

Note

STUDY OF DYE-SENSITIZED SYSTEMS FOR PHOTOIMAGING*

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Abstract *o*-Chloro-hexaarylbiimidazole (*o*-Cl-HABI) can be sensitized efficiently by cyanine dyes, the cyclopentanone and cyclohexanone dyes, when exposed to xenon lamp (use filter cut $\lambda \leq 400$ nm). The photoreaction between the photoinitiator and the dyes was completed through an electron transfer process. Excellent results have been obtained in photoimaging studies, e.g. the resolution of the image can reach 7 μm . The influence of the content of the dyes and the heat after the exposure on the resolution of the image was investigated.

Keywords Photopolymer, Photoimaging, Hexaarylbiimidazole, Printing plate

INTRODUCTION

In recent years, with the rapid development of Ar⁺ (488 nm), YAG (532 nm) and He-Ne (633 nm) laser imaging technology and photocuring, research work has focused on efficient long-wavelength photopolymerization systems, which can be used in many fields, such as holographic recording, computer-to-plate, photocuring and laser stereolithography^[1-6]. For these photosensitive polymeric materials, photosensitivity is a very important technical criterion, especially for printing plates. Now, the printing plate has been developed to the age of computer-to-plate, which means that image can be developed as soon as exposed to the laser source. Therefore, it is necessary that the sensitivity of photosensitive materials must be very high^[1].

o-Chloro-hexaarylbiimidazole (*o*-Cl-HABI) has received much attention in the near-UV and visible photosensitive initiating systems because of its high sensitivity and excellent stability^[7-10]. Our recent work suggested that the cyanine dyes (C1, 1-ethyl-3'-methylthiacyanine bromide, C2, 3,3'-diethyl thiacyanine iodide) and the cyclopentanone dye (C3, 2,5-bis[2-(1,3-dihydro-1,3,3-trimethyl-2H-indol-2-ylidene)ethylidene]) could be employed to sensitize the photolysis of *o*-Cl-HABI and the free radical was produced to initiate polymerization of MMA. In the present work, we synthesized a new cyclohexanone dye (C4 cyclohexanone, 2,6-bis[2-(1,3-trimethyl-2H-indol-2-ylidene)ethylidene]), and carefully compared the effect of the cyanine dyes C1 and C2, the cyclopentanone dye C3 and the cyclohexanone dye C4 on the resolution of the photoimaging.

EXPERIMENTAL

Materials

C1 and C2 were obtained from Shenyang Xin-cheng Chemical Co. Ltd, 3-mercapto-4-methyl-4H-1,2,4-triazole (MTA) was a product of Fluka, Switzerland. *o*-Cl-HABI was purchased from TCI Corporation. C3 and C4 were synthesized in our own laboratory. Monomer, dipentaerythriol pentaacrylate was a gift of Sartmor Corporation. Binder resin, alkaline soluble polyacrylate was prepared in our lab according to reference^[11].

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Methods

The base solutions prepared according to the formula ingredients listed in Table 2 were coated on 2.5 cm × 1.5 cm aluminum plates that have been electrolyzed and oxidized, followed by drying at 100°C for 2 min, and then 1% aqueous polyvinyl alcohol (PVA) solution was coated and dried at 100°C for 2 min. A presensitized offset printing plate was thus obtained.

Using PS plate signal strip as the mask, the plate was exposed to light generated by a 400 W xenon lamp (use filter cut $\lambda \leq 400$ nm) positioned at a distance of 10 cm. After irradiation, the plate was developed with a solution of 5% Na₂CO₃ at 25°C for 30 s. On washing with water, the image was observed.

RESULTS AND DISCUSSION

Synthesis of C4

To a stirred and heated solution containing 30 mL tertiary butanol and 0.62 g potassium tertiary butanol, 0.603 g 1,3,3-trimethyl-2-methyleneindol-aldehyde was added. The mixture was heated until a solution was obtained, then 0.155 mL cyclohexanone was added slowly and the solution was refluxed for 17 h. The above procedures were conducted under N₂ atmosphere. After completion of the reaction, 50 mL H₂O was added to the product and it was filtered. A red precipitate was obtained. The product was purified by column chromatography. The product yield is 8%. Characterization: m.p. 262°C (decomposed), MS: $M + 2,466$, $M = 464$, elemental analysis (% calculated): C, 82.57 (82.72); H, 7.87 (7.81) and N 5.92 (6.03).

