

DYE-SENSITIZED PHOTOLYSIS OF *o*-CI-HEXAARYLBIIMIDAZOLE AND PHOTOPOLYMERIZATION KINETICS STUDY OF THE LONG WAVE-LENGTH DYE/HEXAARYLBIIMIDAZOLE SYSTEMS*

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Abstract *o*-Chloro-hexaarylbiimidazole (*o*-Cl-HABI) can be sensitized efficiently by the dyes 1-ethyl-3'-methyl thiacyanine bromide (C1), 3,3'-diethyl thiacyanine iodide (C2), and cyclopentanone 2,5-bis[2-(1,3-dihydro-1,3,3-trimethyl-2H-indol-2-ylidene)ethylidene] (C3) through electron transfer processes. When exposed to a xenon lamp (filtered by Pyrex glass), the photosensitive systems composed of *o*-Cl-HABI and the above dyes can produce free radicals which initiate the polymerization of MMA. The photopolymerization kinetics equation was obtained for the *o*-Cl-HABI/C2 system, $R_p = K [C2]^{0.75} [o\text{-Cl-HABI}]^{0.44} [MTA]^{0.12} [MMA]^{1.0}$. A comparison of the influence of different dyes on the conversion of MMA photopolymerization was conducted.

Keywords Photolysis, Photopolymerization, Dye-sensitization, *o*-Chloro-hexaarylbiimidazole, Electron transfer

INTRODUCTION

During the last two decades, photosensitive polymeric materials, such as photoresist, ink, coating and presensitized printing plate, have been developed rapidly. For these photofunctional materials, the photopolymerization rate is a very important technical criterion, especially for printing plates. The printing plate has been developed to computer-to-plate (CTP). The image can be developed immediately on exposure to the laser, which means that the sensitivity of photosensitive materials is exceedingly high.

Several near-UV and visible light photosensitive initiating systems have been reported^[1, 2], and most of them were composed of two or three components. Fouassier and Wu^[3] noted that the intrinsic reactivity in the excited state of sensitizer governed the efficiency of the photosensitive system. To obtain high photosensitive efficiency, the absorption of sensitizer should match the wavelength of light source's emission.

In general, for a bimolecular visible light photosensitive initiating system, electron transfer is the only mechanism, because most photoinitiators can only be excited by 200~300 nm light. *o*-Cl-HABI has received much attention in visible photosensitive initiating systems because of its high excited state energy. So the dye/*o*-Cl-HABI system is very stable in the dark, and when it is exposed to near-UV and visible light electron transfer takes place quickly. Our previous research^[4] suggested that *o*-Cl-HABI can be sensitized by coumarin dyes, thioxanthone dyes under near UV and visible light, and mercapto compound, such as *n*-dodecyl mercaptan, as a coinitiator has high ability to improve the initiating efficiency.

In this work, we synthesized a new cyclopentanone dye. The efficiency of photopolymerization of methylmethacrylate (MMA) and polymerization kinetics formulation of dyes/*o*-Cl-HABI systems in visible light were investigated. Moreover, the mechanism on the photosensitization of *o*-Cl-HABI induced by dyes has been discussed.

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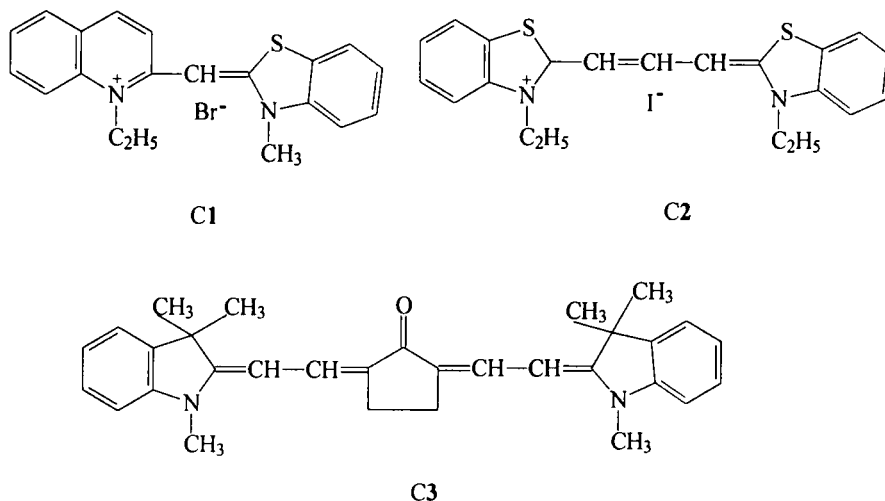
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EXPERIMENTAL

Materials

C1 and C2 were obtained from Shenyang Xin-cheng Chemical Co. Ltd, 3-mercapto-4-methyl-4*H*-1,2,4-triazole (MTA) was a product of Fluka, Switzerland. *o*-Cl-HABI was purchased from TCI Corporation. MMA and trichloromethane were of analytical purity and purified by distillation before use. C3 was synthesized in our laboratory (the structures of C1, C2, C3 are depicted in Scheme 1).



