

# Synthesis and characterization of trimaleimide containing triazine ring

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## Abstract

This paper investigated the preparation methods of Trimaleimide containing *s*-triazine ring. The synthesis was accomplished by convenient methods utilizing cyanuric chloride as raw materials. The best yield was obtained in phase-transfer catalyzed method, it even up to 90%. Up to now, no report about phase-transfer catalyzed method used for synthesise triazine-base maleimide has been found in literature. DSC trace indicates that trimaleimide containing *s*-triazine ring could be thermally polymerized to fire- and heat-resistant laminating resins.

## 1. Introduction

As an important class of matrix resins with higher ratio of properties to price, bismaleimide resins have widely applied in many fields, such as aerospace and aeronautics industries. The disadvantage of the neat resins is their inherent brittleness and poor dielectric property under high frequency. To obtain resins with good properties, usually, the neat resins should be modified. Therefore, many investigations focused on improvement of toughness of bismaleimide resins were carried out in the past 30 years. Polymers containing *s*-triazine rings in the main chain have been attracting attention for a long time, because triazine-based polymers are characterized by good thermal stability, enhanced toughness, low moisture absorption and excellent dielectric property<sup>[1]</sup>. The Skylex BT (Bismaleimide-Triazine) resins marketed by Mitsubishi Gas and Chemical Corporation, gain large commercial success, integrate aforementioned two resins' merit to make it be large-scale applied in electronic industry as multi-layer-printed boards for computer, encapsulation resins, and so on. BT resins is obtained by the polycyclotrimerization of nitrile derivatives, it is now generally accepted that cyanate esters (CEs) and bismaleimides (BMIs) do not co-react in BT resins, but instead from an interpenetrating network (IPN) of homopolymers<sup>[2]</sup>. However, It is well known that the method using nitrile derivatives as raw materials is dangerous and expensive. Triazine-containing polymers also could

be obtained by the polycondensation or polyaddition of monomeric *s*-triazine derivatives. Varma and his co-workers introduced triallyl cyanurate (TAC) to the diamine-chain-extended BMI resins and obtained a new three-component resin with good processibility and mechanical properties<sup>[3]</sup>. Fang qiang synthesizes several novel modifier containing *s*-triazine for bismaleimide via the reaction of cyanuric chloride with 2-allylphenol, and the results shows that the kind modifier can effectively improve mechanical properties of 4,4'-(bismaleimidophenyl)methane (BMDPM) without decreasing heat-resistance<sup>[4,5,6,7]</sup>. The Fang's method using cyanuric chloride as raw materials is of many advantages, such as simply, cheap, little poisonous. So we are greatly interested in it. Both Varma and Fang introduced *s*-triazine into bismaleimide resins via "Ene" reaction of allyl groups with bismaleimides. From the point of view of molecular designs, we hope introducing *s*-triazine into bismaleimide molecular backbone directly. It may make bismaleimide monomer possesses both hard groups and tough groups, and the introducing would not damage thermal property of the resins. Meanwhile, due to more reactive points in the *s*-triazine ring, we can introduce useful functional group into bismaleimide monomer. Thus the synthetic chemistry and structure-properties relationship of maleimide resins containing triazine rings is of great interest.

