Photolysis of hexaarylbiimidazole sensitized by dyes and application in photopolymerization

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Kinetic studies on the near-UV photo-initiating polymerization of methylmethacrylate (MMA) sensitized by dye/hexaarylbiimidazole systems were carried out. When exposed to high-pressure mercury lamp (filtered by Pyrex glass), dye/hexaarylbiimidazole system undergoes quick electron transfer and free radicals are produced. RSH, as hydrogen donor, can improve the polymerization efficiency of MMA. Comparisons of influence of different dyes and different RSH on the conversion of MMA photopolymerization were carried out. Excellent results have been obtained in photoimaging studies, e. g. a minimum exposure energy of the photosensitive systems of 8 mJ/cm² can be reached and the resolution of presensitized printing plate was ca. 10 μm.

Keywords   Hexaaryliimidazole, dye-sensitization, photopolymerization, electron transfer

Introduction

During the last two decades, photosensitive polymer material, such as photoresist, ink, coating and presensitized printing plate, have been developing rapidly. For these photofunctional materials, photopolymerization rate is a very important technical standard, especially in printing plate. The printing plate has been developed to computer-to-plate (CTP). The image can be obtained as soon as exposed to the laser, which means that sensitivity of photosensitive materials is very 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[3] noted that the intrinsic reactivity in the excited state of sensitizer governed the efficiency of the photo-

sensitive system. To obtain high photosensitive efficiency, the absorption of sensitizer should match the wavelength of emission.

In general, for a bimolecular near-UV and visible light photosensitive initiating system, electron transfer is the only mechanism, because most of photoinitiators can only be excited by 200—300 nm light. o-Chloro-hexaaryliimidazole (o-Cl-HABI) has been received much attention in near-UV and visible photosensitive initiating system for its high excited state energy. So dye/o-Cl-HABI system is very stable in dark, and when exposed to near-UV and visible light electron transfer takes place quickly through the singlet state of o-Cl-HABI.

In this paper, the efficiency of photopolymerization of methylmethacrylate (MMA) initiated by dye/o-Cl-HABI systems in near-UV light was estimated. And the mechanisms on the photosensitization of o-Cl-HABI induced by dyes and on the MMA photopolymerization have been discussed. Also, preliminary studies in the presensitized printing plate have been completed.

Materials and methods

Materials

o-Cl-HABI was purchased from TCI and used as received. RSH, n-dodecyl mercaptan (RSH1), pentaerythritol tetra (3-mercaptopropionate) (RSH2), 3-mercapto-4-methyl-4H-1, 2, 4-triazole (RSH3), 1-phenyl-5-mercapto-2,3,4,5-tetraazole (RSH4) were the products of Fluca. Dyes (Scheme 1): DMC was pur-

chased from Aldrich corporation; ITX was supplied by PHT International Inc. DeTX and DiTX were gifts from Prof. S.X. Yu, Beijing Normal University.

Scheme 1
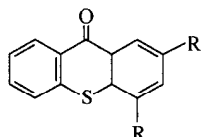
ITX: R=(CH₃)₂CH, R=H;
DiTX: R=(CH₃)₂CH; DeTX: R=C₂H₅
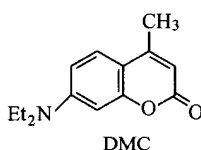
DMC

Methods

(1) Photopolymerization was carried out in a dilatometer ($\Phi = 10$ mm) at 30℃. The sample tubes were rotated around the light source. A high-pressure mercury lamp (500 W) was used, and its short wave-length light (≤ 300 nm) was cut off by two pieces of Pyrex glass filters. The solution was deaearted by bubbling highly pure nitrogen for 30 min. The experimental data were treated by a least-squares method.

(2) The solution composed of photosensitizer (dye), o-Cl-HABI, SH, resin, and monomer was coated on 2.5 cm × 1.5 cm aluminum plates which have been eletrolyzed and oxidated, followed by drying at 100℃ for 2 min, and then 1% polyvinyl alcohol (PVA) solution was coated and dried at 100℃ for 2 min. Using 21-step stouffer wedge as the mask, the plate was exposed to a light of 1 kW high-pressure Hg lamp positioned at a distance of 10 centimeter for 10 sec. After imagewise exposure, the plate was developed with a solution of 5% Na₂CO₃ at 250℃ for 30 sec. After washing with water, the image was obtained.

