

VISIBLE LIGHT PHOTOPOLYMERIZATION OF METHYL METHACRYLATE COINITIATED WITH TITANOCENE AND KETOCOUMARIN DYE*

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Abstract The photosensitive system which can initiate methyl methacrylate with visible light was composed of compound **1** bis(η -5-cyclopentadienyl)-bis[2,6-difluoro-3-(1-H-pyrrolyl)phenyl]titanium (titanocene) and compound **2** [(3,3'-carbonylbis(7-diethylamino coumarin)] (ketocoumarin dye). The high photosensitive initiating efficiency of this photosensitive system could be very promising for efficient system for laser (Ar^+ 488 nm) to plate and photocuring for thick coating and ink. The variation of UV-visible spectrum of compound **2** during irradiation indicates that photolysis of compound **2** is through its triplet state and it can be quenched by O_2 . The much quicker photobleaching of the photosensitive system suggests that there exists certain quick electron transfer reaction between compounds **1** and **2**.

Keywords Photosensitive system, Photopolymerization, Photobleaching, Photolysis, Electron transfer

INTRODUCTION

In recent years, with the rapid development of Ar^+ (488 nm), YAG (532 nm) and He-Ne (633 nm) laser imaging technology and photocuring, research works have focused on efficient long-wavelength photopolymerization systems^[1, 2], which can be used in many fields such as, holographic recording, computer-to-plate, photocuring and laser stereolithography. One of the most important techniques is how to make the system sensitive to long-wavelength light and gain high sensitivity.

Several visible light photosensitive systems have been reported^[3, 4], and most of the photosensitive systems were composed of two or three components. Fouassier^[5] noted that photoinitiating with visible light is induced through two different processes: a) direct absorption of light by photosensitive system, b) sensitized formation of initiating system.

In both cases, the reactivity in the excited states will govern the efficiency of the photosensitive systems.

Titanocene was claimed to be useful as a photopolymerization initiator offering several advantages over conventional UV polymerization initiators (high photospeed, sensitivity to visible light and photobleaching), thus they can be used computer-to-plate and for photocuring for thick coating and ink^[6-8]. It is well known that ketocoumarin, especially 7-alkylamino coumarin, can make the photosensitive system sensitive to visible light efficiently and obtain high initiating

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efficiency^[9, 10]. In these systems, sensitization is always related to electron transfer between coumarin dye and photoinitiator.

In this paper, the photosensitive system composed of compounds **1** and **2**, and which is suitable for Ar⁺ (488 nm) laser, can initiate methyl methacrylate (MMA) efficiently with visible light. Also, the preliminary discussion on the mechanism of sensitization of compound **1** induced by compound **2** has been presented. We think there exists certain rapid electron transfer between them through compound **2**'s triplet state.

EXPERIMENTAL

Materials

Compound **1** was supplied by Ciba Corporation. Compound **2** was synthesized according to a previous work of Eastman Kodak^[14], and its melting point and NMR are consistent with those reported in Ref.[14] (both structures are depicted in Scheme 1). Trichloromethane and MMA were available commercially and purified by distillation before use.

Methods

Photopolymerization was carried out in a dilatometer ($\Phi = 10$ mm) at 30°C with the sample tubes rotated around the light source. A xenon lamp (400 W) was used and the short wavelength light (< 300 nm) was filtered by two Pyrex glass filters. The solution was deaerated by bubbling argon for 30 min.

UV-visible spectra were measured with Hewlett-Packard 8451A diode array spectrophotometer, fluorescence spectrum was measured with Hitachi MPF-4 and Perkin Elmer Ls-5.

RESULTS AND DISCUSSION

Spectra

The UV-visible spectrum of compound **1** in trichloromethane with a concentration of 3×10^{-5} mol/L displays a strong broad band at $\lambda_{\max} = 242$ nm and $\epsilon_{\max} = 4.38 \times 10^4$ mol⁻¹ · L · cm⁻¹, which can be assigned to (π , π^*) transition, as seen in Fig. 1a. Figure 1a shows two obvious weak absorption $\lambda_{\max 1} = 396$ nm, $\epsilon_{\max 1} = 1.15 \times 10^3$ mol⁻¹ · L · cm⁻¹ and $\lambda_{\max 2} = 464$ nm, $\epsilon_{\max 2} = 1.13 \times 10^3$ mol⁻¹ · L · cm⁻¹, which can be assigned to ligand-Ti charge transfer (LMCT) transitions^[11]. The molar extinction coefficient in the visible light is a little smaller, and it is expected that the addition of sensitizer may be necessary in order to increase greatly the photosensitivity in the system if it is used in practice. No fluorescence can be detected for compound **1**.