General

It was established that *o*-Cl-HABI could only be excited by 200–300 nm light^[12]. Therefore, it is estimated preliminarily that the photosensitized reaction between *o*-Cl-HABI and the visible dyes is mainly through electron transfer when exposed to visible light. The main reason is that the energy of the excited singlet state of *o*-Cl-HABI is much higher than that of the dyes (Table 1). Moreover, there is no overlap between the absorption of *o*-Cl-HABI and the emission of the dyes. Therefore, it is difficult for the energy transfer to take place efficiently in these cases.

Table 1. The energy of excited singlet state (kJ · mol⁻¹)

Compd.	E_s
C1	< 215
C2	< 187
C3	< 200
C4	< 208
<i>o</i> -Cl-HABI	352 ^[7]

The Photosensitive Initiating Systems

Besides the photosensitizer and the photoinitiator, the photosensitive initiating systems were composed of co-initiator, MTA, monomer, dipentaerythriol pentaacrylate, and binder resin, alkaline soluble polyacrylate.

The content and the maximum absorption of each component in the photosensitive initiating systems are shown in Table 2. It can be seen that the maximum wavelength of the dyes lies within the visible light region. Moreover, the contents of the photosensitizer and the photoinitiator are much lower than that of the other components, though they play a key role in initiating polymerization of monomer.

Condition Experiment

Without photosensitizer

When the photosensitive initiating systems without any dye were exposed to visible light, no image could be obtained, even when the irradiation time was extended to 20 min. It is well known that *o*-Cl-HABI can not be excited by visible light, and the monomer can not be initiated.

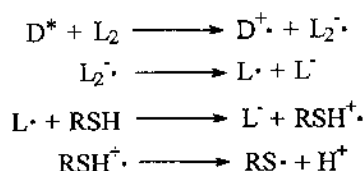
Table 2. The basic components of the offset printing plate

Component	Content (wt%)	$\lambda_{a, \max}$ (nm)
Dye	1~2	C1, 494
		C2, 568
		C3, 532
		C4, 510
<i>o</i> -Cl-HABI	2~4	270
MTA	1~2	258
Monomer	45~50	265
Binder resin	45~50	273

With photosensitizer

In this experiment, we studied carefully the influence of the content of the photosensitizer and the heat after exposure on the photoimaging.

When the content of the dyes was 2~4 wt%, a clear image can be obtained for the four photosensitive systems (Table 3). The process was as follows: the dyes were first excited by visible light and then transferred an electron to *o*-Cl-HABI (L_2) to produce a dye cationic radicals and an *o*-Cl-HABI anionic radical ($L_2^{\cdot -}$). The latter soon dissociated, and then produced an anion (L^-) and a free radical ($L^{\cdot}$), which can undergo hydrogen or electron transfer with MTA to produce a mercapto radical, which initiated the polymerization of the monomer.



The difference in the solubility of the polymeric material in the irradiated region and the unirradiated region became greater and greater with increasing irradiation time. During developing, the material in the unirradiated region was dissolved in the developer and so an image was formed. Fouassier and Wu^[13] noted that the intrinsic reactivity in the excited state of the sensitizer governed the efficiency of the photosensitive system. For a particular photosensitive system, the shorter the irradiation time needed to obtain a clear image, the higher the sensitivity of the system was. So C1 might have the highest reactivity of excited state among the four dyes.

After exposure, the presensitized offset printing plate was immediately placed in an oven and heated at 110°C for 10 min. We found that the irradiation time needed to obtain the clear image becomes shorter (*cf.* Table 3, 4, 5, 6). This shows that applying heat will promote further polymerization of the monomer and improve the sensitivity of the system.

Table 3. The results of photoimaging with a dye content of 2~4 wt%

Conditions	Dyes			
	C1	C2	C3	C4
A*	3 min	5 min	20 min	10 min
B*	2 min	3 min	15 min	5 min
C*	Slightly change	Pink to baby pink	Amaranth to lilac	Brown and red to slightly brown
Resolution	10 μ m	10 μ m	—	—

* A: the shortest irradiation time to obtain a clear image

B: the effect of heat on irradiation time

C: the change of dye's color after irradiation

It was interesting to note that the color of the dyes shows an obvious change when exposed to visible light, which improves the resolution of the image. It may be caused by electron transfer from the photosensitizer to the photoinitiator, and the dye changes its color by an oxidation reaction. The large color difference in the irradiated

region and the unirradiated region indicates that the above four systems could also be used as the photorecording materials.

