

# EFFECT OF THIOL GROUP ON THE CURING PROCESS OF ALKALINE DEVELOPABLE PHOTORESISTS <sup>(1)</sup>



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## **I. Abstract**

Photosensitivity of a conventional radical photoinitiator in an alkaline developable photoresist is boosted by substitution with a thiol group. Evidence is presented that the thiol group acts via a chain transfer mechanism.

## **II. Introduction**

Currently the most efficient radical photoinitiators for a variety of resist applications belong to aminoacetophenone type. A typical example of a widely used initiator out of this class is 2-Methyl-1[4-(methylthio)phenyl]-2-morpholinopropane-1-one which is traded by Ciba Specialty Chemicals under the name of Irgacure 907. In combination with thioxanthone as a photosensitizer, Irgacure 907 shows excellent curing performance. Due to the general trend in electronics industry to higher packaging densities and therefore finer resist pattern and the industry's demand for higher throughput, a novel photoinitiator showing higher photosensitivity and better resolution is desired.

Usual approaches to design a new photoinitiator to obtain high performance are:

- i) to optimize UV absorption profile,
- ii) to achieve a high quantum yield for cleavage,
- iii) to produce a highly active photo fragment for initiation upon cleavage.

In this paper we report of a new approach to improve photosensitivity by attaching thiol group to Irgacure 907. The observed improvement of the performance of the photoinitiator is explained by a mechanism based on radical chain transfer.

## **III. Experimental**

### Model alkaline developable photoresist formulation

To represent Type I formulation (see figure 5 for details), ACA200M (Daicel Chem.) as an alkaline soluble prepolymer and DPHA as a monomer are used. To represent Type II formulation, Carboset 525 as an alkaline soluble binder and TMPTA as a monomer are used.

### Photosensitivity evaluation

The photo-sensitivity of the resist was evaluated based on reproduced maximum step number after UV exposure through Stouffer stepwedge and subsequent development. Metal halide lamp is used as UV light source.

## Evaluation of acrylate double bond conversion

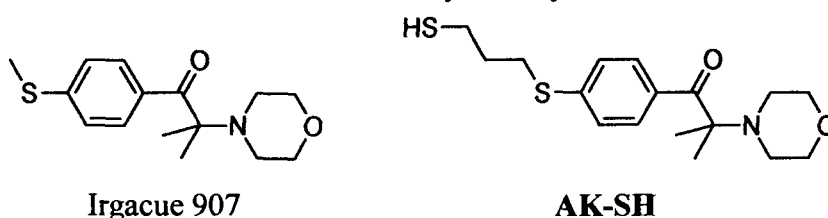
The resist formulation was applied on a silicone wafer as an IR transparent substrate. By stepwise exposure acrylate double bond conversion was traced by IR absorption at  $809\text{ cm}^{-1}$ .

## Molecular weight analysis of photo-polymerized methylmethacrylate(MMA)

THF solution of 5.0 mol/l MMA was irradiated in glass vial after  $\text{N}_2$  bubbling (photoinitiator: 0.1 mol/l, n-dodecylmercaptan (DSH): 0.1 mol/l). The reaction mixture is diluted by THF and analyzed by GPC. The molecular weight of the polymerized MMA was determined from retention time at a GPC peak using polystyrene as a standard.

## IV. Results and discussion

Irgacure 907 is substituted with thiol (**AK-SH**). Thiol group is introduced through a methylene chain on sulfur atom on the benzoyl moiety.



### 1. UV absorption spectra

Figure 1 shows the absorption spectra of Irgacure 907 and **AK-SH** in acetonitrile. The thiol-substitution has no influence on the chromophore.  $\lambda_{\text{max}}$  and the edge of the absorption spectra is the same as for Irgacure 907. Due to the increased molecular weight, absorbance at the same weight % concentration is slightly reduced.

