

**STUDY ON SYNTHESIS, APPLICATION AND MECHANISM OF  
BENZOPHENONE/AMINE INITIATOR**




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**ABSTRACT**

Through Michael addition reaction of trimethylolpropane triacrylate (TMPTA) with diethylamine (DEA), a new kind of tertiary amine derivative was synthesized and its structure was identified by <sup>1</sup>H-NMR. When used in combination with benzophenone, this amine presented excellent curing speed and could be a substitute for initiator Darocur  1173, which is effective but expensive. If so, the cost of UV-curable coatings can descend apparently. The functioning mechanism of benzophenone/amine bimolecular initiator was studied.

**KEYWORDS** UV coating Tertiary amine Initiator

**I. INTRODUCTION**

UV coatings are well known because of their low energy consumption, low pollution and high curing speed. They have been getting wider and wider applications in many fields, such as wood and building materials(1), automotive(2) and Flexo printing(3).

However, UV-curable coatings are expensive due to the essential parts, photoinitiators, which cover almost 1/3 of the total cost. In order to decrease the expenses, we developed benzophenone/amine initiator, a cheap and well-performing initiator. Besides its low cost, the major advantage of such bimolecular initiator is its fast surface cure.

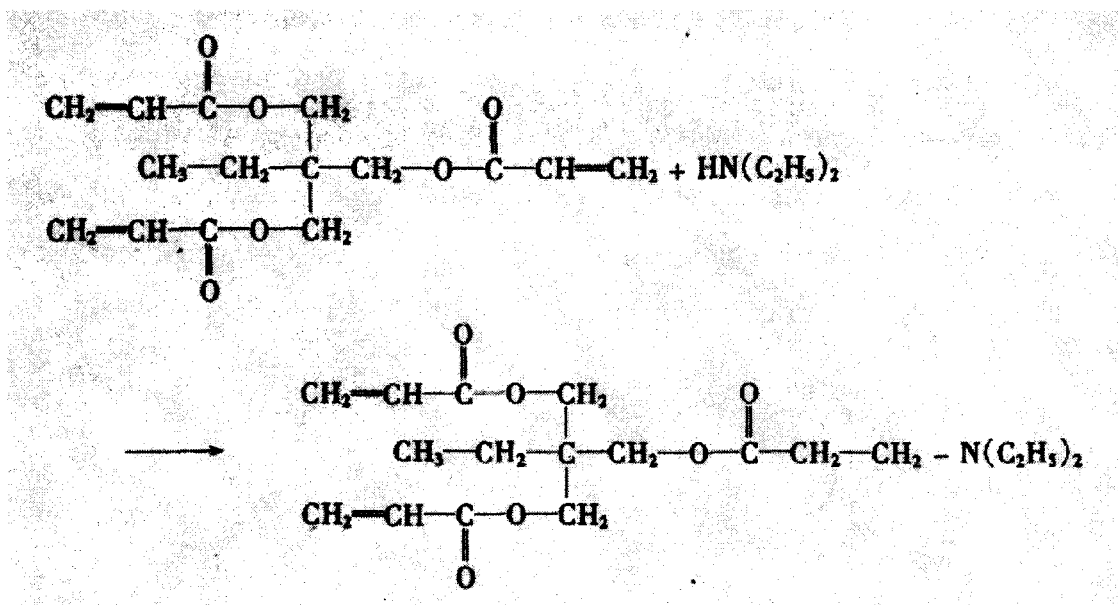
## II. EXPERIMENTAL

### i. Test method

Tertiary amine value: methylthionini chloridum-dimethyl amino----  
azobenzene (4)

Curing speed: measured with a Ultraviolet machine (made in Hunan Univ.,China), coatings were cured with 3.2kw UV-lamp suspended 20cm from substrate. Curing speed was measured by the speed of transmission belt(m/min).

