

# Photoreactive inclusion complex of aryliodonium salt encapsulated by methylated- $\beta$ -cyclodextrin

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## Abstract

A novel photoreactive inclusion complex (PIC) with an excellent water solubility was obtained by the complexation of methylated- $\beta$ -cyclodextrin (Me- $\beta$ -CD) with the hydrophobic 4,4'-dimethyl diphenyliodonium salt (DMDPI). The photoreactivity of the complex PIC was examined by the kinetic studies in order to evaluate the influence of Me- $\beta$ -CD complexation. The photoreactive rate was enhanced in the photolysis of PIC compared with the uncomplexed DMDPI. By employing the photosensitizer at the visible region composed with PIC, the complex system can be used to initiate the photoreaction even in the visible region.

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**Keywords:** Photoinitiator; Photolysis; Diphenyliodonium salt; Cyclodextrin; Complex

## 1. Introduction

A wide area of supramolecular chemistry focuses on host–guest complexes formed by the binding of substrate to molecular receptors via non-covalent interaction [1–3]. If the components were capable of performing light induced function, a supramolecular architecture may be expected to give rise to photoreactive properties. Cyclodextrins (CDs) are cyclic oligosaccharides built up from 1,4-glucose units exhibit a torus-shaped structure with hydrophobic cavity and hydrophilic exterior [4–6]. Since its inception, it grows much interest in supramolecular chemistry using them as host molecules to form inclusion complexes with various organic compounds with high selectivity [7–10]. These applications had been utilized in several areas, including stereoselective synthesis [11,12], rotaxane chemistry [13,14], drug delivery [15,16] and polymer synthesis [17–22]. Particularly, nowadays the global pollution of atmosphere with volatile organic solvents is one of major challenges. The demand for environmentally friendly production requires the water reaction medium to replace the organic solvents.

The complexation of cyclodextrin provides an efficient way to obtain the water-soluble product directly from the wide varies of commercially available organic-soluble compounds without any chemical modification.

Thermally stable organic onium salts such as diaryliodonium and triarylsulfonium are a kind of important photoreactive reagent. They are utilized as the acid catalyst [23], arylation agent for organic synthesis [24] and photoinitiator for both cationic and radical photopolymerization [25–27]. However, the water-insolubility of aryliodonium limited them to apply in aqueous media and biological systems. In order to obtain good water-soluble aryliodonium compounds from available products, we use the cyclodextrins as the host molecule to encapsulate the hydrophobic aryliodonium compound to form a water-soluble inclusion complex and expect to keep its originally photochemical properties in aqueous solution.

Up to now, Ritter's group and our group have reported the inclusion complex of the UV initiator and investigated their initiating properties in aqueous solution [28,29]. But very few publications were concerned about the photosensitive initiation system of complexed photoinitiator. In this paper a water insoluble diaryliodonium salt (DMDPI) was converted to a good water solubility photoinitiator by encapsulation with Me- $\beta$ -CD. Afterwards this inclusion complex was found to be

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capable of a much higher photoreactive properties even than pure DMDPI.

## 2. Experimental

### 2.1. Materials

Randomly methylated- $\beta$ -cyclodextrin (Me- $\beta$ -CD, the average degree of methylation of 1.8 per glucose unit, Aldrich), 4,4'-dimethyl diphenyliodonium hexafluorophosphate (DMDPI, TH-UNIS Insight Co. Ltd.), fluorescein sodium (FL, Beijing Chemical Reagent Co.), acrylamide (AM, Jiangxi Changjiu Biochemical Engineering Co.) were used as received. All other chemicals were commercially available products of A.R. grade.

### 2.2. Complex of Me- $\beta$ -CD with DMDPI (PIC)

1.56 g of Me- $\beta$ -CD (1.2 mmol) and 0.27 g of DMDPI (0.6 mmol) were dissolved in 10 mL of methanol and then 40 mL of distilled water was added gradually to the methanol solution with stirring. The mixture solution was sonicated for 20 min and then placed in dark stirred for 20 h. The solvent was removed by evaporation, and the solid product PIC was dried under vacuum at 40 °C for 6 h.