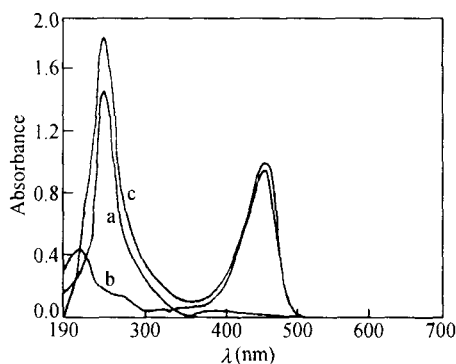


Fig. 1 UV-visible spectra of compound **1** spectrum

a) $[C_1] = 3 \times 10^{-5}$ mol/L, compound **2** spectrum, b) $[C_2] = 1 \times 10^{-5}$ mol/L and the mixture composed of compound **1** and compound **2** spectrum, c) $[C_1] = 3 \times 10^{-5}$ mol/L and $[C_2] = 1 \times 10^{-5}$ mol/L in CHCl_3

The UV-visible spectrum absorption of compound **2** in trichloromethane with a concentration of 1×10^{-5} mol/L is shown in Fig. 1b, in which $\lambda_{\max} = 460$ nm, $\varepsilon_{\max} = 9.70 \times 10^4$ mol $^{-1} \cdot$ L $\cdot$ cm $^{-1}$, which can be assigned to intramolecular charge transfer (ICT), and sensitive to solvent^[12]. The weak fluorescence which appeared in compound **2** comes from the ICT state of the coumarins with a non-twisted 7-dialkylamino group which had undergone a nonemissive TICT states as reported by Jonell *et al.*^[13].

Figure 1c is the UV-visible spectrum of the mixture of compounds **1** and **2** in trichloromethane. As compared with Fig. 1a and Fig. 1b, there is no change and no shift of the maximum absorption in Fig. 1c and the OD of the mixture is equal to the sum of each component. This indicates that there is no formation of 1-2 complex in the ground state.

The Effects of Compound 2 on Photopolymerization in Two-Component Photosensitive System

We have studied the relationship between the photopolymerization rate R_p of MMA and concentration of compound **1** and monomer MMA^[14]. Figure 2 shows the relationship between the R_p of MMA and the concentration of compound **2**. When the concentration of compound **2**, C_2 , is less than 5×10^{-5} mol $\cdot$ l $^{-1}$, $\lg R_p$ is proportional to $\lg C_2$; However, when C_2 is greater than 6×10^{-5} mol $\cdot$ L $^{-1}$, $\lg R_p$ decreases with the increasing of C_2 . This phenomenon of inversion has been observed in other photopolymerization systems^[15]. The molar extinction coefficient of the sensitizer at the wavelength of the source light needs to be high so that it can excite the system effectively. However, on the other hand, a higher concentration of sensitizer will make it difficult for light to pass through the system because the sensitizer absorbs the light effectively and increases the local concentration of reactant. Thus the deactive rate of photosensitive reaction of compound **1** and compound **2** increases, then decreases the polymerization rate of MMA when its concentration is higher than the critical value.

The influence of compound **2** on the polymerization conversion rate of monomer MMA is shown in Fig. 3. For the photosensitive system with compound **2**, the photopolymerization conversion rate of monomer MMA is obviously greater than that without compound **2**. For a particular monomer, the higher the photopolymerization rate and the photopolymerization conversion rate, the higher the photosensitive initiating efficiency and the efficiency of radical generation. The above results prove that compound **2** acts as photosensitizer in a photosensitive system composed of compounds **1** and **2**.