Scheme 1

Methods

Photopolymerization was carried out in a dilatometer ($\Phi = 10$ mm) at 30°C. The sample tubes were rotated around the light source. A xenon lamp (400 W) was used, and its short wavelength light (≤ 300 nm) was cut off by two pieces of Pyrex glass filter. The solution was de-aerated by bubbling highly pure nitrogen for 30 min. The conversion of polymerization can be obtained according to the following equation:

$$C\% = \Delta h \times S / (V_{\text{MMA}} \times 0.233) \quad (1)$$

where C is the polymeric conversion, Δh is the shrinkage height difference in the dilatometer, S is the cross section area of dilatometer, V_{MMA} is the volume of MMA. The experimental data were treated by least-square method.

UV-visible spectra were measured with a Hewlett-Packard 8451A diode array spectrophotometer.

RESULTS AND DISCUSSION

Synthesis of C3

To a stirred and heated solution containing 30 mL *tert*.-butyl alcohol and 0.4 g potassium *tert*.-butyl alcohol, 0.4 g 1,3,3-trimethyl-2-methyleneindol-aldehyde was added. The mixture was heated until a solution was obtained, then 0.09 mL cyclopentanone was added slowly and kept under reflux for 14 h. The above procedures were conducted under N_2 atmosphere. After reaction, 50 mL H_2O was added to the product. On filtration a purple and black precipitate was obtained. The product was purified by column chromatography. The product yield is 15%. Characterization: m.p. 252°C (decomposed); IR (KBr): 1563 cm^{-1} ($\nu_{\text{C}=\text{O}}$), 1309 cm^{-1} ($\nu_{\text{C}-\text{N}}$); MS: $M+2$, 452, $M = 450$; elemental analysis (% (calculated)): C, 82.57 (82.62); H, 7.60 (7.60); N, 6.24 (6.22).

Absorption Spectra

o-Cl-HABI shows strong absorption in the UV region and the $\lambda_{\text{a,max}}$ is at 270 nm. The maximum absorption of the three dyes appears in the visible region in CHCl_3 . As shown in Table 1, the dyes have absorption maxima ranging from 494 to 568 nm. The extinction coefficient varies between 1.6×10^4 and 5.5×10^4 ($\text{mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$). The absorption spectra depend on the chemical constitution of the different dyes.

From Table 1, it can also be seen that compared with C1, the maximum absorption of C2 shows an obvious red shift. This result indicates that the length of the conjugated chain plays a key role in extending the absorption of cyanine dyes. In C3, the carbonyl group acts as an electron acceptor group and the amine group acts as a donor. The red shift of C3 could be due to intra-molecular charge transfer through the conjugated double bond.

Table 1. The spectroscopic parameter of the four dyes*

Compd.	$\lambda_{a,max}$ (nm)	ϵ_{max} (mol ⁻¹ · L · cm ⁻¹)
C1	494	51000
C2	568	16000
C3	532	55000
<i>o</i> -Cl-HABI	270	2580

* In CHCl₃

The absence of any change and shift in the maximum absorption of a mixture composed of dyes and *o*-Cl-HABI suggests that the dyes have no interaction with *o*-Cl-HABI in the ground state. In general, if two compounds form a charge transfer complex (CTC) in the ground state, a new characteristic band always appears. Thus dye/*o*-Cl-HABI systems do not form CTC in the ground state.

Photopolymerization Kinetics Study

It was found that MMA can be initiated by C1/*o*-Cl-HABI, C2/*o*-Cl-HABI and C3/*o*-Cl-HABI systems when exposed to visible light in our experiment, indicating that *o*-Cl-HABI can sensitize the photocleavage to produce triarylimidazole radical. In order to understand further the influence of each component on the photopolymerization, we studied carefully the photopolymerization kinetics of C2/*o*-Cl-HABI system, which was composed of *o*-Cl-HABI, C2, MTA and MMA. They act separately as the initiator, sensitizer, coinitiator and monomer.

