Synthesis and Characterization of N-(2,4,6-tribromophenyl)maleimide

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ABSTRACT: *In this study, N-(2,4,6-tribromophenyl)maleimide (TBPMI) was synthesized using three different catalysts, including stannous chloride, anhydrous acetic acid, and phosphoric acid, respectively. Comparative analysis was carried out on the synthesis conditions and the yields of TBPMI synthesized using different catalysts. Infrared spectroscopy and nuclear magnetic resonance spectroscopy were employed to characterize TBPMI. Results showed that the use of phosphoric acid as the catalyst required harsh reaction conditions and also the catalytic efficiency was poor. On the other hand, under similar conditions, the catalytic efficiency of anhydrous acetic acid was higher than that of stannous chloride, along with the reduction in problems associated with erosion and pollution.*

KEYWORDS: *N-(2,4,6-tribromophenyl)maleimide; Stannous chloride; Anhydrous acetic acid; Flame retardant*

INTRODUCTION

Among the bromine-based organic flame retardants, decabromodiphenyl oxide affords the largest yield and it is the most extensively used material in a broad range of applications. Nonetheless, its use has been restricted by many countries because of anxiety about the toxicity of its combustion cracking products. Therefore, it is imperative to develop a substitute for polybrominated diphenyl ethers; however, the development of a flame retardant with good comprehensive performance is a difficult and challenging task. This is attributed to the fact that although the added small-molecule flame retardant provides flame retardant property to materials, it decreases the heat resistance, mechanical properties, and optical properties. Moreover, it is also difficult to solve the compatibility problem. Reactive bromine-based flame retardants with tetrabromobisphenol A as a representative have the advantages such as good compatibility and long-lasting effect; however, they were used as additive flame retardant in most cases because of their low reactivity.

N-(2,4,6-tribromophenyl)maleimide (TBPMI) has a high bromine (Br) content (up to 58.5%) and conjugated ring structure of maleimide, thus it is very useful in improving the heat resistance and flame retardant property of polymeric materials. It also has other advantages such as good compatibility, low toxicity, good thermal stability, etc., which make the polymer highly heat resistant in addition to improvement in its flame retardant property [1]. Therefore, the synthesis of TBPMI has attracted significant research attention.

Noteworthy, the copolymerization between TBPMI and ethylene, acrylate, etc. can endow superior flame retardant property and unique physical properties to the resulting

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materials. For instance, the TBPMI-styrene copolymer can be processed into high-density, high-absorbent films, which are specifically effective in the separation and purification of cephalosporin C. The reaction product of TBPMI and diaminodicyclohexylmethane can be used as a modifier for polyimide to produce a remarkably soft polyimide film.

The most straightforward synthesis route of TBPMI is the reaction between 2,4,6-tribromoaniline (TBA) and maleic anhydride (MAN). However, due to the electron-withdrawing effect of the three bromine atoms on the benzene ring of 2,4,6-tribromoaniline, exposure of the lone pair of electrons on the amino groups to maleic anhydride becomes difficult, thus the feasibility of the occurrence of reaction is reduced. In general, excess of maleic anhydride or a high-temperature method involving trimethylbenzene solvent is used. As a result, the required reaction temperature is high, the reaction time is too long, the catalytic conditions are harsh, the final yield is low, the product is difficult to purify, the quality is poor, and the cost is also high, which limit the industrial application of TBPMI. Therefore, the low basicity of tribromoaniline and its low reactivity with cis-butenedioic anhydride make it unfeasible to synthesize TBPMI by the method generally used for the synthesis of N-substituted maleimides. Thus, research on TBPMI has rarely been carried out for a long time [2–5].

After the first ever method of synthesis for TBPMI was published in a patent in 1978, research and development of TBPMI grew up rapidly. In the late 1980s, the TBPMI-based products were sold by IMI Company, Israel. Since then, the applications of TBPMI as heat resistant and flame resistant polymeric modifier have been increasing continuously. Development and applications of the heat resistant and flame resistant polymeric materials, closely related to TBPMI, presently make an important subject in the field of polymeric materials. Although brominated flame retardants have been mass produced, their low numbers and high costs have limited their practical applications. Therefore, development of a brominated flame retardant with good performance, in particular, a reactive brominated flame retardant with high bromine content, has attracted significant research attention . Noteworthy, TBPMI as a new type of reactive flame retardant, with dual functions of flame retardancy and heat resistance, has good application prospects. This makes it highly necessary to further discuss novel methods for the synthesis of TBPMI.