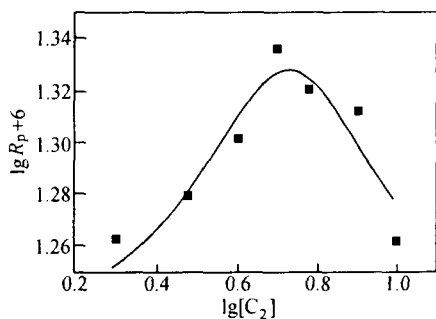


Fig. 2 The relationship between R_p of MMA and the concentration of compound **2** [C_2] $=1 \times 10^{-3}$ mol/L, [MMA] $=2.83$ mol/L in CHCl_3

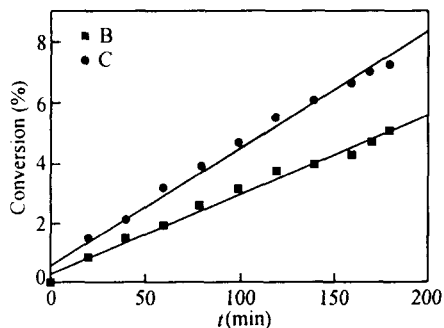


Fig. 3 Influence of compound **2** on the conversion of MMA [C_2] $=1 \times 10^{-3}$ mol/L, [MMA] $=2.83$ mol/L in CHCl_3
Curve B: without compound **2**;
Curve C: with compound **2**, [C_2] $=2 \times 10^{-5}$ mol/L

The above results also prove that the photosensitive system composed of compounds **1** and **2** favors visible light and appears as a very promising one for the design of photosensitive materials

for laser-to-plate and laser photocuring.

The Photoinduced Reaction of Compound 1 and 2

From the above results, we can conclude that compound 1 can be sensitized efficiently by compound 2 with visible light irradiation. The variation of UV-visible absorptions of compound 2 in CHCl_3 and in N_2 during irradiation is shown in Fig. 4. They exhibited a remarkable change due to irradiation with visible light. As shown in Fig. 4, the absorption intensity of compound 2 at 460 nm was decreased by irradiation, and showed blue shift with irradiation time. But the absorption intensity around 360 nm increased gradually with irradiation time, and an isosbestic point appeared. Obviously, a photolysis reaction occurred and thus destroyed its original conjugate structure. For comparison, the variation of UV-visible spectrum of compound 2 with irradiation time in air was studied. In air, the UV-visible spectrum of compound 2 in CHCl_3 did not exhibit any change. This indicated that photolysis reaction of compound 2 is sensitive to O_2 . Because compound 2 has a very large isc value (0.92)^[16], it is easy for it to transit from singlet state to triplet state. It was reported that the energy of the triplet state of compound 2 is 212.3 kJ/mol^[16], the energy of the triplet state of O_2 is 96.1 kJ/mol^[17], therefore the triplet state of compound 2 can be quenched efficiently by O_2 . The results also prove that the photolysis of compound 2 proceeds through its triplet state. The mechanism of photolysis reaction of compound 2 can be expressed as follows:

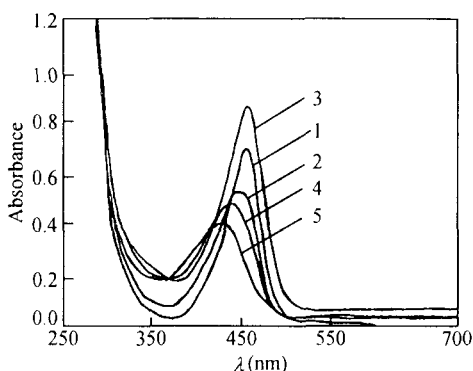
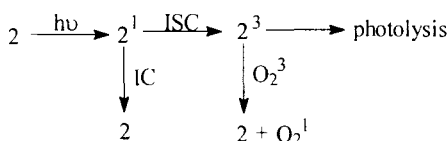


Fig. 4 The variation of the UV-visible spectra of compound 2 in CHCl_3 , $[\text{C}_2] = 1 \times 10^{-5}$ mol/L and under N_2
Time of irradiation: 1) 0, 2) 1 min, 3) 2 min, 4) 3 min, 5) 4 min

The variation of UV-visible absorption of compound 1 in CHCl_3 and in argon with irradiation was studied. In Fig. 5a, the absorption 390–460 nm decreased gradually with irradiation time and finally disappeared, while a new absorption 550–650 nm and an isosbestic point appeared with irradiation time, which is somewhat different from that of bis(η -5-cyclopentadienyl)-bis[(pentafluorophenyl)titanium (compound 3). No new absorption and no isosbestic point were observed when compound 3 was irradiated^[6], and this indicated that their nature may be different. The above results also prove that irradiation of compound 1 leads to the scission of its ligand-metal bond.

