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PREPARATION AND STUDY OF PROPERTIES OF DI(TRIMETHYLOLPROPANE) 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. Furthermore, the flame-retardant combustion performance has been tested by vertical burning test. 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. After discussing the different flame-retardant effects on different fabrics, the conclusions have been drawn: The Di(trimethylolpropane) biphosphate ethanolamine salt has different flame-retardant effects on polyester, acrylic, chinlon, cotton and blended fabrics, of which the flame-retardant effect on chinlon, polyester and cotton is fairly good, but the flame-retardant effect is unremarkable for blended fabrics and acrylic.

KEYWORDS

Ditrimethylolpropane, preparation, performance, Flame retardant effect, Characterization.

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 [1-4]. However, most polymer materials are easily decomposed and combusted at high temperatures; In the event of a fire, they are ignited in the air [5-9]. Furthermore, their molten droplets may also ignite other combustibles, and as a result, fires are caused and there are serious fire hazards. Flame retardants belong to a class of additives that may prevent or inhibit the combustion of polymers.

The serious drawback of halogen flame retardants is that they generate a large amount of toxic and corrosive gases when they are burned; 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 [10-13]. 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 [14-16].

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.

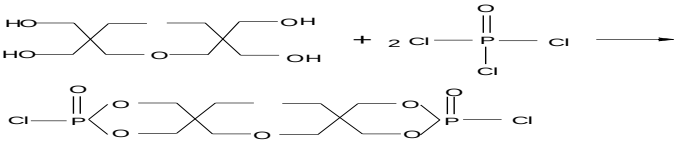
2. EXPERIMENTAL PART

2.1 Main experimental drugs

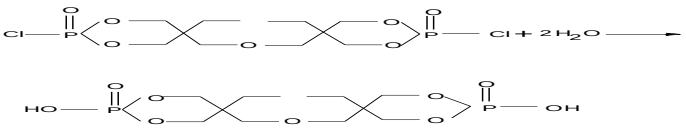
The main drugs are Di(trimethylolpropane) (PetroChina Jilin Petrochemical Company); Phosphorus oxychloride (Jihua Group Lianhua Fuli Chemical Factory); Dioxane (Tianjin Damao Chemical Reagent Co., Ltd.); Ethanolamine (Tianjin Yongda Chemical Reagent Co., Ltd.)

2.2 Experimental principle

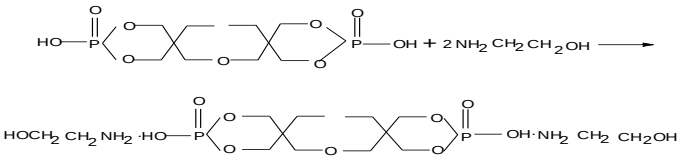
(1) Synthesis of Di(trimethylolpropane)bisphosphate



(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 parker sing, hydrolysis and amination, 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; 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 Discussion of the synthetic process factors

3.1.1 Influence of reaction temperature on the yield

Other reaction conditions were fixed, i.e., the molar ratio among Di(trimethylolpropane), phosphorus oxychloride and water were 1:4:2, only the reaction temperatures of various steps were changed, thus the experimental results as shown in table 1 were obtained.

Table 1: Influence of reaction temperature on the yield

No.	Reaction temperature of the 1st step	Reaction temperature of the 2nd step	Yield/%
1	60	75	78.72
2	60	80	80.51
3	60	85	81.25
4	70	75	84.29
5	70	80	86.49
6	70	85	85.64
7	80	75	80.30
8	80	80	86.93
9	80	85	83.52

The following conclusions were drawn from table 1: For ethanolamine, the yield is the highest when the phosphating reaction temperature in the 1st step is 70°C and the amination reaction temperature in the 3rd step is 75～80°C.The reason is that there will be more side reactions when the temperature is too high, on the other hand, the reaction proceeds insufficiently, affecting the yield when the temperature is low.

3.1.2 Influence of phosphating reaction time on the yield of the intermediate

The following conditions were selected: the reaction temperature was 70°C, the molar ratio between Di(trimethylolpropane) and phosphorus oxychloride is 1:4, the reaction time was regarded as the variable. The results are as shown in Table 4.