EXPERIMENTAL SECTION

Synthesis methods

Using stannous chloride as the catalyst

(1) MAN/TBA = 2.5:1

MAN (24.5 g), TBA (33 g), and stannous chloride catalyst (1 g) were taken in a 250 mL three-necked round bottom flask, placed in a constant temperature oil bath, and the contents were stirred for 2 h at 150 °C. After cooling to 90 °C, water (50 mL) at a temperature of 90 °C was added under rapid stirring. The supernatant liquid (first recycle liquid) was recycled and the solid was dried. The weight of the product was 45 g.

(2) MAN/TBA = 4:1

MAN (39.2 g), TBA (33 g), and stannous chloride catalyst (1 g) were taken in a 250 mL three-necked round bottom flask, which was placed in a constant temperature oil bath, and the contents were stirred for 2 h at 150 °C. After cooling to 90 °C, water (50 mL) at a temperature of 90 °C was added under rapid stirring. The supernatant liquid (first recycle liquid) was recycled and the solid was dried. The weight of the product was 38.3 g.

Using anhydrous acetic acid as the catalyst

(1) MAN/TBA = 2.5:1 (the catalyst loading was 1 g, 0.33 g, and 0.23 g)

MAN (24.5 g), TBA (33 g), and appropriate quantity of anhydrous acetic acid catalyst were taken in a 250 mL three-necked round bottom flask, placed in a constant temperature oil bath. The contents were stirred for 2 h at 150 °C. After cooling to 90 °C, water (50 mL) at a temperature of 90 °C was added under rapid stirring. The supernatant liquid (first recycle liquid) was recycled and the solid was dried. The weight of the product was 38.9 g.

(2) MAN/TBA = 4:1

MAN (39.2 g), TBA (33 g), and anhydrous acetic acid catalyst (1 g) were taken in a 250 mL three-necked round bottom flask, placed in a constant temperature oil bath, and the contents were stirred for 2 h at 150 °C. After cooling to 90 °C, water (50 mL) at a temperature of 90 °C was added under rapid stirring. The supernatant liquid (first recycle liquid) was recycled and the solid was dried. The weight of the product was 40.8 g.

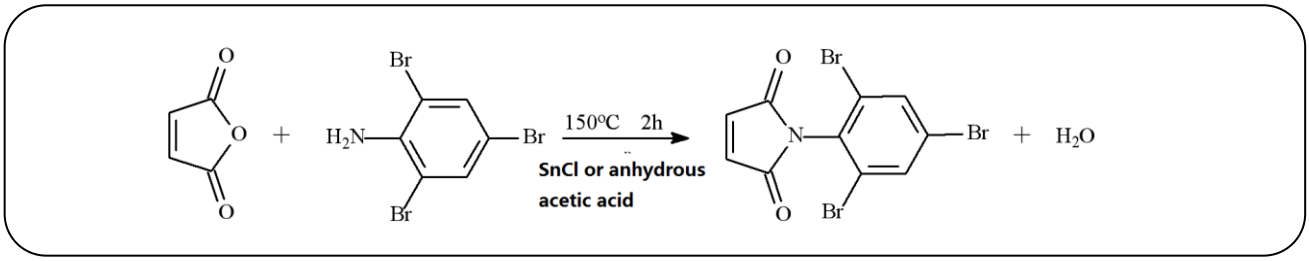

Fig. 1: Schematic illustration of synthesis reaction.

Using phosphoric acid as the catalyst (MAN/TBA = 2.5:1)

MAN (24.5 g), TBA (33 g), and catalyst (1 g) were taken in a 250 mL three-necked round bottom flask, placed in a constant temperature oil bath and stirred together for 3 h at 180 °C. After cooling to 90 °C, water (50 mL) at a temperature of 90 °C was added under rapid stirring. The supernatant liquid (first recycle liquid) was recycled and the solid was dried. The weight of the product was 45 g.

Purification of the product

Sodium hydroxide (10% solution) was used for the purification of the dried flame retardant product. After washing with water and drying, the weights of the flame retardant materials obtained following the above mentioned procedures were 32.5, 31, 34.8, 32.3, and 38.4 g, sequentially.