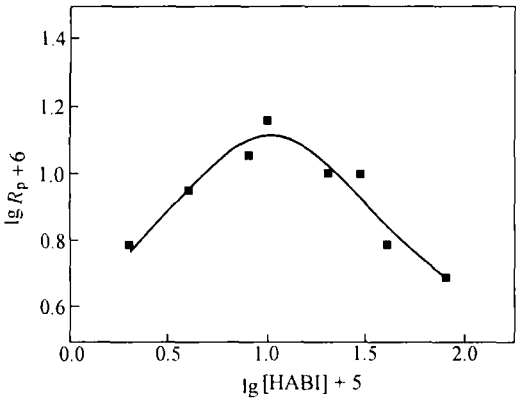


Fig. 1 Influence of *o*-Cl-HABI on the photopolymerization rate of MMA
[C2] = 4 × 10⁻⁵ mol/L
[MTA] = 2 × 10⁻⁴ mol/L
[MMA] = 2.86 mol/L

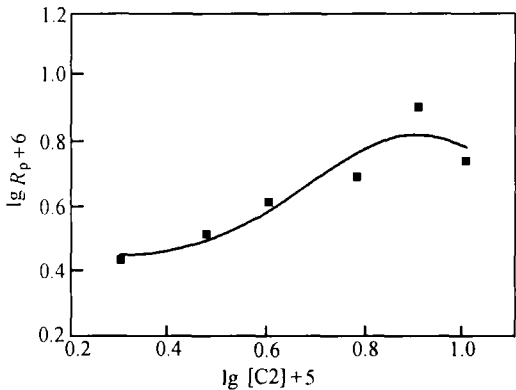


Fig. 2 Influence of C2 on the photopolymerization rate of MMA
[HABI] = 4 × 10⁻⁴ mol/L
[MMA] = 2.86 mol/L
[MTA] = 2 × 10⁻⁴ mol/L

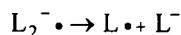
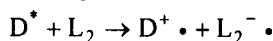
Reactive Exponent of Initiator, *o*-Cl-HABI

Figure 1 shows the relationship between the photopolymerization rate of MMA (*R_p*) and the concentration of *o*-Cl-HABI. When the concentration is lower than 1.0 × 10⁻⁴ mol/L, lg*R_p* is proportional to lg[HABI]. As the concentration increases further, *R_p* decreases. The main reason is that triarylimidazolyl radicals (L•) with a maximum absorption at 550 nm can absorb visible light and recombine to form *o*-Cl-HABI reversibly. From Fig. 1, the reaction exponent is obtained as 0.49, which indicates that the polymerization reaction of MMA is through a free radical initiation mechanism.

Reactive Exponent of Sensitizer, C2

Figure 2 shows the relationship between R_p and the concentration of C2. When the concentration is less than 8×10^{-5} mol/L, $\lg R_p$ is proportional to $\lg[C2]$.

For the molar extinction coefficient of the sensitizer in the visible light range, its wavelength should be high so that the system can be excited effectively. When its concentration is higher than a certain critical value, the local concentration of reactant will be increased and thus decreases the polymerization rate of MMA. The other reason is that the C2 cationic radical could be a chain terminator. According to our previous study^[4], the sensitized process of *o*-Cl-HABI by dyes can be expressed as following.



The reactive exponent of C2 is estimated to be 0.75, from Fig. 2. This high reactive exponent proves further that the photoinitiator, *o*-Cl-HABI, can be sensitized efficiently by photosensitizer C2.

Reactive Exponent of Coinitiator, MTA

o-Cl-HABI can be sensitized by dye to produce triarylimidazolyl radical when it is exposed to visible light. Triarylimidazolyl radical can initiate the polymerization of MMA, but is not very efficient due to its large size. MTA, as hydrogen donor, can undergo hydrogen or electron transfer with triarylimidazolyl radical and produces mercapto radical^[5], which is effective in initiating the polymerization. The reaction exponent of MTA, calculated from the relationship of concentration of MTA and R_p is 0.12. This low value shows that mercapto radical is the secondary free radical. Figure 3 shows the relationship between the concentration of MTA and R_p .

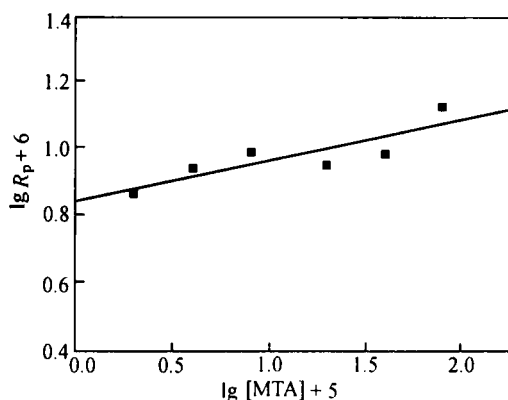


Fig. 3 Influence of MTA on the photopolymerization rate of MMA
 $[C2] = 2 \times 10^{-5}$ mol/L
 $[HABI] = 3 \times 10^{-4}$ mol/L
 $[MMA] = 2.86$ mol/L