### 2.3. Photolysis and photopolymerization

The light source for photosensitized photolysis and visible photopolymerization was 400 W Xenon lamp. A filter was used to cut off the light with  $\lambda < 300$  nm. The light source for direct photolysis was a 300 W high-pressure mercury lamp. The comparative experiments were carried out in neat aqueous solution for PIC and in mixed solvent ( $\text{CH}_3\text{OH}/\text{H}_2\text{O} = 1:9$ , v/v) for DMDPI, respectively. The polymerization rates were measured with dilatometers, which rotated around the light source at 6 rpm on merry-go-round photoreaction set at room temperature. The conversion was less than 15%. The experimental data were treated by a least-squares method.

### 2.4. Measurement

The  $^1\text{H}$  NMR spectra were recorded on a Bruker DPX 400 in  $\text{D}_2\text{O}$ . Chemical shifts were referred to the internal standards TMS. The fluorescence measurements were carried out on a Hitachi F-4500 fluorescence spectrophotometer. Fluorescence lifetime measurements were made on a multiplexed time-correlated single-photocounting fuoremeter FL900 Edinburgh Instruments Spectrometer. UV-vis spectra were recorded on a JASCO V-530 instrument.

## 3. Results and discussion

### 3.1. Inclusion complexation

The cyclodextrin employed in this study was a methylated derivative of  $\beta$ -cyclodextrin (Me- $\beta$ -CD) because the water-solubility of the methylated  $\beta$ -CD (150 g/100 mL, 25 °C) is much larger than that of native  $\beta$ -CD (1.85 g/100 mL, 25 °C). We found that DMDPI, a UV water-insoluble photoinitiator, readily becomes a sufficiently water-soluble product after the complexation with Me- $\beta$ -CD, whereas the complex with native  $\beta$ -CD is hardly soluble in water. The structure of the inclusion complex of Me- $\beta$ -CD with iodonium (DMDPI) was further characterized by spectrometries. NMR spectroscopy is a useful tool for the investigation of CD complexes. Especially aromatic guests with their strong shield tensors can induce proton shifts in the CD and therefore, give valuable information about complexation [28]. The complex PIC NMR spectra were recorded in deuterium oxide ( $\text{D}_2\text{O}$ ). Fig. 1 illustrates characteristic  $^1\text{H}$  NMR spectra of complex PIC in comparison with the single Me- $\beta$ -CD. The spectrum shows highly resolved and signals for the phenyl group and methyl group in higher and lower field, respectively. The appearance of two signals for Me- $\beta$ -CD-C1-H can be explained by the fact that there are methylated and nonmethylated C2-OH group present in the Me- $\beta$ -CD molecule [19]. The inner Me- $\beta$ -CD proton C3-H and C5-H shifted towards a higher field indicating that the guest molecule is positioned within the cavity of the Me- $\beta$ -CD.

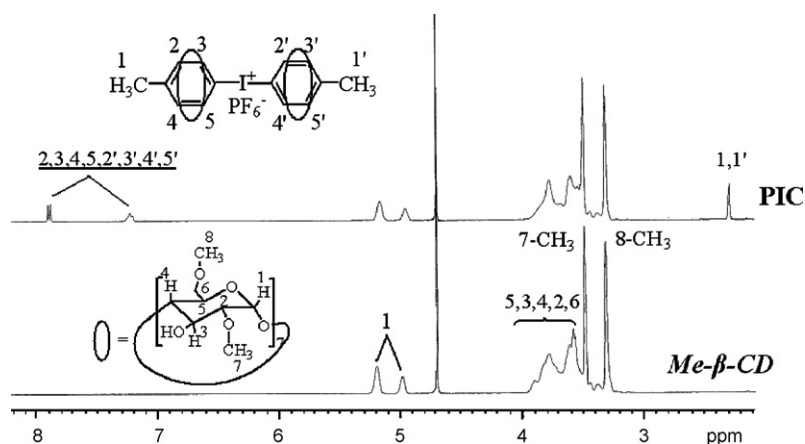


Fig. 1.  $^1\text{H}$  NMR spectrum of PIC and Me- $\beta$ -CD in  $\text{D}_2\text{O}$ .