After washing with alkaline solution, the flame retardant was treated with ethanol to remove colored impurities. After drying, the weights of the flame retardants obtained from the above mentioned procedures were 30.6, 30.2, 34.4, 31.1, and 36.6 g, sequentially.

RESULTS AND DISCUSSION

Synthesis

Fig. 1 shows the schematic illustration of synthesis reaction. In this reaction system, one of the reactants, MAN, also acted as the solvent for reaction. Therefore, the dosage of MAN exhibited significant influence on the reaction. The ring-opening reaction in MAN occurs at around 100 °C; therefore, a large amount of water is produced during the reaction. This leads to side reactions, generating fumaric acid as the by-product. Therefore, open system should be used to expel out the water produced during the reaction from time to time, which would consequently prevent the occurrence of side reactions. The reaction product was highly viscous. Therefore, to prevent the product from sticking to the walls of the flask, in this study, water at 90 °C was added before sufficiently cooling the reaction system (the products were cooled to 90 °C). Then the reaction mixture was rapidly stirred to obtain the product in a powdered form, which could then be easily extracted.

For the synthesis of TBPMI using inorganic halides such as $ZnCl_2$ and $SnCl_2$ as catalysts, erosion of the reaction system due to the metal ions was a serious issue. Moreover, the catalysts were non-recyclable, causing severe pollution, which made it difficult to apply them for industrial production. Therefore, we speculated that anhydrous acetic acid can be used as a substitute for inorganic halides containing metal ions. This catalyst does not contain metal ions and the reaction system is non-erosive, making it a prospective candidate for industrial use.

Comparison of TBPMI syntheses under different reaction conditions

When H_3PO_4 was used as the catalyst, the formation of TBPMI was relatively slow and a very small amount of water was produced during the reaction (anhydrous cupric sulfate was used for testing and no significant color change of anhydrous cupric sulfate was observed). Moreover, the melting point of the product was only 133 °C. All these results indicated that only a little amount of TBPMI was produced in the reaction. Table 1 presents that when H_3PO_4 was used as the catalyst, the reaction required a higher temperature and the reaction time was relatively more with high catalyst loading. Moreover, H_3PO_4 is a moderately-strong acid, thus the reaction system was somewhat corrosive and H_3PO_4 was not a suitable catalyst for this reaction.

When $SnCl_2$ and anhydrous acetic acid were used as the catalyst system, the results were almost similar, but at 150 °C.

The reaction started after 4–5 min of stirring and the color changes were basically similar (changed from yellow

Table 1: Comparison of synthesis conditions and effects on the yields of TBPMI.

Catalyst	Catalyst loading (g)	MAN/ TBA	Reaction temperature (°C)	Reaction time(h)	Unpurified TBPMI (g)	TBPMI washed with base (g)	Ethanol purified TBPMI (g)	Yield (%)
$SnCl_2$	1	2.5:1	150	2	45	32.5	30.6	74.63
$SnCl_2$	1	4:1	150	2	38.3	34.8	34.4	83.9
$SnCl_2$+Anhydrous acetic acid	0.5+0.5	2.5:1	150	2	41.5	36.2	34.9	85.12
Anhydrous acetic acid	0.23	2.5:1	150	2	41.2	34	32.8	80
Anhydrous acetic acid	0.33	2.5:1	150	2	42.7	36	33.6	81.95
Anhydrous acetic acid	1	2.5:1	150	2	38.9	32.6	31.8	77.56
Anhydrous acetic acid	1	4:1	150	2	43.5	38.8	36.7	89.51
H_3PO_4	3.3	2.5:1	180	3	45	48.4	36.6	—

Notes: catalyst used is $SnCl_2$, data with ratio of reactants as 2.5:1 are illustrated in the text.

at the initial dissolving stage to dark brown after reaction, then turned gradually light, then changed to coffee color, and finally turned light stone yellow). There were also little variations in the amounts of water generated. Thus it was hard to note the differences in their reaction phenomena.

Keeping the catalyst same (either $SnCl_2$ or anhydrous acetic acid), the influence of MAN to TBA ratio on the yield was found to be large. Table 1 presents that the yield of the product obtained using a ratio of 4:1 was obviously higher than that obtained with a ratio of 2.5:1. In the synthesis of TBPMI, MAN was not only the reactant, but also acted as the solvent and dehydrating agent. Moreover, due to the characteristic thermal sublimation property of MAN, the presence of excess amount of MAN was beneficial for the progress of the reaction thereby affording a high yield.

