

EFFECT OF ACIDITY ON ACID-SENSITIVE UV CURING SYSTEM*

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Abstract By using diphenyliodonium salts with different counterions as photo acid generators (PAGs), the effect of acidity on ring-opening polymerization of epoxy monomers and polycondensation of polyol with hexamethoxymethyl melamine (HMMM) was studied. The result shows that the rate of ring-opening polymerization is evidently dependent on the acidity of the acid and strong photo-generated acid is required. However, there is a leveling effect in the polycondensation system; if the photo-generated acid is stronger than protonated HMMM, the acidity does not obviously affect the polycondensation rate.

Keywords Photo acid generator, UV curing, Polyaddition system, Polycondensation system

INTRODUCTION

Diaryliodonium salts are important PAGs, which can efficiently decompose and generate acid under irradiation^[1-4]. They are used as the source of acid in acid-sensitive UV curing systems. According to the type of polymerization, the acid-sensitive curing system is classified as polyaddition and polycondensation systems. Generally, the polyaddition system consists of PAG, reactive monomers and epoxy oligomers, and the main components of polycondensation systems are PAG and acid-sensitive resin including polyol and a crosslinking agent (HMMM). Both systems are widely applied in coatings, printings and so on. The polycondensation system is also applied in the region of chemically amplified negative photoresist. Although the PAGs in these two systems are both diaryliodonium salts, the effect of photo-generated acid on the curing rate is different. Further study on this difference is helpful for formulating in practice.

EXPERIMENTAL

Diphenyliodonium salts were synthesized according to the method of Crivello and Lam^[2] and purified by recrystallization. Bisphenol A epoxy resin E51, Irgacure 184 (Ciba-Geigy), Cy179 (Ciba-Geigy) and HMMM (CYTEC) were used as received. Phenothiazine was purified by recrystallization. Novolak was supplied by the Beijing Institute of Chemical Reagent.

Preparation of Diphenyliodonium Salts^[2]

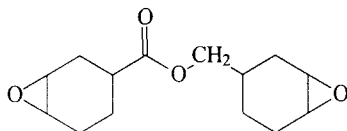
Into a 250mL three-necked round-bottom flask equipped with a mechanical stirrer, a thermometer and a dropping funnel, was added a mixture of KIO₃ (18.8 g), benzene (30.2 mL), acetic acid (18.8 mL) and CH₂Cl₂ (90 mL). To this solution, a mixture of acetic anhydride (18.8 mL) and concentrated sulfuric acid (15.0 mL) was added slowly below 0°C. After the mixture was stirred

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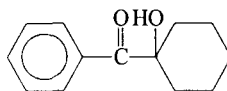
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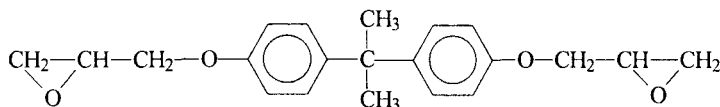
for 12 h at room temperature, an aqueous solution of *p*-toluenesulfonic acid (TsOH) was added and left to react for about half an hour. The organic phase was washed with water, and the aqueous phase was washed with CH_2Cl_2 . Then the organic portions were collected. Acetic acid was added into the organic phase, and a precipitate was formed. Diphenyliodonium salt with counterion of TsO^- was obtained after the filtration of the precipitate. According to the above method, diphenyliodonium salt with counterion of PF_6^- or SbF_6^- was synthesized by replacing TsOH with KPF_6 or KSbF_6 , respectively. These salts were designated as I-1, I-2, I-3. The melting points of I-1, I-2 and I-3 were determined to be 154~155°C, 143~144°C and 148~149°C, respectively.



Cy 179



Irgacure 184



Bisphenol A epoxy resin E51

Measurement of the Gel Time

A mixture was formulated with bisphenol A epoxy resin E51, Cy 179, 1-hydroxyl cyclohexyl-phenyl ketone (Irgacure 184) and diphenyliodonium salt. It was cast onto a glass plate and then exposed to a 125W medium pressure mercury lamp. The thickness of the coating was 200 μm . The time of film formation is defined as the gel time.

Measurement of the Normalized Thickness

Chemically amplified negative photoresist was formulated with novolak, HMMM, diphenyliodonium salt, sensitizer and other additives. It was spin-cast onto a silicon wafer with a SiO_2 surface. The wafer was prebaked at 70 °C for 10 min and exposed to a 125W medium pressure mercury lamp. Then the wafer was postexposure-baked at 117°C for 10 min. After treatment with 2% NaOH-EtOH aqueous solution, the wafer was dried. The ratio of the film thickness after treatment to that before treatment is the normalized thickness.

