Preparation and Study of Properties of Polyhydric Alcohols Biphosphate Ethanolamine Salt

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Abstract: A new type of halogen-free flame retardant has been synthesized with raw materials of Di(trimethylolpropane) and phosphorus oxychloride, and the influence of the raw material ratio, reaction temperature and reaction time on the yield has been discussed. It has been shown in the results that the molar ratio of Di(trimethylolpropane) and phosphorus oxychloride is 1:4, the reaction temperature is 80°C, the reaction time is 4 hours, the intermediates have the highest yield. Furthermore, the flame-retardant effect and thermal stability of the target product on different fabrics have been investigated, and the structures of the intermediates and the target products were characterized by Fourier transform infrared spectrometer.

1. Introduction
In recent several decades, the three major synthetic materials and their products have developed rapidly; Furthermore, polymer materials have the characteristics of energy saving, light weight and good processability, therefore, they are rapidly replacing traditional raw materials such as metals, cement and wood, they are widely used in various fields and has obtained significant economic and social benefits[1-3]. The serious drawback of halogen flame retardants is that they generate a large amount of toxic and corrosive gases when they are burned[4-6]; These can cause corrosion of the circuit system switches and other metal objects, and may cause harm to human respiratory and other organs, these are even life-threatening [7-9]. It has become a trend in the field of flame retardant in the world to develop a kind of halogen-free flame retardant with low-toxicity, low-smoke, low-environmental impact and excellent flame-retardant performance to replace the halogen flame retardants. Confront with increasingly stringent environmental and safety requirements, new flame retardants such as those with no toxicity, high-efficiency and low-smoke toxicity have become their development direction [10-11]. Therefore, the study of flame retardants has played a crucial role in the development and application of new materials. The future research direction of flame retardants is orientated to halogen-free, highly efficient and environment-friendly types. A new type of halogen-free flame retardant has been synthesized with raw materials of Di(trimethylolpropane) and phosphorus oxychloride; This flame retardant has a large molecular weight, with a stable ring structure; The thermal stability is higher than that of commonly used flame retardants, and the flame-retardant effect is better[12-13].

2. Experimental part
2.1 Main experimental drugs

The main drugs are shown in Table 1:

| No. | Chemical name            | Chemical formula | Molecular weight | Specification       | Manufacturer                                      |
|-----|--------------------------|------------------|------------------|---------------------|---------------------------------------------------|
| 1   | Di(trimethylolpropane)   | C₁₂H₂₆O₅         | 250.33           | Industrial pure     | PetroChina Jilin Petrochemical Company             |
| 2   | Phosphorus oxychloride   | POCl₃            | 150.33           | Industrial pure     | Jihua Group Lianhua Fuli Chemical Factory          |
| 3   | Dioxane                  | C₄H₈O₂           | 88.11            | Analytically pure   | Tianjin Damao Chemical Reagent Co., Ltd.           |
| 4   | Ethanolamine             | C₂H₇NO           | 61.08            | Analytically pure   | Tianjin Yongda Chemical Reagent Co., Ltd.          |

2.2 Experimental principle

(1) Synthesis of Di(trimethylolpropane)bisphosphate

(2) Synthesis of Di(trimethylolpropane) diphosphoryl chloride as the intermediate Hydrolysis of the intermediate to form Di(trimethylolpropane)bisphosphate

(3) Synthesis of Di(trimethylolpropane) biphosphate ethanolamine salt as the target product

2.3 Experimental procedure

The experimental procedure was as follows: Assembling, adjusting the experimental device and checking the air tightness. Di(trimethylolpropane) was added to a four-necked flask equipped with a thermometer, stirrer, and spherical condenser tube according to the usage amount; After heating to about 50°C, phosphorus oxychloride was weighed & put into a four-necked flask: the stirrer & condenser were opened and the Di(trimethylolpropane) was weighed and put into the flask. After the Di(trimethylolpropane) was completely dissolved to form a light yellow solution, the temperature was raised to 70°C, the temperature was controlled at about 70°C for 5 hours (calculated from the time when the temperature was raised to the specified temperature point). The HCl gas generated during the reaction was absorbed with an aqueous NaOH solution (containing phenolphthalein). A small amount of evaporated POCl₃ was refluxed through a spherical condenser pipe. The vacuum pump was turned on.
at 2.5 hours after the start of the reaction, unreacted phosphorus oxychloride and HCl gas generated during the reaction were pumped out. After heating up to 75°C, a certain amount of distilled water was added to a constant pressure dropping funnel and dripped into a four-neck flask to carry out reaction for 1.5 hours. The vacuum pump was turned on at 0.5h hours after the start of the reaction; After 1.5 hours of reaction, the reaction was stopped. The temperature was controlled at 80 °C, ethanolamine was weighed (using a constant pressure dropping funnel), condensate water was turned on, and reaction was carried out for 4h (starting from the adding of neutralization reagent). The vacuum pump was turned on for 20min at 2h after the start of the reaction; Then HCl gas generated during the reaction was pumped out, and absorbed with NaOH aqueous solution (containing phenolphthalein) . The vacuum pump was turned off, the content in four-necked flask was the target product Di(trimethylolpropane) bisphosphonate ethylamine salt.

