

SENSITIZED PHOTOINITIATING SYSTEM USED IN PHOTOPOLYMER FILMS

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ABSTRACT

Photopolymer films are widely used in printing and electronic industries, and their usage is expanding to encompass holography, data storage and data processing, optical waveguides and compact disks, etc.

One of widely used photopolymerization initiator, 2-chloro-hexaarylbiimidazole (o-Cl-HABI), is studied by laser flash photolysis in dichloromethane solution in the absence and presence of the visible light photosensitizing dye, 2,5-bis[(2,3,6,7 - tetrahydro- 1H,5H -benzo [i,j,] quinolizin -1-yl) methylene]-cyclopenta-none, (JAW). In the presence of JAW, an increase in triarylimidazolyl radicals L \cdot formation is observed in relative to the absence of JAW. The mechanism of this photosensitizing dissociation is concluded as the dissociation of the o-Cl-HABI radical anion formed by the electron transfer from excited singlet state of JAW to o-Cl-HABI. The observed formation of L \cdot radicals exhibits a linear dependence on o-Cl-HABI concentration. The rate constant of electron transfer obtained from this dependence is equal to $(1.0 \pm 0.2) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. No reaction between the excited triplet state of JAW and o-Cl-HABI is found.

1. INTRODUCTION

The development of photosensitive materials in general and photoreactive polymers in particular is responsible for major advances in the information, imaging and electronic industries. With the recent growth of laser technology and electronic imaging, the use of inexpensive long wavelength emitting lasers is increasing. The interests in holographic recording media for head-up displays, light scanners and data storage stimulates development of reconfigurable and visible light sensitive materials¹.

One of the most attractive photopolymers with many outstanding features and mainly used in holographic recording has been developed in E.I.Du Pont de Numours & Co.¹ The photopolymer film consists mainly a photosensitizing dye S, an initiator I, an acrylic monomer M as shown in figure 1.

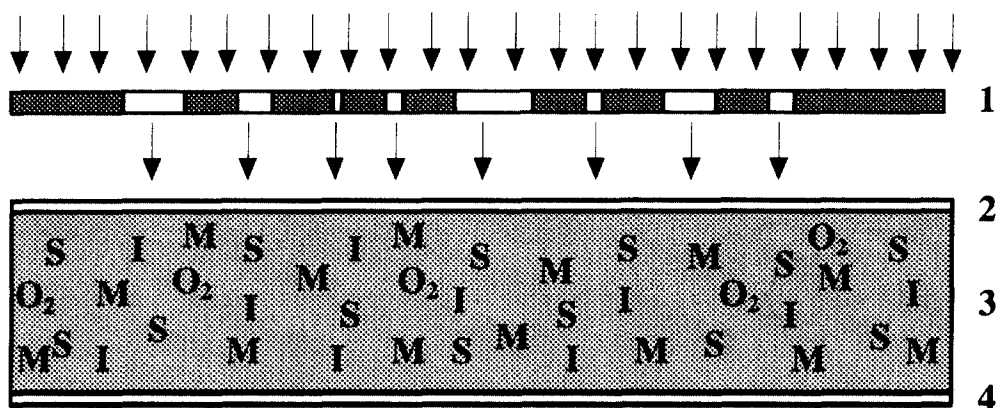
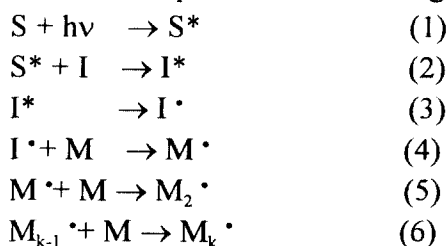


Figure1. Diagram of photopolymer film containing photosensitizer S, initiator I, monomer M and Oxygen. 1 mask; 2 cover film; 3 photopolymer film; 4 cover film.

Hexaarylbiiimidazole (HABI, or Lophine dimer, L_2) and its derivatives, especially, 2-chloro-hexaarylbiiimidazole (o-Cl-HABI, see figure 2) have been used as free radical initiators in this film¹⁻³. The application of HABI is based on well-established property of thermal or UV photolytic dissociation. The homolysis of HABI produces long lived 2,4,5 -triarylimidazolyl radicals (lophyl radicals, $L\cdot$)²⁻⁴. o-Cl-HABI has a strong absorption band in the UV region with $\lambda_{max} = 265 \text{ nm}$ and $\epsilon = 2.79 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$.

Aromatic aminoketones, such as 2,5-bis[(2,3,6,7 - tetrahydro- 1H,5H -benzo [i,j,] quinolizin -1-yl)methylene]-cyclopenta-none (JAW, see figure 2) with broad visible absorption band around 500 nm, have been employed as the visible sensitizer.