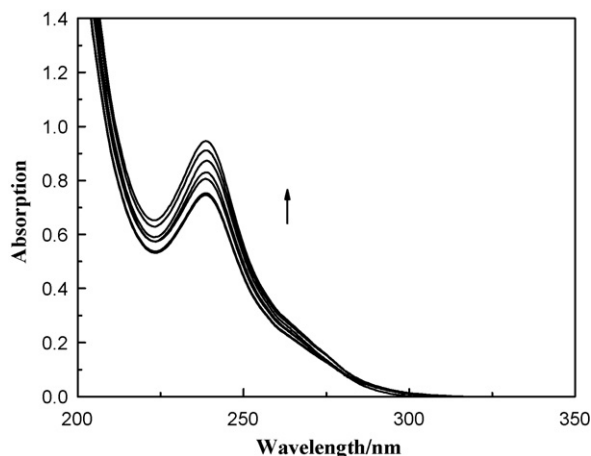


Fig. 2. Absorption spectra of DMDPI ( $2.5 \times 10^{-5}$  mol/L) at various concentrations of Me- $\beta$ -CD (mol/L) in aqueous solution: (1) 0; (2) 0.003; (3) 0.006; (4) 0.007; (5) 0.008; (6) 0.01.

To further prove DMDPI encapsulated by Me- $\beta$ -CD, the UV absorption spectra were employed. Fig. 2 shows the absorption spectra of DMDPI at different Me- $\beta$ -CD concentrations in aqueous solution. It can be seen that the absorption maximum at 239 nm increases with increasing of Me- $\beta$ -CD concentration indicating the formation of an inclusion complex between Me- $\beta$ -CD and DMDPI. The Me- $\beta$ -CD concentration dependence of onium absorbance can be analyzed by the Benesi–Hildebrand [30] linear regression, which provides reliable information on the stoichiometry of Me- $\beta$ -CD with DMDPI.

The Benesi–Hildebrand equation for the 1:1 complex (Case 1) and 1:2 complex (Case 2) between Omnicat 820 and Me- $\beta$ -CD as shown follows:

Case 1, the 1:1 complex:

$$\frac{1}{A - A_0} = \frac{1}{(A' - A_0)K_a C_{CD}} + \frac{1}{A' - A_0}$$

Case 2, the 1:2 complex:

$$\frac{1}{A - A_0} = \frac{1}{(A' - A_0)K_a C_{CD}^2} + \frac{1}{A' - A_0}$$

where  $K_a$  is the association complex constant and  $A_0$  and  $A$  are the absorption intensities of guest in the absence and pres-

ence of host.  $A'$  is the absorption intensity of the inclusion complex.

The Benesi–Hildebrand plots for the complexation of Me- $\beta$ -CD with DMDPI are shown in Fig. 3. Evidently the linear correlation can be obtained only in the case 2 supporting the formation of 1:2 inclusion complex. It means that the compound DMDPI associates with two Me- $\beta$ -CD molecules to form a sufficiently water-soluble guest/host complex (PIC). From the slope and intercept of the double reciprocal plot (B) the association constant  $K_a$  was determined to be  $9.2 \times 10^4$  (mol/L) $^{-2}$ .

Based on the results of  $^1\text{H}$  NMR and the absorption spectra, the structure of the complex PIC (as shown in Scheme 1) could be proposed, in which the phenyl ring of both sides is positioned in the cavity of cyclodextrin, where the iodonium cation, photoreactive sit, is situated in the exterior of CD. As a result the complex PIC is expected to exhibit good water-solubility and high photoactivity identical to the uncomplexed form of onium DMDPI.

### 3.2. Direct photolysis

DMDPI is a thermally stable arylidonium salts. Direct photolysis of these salts is reported to result in the cleavage of carbon–iodine bond to yield reactive aryl radical and radical cation (Eq. (1)) [31]. The radical cation is postulated to undergo H-abstraction from medium to generate Brønsted acid  $\text{H}^+$  (Eq. (2)).



where HR is the medium.