(3) The photosensitivity (E, mJ/cm²) was defined as the minimum exposure energy insolubilizing the layer, and is calculated

$$E = I_0 \times T \times t \qquad (1)$$

where I_0 is the incident light intensity (mJ/cm²s), T is the transmittance of the step at which photosensitive lay-

er begins to be insolubized and t is exposure time (s).

The same procedure as described in (2) was repeated, except for using the resolution and halftone dot signal strip in place of 21-step stouffer wedge. So the resolution and halftone dot repetition can be obtained.

Results and discussion

Spectra

o-Cl-HABI has strong absorption in the UV region and the $\lambda_{a,max}$ is at 270 nm, The maximum absorption of the four dyes is in the near-UV region in CHCl₃. As shown in Table 1, the dyes have absorption maxima ranging from 374—391 nm. The extinction coefficient varies between 675 and 2400 (mol⁻¹·L·cm⁻¹). The absorption spectra depend on the chemical constitution of the different dyes.

The maximum absorption of DMC can be assigned to intra-molecular charge transfer (ICT),[4] and is sensitive to solvent ; DMC has strong fluorescence (Φ = 0.649, $\lambda_{f,max}$ = 421 nm), which comes from ICT state of the coumarin dye with a non-twisted 7-diethylamino group in CHCl₃.

It is assumed[5] that for thioxanthone dyes, ITX, DiTX, DETX, the carbonyl group acts as an electron acceptor group and sulphur atom as a donor. The conjugation between the donor and the acceptor group through their connecting – C = C – double bond is responsible for the longest wavelength absorption and emission. DiTX and DETX have stronger fluorescence than ITX.

Table 1   Spectroscopic parameter of the four dyes

Compd.	$\lambda_{a,max}$ (nm)	ε_{max} (mol⁻¹·L·cm⁻¹)
DMC	374	2400
ITX	383	867
DeTX	390	699
DiTX	391	675
o-Cl-HABI	270	2580

No characteristic absorption band was observed for the dye/o-Cl-HABI mixture and it is noted that the optical density value of the mixture is equal to the amount of optical density value of components. The absence of any change and shift in the maximum absorption suggest that dyes have no interaction with o-Cl-HABI in the ground state. In general, if two compounds can form a charge

transfer complex (CTC) in the ground state, a new characteristic band always appears. So dye/o-Cl-HABI systems do not generate free radical for polymerization through the excitation of CTC when exposed to high-pressure mercury lamp.

Effects of concentration of the components (DMC, o-Cl-HABI, RSH1, MMA) *on the photopolymerization rate of MMA*

Initiator, o-Cl-HABI

Fig. 1 shows the relationship between the photopolymerization rate of MMA (R_p) and the concentration of o-Cl-HABI. When the value of concentration is lower than 5.01×10^{-3} mol/L, $\lg R_p$ is proportional to $\lg[\text{HABI}]$. While the concentration increases further, R_p decreases. The main reason is that triarylimidazolyl radicals ($L^{·}$), whose maximum absorption is at 550 nm, can absorb visible light and recombine to form o-Cl-HABI reversibly. It is noted that the size of the tri-arylimidazole radical is so big that the value of photoinitiating efficiency initiated by o-Cl-HABI alone is low.
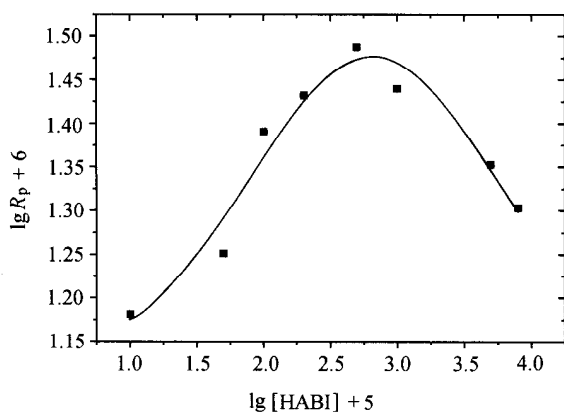
Therefore, it is needed to add RSH to produce small free radical for initiating MMA. From Fig. 1, the reaction exponent can be obtained as 0.17. The added excess photoinitiator can lead to the decrease of molecular weight of photopolymer, which need to be noted in application.