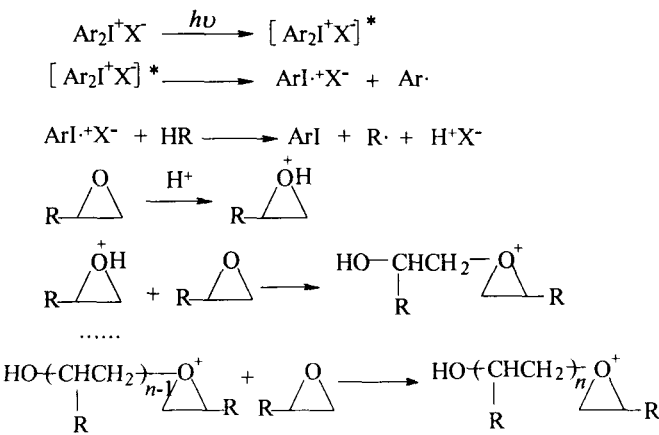
RESULTS AND DISCUSSION

The Effect of Acidity on the Polyaddition System

The ring-opening polymerization of epoxy under irradiation can be described as follows (Scheme 1)^[1,5].

When exposed to UV, the diphenyliodonium salt decomposes and generates acid. The photo-generated proton initiates the ring-opening polymerization via the initial formation of secondary oxonium ion, which can react with the second monomer molecule to form the tertiary oxonium ion. The extent of polymerization is obviously affected by the nucleophilicity of the counterion. For weak acid, the anion is sufficiently nucleophilic to react with the monomer. Thus only very low-molecular-weight products are produced and curing becomes impossible. On the contrary, if the acidity of the photo-generated acid is very strong, the nucleophilicity of the counterion is too weak to terminate the propagating process. As a result, the counterion of PAG affects the rate of curing obviously^[6]. The gel times of samples with different diphenyliodonium salts were tested and are

listed in Table 1. From Table 1, we can see that the stronger the photo-generated acid is, the faster the system will cure. This result is consistent with those reported in the references^[7,8].



Scheme 1. UV curing of epoxy resin

It has been proved that the photo-sensitizer such as phenothiazine can accelerate the decomposition of diaryliodonium salts by electron transfer mechanism^[9]. Some amines such as N, N-dimethylaniline can also promote the photolysis of diaryliodonium salts^[10,11]. However, as is shown in Table 1, if phenothiazine or N, N-dimethylaniline was added into the system, the curing rate descended sharply. This is due to the basicity of these compounds, which leads to the rapid reaction of these compounds with the photo-generated acid. Although the efficiency of photolysis is increased, the total efficiency of UV curing is reduced greatly. By consequence, the curing rate of the acid-sensitive polyaddition system could not be increased by basic compounds.

Table 1. The effect of acidity on polyaddition system*

Onium salts	Photo-generated acid	Additives	Gel time
I-1	TsOH		> 5min
I-2	HPF ₆		22s
I-3	HSbF ₆		17s
I-2	HPF ₆	Phenothiazine	> 5min
I-2	HPF ₆	N, N-dimethyl aniline	> 5min

* Diphenyliodonium salt 3.0%, Irgacure184 3.0%, Cyl179 44%, Bisphenol A epoxy resin 50%

The Effect of Acidity on the Polycondensation System

To investigate the effect of acidity on the polycondensation system, the normalized thickness of samples with different diphenyliodonium salts in different dosages was measured (Fig.1). From this figure, we can conclude that if the acidity of the acid is strong enough, it will not affect the curing rate significantly.

The condensation reaction of polyol with HMMM via transesterification or aromatic electrophilic substitution^[12-14] has been pointed out to be specific-acid catalyzed^[15]. The rate is proportional to the concentration of solvated proton [SH⁺]. If the acid which is added to the solvent S is stronger than SH⁺, no matter how strong the acid is, it is solvated rapidly due to the leveling effect and cannot be distinguished from SH⁺.

