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RAPID COMMUNICATION

Synthesis of a novel triazine flame retardant containing sulfur and its application to cotton fabrics

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Abstract−A novel triazine flame retardant (**FR**) has been successfully synthesized by the reaction of cyanuric chloride with sodium sulfanilate followed by diethanol amine. Its structure has been fully characterized by IR and ^{1}H NMR spectroscopy. The effects of reaction solvent, acid-binding agent, reaction temperature, and molar ratio of starting materials on the yield of **FR** were investigated in detail. Experiments showed that when the molar ratio of intermediate **I** to diethanol amine is 1 to 1.2 in the presence of sodium carbonate as acid-binding agent in acetone-water at 45 °C, the yield of the obtained **FR** reaches 81.4%. Thermogravimetry (TG) test indicated that the **FR** has good thermostability and char-forming ability. In addition, the flame retardancy and thermal behavior of the cotton fabrics treated with **FR** were studied by limiting oxygen index (LOI), vertical flammability test, and thermogravimetry (TG) to evaluate the flame-retardant performance of the target **FR**. These results demonstrated that the flame retardancy and thermal stability of the cotton fabrics treated with **FR** were clearly improved.

Key words: Triazine, Flame Retardant, Synthesis, Thermal Stability, Cotton Fabrics

INTRODUCTION

It is common that formaldehyde-containing or halogen-containing flame retardants show remarkable flame retardancy. However, they generate large amounts of toxic and corrosive fumes during combustion [1] and have restricted applications in many fields [2,3]. Triazine and its derivatives are known as flame-retardant materials and good charring agents because they contain stable triazine rings and form high-quality char layer during burning [4,5]. Furthermore, triazines are of beneficial merit as commercially available, comparatively cheap, and environmentally clean materials. However, the flame retardancy of triazines that have been applied to some polymers still has not been studied sufficiently [6-9]. These strongly enable us to prepare the triazine flame retardant with the sulfur-nitrogen synergistic effect [10,11] and apply it to the flame-retardant treatment of cotton fabrics.

In this paper, a triazine flame retardant (**FR**) was synthesized for the first time by the reaction of cyanuric chloride with sodium sulfanilate followed by diethanol amine to give a target **FR**. The molecular structure of **FR** was structurally characterized by IR and ^{1}H NMR spectroscopy. Thermogravimetry (TG) test indicated that the **FR** has good thermal stability and char-forming ability. Meanwhile, the flame retardancy and thermal behavior of the cotton fabrics treated with **FR** were investigated by limiting oxygen index (LOI), vertical flammability test and thermogravimetry (TG). These results demonstrate that the flame retardancy and thermal stability of the cotton fabrics treated with **FR** is clearly improved when the prepared **FR** is applied to the cotton fabrics.

MATERIALS AND METHODS

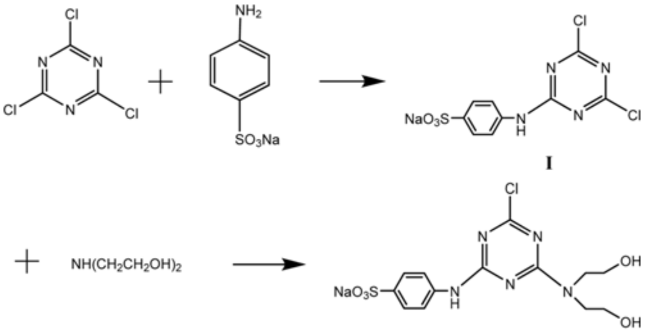
1. Materials

Cyanuric chloride and sodium sulfanolate were purchased from the Yingkou Sanzheng Organic Chemical Industry Company. Diethanol amine, acetone, and sodium carbonate were obtained from the Tianda Chemical Reagent Factory. All the starting materials and solvents were commercially available and used without further purification. 100% Cotton fabrics with density of 184 g/m^2 was supplied by Santai Fire Resistant Products Co., Ltd.

2. Synthesis of FR

The intermediate **I** was prepared according to the reported literature [12].

The target compound **FR** was prepared as shown in Scheme 1. In a typical experiment, the intermediate **I** (10 mmol) was added to a mixed solution of water and acetone in 250 mL four-neck flask, and then the mixture was stirred for 0.5 h at 25 °C. The aqueous



Scheme 1. Synthetic route of FR.