Sensitizer, DMC

Fig. 2 shows the relationship between R_p and the concentration of DMC. When the concentration is less than 1×10^{-3} mol/L, $\lg R_p$ is proportional to $\lg[\text{DMC}]$. However, when the concentration increases further, R_p decreases.

The molar extinction coefficient of the sensitizer at the wavelength of light is necessary to be high so that the system can be excited effectively. While the local concentration of reactant can be increased, the polymerization rate of MMA is decreased when its concentration is higher than the critical value. The other reason is that the coumarin cationic radical can be chain terminator (see the discussion in mechanism). The reaction exponent of DMC can be estimated as 0.53, from Fig. 2.
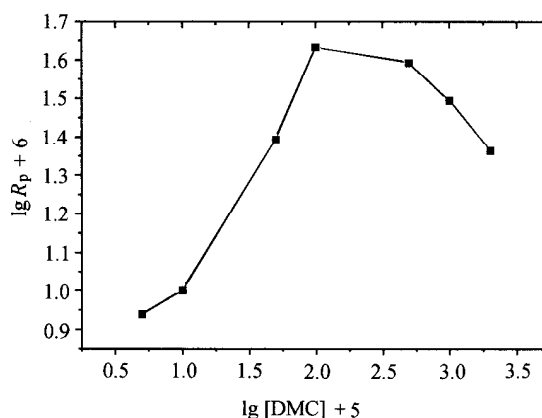

Fig. 1 Influence of o-Cl-HABI on the photopolymerization
rate of MMA, [DMC] = [RSH1] = 1 × 10⁻² mol/L,
[MMA] = 2.86 mol/L.

Fig. 2 Influence of DMC on the photopolymerization rate of
MMA, [o-Cl-HABI] = 5 × 10⁻⁴ mol/L, [MMA] =
2.86 mol/L, [RSH1] = 1 × 10⁻² mol/L.

Coinitiator, RSH1

Seen from the above results, o-Cl-HABI can be sensitized by dye when exposed to near-UV light to produce triarylimidazolyl radical. Triarylimidazolyl radical can initiate the polymerization of MMA, but is not very

efficient due to its big size. RSH, as hydrogen donor, can undergo hydrogen or electron transfer with triarylimidazolyl radical and produced RSH radical.[6] RSH free radical is more effective in initiation, so the polymerization is prompted . The reaction exponent of RSH 1, 0.46, can be calculated from the relationship of concen-

tration of RSH and R_p. Fig. 3 showed the relationship of concentration of RSH1 and R_p.

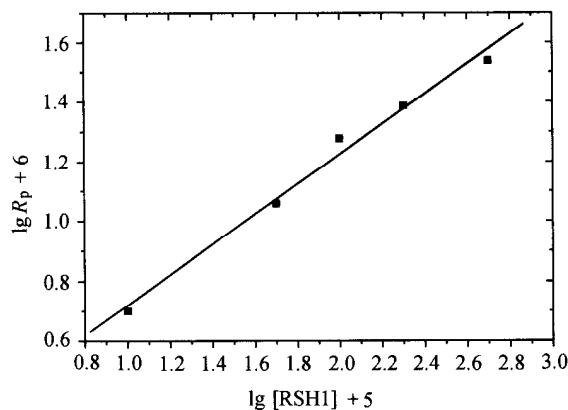The influence of different RSH1 on the photopoly-

Fig. 3   Influence of RSH1 on the R_p of MMA, [o-Cl-HABI] = 5×10^{-4} mol/L, [MMA] = 2.86 mol/L, [DMC] = 1×10^{-3} mol/L.

In our experiment, the influence of different dyes on the conversion of PMMA was examined. Seen from Fig.5, o-Cl-HABI can all be sensitized by the four dyes to produce radicals, and DiTX is the best sensitizer, which could be attributed to the intrinsic reactivity of its excited state.
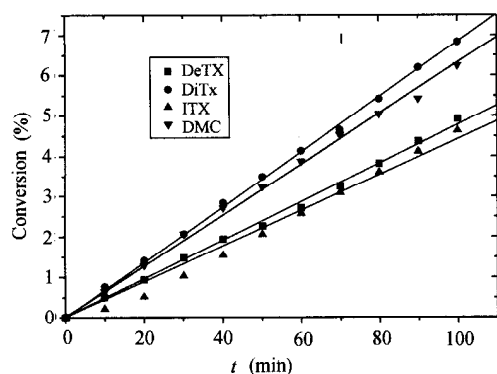

Fig. 5   Influence of dyes on the conversion of PMMA, [RSH1] = 1×10^{-2} mol/L, [o-Cl-HABI] = 5×10^{-4} mol/L, [MMA] = 2.86 mol/L, [DiTX] = [DeTX] = [ITX] = [DMC] = 1×10^{-3} mol/L.