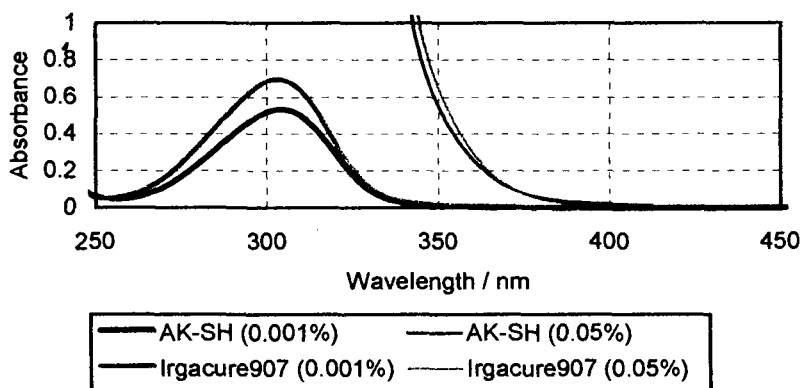


Figure 1 Absorption spectra of **AK-SH** measured in acetonitrile

### 2. Photo sensitivity

In spite of similar absorption spectra, **AK-SH** exhibits 4 steps higher photosensitivity than Irgacure 907. This means **AK-SH** can offer 4 times faster photo speed than Irgacure 907. The photosensitivity data also show that **AK-SH** can be sensitized by isopropylthioxanthone (ITX). ITX addition increases the sensitivity by two steps. This photo sensitization is practically very important for depth curing, curing of

pigmented coatings and thick photoresist coatings being exposed through a photo-mask.

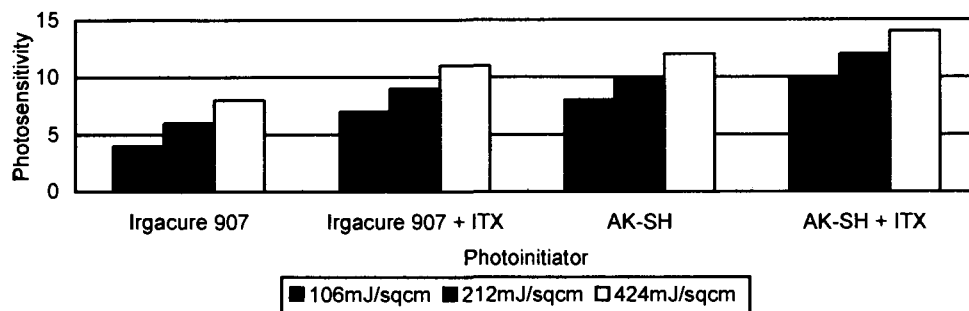


Figure 2 Stepwedge photosensitivity of alkaline developable photoresist using **AK-SH** as photoinitiator in comparison to Irgacure 907.

Double bond conversion of resist coatings using Irgacure 907 and **AK-SH** are compared under irradiation (Figure 3). Typically, at an early stage of irradiation, **AK-SH** results in faster double bond conversion than Irgacure 907.

Therefore, **AK-SH** is expected to allow for high throughput in photocuring processes.

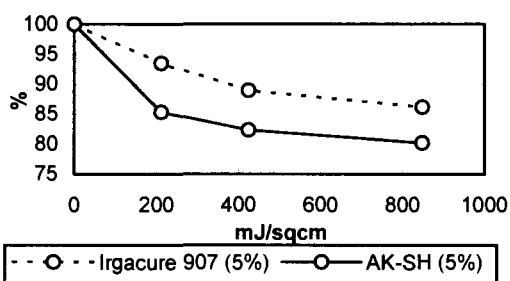
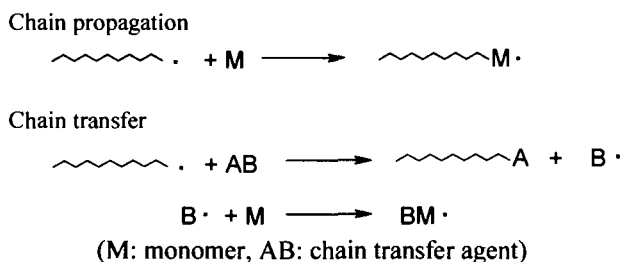


Figure 3 Comparison of double bond conversion of photoresist using Irgacure 907 and **AK-SH** as photoinitiator under irradiation

### 3. Mechanism of increased photo sensitivity boosted by thiol substitution

#### 3.1. Influence of chain transfer reaction on radical propagation<sup>(2)</sup>

A chain transfer reaction is a reaction which competes with a chain propagation reaction. A propagating radical (chain-)end can be terminated by a chain transfer agent (CTA) and a newly generated radical fragment initiates a polymerization with a monomer, resulting in the growth of a new polymer chain.