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solution of diethanol amine (12 mmol) was slowly dropped into the above reaction vessel for 0.5 h, in which 20% aqueous solution of sodium carbonate was added to keep pH=8-9. The reaction process was monitored by thin layer chromatography (TLC) on silica gel elution with methanol-toluene (2 : 3, v : v). When the reaction was completed, the reaction solvent was removed on a rotary evaporator. The crude product obtained was poured into anhydrous alcohol, washed with anhydrous alcohol and dried at room temperature. Finally, the target product was afforded as a white powder (Yield: 81.4%). ^{1}H-NMR (400 MHz, d$_6$-DMSO, δ/ppm): 10.10 (s, 1H, NH), 7.52-7.61 (2s, 4H, PhH), 4.84 (s, 2H, OH), 3.57-3.70 (m, 8H, NCH_2 CH_2O); IR (KBr, ν/cm^{-1}): 3,478, 3,272, 1,563, 1,380, 1,230, 1,173, 1,038, 610 [13].

RESULTS AND DISCUSSION

1. Synthetic Condition of FR

1-1. Influence of Reaction Solvent on the Yield of FR

The influence of solvent on the reaction to yield of **FR** was first considered for the optimal synthetic conditions. As the molar ratio of intermediate **I** and diethanol amine is 1 to 1.2 in the presence of sodium carbonate as acid-binding agent at 45 °C, we investigated the influence of several reaction solvents on the yield of FR and the results are presented in Table 1.

Table 1 shows that the yield of **FR** was 76.0% when the solvent was water that was regarded as an environmentally-friendly solvent. However, the maximum yield of **FR** increased to 81.4% as the solvent was water-acetone. One reason is that diethanol amine, which is a viscous liquid and has better solubility in water than in ethanol, must be dissolved in water before dropping. Another is that the solubility of the target product in acetone is relatively higher than the one in water, resulting in the increase of the yield of **FR**. Therefore, we selected the water-acetone as the optimal reaction solvent.

1-2. Influence of Acid-binding Agent on the Yield of FR

As the molar ratio of intermediate **I** and diethanol amine is 1 to 1.2 in water-acetone at 45 °C, we studied the influence of different acid-binding agent on the yield of **FR** and the results are listed in Table 2. It was noted that the addition of the appropriate acid-binding agent could efficiently accelerate the reaction when hydrogen chloride was produced during the reaction, which was based on the principle of the chemical equilibrium shift. The common acid-binding agents were composed of the inorganic bases (sodium hydroxide, sodium carbonate, etc.) and organic bases (pyridine, triethylamine, etc.). However, the inorganic bases are the best choice as they are lower-cost and environmentally friendly.

Table 1. Effect of reaction solvent on the yield of FR

Solvent	Water	Water-acetone	Acetone	Water-ethanol
Yield/%	76.0	81.4	53.5	49.0

Table 2. Effect of acid-binding agent on the yield of FR

Acid-binding agent	Sodium carbonate	Sodium hydroxide
Yield/%	81.4	55.8

Table 2 shows that the yield of **FR** reached 81.4% when acid-binding agent was sodium carbonate. This is because sodium hydroxide is more basic than sodium carbonate, which might cause the appearance of some side reaction. Thus, we chose sodium carbonate as the optimal acid-binding agent.

1-3. Influence of Reaction Temperature on the Yield of FR

As the molar ratio of intermediate **I** and diethanol amine is 1 to 1.2 in the presence of sodium carbonate as acid-binding agent in water-acetone, the influence of reaction temperature on the yield of **FR** was investigated and the results are displayed in Fig. 1.

Fig. 1 shows that a different reaction temperature had a certain effect on the yield of **FR**. When the reaction temperature was 45 °C, the yield of **FR** reached the maximum. According to the different reactivity of three chlorine atoms in cyanuric chloride, the first chlorine atom can react at 0-5 °C and the second chlorine atom can react at 40-60 °C [14]. For the general reaction, the increase of temperature can enhance the probability of the intermolecular effective collision, resulting in the rise of the reaction rate. Obviously, the yield of **FR** showed little change as the reaction temperature was above 45 °C.

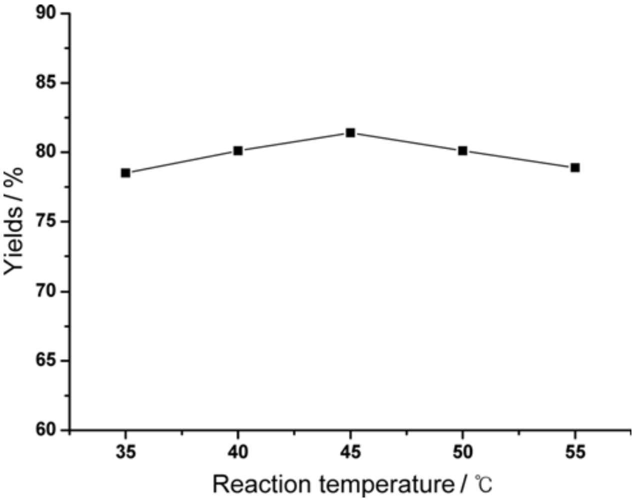

Fig. 1. Influence of reaction temperature on the yield of FR.