Monomer, MMA

The relationship between the concentration of MMA

merization conversion of MMA was carried out. Seen from Fig. 4, RSH1 is the best coinitiator, which could be attributed to small size of RSH1 radical.
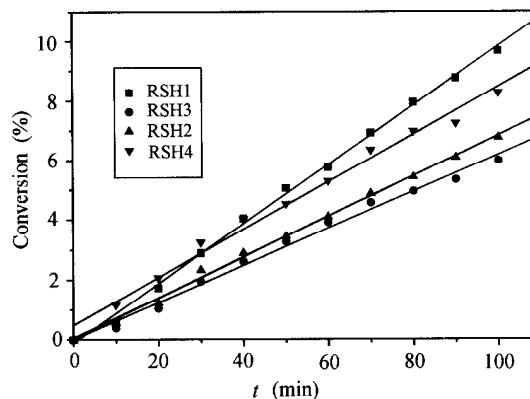

Fig. 4   Influence of RSH on the conversion of PMMA, [o-Cl-HABI] = 5×10^{-4} mol/L, [RSH1] = [RSH2] = [RSH3] = [RSH4] = 1×10^{-3} mol/L, [DMC] = 1×10^{-3} mol/L, [MMA] = 2.86 mol/L.

and Rp was linear and the reaction exponent is 1.0. The more monomer, the higher photopolymerization rate is.

Near-UV *photoinduced reaction of* o-Cl-HABI *and dyes*

From the above results, we can draw a conclusion that o-Cl-HABI can be sensitized efficiently by DMC. In the same concentration of DMC, the variation of UV-visible absorption spectra of DMC as well as the mixture composed of DMC and o-Cl-HABI during irradiation in air is shown in Fig. 6 and Fig. 7. As shown in Fig. 6, the maximum absorption of DMC was decreased by near-UV irradiation, while optical density of its maximum absorption was great after irradiation for 20 s. The results could be the photolysis of DMC. As compared with Fig. 6, the maximum absorption of the mixture was decreased quickly by near-UV light irradiation and disappeared after irradiation for 12 s, while the absorption around 315 nm increased greatly with irradiation, and an isosbestic point (410 nm) was found. Obviously, a new product was produced and increased greatly with irradiation in near-UV light. Seen from the above results, photoreaction of DMC is very different from that of the mixture. The above results further demonstrate that there exists rapid electron transfer between DMC and o-Cl-HABI, thus DMC improves the initiating efficiency of the photo-
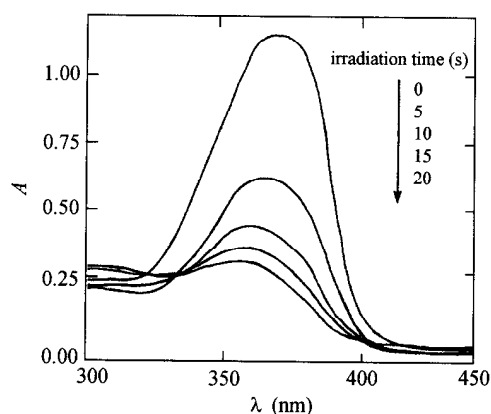
sensitive initiating system.

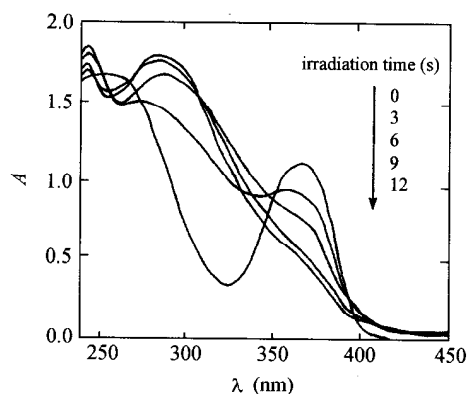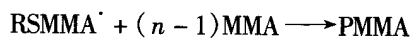**Fig. 6**   UV-visible absorption of DMC at different irradiation time, [DMC] = 5 × 10⁻⁵ mol/L.
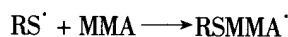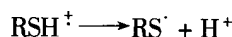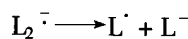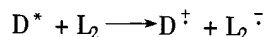

Fig. 7   UV-visible absorption spectra of the mixture DMC and o-Cl-HABI at different irradiation time, [DMC] = [o-Cl-HABI] = 5 × 10⁻⁵ mol/L.