As compared with compound 2, the mixture of compound 1 and compound 2 showed much quicker photobleaching in CHCl_3 and in argon during irradiation (cf. Fig. 5c). Both the maximum

absorbance of compounds **1** and **2** in the visible region disappeared at the end of the irradiation process. This means the photosensitive system composed of compounds **1** and **2** can be used in photocuring for thick coating and ink. But no changes such as those seen in Fig. 4 have taken place for compound **2**. The results demonstrate that there exists certain rapid electron transfer between compound **1** and **2**, which improves the efficiency of the photosensitive system. Eaton^[18] has reviewed many cases of dye-sensitized photopolymerization and indicated that for nearly all polymerizations initiated by visible light, electron transfer explanation is the only viable mechanism. Because compound **2** has a very large value of i_{sc} , the electron transfer reaction may proceed through compound **2**'s triplet state. In fact, the UV-visible spectrum of mixture of compounds **1** and **2** in air during irradiation has similar changes as that of compound **1** in air (cf. Fig. 5b and Fig. 5d), and after the irradiation was completed, the UV-visible spectrum becomes the same as that of compound **2**. This means that compound **2**'s triplet state is quenched by O_2 and therefore electron transfer reaction between them is inhibited. The above results basically prove that the electron transfer reaction between compounds **1** and **2** proceeds through compound **2**'s triplet state.

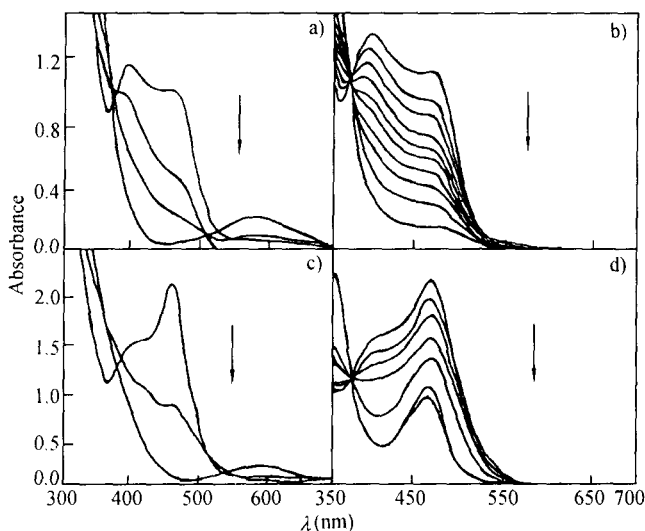


Fig. 5 The variation of UV-visible spectra of compound **1** and the mixture composed of compound **1** and compound **2** with irradiation time in $CHCl_3$ solvent

a) compound **1** under Ar atmosphere, $[C_1] = 1 \times 10^{-3}$ mol/L, irradiation time interval = 20 s, b) compound **1** under air atmosphere, $[C_1] = 1 \times 10^{-3}$ mol/L, c) compound **1** + compound **2** under Ar atmosphere, $[C_1] = 1 \times 10^{-3}$ mol/L, $[C_2] = 1 \times 10^{-5}$ mol/L, d) compound **1** + compound **2** under air atmosphere, $[C_1] = 1 \times 10^{-3}$ mol/L, $[C_2] = 1 \times 10^{-5}$ mol/L.

CONCLUSIONS

Compound **1** was sensitized efficiently by compound **2** with visible light irradiation, and the photosensitive initiating efficiency of the photosensitive system composed of compound **1** and **2** is also improved. Therefore the photosensitive system composed of compounds **1** and **2** can be used in computer-to-plate and thick photocuring; the photolysis of compound **2** occurred through its triplet state and can be quenched by O_2 . The sensitization of compound **1** induced by compound **2** is completed through electron transfer between them.

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