### ii. Michael addition reaction (5)



In this paper , the structure of Michael addition product is substituted by RN C<sub>2</sub>H<sub>5</sub> 2

### iii. Synthesis process:

Both 296g TMPTA(1 mol) and 1.2 g MEHQ (hydroquinone monomethyl ether, used as inhibitor) was added into a four-mouth flask equipped with agitator, condensor and thermometer, then 95g DEA (1.3 mol) was added in drops with stiring and cooling. During dripping, the mixture temperature was maintained at 40±2<sup>0</sup>c. After adding of DEA, the

reaction system was kept at 60<sup>o</sup>c for 2 hours and kept agitating efficiently. When tertiary amine value reached 185 ±5 mg KOH/g, the reaction was stopped. Then, excess DEA was removed by using a vacuum apparatus. Finally, 0.5 g MEHQ was added into the mixture.

iv. Structure analysis of tertiary amine.

i) At the beginning of reaction

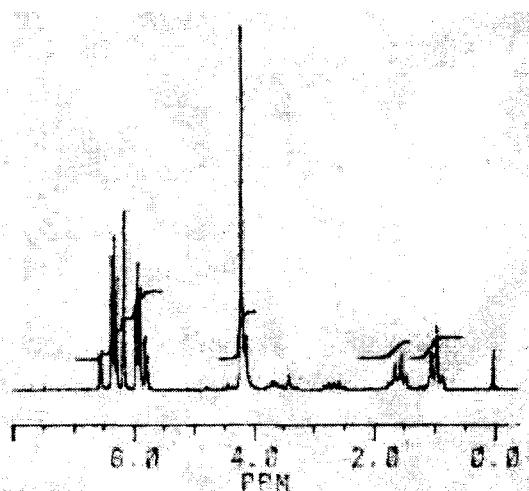


Fig.1 <sup>1</sup>H-NMR spectra of TMPTA, 80MHZ

Fig.1 shows clearly that the ratio of H number in TMPTA exactly corresponds with that of peak area, which is listed in Table 1.

Table 1 . Correspondence between H number in TMPTA and peak area in Fig.1

Shift of H/ppm	6.6~5.8	4.2~4.1	1.6~1.5	1.1~0.9
Corresponding H	CH <sub>2</sub> =CH-	-O-CH <sub>2</sub> -	$\begin{array}{c} \diagup \\ \text{C} \\ \diagdown \end{array}$ -CH <sub>2</sub> -	-CH <sub>3</sub>
Ratio of H number	9	6	2	3
Ratio of peak area	9	6	2	3

ii) At the end of reaction

After reaction, product was analyzed by <sup>1</sup>H-NMR as shown in Fig.2

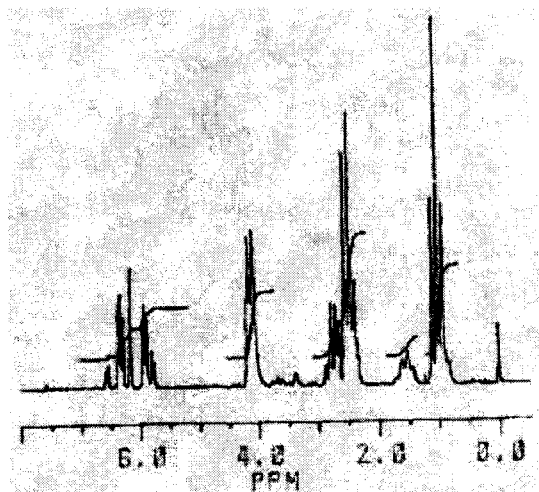


Fig.2 <sup>1</sup>H-NMR spectra of Michael addition product, 80MHZ

Through the aboved synthesis process, Michael addition reaction was carried out just as known in table 2.

Table 2. Correspondence between H number in Michael addition product and peak area in Fig.2

Shift of H/ppm	6.6~5.8	4.2~4.1	1.6~1.5	1.1~0.9	2.9~2.4
Corresponding H	CH <sub>2</sub> —CH	—O—CH <sub>2</sub>	—C—CH <sub>2</sub>	—CH <sub>3</sub>	the rest of H
Ratio of H number	5.1	6.0	2.0	10.8	15.6
Ratio of peak area	5.2	6.5	2.0	9.8	13.8

The reason why the ratio of H number is not exactly equal to that of peak area is the existence of foreign matter in the product and uncompleted reaction. However, this does not affect application of tertiary amine in UV-curable coating.

#### v. Application of tertiary amine

##### i) Non Benzophenone/Amine formulation

Before the development of Benzophenone/Amine combined initiator, we used the following formulation for UV-curable PVC coating.

Table 3. Non Benzophenone/Amine formulation:

Component	Epoxy acrylate	TMPTA	TPGDA	NPGDA	HDDA	Initiator 1173	additive
Content, wt%	44	15	12	8	13	6	2

Note: TPGDA means tripropylene glycol diacrylate

NPGDA means neopentylene glycol diacrylate

HDDA means 1,6-hexanediol diacrylate

For this formulation, curing speed is 38 m/min.

total cost is 33,850 RMB/Ton

#### ii) Benzophenone/Amine formulation

Using benzophenone/amine as initiator, the formulation for PVC coating is as follows.