The acid-photogeneration from the direct photolysis of DMDPI was determined by the titration with aqueous NaOH to the phenol–phthalein end point. Fig. 4 shows the results of acid generation of the photolysis for the complex PIC and DMDPI in aqueous solution and mixed solvent ( $\text{CH}_3\text{OH}/\text{H}_2\text{O} = 1:9$ , v/v), respectively. It was found that the acid yields increased with UV irradiation time along with the precipitation which formed by the recombination of the photolysis product. However, the rate of acid-generation is remarkably higher and the turbidity of reaction solvent is obviously lower for complex PIC than those for DMDPI. These differences can be

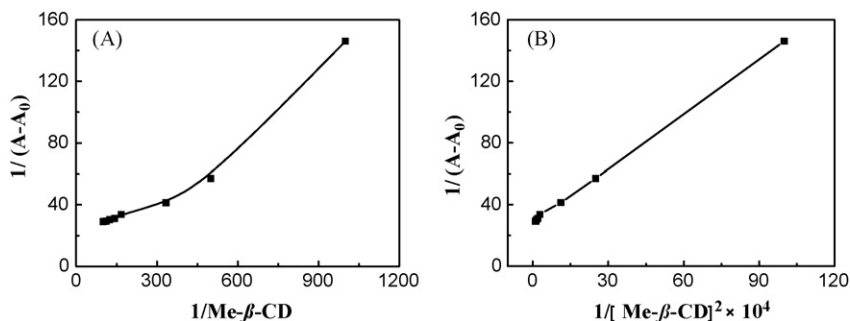


Fig. 3. Benesi–Hildebrand plot of (A)  $1/(A - A_0)$  against  $1/[\text{Me-}\beta\text{-CD}]$  and (B)  $1/(A - A_0)$  against  $1/[\text{Me-}\beta\text{-CD}]^2$ .

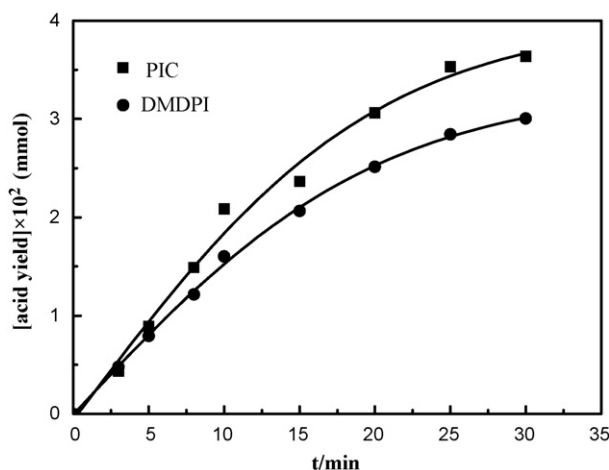


Fig. 4. The direct photolysis of PIC and DMDPI in aqueous solution and mixed solution ( $\text{CH}_3\text{OH}/\text{H}_2\text{O} = 1:9$ , v/v),  $[\text{PIC}] = [\text{DMDPI}] = 2 \times 10^{-3}$  mol/L.

attributed to the Me- $\beta$ -CD complexation which can act as the H-donor and increases the water-solubility of the recombination products.

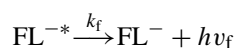
### 3.3. Photosensitized photolysis

Most of the onium salts only absorb light at the UV region which limits their application field. But photosensitized by different dyes, its application can be prolonged to the entire visible and near-IR region. In this work the fluorescence dye FL was selected as a visible photosensitizer in the combination with the complex PIC to constitute a water-soluble photosensitive system. As reported [32,33] previously the irradiation with visible light the photosensitization system proceeds electron transfer from excited FL dye to iodonium cation to form a radical pairs which rapidly undergo C–I bond cleavage leading to a generation of active radical and subsequent photobleaching of dye as a result of radical couple to form Leuco form of dye. The main photochemical process is described as follows:

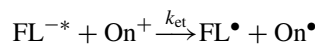
excitation



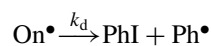
emission



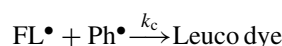
electron transfer



cleavage



couple

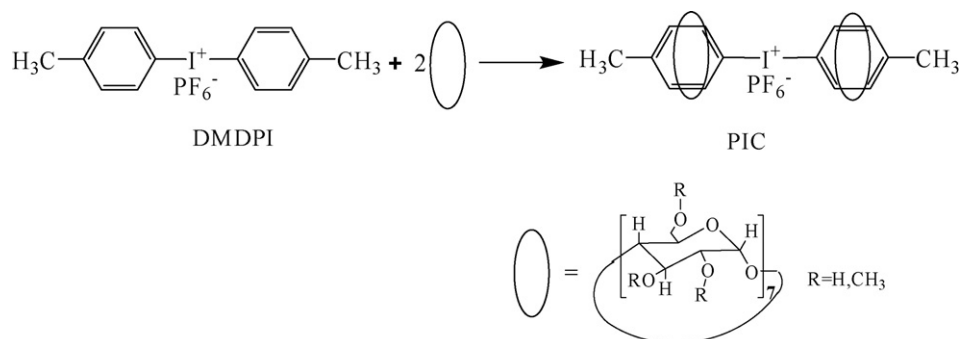


where  $\text{On}^+$  is the onium cation.

According to these reaction processes two methods were proved efficiently in this dye sensitized photolysis system, (a) the fluorescence quenching of FL dye by onium salt which is directly related with primary electron transfer process can be measured by the fluorescence spectrophotometer; (b) the photobleaching of the photosensitizer can be monitored by the spectrophotometer.

#### 3.3.1. Fluorescence quenching

FL dye is an efficient fluorophore with high fluorescence quantum. The fluorescence quenching experiment provided a useful method to investigate the sensitizing interactions with onium salts at singlet excited state. The FL fluorescence quenching and lifetime composed with PIC and DMDPI was carried out in aqueous solution and mixed solution ( $\text{CH}_3\text{OH}/\text{H}_2\text{O} = 1:9$ , v/v), respectively. Fig. 5 shows the relative emission intensity ( $I_0/I$ ) of the onium salt concentration dependence of DMDPI was consistent with the Stern–Volmer relationship. The quenching constant  $k_q$  was  $8.7 \times 10^{10} \text{ M}^{-1} \text{ S}^{-1}$  ( $\tau_0 = 4.8 \text{ ns}$ ) in order of magnitude agreement with value ( $k_q = 3.4 \times 10^{10} \text{ M}^{-1} \text{ S}^{-1}$ ) obtained by life time measurement in the range of diffusion controlled process, while the Stern–Volmer dependence for complexed onium PIC deviates from the linear relationship at



Scheme 1. Chemical structure of the inclusion complex PIC.





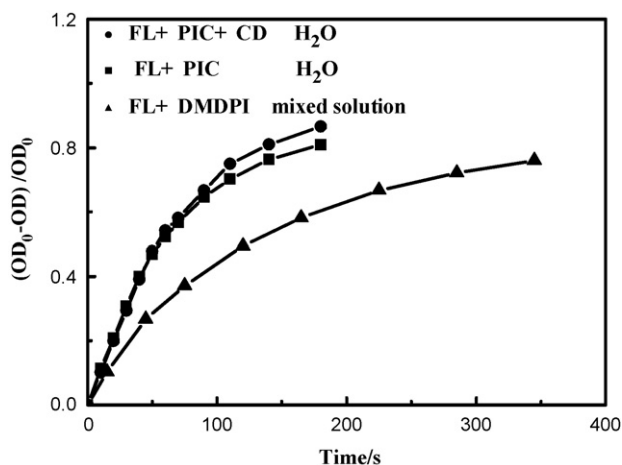


Fig. 8. Photobleaching of FL/PIC and FL/DMDPI in water and mixed solution ( $\text{CH}_3\text{OH}/\text{H}_2\text{O}=1:9$ , v/v).  $[\text{FL}]=3 \times 10^{-5}$  mol/L,  $[\text{PIC}]=[\text{DMDPI}]=3 \times 10^{-4}$  mol/L.

