

PHOTOPOLYMERIZATION OF MMA INITIATED BY CYANINE DYE AND HEXAARYLBIIMIDAZOLE*

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Abstract The photoinitiating system composed of 1-ethyl-3'-methyl thiocyanine bromide (C-I), 2-chlorohexaarylbiimidazole (o-Cl-HABI) and 3-mercapto-4-methyl-4H-1, 2, 4-triazole (MTA), which act 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 dilatometry. The relation between the polymerization rate and the concentrations of C-I, o-Cl-HABI, MTA and MMA was studied.

Keywords Biimidazole; Photopolymerization; Dye sensitization

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-thioxanthene^[2] and aromatic aminoketone-hexaarylbiimidazole^[3]. We have reported two hexaarylbiimidazole systems before^[4~5]. In this work, we used a cyanine dye as sensitizer (C-I) and studied a new photosensitive initiating system composed of C-I, o-Cl-HABI and MTA. Up to date, there is no report concerning the kinetic study of above photosensitive initiating system.

EXPERIMENTAL

Materials

o-Cl-HABI was prepared according to a known procedure^[6]. Its structure was

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confirmed by mass spectrometry (MS), nuclear magnetic resonance (NMR), infrared spectrometry (IR) and elementary analysis.

C-I was obtained from Shenyang Xincheng Chemical Co. Ltd., MTA was a product of Fluka, Switzerland. MMA, trichloromethane was of analytical purity and purified by distillation before use.

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 filtered by two Pyrex glass filters. The solution was deaerated by bubbling highly pure nitrogen for 30 min.

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

RESULTS AND DISCUSSIONS

Absorption spectra

The absorption spectrum of C-I in trichloromethane displays a strong broad band in the visible region: $\lambda_{\text{max}} = 494$ nm and $\epsilon_{\text{max}} = 5.1 \times 10^4 \text{ mol}^{-1} \text{ L cm}^{-1}$, 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: $\lambda_{\text{max}} = 265$ nm and $\epsilon_{\text{max}} = 2.9 \times 10^4 \text{ mol}^{-1} \text{ L cm}^{-1}$, 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: $\lambda_{\text{max}} = 258$ nm and $\epsilon_{\text{max}} = 1.78 \times 10^4 \text{ mol}^{-1} \text{ L cm}^{-1}$.

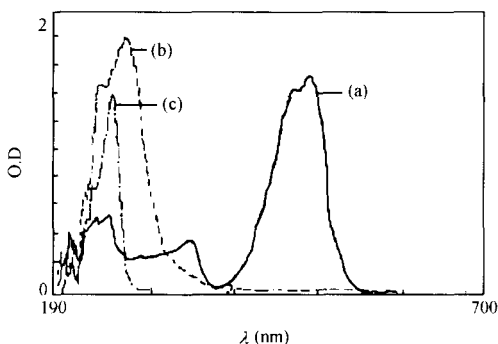


Fig.1 Absorption spectra of C-I ($3 \times 10^{-5} \text{ mol/L}$) (a), o-Cl-HABI ($6 \times 10^{-5} \text{ mol/L}$) (b), MTA ($8 \times 10^{-5} \text{ mol/L}$) (c) in CHCl_3

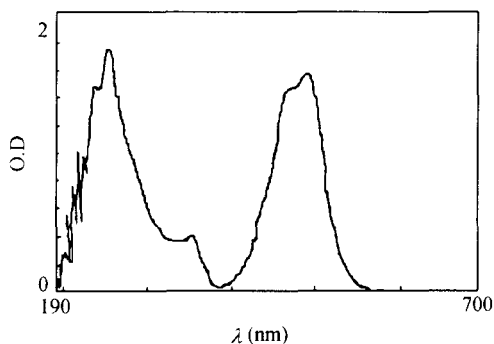


Fig.2 Absorption spectrum of C-I ($3 \times 10^{-5} \text{ mol/L}$), o-Cl-HABI ($3 \times 10^{-5} \text{ mol/L}$) and MTA ($3 \times 10^{-5} \text{ mol/L}$) mixed in CHCl_3

Fig.2 is the absorption spectrum of the mixture of C-I, o-Cl-HABI and MTA in trichloromethane. Compared with Fig.1, no shift of the absorption maximum

occurred. This indicated that there is no formation of (C-I)-(o-Cl-HABI) complex in the ground state.

