

DYE-SENSITIZED PHOTOPOLYMERIZATION OF METHYL METHACRYLATE INITIATED BY COUMARIN DYE/IODONIUM SALT SYSTEM*

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Abstract The photosensitive initiating system composed of 7-diethylamino-3-(2'-benzimidazolyl)coumarin dye (DEDC) and diphenyliodonium hexafluorophosphate (DIHP) which act as the sensitizer and the initiator respectively, can be used to initiate the polymerization of methyl methacrylate (MMA). The results showed that when exposed to visible light, coumarin dye/iodonium salt undergoes quick electron transfer from DEDC to DIHP and free radicals are produced. The visible light photoinduced reaction between DEDC and DIHP is mainly through the excited singlet state of DEDC and thus it is a little sensitive to O_2 . The influence of concentration of DEDC, DIHP and MMA on the rate of photopolymerization of MMA was also investigated.

Keywords Dye-sensitization, Photopolymerization, Electron transfer, Iodonium salt

INTRODUCTION

Most photopolymerization compositions used in industrial fields are sensitive only to UV light. Recently, with the development of laser technology and imaging, research work has been focused on the efficient long wavelength photopolymerization system. By now only a little success have been obtained in the efforts to extend the photoresponse of useful free radical photoinitiator to the visible light region. For these reasons, dye sensitization systems are again attracting much attention. One of the most important techniques is how to make system sensitive to long wavelength and gain high sensitivity.

Several visible light or near-IR photosensitive systems have been reported^[1, 2], and most of the photosensitive systems were composed of two or three components. Fouassier^[3] noted that the photosensitization in long wavelength light is induced through two different processes: 1) direct absorption of light by photosensitive system and 2) formation of photoreactive state of initiating system. In both cases, the reactivity of the excited states governs the efficiency of the photosensitive systems.

In general, for a bimolecular visible light photosensitive imaging system, electron transfer process is the one and only mechanism^[4]. It is well known that coumarin dyes, especially 7-alkylamino coumarin dyes used as the electron donor, can improve the photosensitive initiating efficiency of photosensitive systems when exposed to visible light^[5]. Most iodonium salts, which can be used as efficient UV initiators, have received much attention in visible light photosensitive systems for its low negative oxidation-reduction electric potential ($E_{red} = -0.2$ V) and high excited energy ($E_s = 384.6$ kJ/mol^[6]), therefore the photosensitive system of dye/ iodonium salts system is

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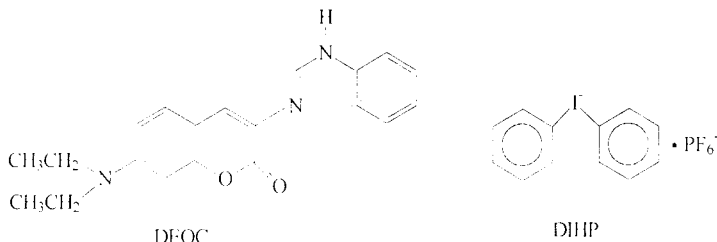
stable in the dark and electron transfer quickly takes place between them when exposed to visible light.

In this paper, the efficiency of photopolymerization of methylmethacrylate (MMA) in visible light initiated by coumarin dye/iodonium salt system, which is suitable for Ar^+ (488 nm) laser, was estimated. The mechanism of the photosensitization of DIHP induced by DEDC and of the photopolymerization of MMA in visible light is discussed. It is suggested that there exists a rapid electron transfer mainly through DEDC's excited singlet state in DEDC/DIHP system when it is exposed to visible light.

EXPERIMENTAL

Material

DEDC was synthesized and purified according to the literature^[7]. DIHP was prepared according to a known procedure^[8] and recrystallized from methyl alcohol before use. Their structures (Scheme 1) were confirmed by MS, NMR, IR and elementary analysis. MMA and trichloromethane and dimethyl sulfoxide (DMSO) were of analytical reagent and were purified by distillation before use.



Scheme 1

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. Its short wavelength lights (less than 300 nm) were filtered by two Pyrex glass filters. The experimental data were treated by a least-squares method.

UV-visible absorption spectra and fluorescence spectra were recorded on a Hitachi 557 UV-Visible spectrometer and a Hitachi MPF-4 fluorimeter.

