Kinetic Study of Long Wave-length light Photopolymerization initiated by Cyanine Dye and Hexaarylbiimidazole

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The long-wavelength sensitive photoinitiating system composed of 3-n-propylsulfonic acid -2-[S-(3-n-propylsulfonic acid triethylamine-2-benzothiazolinylidene)-1,3-pentadienyl]-benzoxazolium inner salt (SP-36), 2-chlorohexaarylbiimidazole (o-cl-HABI) and 3-mercapto-4-methyl-4H-1,2,4,-triazole(MTA), which acted as sensitizer, initiator and hydrogen-donor respectively, can be used to initiate the polymerization of methyl methacrylate (MMA). The kinetic study was carried out in trichloromethane solution at 30 °C by using dilatometer. The relation between the polymerization rate and the concentrations of SP-36, o-cl-HABI, MTA and MMA was studied. The kinetic formula was deduced: \( Rp=K\cdot[SP-36]^{0.45}[HABI]^{0.40}[MTA]^{0.24}[MMA]^{1.0} \). The photopolymer system can record stable hologram under Helium neon laser.

Key words biimidazole, photopolymerization, dye sensitization

1. Introduction
With the recent development of laser technology and imaging, research work has been focused on efficient long-wavelength photopolymerization system, which can be used in many fields such as holographic recording, computer-to-plate and photocuring. One of the most important techniques is how to make the system sensitive to long-wavelength light and gain high sensitivity.

Several visible light photoinitiating systems have been reported, such as Eosin-onium salt\(^1\), N-phenylglycine-thioxanthane\(^2\) and Aromatic aminoketone-Hexaarylbiimidazole\(^3\). We have reported two Hexaarylbiimidazole systems before\(^4,5\). In this paper, we further our study and use SP-36 as the sensitizer, whose maximum absorption lies in 619nm.

2. Experimental Materials
o-cl-HABI was prepared according to a known procedure\(^6\). The structure was confirmed by mass spectrometry (MS), nuclear magnetic resonance (NMR), infrared spectrometry (IR) and elementary analysis.

SP-36 was obtained from Nippon Kankoh Shikiso Kenkyusho Co. Ltd. without further purification. MTA was a product of Fluca, Swaziland.

MMA and its solvent, trichloromethane, were of analytical purity and purified by distillation before using.
Methods
Photopolymerization was carried out in dilatometer (Φ=10mm) at 30 °C. The sample tubes were rotated around the light source. A xenon lamp (400W) was used and its short wavelength light (<300nm) was removed by two Pyrex glass filters. The solution were deaerated by bubbling highly pure nitrogen for 30 minutes.

3. Results and discussions
I Absorption Spectra
The absorption spectrum of SP-36 in trichloromathane displays a strong broad band in the visible region: $\lambda_{\text{max}}=619\text{nm}$ and $\epsilon_{\text{max}} =7.48 \times 10^4\text{mol}^{-1}\text{L.cm}^{-1}$, as shown in Fig. 1(a). o-cl-HABI has a very weak absorption in the visible region but absorbs strongly in the UV region: $\lambda_{\text{max}}=265\text{nm}$ and $\epsilon_{\text{max}} =2.82 \times 10^4\text{mol}^{-1}\text{L.cm}^{-1}$, as shown in Fig. 1(b). The bond energy of C-N in o-cl-HABI is very low which leads to the easy homolysis of HABI when exposed in UV light or heated.$^{(7)}$ Fig. 1(c) shows the absorption of MTA: $\lambda_{\text{max}}=258\text{nm}$ and $\epsilon_{\text{max}} =1.78 \times 10^4\text{mol}^{-1}\text{L.cm}^{-1}$.

Fig. 2 is the absorption spectrum of the mixture of SP-36 and o-cl-HABI in trichloromathane. Compared with Fig. 1, no shift of the maximum absorption occurred. This indicated that there was no formation of (SP-36)- (o-cl-HABI) complex in the ground state.

<table>
<thead>
<tr>
<th>Sensitizer SP 36</th>
<th>Initiator o-Cl-HABI</th>
<th>Hydrogen-donor MTA</th>
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<tbody>
<tr>
<td><img src="image1.png" alt="Compound Structure" /></td>
<td><img src="image2.png" alt="Compound Structure" /></td>
<td><img src="image3.png" alt="Compound Structure" /></td>
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Table 1. The compound structure of photosensitive initiating system
In our study, the solution of o-cI-HABI and MMA (monomer) in trichloromethane were exposed in the visible light (λ > 510nm). No photopolymerization occurred. The reason is that the absorption of o-cI-HABI is nearly all in the UV region, thus cannot produce free radicals in the visible light. When SP-36, the sensitizer, was added, the photo-polymerization occurred efficiently.