Table 1  
Photobleaching rate of FL/PIC and FL/DMDPI

	FL/PIC + CD	FL/PIC	FL/DMDPI
$R_b \times 10^3 \text{ s}^{-1}$	9.75	9.40	5.88
$\Phi_i \times 10^2$	3.16	2.84	2.01

$[\text{FL}]=3 \times 10^{-5}$  mol/L,  $[\text{PIC}]=[\text{DMDPI}]=3 \times 10^{-4}$  mol/L.

accelerated. It did not occur in polar media because of the high dissociation for ion-pair complex. These results implicate that the stable complex (II) formed between anion FL dye and cationic iodonium salt PIC in water is probable due to the protection of bulk CD cycle. From the above results, we can conclude electron transfer photosensitized photolysis of PIC by FL was enhanced significantly due to the intermolecular association occurred in the reaction system.

### 3.3.2. Photobleaching

When the FL/PIC system is exposed to visible light, the dye-bleaching phenomenon was observed, and the absorption peak of FL monotonously decreased with irradiation time. The solutions were deoxygenated with  $\text{N}_2$  at least 30 min. These changes can be illustrated in Fig. 7.

The photoreaction kinetic study was performed by monitoring the relative change in the optical density of the FL at 489 nm with different irradiation time. As shown in Fig. 8, it was found that the photobleaching rate for PIC is much higher than the value for DMDPI. With adding excessive Me- $\beta$ -CD the system some positive effect on the photobleaching was found. The photobleaching rate  $R_b$  and quantum yield  $\Phi_i$  calculated from these kinetic curves are given in Table 1. The relative high quantum yield  $\Phi_i$  for FL/PIC compared with the value for FL/DMDPI indicates that the interaction between FL and PIC play an important role. The enhanced reactivity can be explained by the fact that the formation of complex between FL and PIC, which probably enhanced the access to the active site of onium cation and produced a favorable microenvironment thus leading to significantly promoting the electron transfer reaction and decreasing

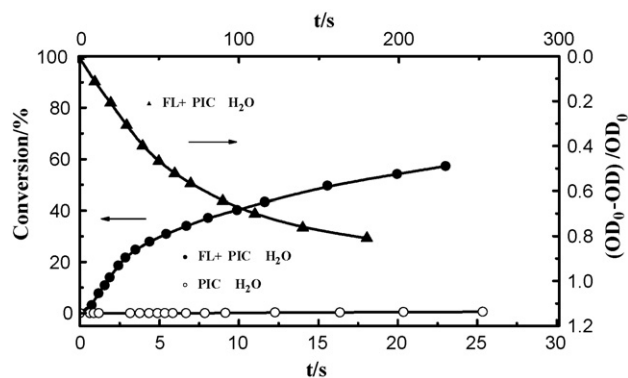


Fig. 9. Photopolymerization of AM initiated by FL/PIC.  $[\text{AM}]=1.8$  mol/L,  $[\text{FL}]=3 \times 10^{-5}$  mol/L,  $[\text{PIC}]=3 \times 10^{-4}$  mol/L.

the back electron transfer rate. Devoe et al. [35] also indicated that the association of the donor photosensitizer with iodonium cation may affect either the decomposition rate of the photoproducted dipheylido radical or decrease the back electron transfer rate by altering the reorganization energy.

### 3.4. Photopolymerization

As mentioned above, the FL/PIC appears to be a visible radical and acid photogeneration source. Since cationic polymerization cannot be carried out in aqueous solution, the photosensitized PIC can be used as an efficient water-soluble radical photoinitiation system for visible photopolymerization.

The photopolymerization experiments of acrylamide (AM) initiated by FL/PIC complexed systems were carried out in aqueous solution at room temperature. After the addition of the FL/PIC, the solution of AM was still kept transparent, indicating that the competitive complex between the DMDPI and AM can be neglected. The results obtained as expressed in Fig. 9 show that the polymerization of the AM proceeds efficiently, along with dye photobleaching, while it can be seen that the iodonium salt alone cannot induce the polymerization on irradiation of visible light.