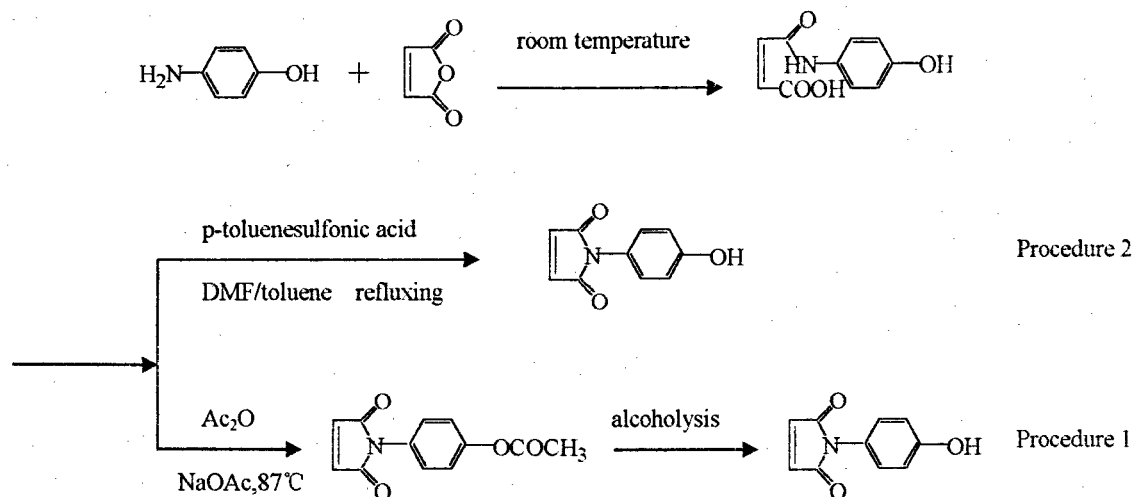
In this paper, the aim of our work is to investigate the preparation methods of trimaleimide monomer containing *s*-triazine ring using cyanuric chloride as raw material to study the synthetic chemistry, it can be used as base of preparation of bismaleimide possessing the desirably functional group for improving properties.

## 2. Study on maleimides containing triazine rings

A literature survey revealed that introducing *s*-triazine into maleimide molecular backbone directly have only been reported in a Japanese patent<sup>[8]</sup> and Melissaris who is a doctor of Grecian Patras university and his co-worker's work<sup>[9]</sup>. Both them all prepared trimaleimide containing *s*-triazine ring from cyanuric chloride as raw materials. Melissaris firstly synthesized 2,4,6-tris(4-nitrophenoxy)-*s*-triazine, then hydrogenated to 2,4,6-tris(4-aminophenoxy)-*s*-triazine. Finally, trimaleimide was prepared by reacting 2,4,6-tris(4-aminophenoxy)-*s*-triazine with maleic anhydride in the presence of acetic anhydride and sodium acetate as catalyst. The other is firstly to synthesize *N*-(4-hydroxyphenyl)maleimide, then the product react with cyanuric chloride. To avoid hydrogenation of 2,4,6-tris(4-aminophenoxy)-*s*-triazine with expensive palladium as catalyst and requiring rigorous equipment, we chose the latter method. Our overall reaction sequences for the synthesis of the trimaleimide containing *s*-triazine are outlined in Schemes. In Japanese patent's method, firstly, *N*-(4-hydroxyphenyl)maleimide was prepared by reacting maleic anhydride with an equimolar amount *p*-aminophenol in DMF at ambient temperature and subsequent heating of the reaction mixture in the presence of acetic anhydride and sodium acetate, then cyanuric chloride reacted with the cyclodehydrated product in *N,N*-dimethylacetamide in the presence of an acid acceptor such as triethylamine. It must indicate that the aforementioned preparation method raises several inquiries

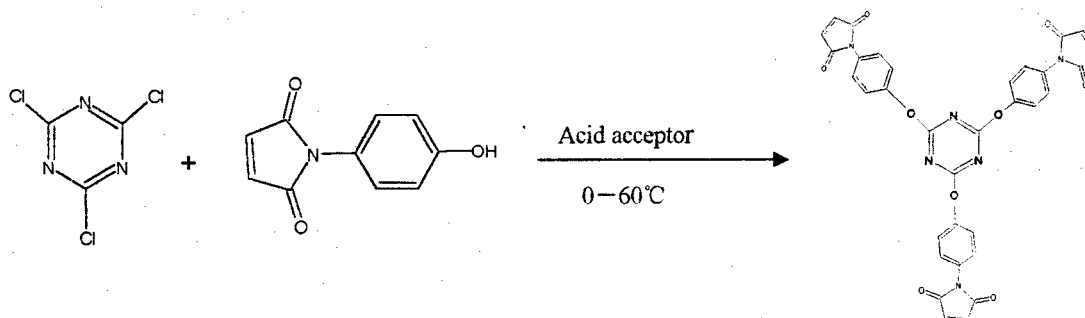
about its efficiency. In subsequent discussion, those inquiries will be mentioned one by one.