From Fig. 1 and Fig. 2, we found that the maximum absorption band of o-cI-HABI and SP-36 (265nm and 619nm respectively) are too far away to have any overlay. It is difficult for energy transfer in this way. Therefore, we consider that the photopolymerization mechanism in this system was also electron transfer: SP-36 was excited by visible light and then transferred an electron to o-cI-HABI (L2). A dye cation radical and an o-cI-HABI anion radical (L2⁻) were produced. The latter soon dissociated and produced an anion (L') and a free radical (L'), which can initiate the photo-polymerization of MMA. The following is the procedure:

\[
\begin{align*}
\text{SP-36} & \xrightarrow{h_v} \text{SP-36}^* \\
\text{SP-36}^* + \text{L}_2 & \rightarrow \text{SP-36}^+ + \text{L}_2^- \\
\text{L}_2^- & \rightarrow \text{L}' + \text{L}^- \\
\text{L}' + \text{MMA} & \rightarrow \text{LMMA}' \\
\text{LMMA}' + (n-1)\text{MMA} & \rightarrow \text{PMMA}
\end{align*}
\]

### Effects of the Concentrations of the Components

**Sensitizer, SP-36**

Fig. 3 shows the relationship between the polymerization rate (Rp) and the concentration of SP-36. When the concentration is less than 6 \times 10^5 M, LGp is proportional to LG[SP-36]. The exponent value is 0.45, which was calculated from the slope of the linear. However, when the concentration increases furthermore, Rp decreases. This phenomenon of inversion has been observed in other photopolymerization systems. The molar extinction coefficient of the sensitizer at the wavelength of the source light is necessary to be high so that it can excite the system effectively. However, on the other hand, it makes the light difficult to pass through the system and then decreases the polymerization rate when its concentration is higher than the critical value.

**Initiator, o-cI-HABI**

Fig. 4 shows the relationship between Rp and the concentration of o-cI-HABI. When the concentration is less than 2 \times 10^{-5} M, LGp is proportional to LG[HABI]. The exponent value is 0.40 according to the slope of the linear. While the concentration increases furthermore, Rp decreases. The reason is that triarylimidazolyl radicals (L'), whose maximum absorption is at 550nm, can absorb visible light and recombine to form o-cI-HABI reversibly, as shown in Fig. 5.

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**Graphs and Figures:**

- Fig. 3: Relationship between Rp and [SP-36]
  - \([\text{o-cI-HABI}]=2 \times 10^{-4} \text{ mol/L} \quad [\text{MTA}]=2 \times 10^{-4} \text{ mol/L} \quad [\text{MMA}]=2.86 \text{ mol/L}\)

- Fig. 4: The influence of [o-cI-HABI] on Rp
  - \([\text{SP-36}]=4 \times 10^{-5} \text{ mol/L} \quad [\text{MTA}]=2 \times 10^{-4} \text{ mol/L} \quad [\text{MMA}]=2.86 \text{ mol/L}\)

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Monomer, MMA
Polymerization rate has very nice linear relationship with the concentration of MMA, as Fig.6 shows. The exponent value is 1.0.

Hydrogen-donor, MTA
Triarylimidazolyl radicals can initiate the polymerization of MMA, while it is not very efficient due to the big size. MTA is a hydrogen donor which can reduce SP-36 cation radicals to generate MTA free radicals. MTA free radicals have more effective initiation, so the polymerization is prompted. Fig.7 is the monomer conversion curve with (A) and without (B) MTA. The effect of the MTA concentration on Rp is illustrated in Fig.8. The exponent value is 0.24.

IV Kinetic Formula
From the result obtained above, the kinetic formula of Rp may be concluded as:

\[
Rp = K[SP-36]^{0.45}[o-cl-HABI]^{0.40}[MTA]^{0.24}[MMA]^{1.0}
\]

4. Application
The solution composed of SP-36, o-cl-HABI, MMT, active monomer and binder was coated onto glass plate, dried and exposed with He⁺-Ne⁺ laser. It can be used to record hologram.

5. Conclusion
The electron transfer reaction between the excited state of Cyanine dye SP-36 and the ground state of o-cl-HABI generated triarylimidazoyl radicals which can initiate the polymerization of
MMA. The effects of the concentrations of the components on the polymerization rate have been investigated and the kinetic formula has been deduced.

Acknowledgment
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