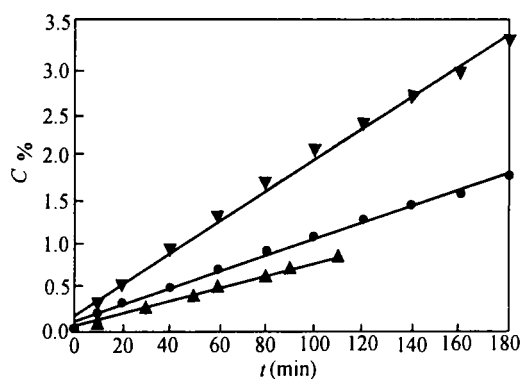


Fig. 4 Influence of dyes on the conversion of PMMA
 $[HABI] = [MTA] = 2 \times 10^{-4}$ mol/L
 $[MMA] = 2.86$ mol/L
 $[Dyes] = 4 \times 10^{-5}$ mol/L

Reactive Exponent of Monomer, MMA

The relationship between the concentration of MMA and R_p was found to be linear and the reaction exponent is 1.0. This means that the more monomer, the higher photopolymerization rate is. While the more monomer will induce the decrease of the molecular weight of polymer, thus will affect further the rigidity of photopolymer material. The reaction exponent, 1.0, suggests again that the initiation mechanism is through free radical initiation.

So, the polymerization kinetics formulation, $R_p = K[C2]^{0.75}[o\text{-Cl-HABI}]^{0.44}[MTA]^{0.12}[MMA]^{1.0}$, can be obtained from the above experiment. In our experiment, the influence of different dyes on the conversion of

PMMA was investigated. As can be seen from Fig. 4, *o*-Cl-HABI can be sensitized by the three dyes to produce free radicals, and C1 is the best one. This could be attributed to the intrinsic reactivity of its excited state.

Visible Light Sensitization Reaction of Dyes and *o*-Cl-HABI

In order to verify that electron transfer can be used to explain the photosensitization of *o*-Cl-HABI by dyes, we estimated the energy of excited states (Table 2). It can be seen from Table 2, that the energy of the excited state of *o*-Cl-HABI is much higher than that of the dyes. Moreover, there is not any overlap between the absorption of *o*-Cl-HABI and the emission of the dyes. So, it is difficult for energy transfer to take place efficiently in this case. It can be deduced preliminarily that the photosensitization mechanism in three systems corresponds to an electron transfer reaction: Dyes were excited by visible light and then transferred an electron to *o*-Cl-HABI (L_2), dye cationic radicals and an *o*-Cl-HABI anionic radical ($L_2^{\cdot-}$) were produced. The latter soon dissociated and produced an anion (L^-) and a free radical ($L^{\cdot}$), which can initiate the photopolymerization of MMA.

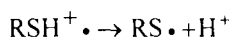
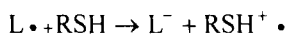
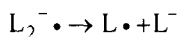
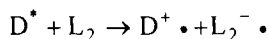


Table 2. The energy of excited singlet state ($\text{kJ} \cdot \text{mol}^{-1}$)

Compd.	E_s
C1	< 215
C2	< 187
C3	< 200
<i>o</i> -Cl-HABI[6]	352

The fluorescence of dyes can be quenched by *o*-Cl-HABI in agreement with Stern-Volmer equation. According to the above results, this quenching process may result from electron transfer.

It is interesting to note that photosensitive systems, C2/*o*-Cl-HABI and C3/*o*-Cl-HABI, show photobleaching ability when exposed to visible light. Fig. 5 shows that the intensity of maximum absorption of C2/*o*-Cl-HABI is decreased quickly by visible light irradiation and the maximum absorption wavelength displays a blue shift. The results (Table 3) indicate that there exists rapid electron transfer between dyes and *o*-Cl-HABI, and dyes are oxidized by the photoinitiator.

Table 3. The changes of some optical properties of photosensitive system after visible light irradiation*

Photosensitive system	Before irradiation	After irradiation	Photobleaching
	$\lambda_{a,max}$ (nm)	$\lambda_{a,max}$ (nm)	
C2/ <i>o</i> -Cl-HABI	568	550	obvious
C3/ <i>o</i> -Cl-HABI	532	472	obvious

* In CHCl_3

Application

All the above three systems have been used to record words and images when exposed to visible light, and excellent results were obtained, which will be reported in another paper.

CONCLUSION

o-Cl-HABI can be sensitized by dyes, C1, C2 and C3, through an electron transfer process. When exposed to visible light, the dyes/*o*-Cl-HABI can produce free radicals and initiate the polymerization of MMA. The difference in initiating efficiency of three photosensitive systems may result from different reactivity of the excited state of the dyes.

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