### a) Shorter polymer chain length

As expected from the chain transfer reaction scheme, the produced polymer chain length becomes shorter in the presence of CTA. Therefore, at the same double bond conversion ratio, slower viscosity increase during the curing process is expected in the presence of CTA. The less viscous environment makes the radical chain end easier to migrate and to undergo further propagation reactions. This may be one of the reasons for the observed higher double bond conversion with **AK-SH** compared to Irgacure 907.

As shown in Figure 4, it is experimentally confirmed that the molecular weight of photo-polymerized methylmethacrylate (MMA) with **AK-SH** is smaller than that with Irgacure 907. Therefore, we conclude that the thiol group on **AK-SH** structure actually works as a radical chain transfer group.

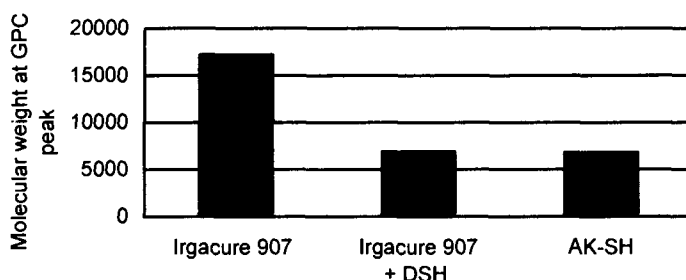
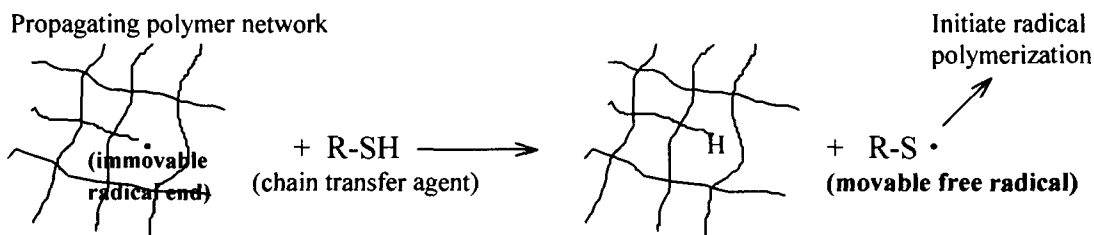


Figure 4 Molecular weight comparison of photopolymerized MMA with Irgacure 907, Irgacure 907 + DSH and **AK-SH**

### b) Release movable free radical

Another expected role of chain transfer function is the release of a mobile free radical (see scheme below).

Under irradiation, the crosslinking among multi-functional acrylates proceeds very rapidly and a radical propagation end is easily trapped in the highly crosslinked domain to become inaccessible for further propagation. However, when a chain transfer agent is present in the system, it reacts with the trapped radical end and generates a new mobile radical to reinitiate a propagation reaction. This role of chain transfer group may also contribute to the higher double bond conversion.



### 3.2. Influence of chain transfer group on the photo sensitivity of an alkali developable photoresist

Two typical types of alkaline developable, negative photoresist are described in Figure 5. The thiol substitution boosts the sensitivity in both type systems, but the effect is much more pronounced in Type I system.

In negative resist systems UV irradiation causes the exposed resist areas to become insoluble in a developing solution. In the both types, -COOH attached to a prepolymer or a binder polymer makes the uncured resist soluble in aqueous alkaline developers. The mechanism of insolubilization is, however, different in the two systems. In Type I case (Figure 5), the prepolymer itself contains acrylate double bond. The photo-crosslinking reaction of those double bonds attached to the prepolymer makes it easily insoluble in the developer. There is no growth of a long chain required for obtaining an insoluble system. Therefore, the shortened chain length by the chain transfer reaction is not detrimental in Type I formulations. Thus, for this system the increased double bond conversion results in a higher photosensitivity.

In Type II case, there is no reactive double bond on the binder polymer, therefore, the growing polymer network formed by acrylate monomers have to have a certain chain length to make the binder insoluble. Thus, the shortened chain length has a negative effect on the photo-crosslinking process. As a result, the sensitivity boost by the chain transfer group for Type II is small.