Table 4. Benzophenone/Amine formulation

Component	Epoxy acrylate	TMPTA	TPGDA	NPGDA	HDDA	Initiator	additive
Content, wt%	43	14	12	10	11	8	2

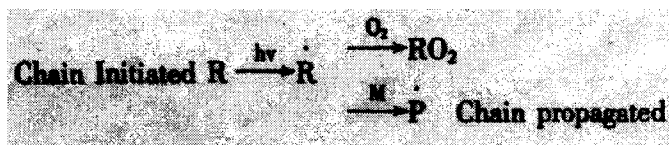
For this formulation, curing speed is 40 m/min

total cost is 26,650 RMB/Ton

### III. DISCUSSION

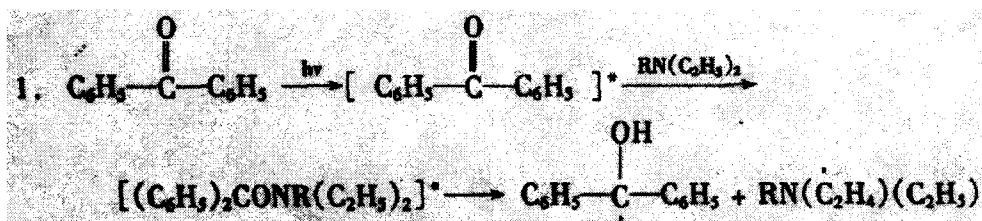
Table 3 and Table 4 show that the benzophenone/amine combined initiator not only makes contribution to fast curing, but also decreases coating cost greatly. Therefore, this bimolecular initiator is an excellent substitute for initiator 1173. Here we discuss the mechanism of benzophenone/amine.

It is a common knowledge that oxygen in air will substantially decrease UV curing rate. According to Decker et al [ 6 ], the mechanism of oxygen inhibition effect is as follows:

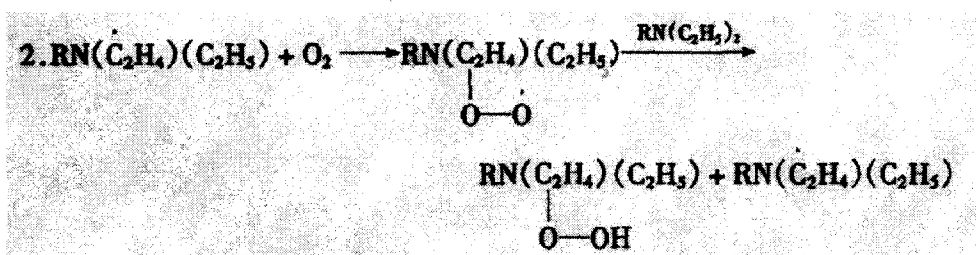


Therefore, only when the eliminating rate of resolved oxygen in coating is faster than the rate of oxygen diffusing into coating from air, the chain propagating can be maintained.

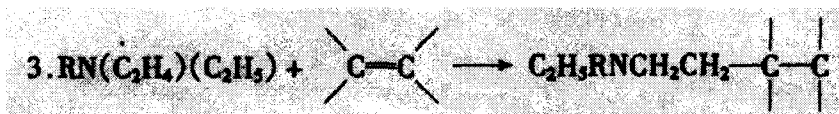
The tert-amine derivative which we synthesized can solve this problem. It can absorb the resolved oxygen in coating. The mechanism is outlined below.



Absorption of UV light results in the formation of triplets of excited benzophenone, which when combine with tert-amine molecules to form charge-transfer complexes. Subsequently, hydrogen transfer occur in the complexes, yielding tert-amine radicals.



Tert-amine radicals absorb resolved oxygen and change into peroxide radicals, which further react with tert-amine molecules releasing tert-amine radicals.



Tert-amine radicals initiate the polymerization of double bonds. As a result, polymerization is initiated while oxygen is consumed.

#### IV. CONCLUSIONS

1. Benzophenone/Amine initiator developed in this paper can greatly accelerate the curing of the formulated UV-curable coating.
2. By the replacement of cheap Benzophenone/Amine initiator for expensive 1173 initiator, the total cost of coating can descend drastically.
3. Benzophenone/Amine can act as an effective initiator because tert-amine eliminate resolved oxygen in coating.

#### V. REFERENCES

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