Finally the target product Di(trimethylolpropane) bisphosphonate ethylamine salt was taken out, and sealed & stored. All power supplies and condensate were turned off.

2.4 Measurement
Nicolet 6700 type red infrared spectrometer was used to identify the product structure; The thermal stability of the product was measured using a SDT-Q600 type synchronous thermal analyzer; Furthermore, the flame-retardant combustion performance was tested with fabric vertical burning test; Please refer to GB/T 5455-1997 «Textile burning performance test vertical method» for testing.

3. Results and discussion

3.1 Influence of material ratio on the yield of intermediate products
The molar ratio between Di(trimethylolpropane) and phosphating agent as the reactive materials is the main factor that affects the composition and performance of the product. When the reaction is carried out at 70°C for 5 hours at constant temperature according to the different raw material ratio, the results in table 2 can be obtained.

| No. | N (Di-TMP) : n (POCl₃) | Yield/% | Product color and shape          |
|-----|------------------------|---------|---------------------------------|
| 1   | 1:2                    | 67.20   | Viscous milk white paste        |
| 2   | 1:3                    | 75.33   | Viscous milk white paste        |
| 3   | 1:4                    | 89.56   | Viscous milk white paste        |
| 4   | 1:5                    | 78.27   | Viscous milk white bronzing     |

It can be seen from Table 2 that raw material ratio has a great influence on the reaction. The phosphorus oxychloride content in the reaction is too low (less than 2:1), and it may cause incomplete reaction of Di(trimethylolpropane), and it is difficult to form a stable ring structure; so the product flame retardant property may be affected; When the phosphorus oxychloride content in the reaction is too high (higher than 2:1), although the degree of reaction can be increased, and the yield can achieve over 90%, however, the intermediates contain more phosphorus oxychloride, and it can't be easily removed, in addition, partial carbonation of the products affects the purity of the product; Furthermore, due to large steric hindrance of the product, excessive phosphorus oxychloride is not conducive to the full formation of the ring structure. Considering comprehensively, it is more appropriate to choose 4:1 as the raw material ratio.

3.2 Influence of amination reaction time and temperature on the yield of target product
The selected reaction conditions are as follows: phosphating reaction temperature is 70°C, the hydrolysis temperature is 75°C, the molar ratio of materials is as follows: Di(trimethylolpropane): phosphorus oxychloride: ethanol amine is 1:4:2; The reaction time and temperature of the amination reaction stage are used as variables to explore their influence on obtaining the target product; The data in the following table 3 is obtained.

Table 3 Experimental data of the third step reaction time and temperature
| No. | Temperature/°C | Reaction time/h | Product yield/% | Color |
|-----|----------------|-----------------|-----------------|-------|
| 1   | 70             | 3               | 70.31           | Milk white |
| 2   | 75             | 3               | 72.46           | Milk white |
| 3   | 80             | 3               | 72.02           | Milk white |
| 4   | 70             | 4               | 76.35           | Light yellow viscous material |
| 5   | 75             | 4               | 76.83           | Light yellow viscous material |
| 6   | 80             | 4               | 77.96           | Light yellow viscous material |

It can be seen from the data that the influence of the reaction temperature on the yield in this step is less than that of the time; the reaction is insufficient when time is too short, and the target product yield is low; Furthermore, this may also cause unreacted intermediates to undergo side reactions and reduce flame retardant properties.

It has been shown through comprehensive consideration that the preferable conditions should be the following: molar ratio between Di(trimethylolpropane) and phosphorus oxychloride is 1:4, phosphating reaction temperature is 70°C, the reaction time is 5 hours, The molar ratio of hydrolysis reaction is 1:2, the reaction temperature is 75°C, the reaction time is 1.5 hours, The molar ratio of amination reaction is 1:2, the reaction temperature is 80°C, and the reaction time is 4h in order to obtain the product in a good manner.