### Step I synthesis of *N*-(4-hydroxyphenyl)maleimide



scheme I

### Step II Etherification of cyanuric chloride with *N*-(4-hydroxyphenyl)maleimide



scheme II

## 2.1 Synthesis of *N*-(4-hydroxyphenyl)maleimide

The first problem of Japanese patent's method is cyclodehydration of *N*-(4-hydroxyphenyl)maleamic acid by acetic anhydride leads undoubtedly to acetylate the free hydroxyl group. We adopted two procedure to synthesize *N*-(4-hydroxyphenyl)maleimide. The first step is same in two procedure, *N*-(4-hydroxyphenyl)maleamic acid was prepared by reacting *p*-aminophenol with slightly excessive maleic anhydride in acetone at room temperature. In the case of procedure 1, *N*-(4-hydroxyphenyl)maleamic acid is cyclodehydrated by chemical means utilizing acetic anhydride and sodium acetate as dehydrating agent, then the product, *N*-(4-acetoxyphenyl)maleimide, alcoholysize with methanol in the presence of *p*-toluenesulfonic acid. In the case of procedure 2, *N*-(4-hydroxyphenyl)maleimide

is directly obtained by cyclodehydration of *N*-(4-hydroxyphenyl)maleamic acid in the presence of *p*-toluenesulfonic acid.

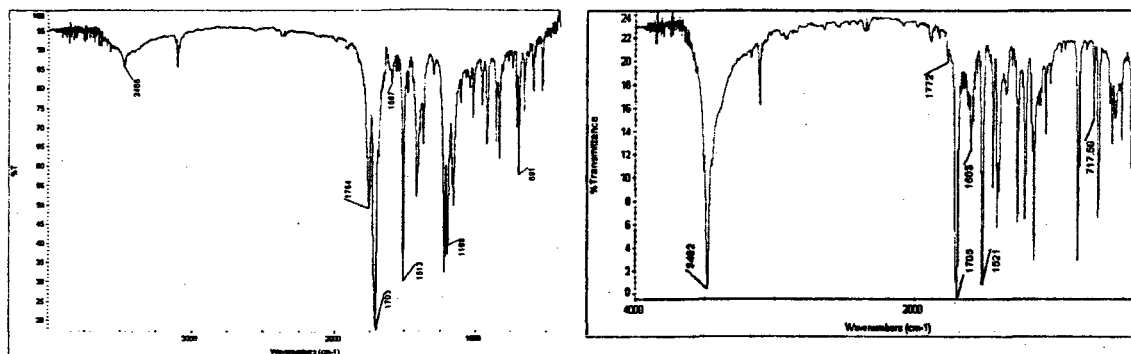


Fig.1 FTIR spectrum of *N*-(4-acetoxyphenyl)maleimide .2 FTIR spectrum of *N*-(4-hydroxyphenyl)maleimide

Fig.1 is FTIR spectrum of the product that *N*-(4-hydroxyphenyl)maleamic acid directly cyclodehydrated with acetic anhydride and sodium acetate as dehydrating agent and fig.2 is FTIR spectrum of the product cyclodehydrated with *p*-toluenesulfonic as dehydrating agent, respectively. From fig.1, we can easily find characteristic absorption appears at  $1187\text{cm}^{-1}$  are assigned to C-O stretching and Characteristic absorption peaks near  $3470\text{cm}^{-1}$  diminishes due to hydroxyl groups' etherification. It clearly demonstrated that acetylation of the free hydroxyl groups has occurred in the course of dehydration. After alcoholysis with methanol, FTIR spectrum of the product accords with that of procedure 2. That is to say, procedure 1 is of lower yield, more expensive, and complicated. The main characteristic absorption and melting point of main intermediate and target product are listed in Table 1.