The main steps of sensitized image formation in this film can be written as:



In this kinetic scheme, the most interesting steps for us are radical formation reactions of (2)-(3), where the sensitizer JAW absorbs visible light to form an excited state that will react with the ground state of HABI to produce the $L\cdot$ radical. Reaction (2) (3) can occur by energy transfer as in many sensitized initiating systems, or charge (electron or proton) transfer process, or can be other type of chemical reactions. In this study, we attempted to classify the radical formation reaction in this JAW-HABI system. The study of the direct and dye sensitized dissociation of o-Cl-HABI by the 480nm-laser flash photolysis is presented below.

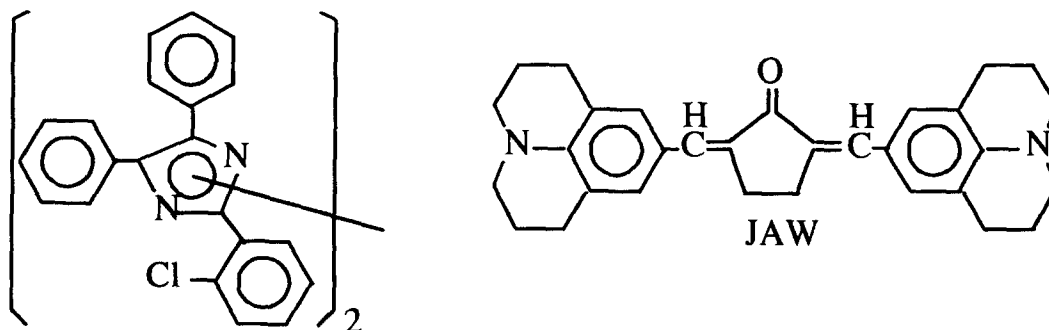


Figure2. Structure of o-Cl-HABI and JAW.

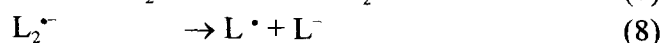
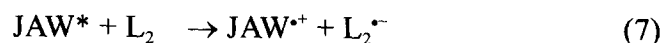
2. EXPERIMENTAL

The excitation source used in this experiment was a Lambda Physik FL 3002 dye laser, pumped by a Questek 2440 excimer laser. The duration of the dye laser pulse was ~ 20 ns, and the maximum output energy was 20 mJ / pulse. A kinetic spectrophotometer was used to monitor the transient absorption and emission. A Tektronix digitizing signal analyzer, DSA 601 was used to record transient signals. The data acquisition was controlled by a labVIEW program that installed on a Macintosh IIx computer. Between 4 and 20 laser pulses were used for signal averaging⁵⁻⁶.

3. RESULTS AND DISCUSSION

The flash photolysis of dichloromethane solutions containing only o-Cl-HABI (10^{-3} - 10^{-1} M) and both JAW (10^{-5} M) and o-Cl-HABI (10^{-3} - 10^{-1} M) was carried out by 480 nm laser excitation. The absorption of the L• radical around 550 nm was studied quantitatively in these two cases and the data are shown in Figure 3. The concentration dependence of sensitized dissociation of HABI is plotted as the reciprocal of quantum yield of formation of lophyl radicals $1 / \Phi[L^{\bullet}]$ as a function of HABI's concentration (Stern- Volmer plot), a straight line is obtained as shown in Figure 4.

The sensitized dissociation of HABI is not possible by energy transfer because the energy of ether singlet or triplet states of dye is much lower than that of singlet excited state of HABI (from their absorption and emission spectra)⁵⁻⁶. The charge transfer is more likely the source for lophyl radicals. The HABI anion radical formed in this single electron redox reaction will dissociate to form lophyl radicals as shown below:



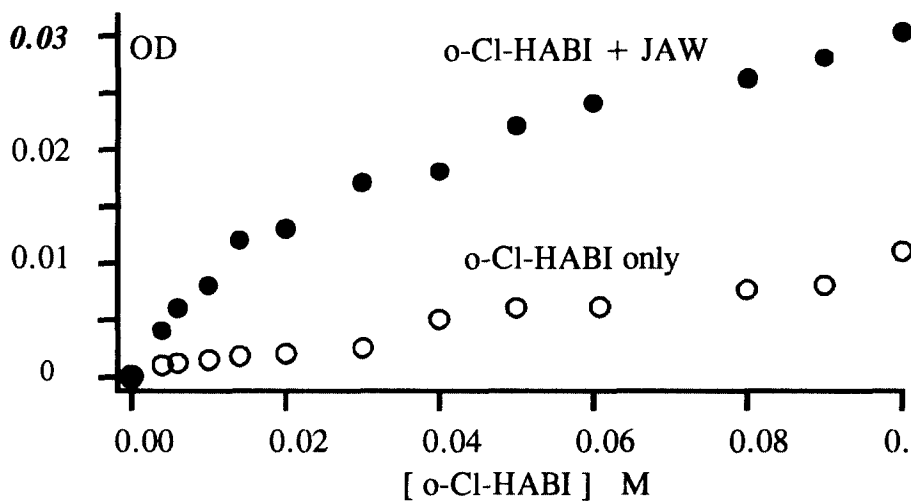


Figure 3. Production of lophyl radicals vs. O-Cl-HABI concentrations in 480 nm laser photolysis with absence and existence of photosensitizer JAW.

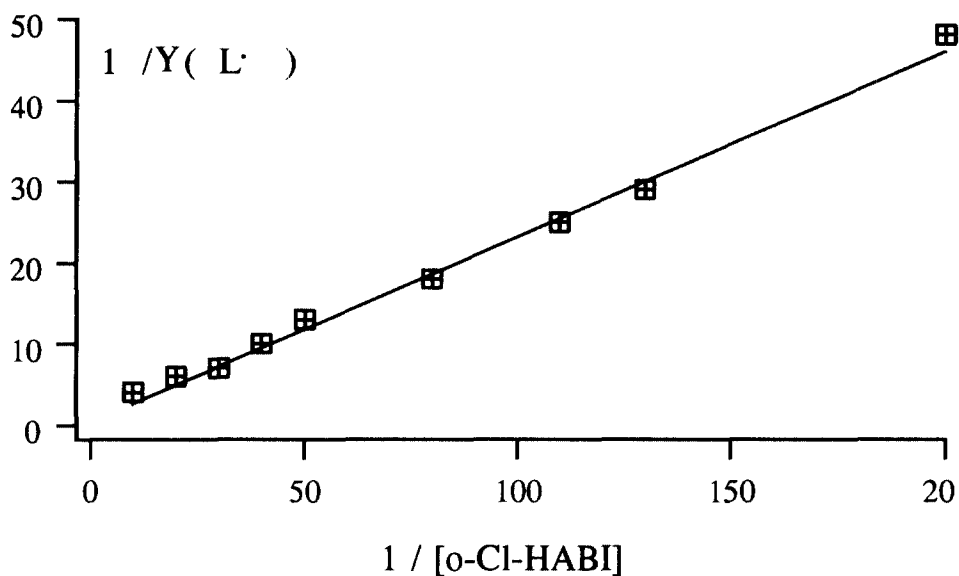


Figure 4. Stern-Volmer plot of Yield of lophyl radicals vs. Concentrations of HABI.

Our time-resolved fluorescence quenching measurements using single photon counting technique has confirmed this mechanism⁷. Eaton has reviewed many cases of the dye sensitized photopolymerizations and indicated that for nearly all photopolymerizations initiated by absorption of visible light, electron transfer is the only viable mechanism⁸.

From Stern-Volmer plot, the rate constant of the electron transfer from ¹JAW* to o-Cl-HABI was derived as $(1.0 \pm 0.2) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. This rate is close to diffusion controlled reaction rate constants. This indicates that sensitization of HABI is a process with low activation energy and perhaps has little if any orientation restrictions. From the work of Lin and co-workers at this laboratory⁷ we know that the electron transfer in HABI –JAW* system is a relatively short -distance process (<12 Å). Indeed, the short range of electron transfer and it's restriction only by the rate of HABI-JAW* contact would require close proximity of sensitizer and HABI in order to initiate the photopolymerization efficiently. Together with the short life time of JAW*, we can explain why in the imaging materials based on HABI and visible dye sensitizer the HABI has to be present at relatively high concentration (1-3% in weight). Further improvements in the efficiency of lophyl radical production should be also possible by developing a sensitizer having a longer-lived excited singlet state.

4. CONCLUSIONS

The industrial use of dyes for the visible light sensitization of photopolymerization is expanding. In most cases the dye excited state reacts either with electron donor or electron acceptor initiating photopolymerization. We studied the behavior of one of such initiators, o-Cl-HABI, photosensitized to visible light by JAW. The increase of lophyl radicals yield upon o-Cl-HABI visible light photolysis in the presence of JAW was quantified for the first time. As reported for other visible light sensitized radical formation¹, we came to the conclusion that the activation of HABI by JAW involved electron transfer between HABI and excited singlet state of JAW. We hope that additional confirmation of the charge transfer as a path for visible light photosensitization will make further selection of suitable sensitizers a simpler task.

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