Table 4. The results of photoimaging with a dye content of 1~2 wt%

Conditions	Dyes			
	C1	C2	C3	C4
A*	3 min	15 min	5 min	5 min
B*	2 min	10 min	3 min	3 min
Resolution	10 μ m	10 μ m	10 μ m	10 μ m

* A: the shortest irradiation time to obtain a clear image

B: the effect of heat on irradiation time

Table 4 shows that as the content of the dyes decreases, the sensitivity of the C3 system and the C4 system is increased dramatically. The time needed to get a clear image becomes shorter. We presume that this result could be attributed to the spectral properties of the dyes. C3 and C4 have high extinction coefficient and thus the high content of photosensitizer can prevent the light from reaching the substrate, and it further improves the self-deactivation rate of the excited state of the dyes. Therefore, a decrease in the content of C3 and C4 enhances the sensitivity of these systems.

Table 5. The influence of content of C3 on the resolution of image

Conditions	Content (wt%)			
	2~4	1~2	0.5~1	0.25~0.5
A*	20 min	5 min	2 min	4 min
B*	15 min	3 min	1 min	2 min
Resolution	-	10 μ m	10 μ m	10 μ m

* A: the shortest irradiation time to obtain a clear image

B: the effect of heat on irradiation time

In order to verify the above presumption, we studied the resolution of the photoimaging when the content of C3 and C4 was 0.5~1 wt% and 0.25~0.5 wt%, respectively. The results are listed in Table 5 and Table 6. With the decrease of dye content, the sensitivity of the systems is improved. As the content decreases further, the sensitivity of the systems also decreases. This indicates that there is a critical content for the particular dye.

Table 6. The influence of content of C4 on the resolution of image

Conditions	Content (wt%)			
	2~4	1~2	0.5~1	0.25~0.5
A*	10 min	5 min	30 s	2 min
B*	5 min	3 min	15 s	1 min
Resolution	-	10 μ m	7 μ m	10 μ m

* A: the shortest irradiation time to obtain a clear image

B: the effect of heat on irradiation time

It can also be seen from Table 3 and Table 4 that a decrease in the content of C1 has little effect on the sensitivity of the system, while for C2, the sensitivity decreases with a decrease of content of C2. These results indicate that the critical content of C1 and C2 is higher than 2~4 wt%. In fact, we have found that when the content of C1 and C2 was 6~8 wt%, the sensitivity of the systems was improved. When the content of C1 and C2 increases further (10~12 wt%), the sensitivity of the systems was decreased.

REFERENCES

- 1 Monroe, B.M. and Weed, G.C., *Chem. Rev.*, 1993, 93: 435
- 2 Yang, W.D., Yang, Y.Y. and Wang, J.S., *J. Photopolym. Sci. Tech.*, 1994, 7: 187
- 3 Allen, N.S., *Photochem.*, 1996, 27:303
- 4 Chen, Y.H., Kageyama, T. and Takahashi, T., *J. Imaging. Sci. Tech.*, 1997, 41: 178
- 5 Lessard, R.A. and Manivannan, G., *J. Imaging. Sci. Tech.*, 1997, 41: 228
- 6 Allen, N.S., Marin, M.C. and Edge, M., *J. Photochem. Photobiol. A: Chem.*, 1999, 126: 135
- 7 Zhu, Q.Q., Fink, M. and Seitz, F., *J. Photochem. Photobiol. A: Chem.*, 1991, 59: 255
- 8 Davidson, R.S., *J. Photochem. Photobiol. A: Chem.*, 1993, 73: 81
- 9 Zhao, C.Y., Yang, Y.Y. and Li, L.D., *Chin. J. Polym. Sci.*, 1998, 16: 310
- 10 Gao, F., Yang, Y.Y. and Mao, W.M., *J. Chin. Appl. Chem. (in Chinese)*, 1999, 16: 24
- 11 Xu, J.Q., Yang, Y.Y. and Li, L.D., *J. Photopoly. Sci. Tech.*, 1998, 11: 105
- 12 Li, L.D., Yang, Y.Y. and Zhao, C.Y., *Photogra. Sci. Photochem. (in Chinese)*, 1998, 16: 1
- 13 Fouassier, J.P. and Wu, S.K., *J. Applied Polym. Sci.*, 1992, 44: 1779