Effects of the Concentrations of the Components

The photosensitive initiating system is composed of C-I, o-Cl-HABI and MTA, which act as sensitizer, initiator and hydrogen-donor respectively. Their chemical structures are shown as follows:

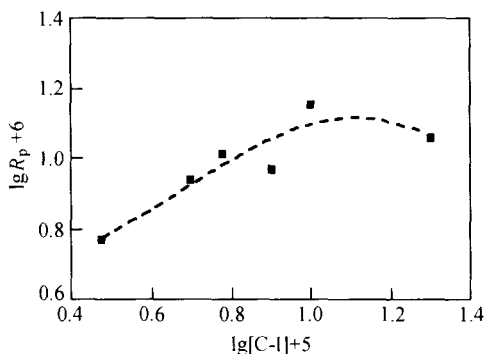
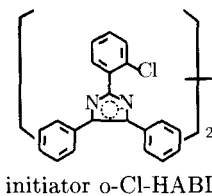
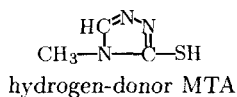
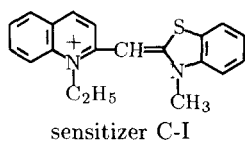


Fig.3 Relationship between R_p and $[C-I]$
[HABI]: 4×10^{-4} mol/L, [MTA]: 2×10^{-4} mol/L; [MMA]: 2.83 mol/L

Sensitizer, C-I Fig.3 shows the relationship between the polymerization rate (R_p) and the concentration of C-I. When the concentration is lower than 10^{-4} mol/L, $\lg R_p$ is proportional to $\lg [C-I]$. The exponent value which was calculated from the slope of the linear section of the curve is 0.63. However, when the concentration is further increased, R_p decreases. This phenomenon of inversion has been observed in other hand, photopolymerization systems^[8]. A high molar extinction

coefficient of the sensitizer at the wavelength of the source light is necessary in order that it can excite the system effectively. However, on the otherhand, it makes the light difficult to pass through the system because the sensitizer absorbs the light effectively, then decreases the polymerization rate when its concentration is higher than the critical value.

Initiator, o-Cl-HABI Fig.4 shows the relationship between R_p and the concentration of o-Cl-HABI. When the concentration is lower than 3×10^{-5} mol/L, $\lg R_p$ is proportional to $\lg [HABI]$. The exponent value obtained from the slope of the linear section of the curve is 0.44. When the concentration increased, R_p decreases. The reason for this effect is that triarylimidazolyl radicals ($L\cdot$), whose absorption maximum is at 550 nm, can absorb visible light and recombine to form o-Cl-HABI

reversibly.

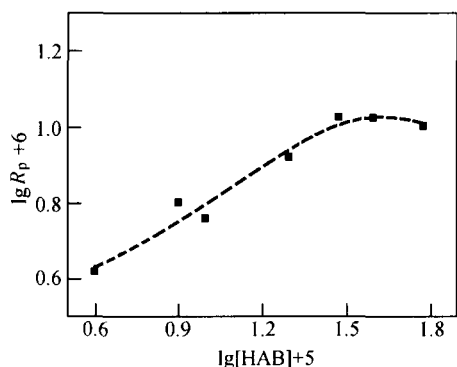


Fig.4 Relationship between R_p and $[\text{HABI}]$
 $[\text{C-I}]$: $4 \times 10^{-5} \text{ mol/L}$, $[\text{MTA}]$: $2 \times 10^{-4} \text{ mol/L}$, $[\text{MMA}]$: 2.83 mol/L

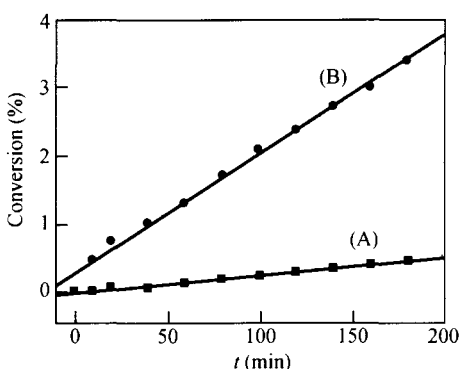


Fig.5 Influence of initiator on conversion
 (A) without initiator, (B) with initiator
 $[\text{C-I}]$: $4 \times 10^{-5} \text{ mol/L}$, $[\text{HABI}]$: $4 \times 10^{-4} \text{ mol/L}$, $[\text{MTA}]$: $2 \times 10^{-4} \text{ mol/L}$, $[\text{MMA}]$: 2.83 mol/L

Fig.5 shows the influence of HABI on the conversion of monomer. When the system contains no HABI (Curve A), the conversion is low and becomes a horizontal straight line. It illustrates that there is no reaction between C-I and MTA when HABI is absent.

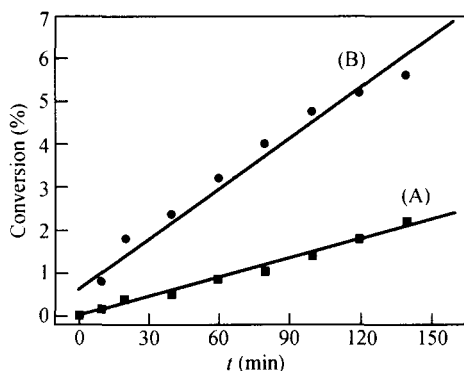


Fig.6 Influence of $[\text{MTA}]$ on monomer conversion
 (A) without hydrogen-donor; (B) with hydrogen-donor
 $[\text{C-I}]$: $4 \times 10^{-5} \text{ mol/L}$; $[\text{HABI}]$: $4 \times 10^{-4} \text{ mol/L}$; $[\text{MTA}]$: $8 \times 10^{-4} \text{ mol/L}$; $[\text{MMA}]$: 2.83 mol/L