RESULTS AND DISCUSSION

Spectra

The absorption spectrum of DIHP in trichloromethane displays a strong band in the UV region, which is assigned to the (π, π^*) transition. No absorption in the visible region can be detected for DIHP, thus it is impossible to initiate the polymerization of monomer by DIHP in visible light without an appropriate sensitizer.

The maximum absorption of DEDC in trichloromethane appears in the visible light region, $\lambda_{\text{max}1} = 438$ nm, $\epsilon_{\text{max}1} = 5.23 \times 10^4$ L/mol $\cdot$ cm, $\lambda_{\text{max}2} = 459$ nm, $\epsilon_{\text{max}2} = 5.13 \times 10^4$ L/mol $\cdot$ cm⁻¹, which is assigned to the intra-molecular charge transfer (ICT), and sensitive to solvent; DEDC has strong fluorescence, which comes from the ICT state of the coumarin dye with a non-twisted 7-diethylamino group followed by undergoing a non-fluorescence TICT (twisted ICT) state in many strong polar solvents^[9].

No characteristic absorption band was observed for the DIHP/DEDC mixture and it is noted that the optical density value of the mixture is equal to the sum of the optical density value of the components. No change and no shift in the maximum absorption suggest that DIHP has no

interaction with DEDC in the ground state. In general, if two compounds can form a charge transfer complex (CTC) in the ground state, a new characteristic band should always appear^[10]. So DEDC/DIHP system does not generate free radical for the polymerization through the CTC when it is exposed to visible light. This fact can be attributed to the weaker electron donor ability of the diethylamino group as compared with the triethylamine.

Effects of the concentration of the components

In Fig. 1, polymerization conversion of MMA initiated by DEDC/DIHP system and DIHP alone is compared. For the high energy level of the excited state of MMA ($E_T = 286.33 \text{ kJ/mol}^{[11]}$), the excited state of DEDC can not be quenched by MMA. For a particular monomer of photosensitive initiating system, the higher the polymerization rate, the higher are the photosensitization efficiency and the efficiency of free radical generation. The above results demonstrate that the visible light photoinduced reaction between DEDC and DIHP is efficient.

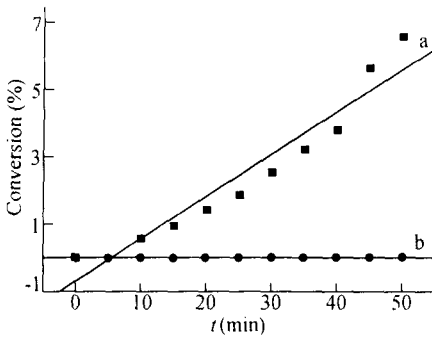


Fig. 1 Influence of sensitizer on the conversion of MMA
a) with sensitizer, b) without sensitizer; [MMA]=2.83mol/L, [DIHP]= 2×10^{-2} mol/L, [DEDC]= 6×10^{-4} mol/L, in DMSO; irradiation distance: 6 cm, irradiation intensity: 16.10 mW/cm², $\lambda > 300\text{nm}$

Compared with nitrogen atmosphere, photopolymerization of MMA initiated by DEDC/DIHP system in air in visible light showed a longer induction period but its rate dropped slightly. This shows that O₂ has significant influence on the induction period of polymerization of MMA and plays a unimportant role in quenching the excited state of DEDC.

Sensitizer, DEDC

The photopolymerization rate (R_p) of MMA initiated by DEDC/DIHP system with different concentrations of DEDC is listed in Table 1. When the concentration is lower than 6×10^{-4} mol/L, $\lg R_p$ improves a little. When the concentration is further increased, R_p decreases dramatically.

Table 1. The influence of concentration of DEDC on the rate of photopolymerization

$\lg[\text{DEDC}] + 5$	1.301	1.602	1.700	1.778	1.903	2.000	2.176	2.301
$\lg[R_p] + 6$	1.740	1.757	1.763	1.773	1.645	1.640	1.588	1.544

* [MMA] = 2.83 mol/L, [DIHP] = 2×10^{-2} mol/L, in DMSO

The molar extinction coefficient of the sensitizer at a given wavelength needs to be high so that it can excite the system effectively and increases the local concentration of reactant, thus decreases the R_p of MMA when its concentration is higher than a certain value.

