton fabrics.

Table 5

MCC data of untreated and treated cotton fabrics

Samples	pHRR/W·g ⁻¹	THR/kJ·g ⁻¹	T _{max} /°C
Untreated	223.9	13.8	358.1
25 wt% DPTA treated	42.8	4.8	290.3

Note: pHRR = peak heat release rate. THR = total heat release.

and further generate a swollen as well as porous char layer (named as intumescent char layer) [18]; (3) the silicon-containing unit in DPTA as inorganic filler can well reinforce the above-formed intumescent char layer, which can act as a big barrier to heat, fuel, as well as oxygen transfer and may effectively inhibit the fire spread of cotton fabrics [19].

3.5.2. Microcombustion calorimetry test (MCC)

The flame-retardant behaviors of untreated and treated cotton fabrics with 25 wt% DPTA are further investigated by microcombustion

calorimetry (MCC). While the MCC curves of untreated and treated samples are displayed in Fig. 8, the corresponding data for these samples are listed Table 5.

It can be seen from Fig. 8 that the presence of the DPTA decreases the onset decomposition temperature for treated cotton fabrics, as observed in the reported phosphorus-containing flame retardants. This is possibly because that the decomposition of phosphorus-containing compound during combustion may catalyze the dehydration of cellulose [16]. It is seen from Fig. 8 and Table 5 that the optimum condition of treated samples exhibits the greatest reduction in pHRR and THR of 80% and 65% respectively, compared to that of untreated sample. This indicated that the presence of DPTA can result in the increase of the residual char, which may further inhibit the transfer of heat. So, the above-mentioned results are consistent with those of TGA and vertical flammability test.

3.6. Surface morphology for untreated and treated cotton fabrics

The difference in the surface morphology of untreated and treated cotton fabrics with 25 wt% DPTA has been studied by scanning electron microscopy (SEM). The morphologies of untreated and treated samples before and after LOI tests are shown in Fig. 9.

For untreated sample, the surface morphology before burning is intact and smoothed (Fig. 9A₁), whereas the char layer after burning is completely destroyed and very loose (Fig. 9A₂). For treated sample with 25 wt% DPTA, the surface morphology before flaming is rough and firm (Fig. 9B₁) in comparison with that of untreated sample, which should be attributed to the successful grafting of DPTA to the fabric matrix during the cross-linking reaction between them as confirmed in the ATR-FTIR spectra of untreated and treated samples. Most importantly, the surface of the char residue of treated sample after flaming is still compact as well as continuous as compared to that of untreated sample; meanwhile, it also displays an intumescent microstructure of char residue (Fig. 9B₂). Such the surface morphology change indicated that the formation of high-quality char layer during flaming plays an important role in protecting the inside of cotton fabrics and in blocking the fire propagation of the combustion process [20]. And it is noted that these results are consistent with the good flame-retardant ability of treated cotton fabrics as indicated in the LOI and vertical flammability tests.

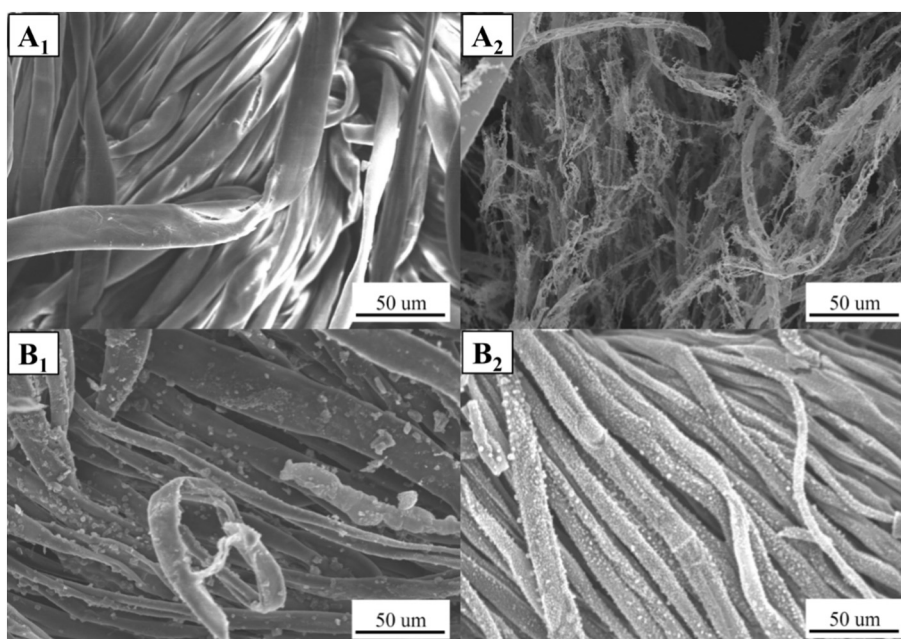


Fig. 9. SEM images of untreated (A₁, A₂) and treated (B₁, B₂) cotton fabrics before and after LOI tests.

4. Conclusions

A novel halogen-free P/N/Si flame retardant monomer (DPTA) with reactive siloxy groups was successfully synthesized, which has been well characterized by elemental analysis, FTIR, ^1H NMR, and ^{31}P NMR spectroscopies. The influence of DPTA on the fire-resistant performance and the thermal degradation behavior of cotton fabrics has been investigated by LOI, VFT, TGA, as well as MCC tests. The LOI data show that DPTA is effective in providing the fire-resistant finishing of cotton fabrics, in which the LOI values of treated sample with 25 wt% DPTA can reach 30.7%. VFT results demonstrate that the flame retardancy of treated sample can achieve the GB/T 5455-1997 vertical burning test B1 grade. The TGA and MCC results indicate that relative to pure cotton fabrics, the treated sample with 25 wt% DPTA possesses ca. 40.1% of the char residues at 700 °C, which results in 80% and 65% reduction in peak heat release rate and total heat release. The surface morphology for treated samples with 25 wt% DPTA before and after burning as observed by SEM demonstrates that DPTA as a reactive flame retardant plays an important role in the formation of the high-quality char layer during flaming. So, these results indicate that treated cotton fabrics with 25 wt% DPTA can possess the obviously enhanced fire-resistant and thermal properties.

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