Table 1 The FTIR characteristic absorption data and melting point of monomers

Monomer	FTIR spectral data (KBr ( $\text{cm}^{-1}$ )) and the corresponding structure	Melting point
<i>N</i> -(4-hydroxyphenyl)maleamic acid	3293(-OH); 2850 ~ 3260 (-COOH); 1700 (C=C); 1608 (C=C); 1506(aromatic ring)	196~198°C
<i>N</i> -(4-acetoxyphenyl)maleimide	1703,691(imide structure); 1587 (C=C), 1513(aromatic ring); 1469(-CH <sub>3</sub> asymmetric deformation); 1372(-CH <sub>3</sub> symmetric deformation)	164~165°C
<i>N</i> -(4-hydroxyphenyl)maleimide	3482(-OH); 1772,1705,691(imide structure); 1603 (C=C); 1521(aromatic ring)	181~182°C

## 2.2 Synthesis of trimaleimides containing triazine rings

Generally speaking, etherification with halocarbon and alcoholic or phenolic compound is achieved with Williamson etherification. That is to say, the presence of strong base, such as NaH, KOH, is the key of the occurrence of the reaction. Furthermore, imide structures is sensitive to the alkaline environment, the presence of alkali rapidly leads a side reaction of imide structure, opening rings to polymerize. According to a literature survey, besides the aforementioned popular procedure, using aqueous or anhydrous alkali as acid acceptor and hydrous mixture system as solvent, there is other way to prepare triazine-base monomers<sup>[7]</sup>. The procedure is a water-free route with high yield, cyanuric chloride reacts with alcoholic or phenolic compound in organic system using tertiary amine or pyridine derivatives such as triethylamine or pyridine as acid acceptor. But we found it gains little yield to use DMAC or DMF as reactive solvent, like Japanese patent's method. In DMAC or DMF reactive solvent system, while adding tertiary amine, quaternary ammonium salt formed by cyanuric chloride and tertiary amine immediately deposits. Because quaternary ammonium salt hardly dissolves in DMF or DMAC, it cannot participate reaction again. Meanwhile, many side reactions occur in the reactive system, we find many byproduct have been produced in the course of reaction via thin layer chromatography. After deposition, resin-like products and a little solid are obtained, FTIR spectra of the products show that imide structures have been damaged. We also found the same phenomenon while using pyridine as acid acceptor. When using DMF and other solvent that possesses good dissolubility of quaternary ammonium salt, we obtained a mixture composed two bismaleimides which molecular weight are 531 and 563 respectively. While choosing adequate solvent system, such as acetone/chloroform, we obtain trimaleimide with yield below 50%.

According to a literature survey, we found it is efficient to utilize the phase-transfer catalyzed reaction for etherifying<sup>[8]</sup>. Meanwhile, in the course of experiment, we found that little quaternary ammonium salt formed in the beginning of reaction, the reactive speed would remarkably accelerated. So we applied phase-transfer catalyzed reaction as the reactive method in the etherification. Adding phase-transfer catalyst in reactive system, we found the etherification can perform in acidic circumstance. This make possible to accomplish the desirable reaction by phase-transfer catalyzed reaction. When we use aqueous carbonate as acid acceptor, the yield vary between 70~80%, of course solvent system also have remarkable effect on yield. There is an interest phenomenon that, opposing our expectation, the reaction using aqueous alkali as acid acceptor is of lower yield than that of using aqueous carbonate. We consider the reason is opening ring of imide structure in the Condition of adding alkali. While using quaternary ammonium salt/tertiary amine, binary catalyst system, the reaction obtained the best yield even up to 90%.

The main characterization of trimaleimide listed in Table 2 and Fig.3, Fig.4 are shown in following.