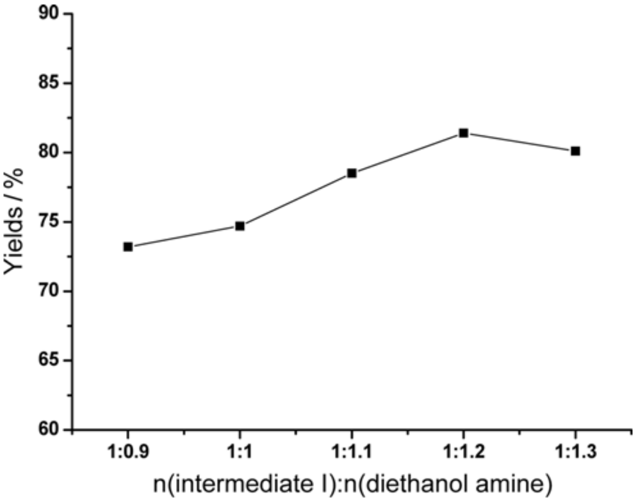

Fig. 2. Influence of n (intermediate I) : n (diethanol amine) on the yield of FR.

Consequently, the optimal reaction temperature was at 45 °C.

1-4. Influence of n (Intermediate I): n (Diethanol Amine) on the Yield of FR

With the condition of water-acetone as reaction solvent, sodium carbonate as acid-binding agent, and reaction temperature at 45 °C, the influence of the molar ratio of intermediate **I** to diethanol amine on the yield of **FR** was studied and the results are presented in Fig. 2.

Fig. 2 shows that the yield of **FR** gradually increased when the range of the molar ratio of intermediate **I** to diethanol amine was from 1 : 0.9 to 1 : 1.2 but sharply decreased as that of intermediate **I** to diethanol amine was 1 to 1.3. Especially considering the cost of starting materials and the pollution of environment, we finally selected n (intermediate **I**) : n (diethanol amine)=1 : 1.2 as the optimal molar ratio of starting materials.

On the basis of the above results, it is concluded for the optimal synthetic conditions that the yield of **FR** reaches 81.4% as the molar ratio of intermediate **I** to diethanol amine is 1 to 1.2 in the presence of sodium carbonate as acid-binding agent in acetone/water at 45 °C.

2. Thermal Stability of FR

Fig. 3 gives the TG and DTG curves of **FR** in an air atmosphere. It can be seen from the TG curve that the initial decomposition temperature is 169 °C and the char residue reaches 36.8% at 600 °C, indicating that **FR** is an efficient char-forming agent. Meanwhile, the DTG curve displays that **FR** has a minor (at about 182 °C) and a major (at about 507 °C) weight-loss stage, which might be assigned to the loss of the unstable compound such as water and the decomposition of sulfamate. These results indicate that **FR** is a potential highly-effective flame retardant.

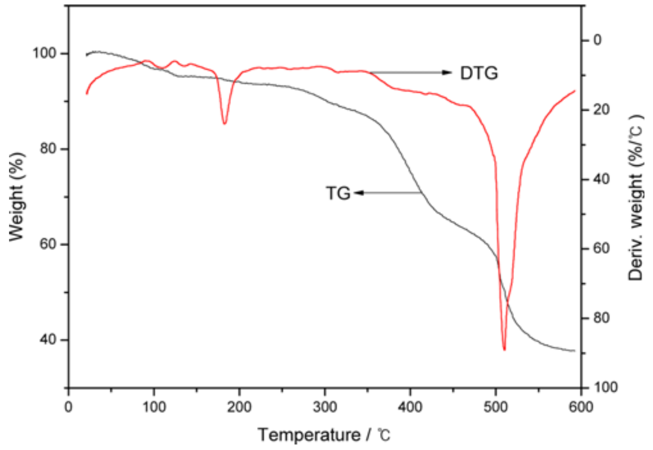

Fig. 3. TG and DTG curves for FR in air (heating rate=10 °C/min).

3. Flame-retardant Study of the Cotton Fabrics Treated with FR

3-1. Flame Retardancy of the Cotton Fabrics Untreated or Treated with FR

To evaluate the flame-retardant performance of **FR**, the results of limiting oxygen index (LOI) and vertical flammability test for the cotton fabrics treated by **FR** are shown in Table 3. When the add-on of **FR** is 10 wt%, the LOI value of cotton fabrics treated is 26.1% and it can reach flame-resistant level. From the vertical flammability test, it is clearly seen that the cotton fabrics untreated can completely inflame, but the cotton fabrics treated have shorter after-flame and after-grow burning with the char length less than 10 cm. Therefore, it is concluded that the addition of **FR** can greatly improve the flame retardancy of the cotton fabrics.