3.3 Infrared spectrum

The synthesized intermediate and the final product were mixed and ground with KBr powder, and the infrared spectrogram data was measured after tableting, the test results were shown in figure 1 and figure 2.

![Infrared spectrum of intermediate Di(trimethylolpropane) diphosphoryl chloride](image)

As shown in figure 1, the spectral band at 1309.5 cm⁻¹ was regarded the stretching vibration of phosphate ester P=O; the spectral band at 1190.3 cm⁻¹ was regarded the anti-symmetric stretching vibration of ether C-O-C; the spectral band at 1060.8 cm⁻¹ was regarded the stretching vibration of alcohol C-OH; the spectral band at 1020.3 cm⁻¹ and 990.0 cm⁻¹ was regarded as the anti-symmetric stretching vibration of P-O-C; the spectral band at 854.2 cm⁻¹ was regarded the symmetric stretching vibration of P-O-C, mainly referring to the stretching vibration of P-O; the spectral band at 577.5 cm⁻¹ was regarded the stretching vibration of residual P-Cl; Through comparison with the infrared spectra of the raw materials Di(trimethylolpropane) and phosphorus oxychloride, the synthesized product proved to be Di(trimethylolpropane) diphosphoryl chloride.
As shown in figure 2, the wave number 3332.8 cm⁻¹ corresponds to formation of intramolecular hydrogen bond -OH; Due to formation of intramolecular hydrogen bond -OH, the reduction of the key force constant occurs, the absorption shifts to lower wave numbers (around 3300 cm⁻¹), the peak type is wide and blunt; The wave number of 2965.1 cm⁻¹ corresponds to -CH₃, the wave number of 2965.1 cm⁻¹ corresponds to -CH₂, the wave number of 2883.4 cm⁻¹ corresponds to carbon-hydrogen bond in -CH₂-OH; Because four absorption peaks are generally visible in the saturated carbon and hydrogen stretching vibrations, among which, 2960cm⁻¹ and 2870cm⁻¹ belong to CH₃, 2925cm⁻¹ and 2850cm⁻¹ belong to CH₂; When CH₃ or CH₂ is connected to an oxygen atom, the absorption shifts to lower wave numbers; The wave number of 1169.8 cm⁻¹ corresponds to symmetric vibration of C-O-C; The wave number of 1064.4 cm⁻¹ corresponds to P-O-C; The wave number of 550.6 cm⁻¹ corresponds to a moderately divergent double peaks P=O double bond. To sum up, the synthesized product was indeed Di(trimethylolpropane) diphosphate ethanol amine salt.

3.4TG-DSC test chart and analysis
The thermal analysis data of the product is shown in Figure 3.

As seen from figure 3, product lost adsorbed water in 20 °C ~ 80 °C; exothermic peaks appeared at 260°C~340°C, decomposition reaction occurs; The endothermic peak appeared at 430°C~470°C, and ethanolamine was removed. Exothermic peaks appeared at 510°C~600°C, and oxidation reaction occurred.

| Table 4 | Product TGA results |
|---------|---------------------|
| Temperature range/°C | 20~120  | 120~340  | 340~470  | 470~590  |
| Weight loss/% | 8.06  | 44.19  | 21.52  | 7.95  |
Table 5 Results of differential scanning calorimetry for the product

| Temperature range/℃ | 20~80 | 260~340 | 430~470 | 510~600 |
|---------------------|-------|---------|---------|---------|
| Results             | Loss of adsorbed water | Decomposition on reaction | Ethanolamine removal | Oxidation reaction |

4. Conclusion
Di(trimethylo1propane), phosphorus oxychloride and ethanol amine were used as the main materials in the experiment, and the intumescent flame retardant, Di(trimethylo1propane) biphosphate ethanolamine salt was synthesized, and the flame-retardant effect of the target product on different fabrics have been tested; Furthermore, the following conclusions have been drawn.

(1) The preferable synthesis process of a halogen-free flame retardant is as follows: The molar ratio between Di(trimethylo1propane) and phosphorus oxychloride is 1:4, the reaction temperature is 80°C, the reaction time is 4h, and the flame-retardant effect of the target product on different fabrics is fairly good.

(2) Infrared spectroscopic analysis and differential scanning calorimetry have been carried out on the final product, and the structure and thermal properties of the product have been characterized.

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