Table 4: Influence of phosphating reaction time on the yield of the intermediate

No.	Reaction time/h	Yield/%	Product color and shape	Cause analysis
1	3	69.72	Viscous milk white liquid	Incomplete reaction
2	4	77.41	Viscous light-yellow paste	Complete reaction
3	5	79.52	Viscous light-yellow paste	Complete reaction
4	6	78.88	Viscous light red brown paste	Complete reaction, with partial carbonization

The following analysis can be carried out from table 4: The intermediate yield increases with the time; the yield of the intermediate product reaches its maximum at 5 h. When the reaction time continues to increase, side reactions of the intermediates occur, the yield begins to decline, and this is not conducive to the experiment.

3.2 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 result was shown in figure 1.

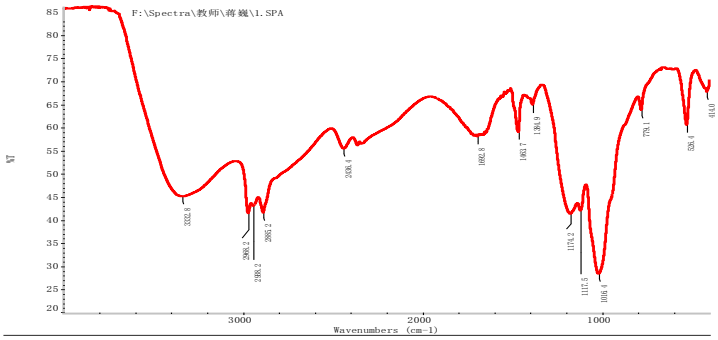


Figure 1: Infrared spectrum of the target product

As shown in figure 1, 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 2965.1cm^{-1} corresponds to -CH_3, the wave number of 2965.1 cm^{-1} corresponds to -CH_2, the wave number of 2883.4 cm^{-1} corresponds to carbon-hydrogen bond in -CH_2-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 CH_3, 2925$cm^{-1}$and 2850cm^{-1} belong to CH_2; When CH_3 or CH_2 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.

3.3 Discussion of flame retardant effect of the product

The molar ratio between Di(trimethylolpropane) and phosphorus oxychloride is 1:4, phosphating reaction temperature is 70°C, the reaction time is 5h, the molar ratio of hydrolysis reaction is 1:2, the reaction temperature is 75°C, the reaction time is 5h, the molar ratio of amination reaction is 1:2, the reaction temperature is 80°C, the reaction time is 4h, and the flame-retardant effect of the target product on different fabrics have been investigated.

The flame-retardant effects of the product on polyester, acrylic, cotton, chinlon and blended fabrics are shown in Figures 4-8.

4

Figure 5: Figure showing flame retardant effect on acrylic

5

Figure 4: Figure showing flame retardant effect on polyester

6

Figure 6: Figure showing flame retardant effect on cotton

7

Figure 7: Figure showing flame retardant effect on chinlon

8

Figure 8: Figure showing flame retardant effect on blended fabrics

It can be concluded through comparing the above diagrams that, the intumescent flame retardant has a remarkable flame-retardant effect on cotton, chinlon and blended fabrics, but the flame-retardant effect on polyester and acrylic is not so good. The reason is as follows: Firstly, the microstructure of each fabric is different, and the product flame retardant property of the fabric may be different; Secondly, the same flame retardant has different affinities to different fabrics and shows different flame-retardant effects. Therefore, it showed different flame-retardant effects on different fabrics.

4. CONCLUSION

Di(trimethylolpropane), phosphorus oxychloride and ethanol amine were used as the main materials in the experiment, and the intumescent flame retardant, Di(trimethylolpropane) 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(trimethylolpropane) and phosphorus oxychloride is 1:4, phosphating reaction temperature is 70°C, the reaction time is 5h,the molar ratio of hydrolysis reaction is 1:2,the reaction temperature is 75°C, the reaction time is 5h, the molar ratio of amination reaction is 1:2, 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) After discussing the flame-retardant effects on different fabrics, it has been shown that the intumescent flame retardant has a better flame-retardant effect on chinlon, cotton and blended fabrics, but the flame-retardant effect on polyester and acrylic is not so good.

(3) 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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