3-2. Thermal Stability of the Cotton Fabrics Untreated or Treated with FR

Fig. 4 shows the TG (a) and DTG (b) curves of cotton fabrics untreated or treated by **FR**. For the cotton fabrics untreated, while the initial decomposition temperature was at 225 °C, it has a minor (at about 311 °C) and a major (at about 392 °C) weight-loss stage, in which it has merely the residues of 8.8% at 600 °C. For the cotton fabrics treated with **FR**, while the initial decomposition temperature was at 234 °C, it has a minor (at about 325 °C) and a major (at about 505 °C) weight-loss stage, where it has a residue of 23.0% at 600 °C. The results indicate that the initial decomposition temperature and char residue of the cotton fabrics treated with **FR** increased significantly, further demonstrating that the addition of **FR** can improve the thermal stability and change the thermal decomposition behavior of the cotton fabrics during combustion. This may be be-

Table 3. Data of LOI and vertical flammability test of cotton fabrics treated and untreated with FR

Samples	LOI (%)	After-flame time (s)	After-glow time (s)	Char length (cm)
Cotton/**FR**	26.1	1.5	12.5	7.8
Cotton	17.5	2.9	32.7	None

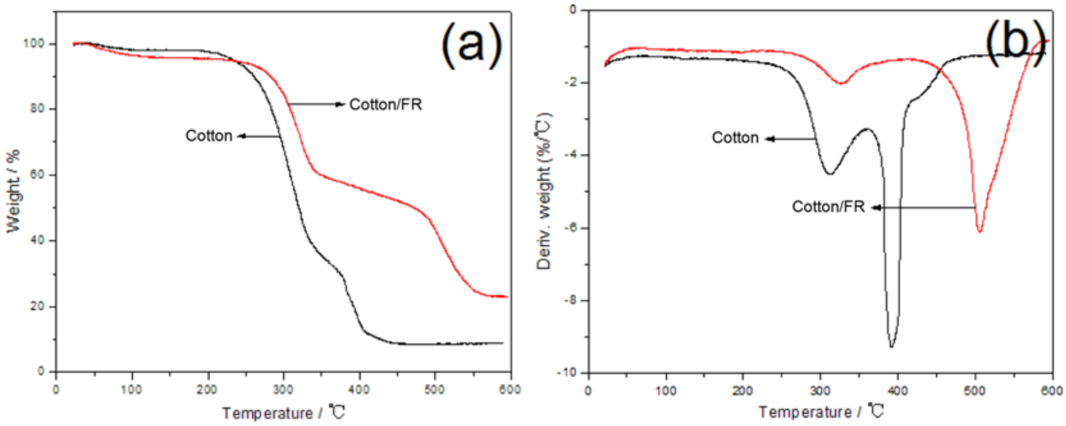

Fig. 4. TG (a) and DTG (b) curves for the cotton fabrics untreated or treated with FR in air (heating rate=10 °C/min).

cause (i) **FR** can form the protective char layer during flaming, which prevents the diffusion of the heat and oxygen in the outside of the cotton fabrics into the inside; (ii) the production of the heat is difficult to be transferred from the char layer to the gas phase area during combustion; (iii) thus the thermal decomposition process of the cotton fabrics treated with **FR** is delayed, which increase the thermal stability of the cotton fabrics.

CONCLUSIONS

A novel triazine flame retardant (**FR**) was successfully synthesized and structurally characterized by means of IR and ^{1}H NMR spectra. Experiments for the optimal synthetic conditions showed that the yield of **FR** reaches 81.4% when the molar ratio of intermediate **I** to diethanol amine is 1 to 1.2 in the presence of sodium carbonate as acid-binding agent in acetone/water at 45 ºC. Thermogravimetry (TG) test indicated that the **FR** has good thermal stability and char-forming ability due to the presence of the triazine ring and benzene ring. Additionally, the limiting oxygen index (LOI) and vertical flammability test demonstrated that the LOI value is 26.1% and reaches flame-resistant level when the cotton fabrics is treated with 10 wt% add-on of **FR**. TG and DTG curves showed that the char residue of the cotton fabrics treated was much higher than the one of the cotton fabrics untreated, which may be ascribed to the sulfur-nitrogen synergistic effect in the flame retardant system of the cotton fabrics treated with **FR**. These results indicated that the target **FR** is a novel nitrogen-sulfur-containing triazine flame retardant, which has good char-forming ability for flame-retardant cotton fabrics.

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