Initiator, iodonium salt

Figure 2 shows the relationship between R_p and the concentration of DIHP. Until the concentration is higher than 4×10^{-2} mol/L, $\lg R_p$ is still proportional to $\lg[\text{DIHP}]$, which is different from the *o*-Cl-HABI/coumarin photosensitive system^[12]. There are two major reasons: 1) the size of free radical

produced by iodonium salt is small, so it is very reactive as compared with HABI radical; 2) DIHP shows no absorption in visible light region, and so it can not initiate monomers solely when exposed to visible light.

Monomer, MMA

The monomer conversion has good relation with irradiation time under different monomer concentration as indicated in Fig. 3. The longer the irradiation time is, the higher the conversion rate of MMA will be. This result can be attributed to the unique initiating mechanism, which only occurs with free radical initiation.

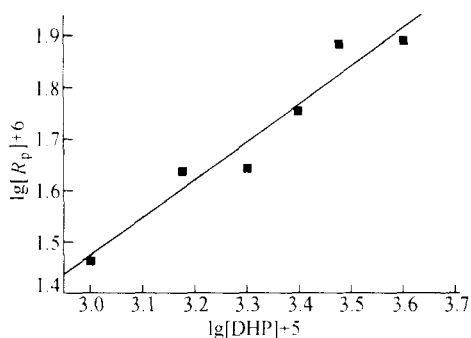


Fig. 2 Relationship between R_p and [DIHP]
[MMA] = 2.83 mol/L. [DEDC] = 1×10^{-3} mol/L,
in DMSO

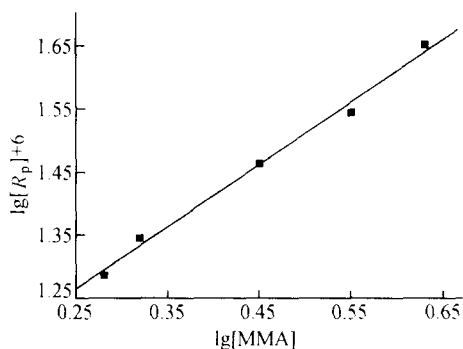


Fig. 3 Relationship between R_p and [MMA]
[Compound] = 1×10^{-3} mol/L.
[Ph₂I⁺] = 1×10^{-2} mol/L. in DMSO

The Visible Light Photoinduced Reaction of DEDC and DIHP

The variation of UV absorption of a mixture composed of DEDC and DIHP during irradiation under N₂ with visible light is shown in Fig. 4. The UV-visible spectra of the mixture exhibited a remarkable change with irradiation time in visible light. As shown in Fig. 4, the maximum absorption of the mixture decreased under irradiation, while the absorption around 470–520 nm increased significantly with irradiation time, and an isosbestic point (458.6 nm) and a new band ($\lambda_{\text{max}} = 484.7$ nm) appeared (indicating a new product was produced) and increased continuously with irradiation time. In fact, the UV-visible spectra of DEDC/DIHP system showed the same changes in air as in N₂ when exposed to visible light. A comparison of the basic photoreaction rates of the mixture composed of DEDC and DIHP (Fig. 5) shows that this photoreaction is somewhat sensitive toward O₂. DEDC has very strong fluorescence ($\Phi = 0.62$, measured by ourselves) and internal conversion is the main decay channel of non-radiative transition for coumarin dye^[13], therefore it is difficult for DEDC to make the transition from excited singlet state to excited triplet state and its phosphorescence is weak. The above facts indicate further that the photoreaction is mainly through the singlet state of DEDC and explain further the results of Table 1.

The UV-visible spectrum of the PMMA initiated by DEDC/DIHP system shows a strong absorption and fluorescence in the visible light region even if the PMMA has been purified many times with alcohol. The above results suggest that the new product produced by visible light photoinduced reaction of DEDC and DIHP is the chain terminating free radical. The higher the concentration of DEDC, the more chain terminating free radical produced. So in high concentrations of DIHP, the rate of photopolymerization of MMA initiated by DEDC and DIHP in visible light decreases rapidly. From the above discussion, the visible light photoinduced reaction mechanism of DEDC and DIHP can be expressed by Scheme 2.