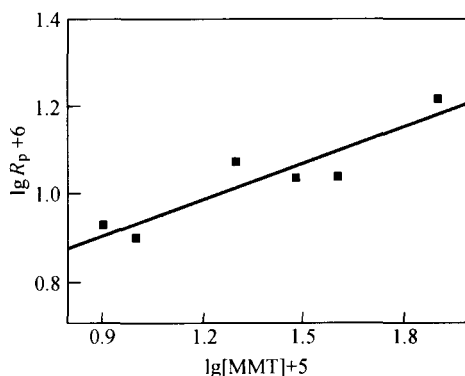


Fig.7 Relationship between R_p and $[\text{MTA}]$
 $[\text{C-I}]$: $4 \times 10^{-5} \text{ mol/L}$; $[\text{HABI}]$: $4 \times 10^{-4} \text{ mol/L}$; $[\text{MMA}]$: 2.83 mol/L

Hydrogen-donor, MTA Triarylimidazolyl radicals can initiate the polymerization of MMA, yet it is not very effective due to its large size. MTA is a hydrogen

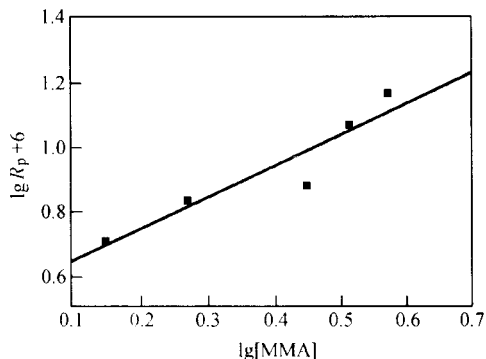


Fig.8 Relationship between R_p and $[MMA]$
 $[C-I]: 4 \times 10^{-5} \text{ mol/L}$, $[HABI]: 4 \times 10^{-4} \text{ mol/L}$, $[MTA]: 2 \times 10^{-4} \text{ mol/L}$

donor which can reduce C-I cation radicals to generate MTA free radicals. MTA free radicals is a more effective initiator, so the polymerization is prompted. Fig.6 is the monomer conversion curves with or without MTA. The effect of the MTA concentration on R_p is illustrated in Fig.7. The exponent value is 0.27.

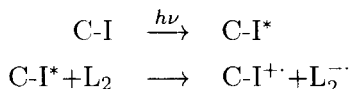
Monomer, MMA polymerization rate has very good linear relationship with the concentration of MMA, as Fig.8 shows. The exponent value is 1.0.

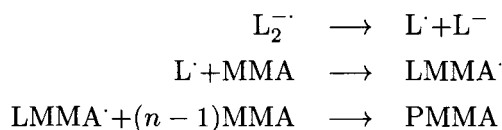
PHOTOPOLYMERIZATION PROCEDURE

Many research works on the dye sensitization mechanism in the polymerization of HABIs have been reported recently. Liu found that it is a process of singlet-singlet electron transfer reaction^[8,9]. Moreover, Eaton pointed out that, for nearly all photopolymerizations initiated by visible light with dye sensitization, electron transfer is the only viable mechanism^[10].

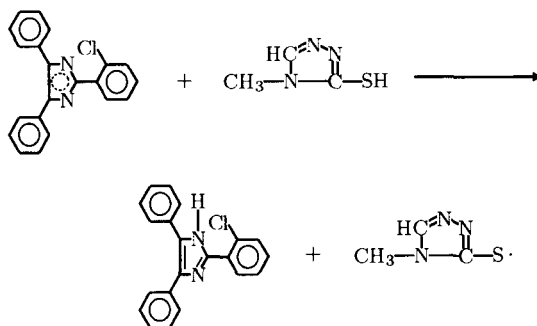
In our study, a solution of o-Cl-HABI and MMA (monomer) in trichloromethane were exposed in the visible light ($\lambda > 510 \text{ nm}$), no photopolymerization occurred. The reason is that the absorption of o-Cl-HABI is nearly all in the UV region, thus can not produce free radicals in the visible light radiation. When C-I, was added, the photopolymerization proceeded efficiently.

From Fig.1 and Fig.2, we found that the maximum absorption bands of o-Cl-HABI and C-I (265 nm and 494 nm respectively) are widely separated. It is difficult for energy transfer in this way. Therefore, we consider that the photopolymerization mechanism in this system is also an electron transfer one, i.e., C-I was excited by the visible light and then transferred an electron to o-Cl-HABI (L_2). A dye cation radical and an o-Cl-HABI anion 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. The process is illustrated as follows:





When the hydrogen-donor, MTA is added, $L^{\cdot}$ can capture its hydrogen and generate MTA free radicals, which are much more efficient than $L^{\cdot}$ and thus can increase the polymerization rate significantly. The formation of MTA free radicals is shown as follows:



APPLICATION

A solution composed of C-I, o-Cl-HABI, MTA, active monomer and binder was coated onto a glass plate, dried and exposed with 488 nm Ar^+ laser. The plate so prepared can be used to record hologram.

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