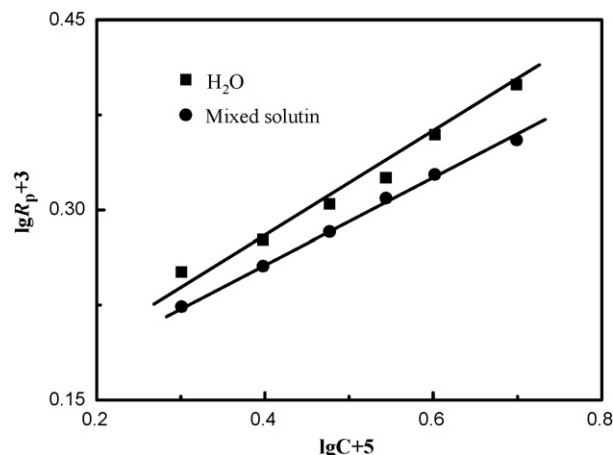


Fig. 10. Concentration influence of FL on polymerization rate  $R_p$ .

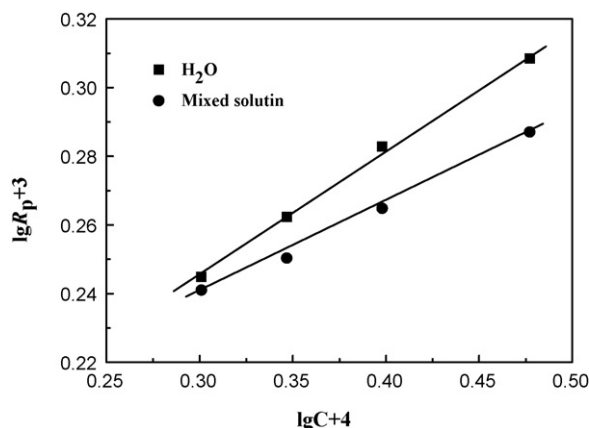


Fig. 11. Concentration influence of photoinitiator on polymerization rate  $R_p$ .

In order to estimate the influence of Me- $\beta$ -CD complexation in the initiation system on the photopolymerization, a comparison of polymerization for FL/PIC and FL/DMDPI was studied in the water and mixed solution ( $\text{CH}_3\text{OH}/\text{H}_2\text{O} = 1:9$ , v/v), respectively.

#### 3.4.1. Influence of the photoinitiator concentration

The polymerization of AM was carried out in the condition of  $[\text{AM}] = 1.8 \text{ mol/L}$  at  $30^\circ\text{C}$ . The initiator concentration dependence of the polymerization rates ( $R_b$ ) were plotted in Figs. 10 and 11. It can be found that with increasing FL or onium salt concentration, the both polymerization rates increased, but the photopolymerization rate for FL/PIC system is obviously faster than that for FL/DMDPI. These results are consistent with the above results observed from fluorescence quenching and photobleaching experiments. The kinetic concentration exponents for FL obtained from the linear plot of curves to be 0.38 and 0.34 for FL/PIC and FL/DMDPI system, respectively. The concentration exponent for PIC and DMDPI is 0.36 and 0.27, respectively.

Obviously the rate enhancement is related with the association between FL and PIC in reaction system which greatly promotes the sensitized photolysis and radical generation, leading to accelerate the radical initiation and influence the overall rate of polymerization. In addition, in the case complex PIC the radical species has the phenyl group inside the hydrophobic cavity of Me- $\beta$ -CD, therefore the concentration in the aqueous phase will be higher than in the system without Me- $\beta$ -CD. This caused the effect of increasing rate of polymerization. Similar phenomenon was also reported in the case of Me- $\beta$ -CD complexed monomer by Ritter and co-workers [28].

## 4. Conclusions

Using Me- $\beta$ -CD as the host to encapsulate the hydrophobic arylonium salt DMDPI, one water-soluble and photoreactive inclusion complex (PIC) was obtained. The influences of Me- $\beta$ -CD on the photoreactivity and the photopolymerization of

DMDPI were examined by the spectroscopic and kinetic studies in comparison with uncomplexed onium system. The obtained results indicated that the photoreactive complex PIC remains keep the original photochemical properties of DMDPI with even much higher reaction efficiency. The rate enhancements for directed photolysis or for FL sensitized photolysis and photopolymerization were observed in the presence of the Me- $\beta$ -CD complexed onium PIC. This new approach opens a new route for converting water insoluble photoinitiator or dyes to water-soluble product. Further work will be applied such photoinitiator system to the photoreactive coatings.

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