Table 1 also presents the effects of keeping the ratio of reactants the same and varying the catalyst used. The catalytic efficiency of anhydrous acetic acid was obviously higher than that of $SnCl_2$. When the dosages of anhydrous acetic acid were 0.23, 0.33, and 1 g, the yields of the corresponding products were higher than those obtained when using $SnCl_2$ catalyst. When a catalyst system containing $SnCl_2$ to anhydrous acetic acid ratio of 1:1 was used, the yield obtained was higher than that obtained using $SnCl_2$ alone as the catalyst. Though the yield of the reaction using anhydrous acetic acid as the catalyst was similar to that using $SnCl_2$ as catalyst, anhydrous acetic acid could overcome some disadvantages of $SnCl_2$, such as absence of metal ions, non-corrosion, no environmental pollution, high catalytic efficiency, relatively mild reaction conditions, shorter reaction time, and low catalyst loading. Therefore, it has the potential to be used as catalyst in industrial production.

IR and NMR spectra of pure product (TBPMI)

Fig. 2 shows the peaks at 3440 and 3320 cm^{-1}, which can be assigned to the asymmetric and symmetric –N–H stretching vibrations, respectively. The peak at 3100 cm^{-1} is due to the =C–H stretching vibrations of the benzene ring, and the peak at 1631 cm^{-1} is attributed to the bending vibrations of N–H. Peaks at 1579, 1559, and 1470 cm^{-1} are the characteristic of the vibrations of the benzene ring skeleton, and the peak at 1080 cm^{-1} is due to the stretching vibrations of C–Br. The peak at 1076 cm^{-1} is ascribed to tetra-substituted benzene ring =C–H (in-plane rocking vibrations), while the peak at ~720–780 cm^{-1} is due to the out-of-plane bending vibrations of the hydrogen attached to the benzene ring.

Fig. 3 shows the presence of a peak at 7 ppm, which can be assigned to the protons of the side chain double bond, while the peak at 8 ppm is due to the protons of the benzene ring. Evidently, the peaks of the amino group in TBA are absent in the spectrum of TBPMI. Moreover, no peaks other than those of TBPMI are present. This shows that the purity of the obtained TBPMI was high, with only a small amount of impurities. The amount of TBA present in TBPMI was less than 0.1%.

CONCLUSIONS

In the study, TBPMI was synthesized through the reaction between MAN and TBA using phosphoric acid,

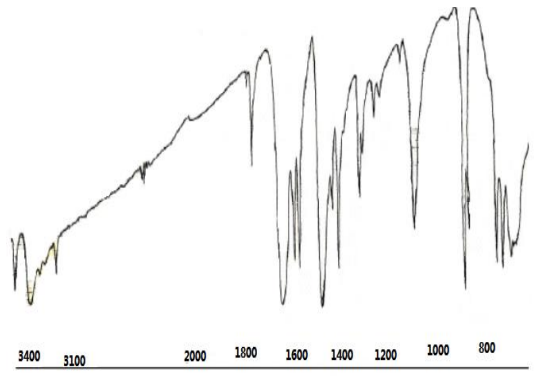

Fig. 2: IR spectrum of purified product (TBPMI).

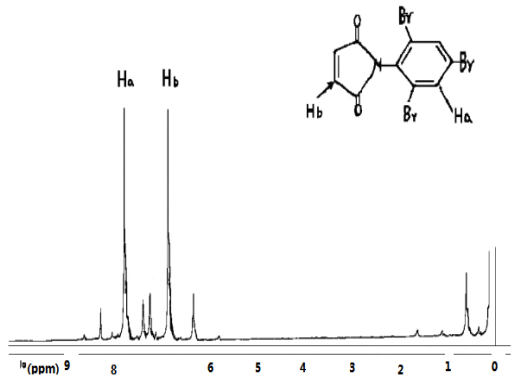

Fig. 3: NMR spectrum of the purified product (TBPMI).

stannous chloride, and anhydrous acetic acid as catalysts, respectively. The reaction product was purified and characterized by infrared and nuclear magnetic resonance spectroscopy. The results indicated that when anhydrous acetic acid was used as catalyst, the catalytic efficiency was higher, the reaction conditions were mild, the reaction time was short, the amount of catalyst used was small, and the purity of the product was higher. Therefore, anhydrous acetic acid as a catalyst exhibits promising applications in industrial production.

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