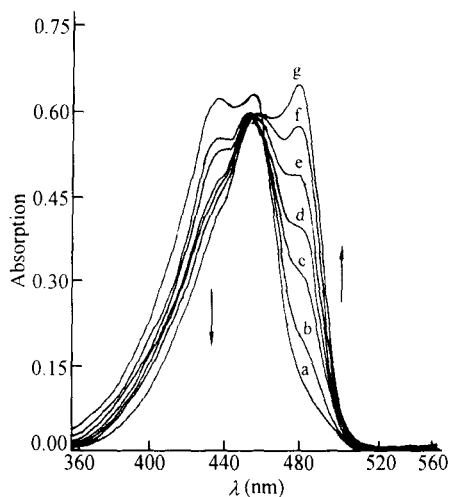


Fig. 4 Change of the absorption of DEDC/DIHP system in trichloromethane during visible light irradiation with irradiation time
 $[\text{DEDC}] = 1 \times 10^{-5} \text{ mol/L}$, $[\text{DIHP}] = 5 \times 10^{-5} \text{ mol/L}$;
 a) 0 s, b) 30 s, c) 60 s, d) 90 s, e) 120 s, f) 150 s, g) 180 s

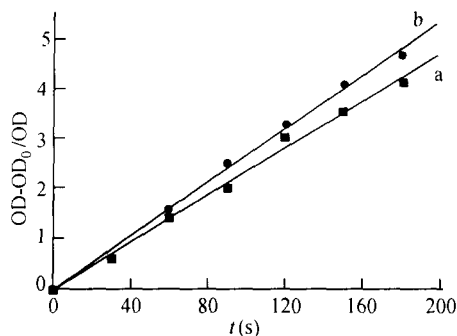
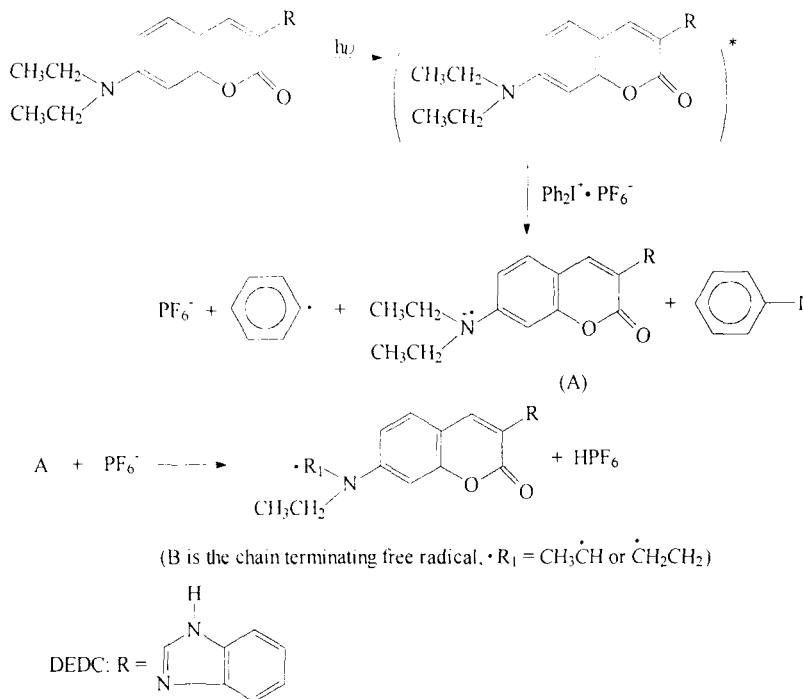


Fig. 5 A comparison of the rate of basic visible light photoinduced reaction of DEDC/DIHP system in N_2 (b line) and in air (a line) (the optical density value of 484.7 nm as reference)
 $[\text{DEDC}] = 1 \times 10^{-5} \text{ mol/L}$, $[\text{DIHP}] = 5 \times 10^{-5} \text{ mol/L}$, in CHCl_3



Scheme 2

Application

A glass plate was coated with a solution composed of DEDC, DIHP, active monomer and binder, dried and exposed to 488 nm Ar^+ laser. This is used to record imaging.

CONCLUSIONS

The visible light photoinduced reaction of DEDC and DIHP can be achieved through electron transfer from DEDC to DIHP (Scheme 2). The excited singlet state of DEDC is the main reactive state and is thus somewhat sensitive to O_2 .

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