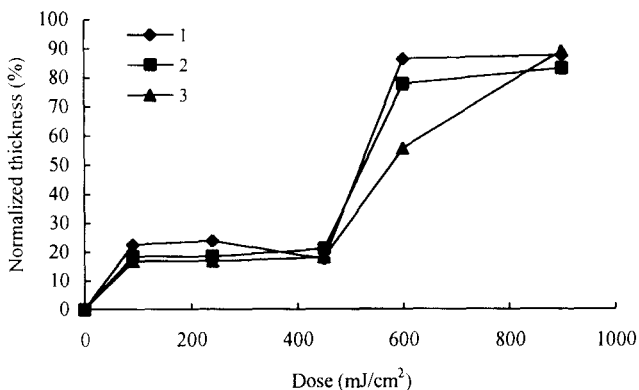
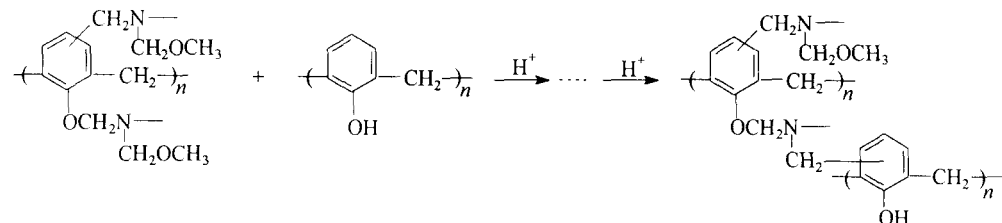
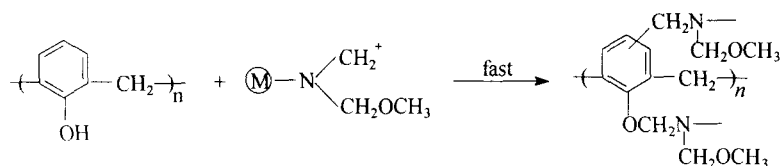
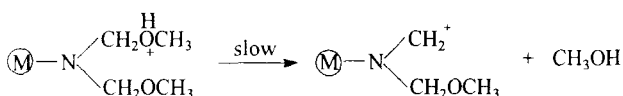
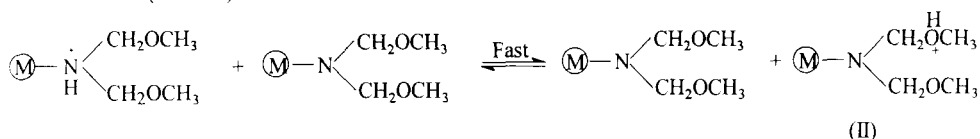
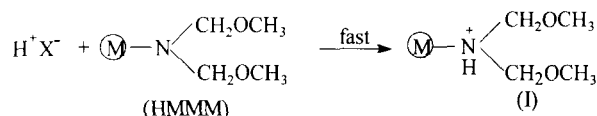
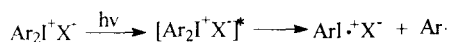


Fig.1 Sensitivity plots of the polycondensation system
1. TsO⁻, 2. PF₆⁻ and 3. SbF₆⁻



Scheme 2. UV curing of polycondensation system

Although in our polycondensation system the solvent is evaporated off, the function of HMMM is similar to the solvent (Scheme 2). The structure of HMMM is analogous to N, N-dimethylaniline. In HMMM, the dimethoxymethyl amino groups are conjugated with an aromatic ring just like the dimethylamino group in N,N-dimethylaniline. Supposing that their basicities are

close to each other, we can assume that the K_a of the conjugate acid of HMMM ($\text{HMMM}^+(\text{I})$) is about 10^{-2} . The acidity of TsOH is much stronger ($K_a = 10^6$). When the diphenyliodonium *p*-toluenesulfonate decomposes and generates acid under irradiation, the photo-generated TsOH first reacts with the amino group of HMMM and turns it into $\text{HMMM}^+(\text{I})$ completely. The equilibrium constant of the reaction is about 10^8 . HPF_6 and HSbF_6 undergo the same situation. In other words, there is also a leveling effect in this system. In fact, the protonated $\text{HMMM}(\text{I})$ is probably the strongest acid existing in this system. Because of the leveling effect, the photo-generated acid does not make a difference with $\text{HMMM}^+(\text{I})$. The curing rate is proportional to the concentration of $\text{HMMM}^+(\text{I})$, and not to the acidity of the photo-generated acid.

In contrast to the ring-opening polymerization system, basic sensitizers can accelerate the curing of the polycondensation system (Table 2). In the polycondensation system, although the basic sensitizers such as phenothiazine or *N*, *N*-dimethylaniline can react with photo-generated acid, the conjugate acids of sensitizers produced can also react with HMMM by rapid proton-exchange. The reaction of basic sensitizers with photo-generated acid could not stop the polycondensation reaction. Thus the curing of the polycondensation system can be accelerated by these basic compounds (Table 2). However, it was found that the basicity of the sensitizer should not be too strong, otherwise, strong bases such as triethyl amine will decrease the rate of curing (Table 2).

Table 2. The effect of basic sensitizer on polycondensation system*

Amine	PK_b	Exposure time (sec)		
		20	30	120
No sensitizer		×	×	×
Phenothiazine	12.8	√	√	√
<i>N</i> , <i>N</i> -dimethylaniline	8.85	O	√	√
iso-Pentyl <i>N,N</i> -dimethyl benzoate		√	√	√
Pyridine	8.83	√	√	√
Triethyl amine	3.28	×	×	×
Phenothiazine + triethyl amine		×	×	×

* √: curing; ×: not curing; O: curing incompletely

CONCLUSION

In acid-sensitive polyaddition systems, the acid acts as the initiator of polymerization. The rate of curing is dependent on the acidity of the acid. The stronger the acid, the faster the system cures. In acid-sensitive polycondensation systems, the acid is the catalyst of the reaction. There is a leveling effect of acid in this systems. If the acidity of acid is stronger than the protonated $\text{HMMM}(\text{I})$, the rate of curing is proportional to the concentration of protonated $\text{HMMM}(\text{I})$, and not to the acidity of the photo-generated acid.

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