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). (Assuming in the intramolecular charge transfer transition the energy difference between singlet and triplet is 36.4 (kJ·mol⁻¹).[7] Seen from Table 2, the energy of excited state of o-Cl-HABI is higher than that of dyes. Moreover, the absorption maxima of o-Cl-HABI and e-mission spectra of dyes are too far away to have a great overlap. It is difficult for energy transfer to take place efficiently in this case. Therefore, we can conclude that the photosensitization mechanisms in three systems were all electron transfer reaction: Dyes were excited by visible light and then transferred an electron to o-Cl-HABI (L₂). 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·), which can initiate the photopolymerization of MMA. The mechanism is as the follows.

$$D^* + L_2 \longrightarrow D^{\cdot+} + L_2^{\cdot-}$$
$$L_2^{\cdot-} \longrightarrow L^\cdot + L^-$$
$$L^\cdot + RSH \longrightarrow L^- + RSH^{\cdot+}$$
$$RSH^{\cdot+} \longrightarrow RS^\cdot + H^+$$
$$RS^\cdot + MMA \longrightarrow RSMMA^\cdot$$
$$RSMMA^\cdot + (n-1)MMA \longrightarrow PMMA$$

Zhu and his coworkers[8] have employed flash photolysis to study the mechanism of photolysis of o-Cl-HABI sensitized by ITX and thought that electron transfer was reasonable between them.

Table 2   Energy of excited state (kJ·mol⁻¹)

Compd.	E_S	E_T
DMC	284.4	248
DiTX	277.8	241.1
DeTX	281.7	245.3
o-Cl-HABI[8]	352	283

The fluorescence of dyes can be quenched by o-Cl-HABI in accord with Stern-Volmer equation. Fig. 8 showed the Stern-Volmer plot of fluorescence quenching of DMC by o-Cl-HABI and the quenching constant was ca. 5 × 10¹¹ mol⁻¹·L·s⁻¹. According to the above results, this process is attributed to electron transfer.
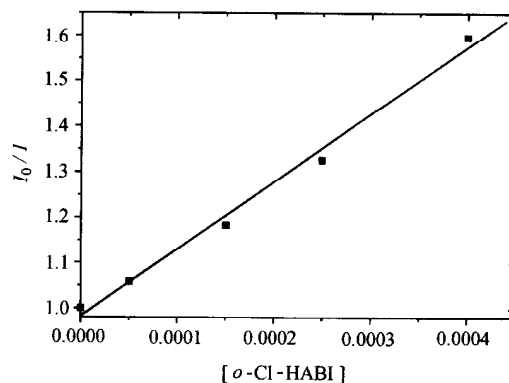

Fig. 8   Plot for Stern-Volmer equation of florescence of DMC quenched by o-Cl-HABI.

Analysis of photosensitivity of the four dye/o-Cl-HABI/RSH1 system

In this work, the four photosensitive initiating systems were composed of a sensitizer (DMC, or DeTX, or DiTX or ITX), a coinitiator RSH1, initiator o-Cl-HABI, and the binder resin [modified poly(styrene-co-maleic anhydride)resin]. The solution was prepared in line with the best rate obtained from the above kinetic experiments. According to experimental methods (2) and (3), many excellent results were obtained (Table 3 and Table 4).

Table 3   Results of photosensitivity of the four photosensitive system

Photosensitive system	DMC	DiTX	DeTX	ITX
E (mJ/cm^2)	7.49	7.04	8.56	8.80

Table 4   Resolution and halftone dot repetition of the four photosensitive

Sensitizer	High-exposure (μm)	Light-exposure (μm)	Halftone dot repetition (%)
DMC	15	10	4
DiTX	10	10	3
DeTX	12	12	4
ITX	15	10	5

Seen from Tables 3 and 4, the four photosensitive systems can all be used in photoimaging, in which DiTX/o-Cl-HABI/RSH1 is the best photosensitive initiating system. The results are similar to those in the above kinetic results.

Acknowledgments

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