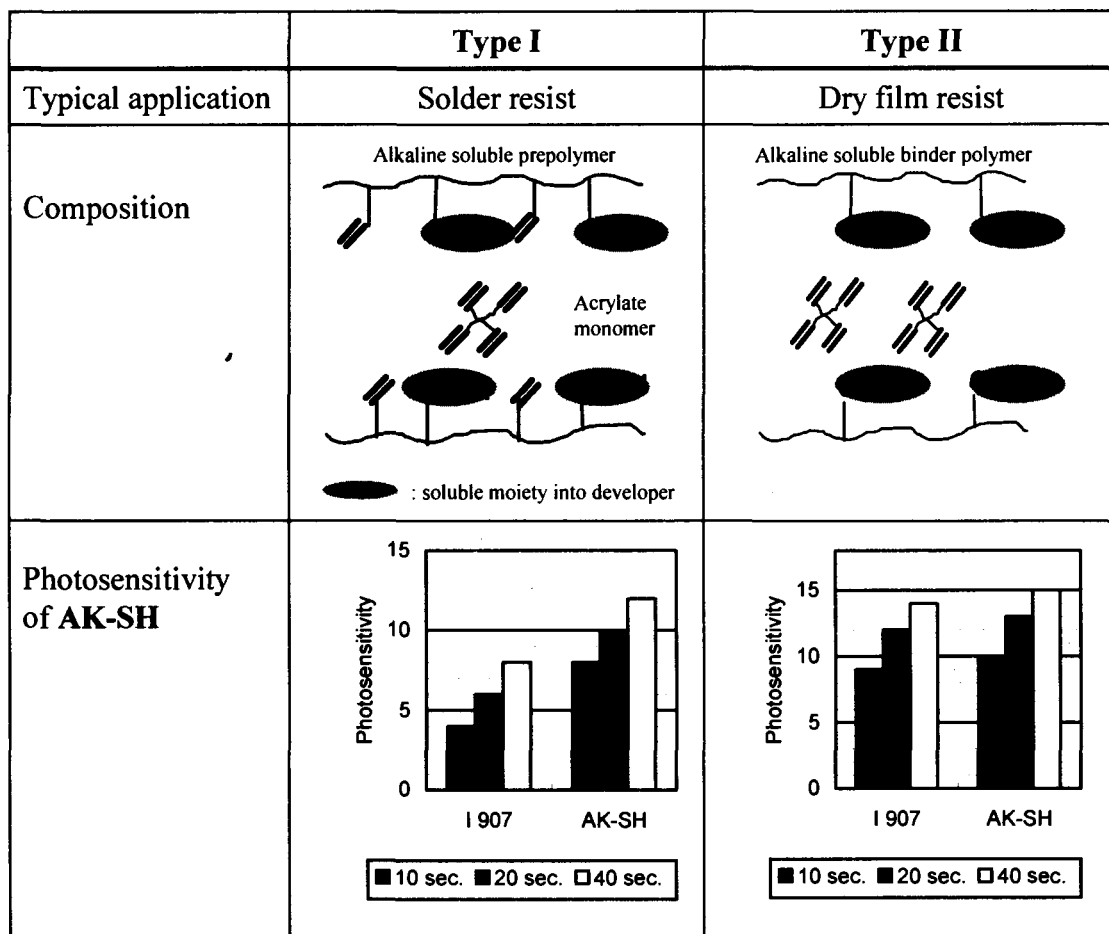


Figure 5 Type of alkaline developable photoresist and photosensitivity comparison between Irgacure 907 and AK-SH in each types

### **3.3. Odor**

Although pure AK-SH was essentially odorless, formulations containing it developed a characteristic thiol odor upon aging. This thiol odor became particularly apparent at higher temperatures, for example at oven drying of the coatings.

Despite the favorable photochemical properties of AK-SH like high photosensitivity and good resolution, the odor problem related to the presence of the thiol group is preventing any large volume use of this compound class. Thus, for industrial processes AK-SH cannot be applied.

### **V. Conclusions**

Thiol substitution of  $\alpha$ -aminoacetophenone has been shown to improve the photocuring and photoimaging properties of negative working acrylate based resist materials. The enhanced photocuring activity could be attributed to a chain transfer mechanism which involves the thiol group. However, the characteristic thiol-type odor of formulations and coatings upon drying so far prevents use of this approach in an industrial environment.

### **VI. References**

- (1) GB 2320027, 1998
- (2) Priola, A., Renzi, F., Cesca, S.J., J. Coatings Technol., 55 (1983) 63