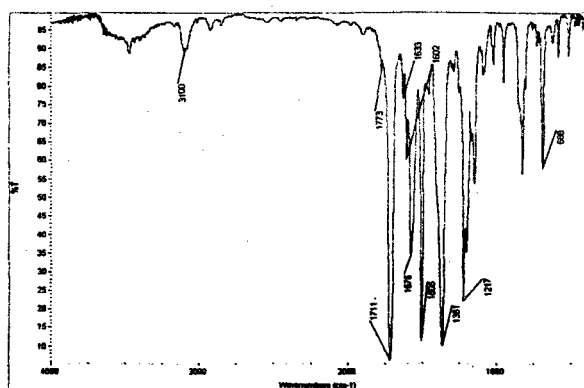


Fig.3 FTIR spectrum of trimaleimide

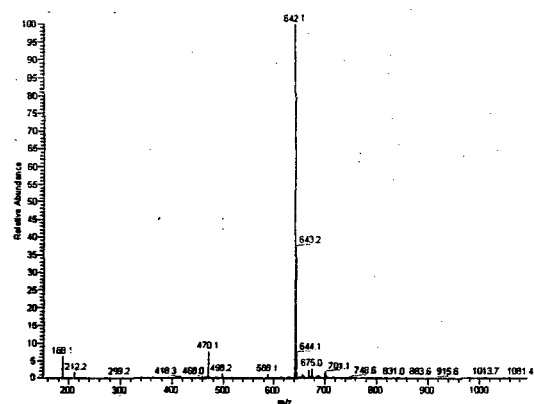
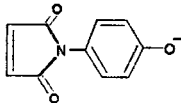
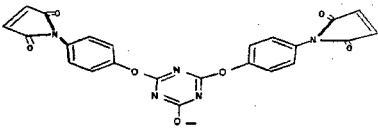


Fig.4 Mass spectrum of trimaleimide

Table 2 The main characteristic data of monomers

trimaleimide	
FTIR spectral data (KBr (cm <sup>-1</sup> )) and the corresponding structure	1786,1732,1382,703(imide structure); 3080,1595, 1522(aromatic ring); 1665(C=N); 1620 (C=C); 1220(ether bond)
The main EI-Mass fragments and the corresponding structure	<p>188 </p> <p>470 </p> <p>642 molecular ion peak (M<sup>+</sup>. )</p>

### 3. Properties of trimaleimide

Trimaleimide monomer only can dissolve in strong polar solvents, such as DMF, DMAC. No melting point of trimaleimide was observed by both differential scanning calorimeter and capillary tube method. The DSC trace shows that board exothermic peak appears in the region of 203°C ~ 269°C due to thermal polymerization of trimaleimide.

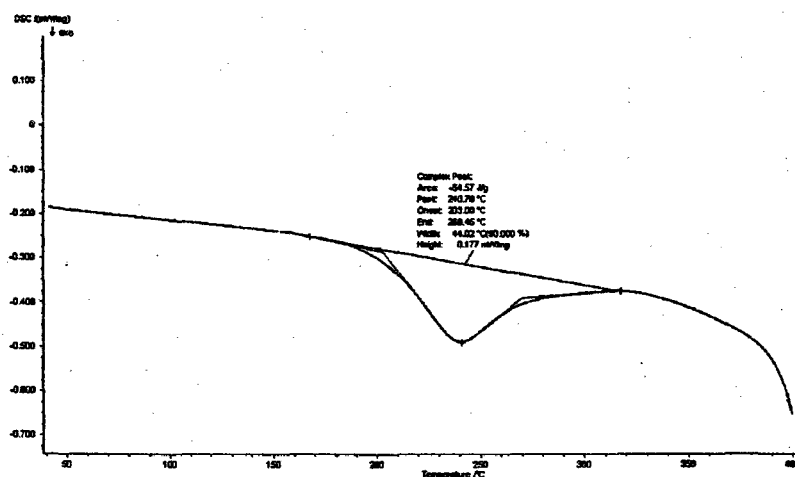


Fig.5 DSC trace of trimaleimide

#### 4. Conclusion

*N*-(4-hydroxyphenyl)maleimide was prepared in two methods. In the method using acetic anhydride and sodium acetate as dehydrator, acetylation of the free hydroxyl groups undoubtedly occurs to form *N*-(4-acetoxyphenyl)maleimide. To obtain the target intermediate, it is necessary to alcoholize *N*-(4-acetoxyphenyl)maleimide with methanol. The FTIR spectra of the product in the two procedures commendably inosculate. That is to say, the latter method is of lower yield, more expensive, and complicated.

We prepare target product, trimaleimide containing triazine ring in three ways. The first method is popular way to use tertiary amine as acid acceptor in adequate solvent system; however, the way is of low yield. And the other two methods with high yield are phase-transfer catalyzed reaction which is a novel synthetic method using for preparation of triazine-containing maleimide. Just one is to use aqueous alkali or carbonate as acid acceptor, and the other is to use binary quaternary ammonium salt/tertiary amine catalyst system. The yield of three methods are in the order the reaction using quaternary ammonium salt/tertiary amine as catalyst system > that using quaternary ammonium salt as catalyst and aqueous carbonate as acid acceptor > that using tertiary amine as acid acceptor, and the first method possesses the best yield even up to 90%.

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