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Host/guest complex of Me-β-CD/2,2-dimethoxy-2-phenyl acetophenone for initiation of aqueous photopolymerization: Kinetics and mechanism

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Abstract

Methylated-β-cyclodextrin (Me-β-CD) was used to complex the photoinitiator, 2,2-dimethoxy-2-phenyl acetophenone (DMPA), yielding a water-soluble host/guest complex. The comparative studies demonstrated that the Me-β-CD complexed DMPA exhibited a high photoreactivity identical to the uncomplexed DMPA, while the CD complex obviously influenced the products of primary photolysis of DMPA and the photopolymerization kinetics due to the steric effect of CD on the subsequent initiation reactions. The photopolymerization rate of acrylamide can be described by the equation: $R_p = K[2a]^{0.62}[M]^{1.37}[I]^{0.5}[\text{Me-}\beta\text{-CD}]^0$. The mechanism of polymerization was also discussed.

Keywords: Host/guest complex; Cyclodextrin; Kinetics

1. Introduction

The demand for environmentally benign processes is growing as the world becomes increasingly aware of environmental issues involving conventional organic solvents. In an effort to promote pollution prevention, the research is directed to promote the design of environmentally benign processes that minimize or eliminate the use of toxic substances such as solvents and reagents. The reaction in aqueous solution is a highly effective approach to use water instead of the organic solvents. Cyclodextrins are cyclic oligosaccharides built up from 1,4-glucopyranose units that exhibit a torus-shaped structure with a hydrophobic cavity and a hydrophilic exterior [1–3]. Due to the special molecular structure they are able to enclose smaller hydrophobic molecules or hydrophobic side groups of polymer as guests into their cavities to form host/guest compounds in aqueous and in emulsion [4–10]. This inclusion complex leads to a significant change of the solution properties and reactivities of the guest molecule, but without any chemical modification [11–17]. And it also attracted more and more attention in recent years because of their potential to serve as molecular devices and molecular machines, as well as nanostructured functional materials, such as cyclodextrin-based light-driven molecular shuttle [18,19] and rotaxane-encapsulated dyes to prevent the chromophore degradation [20].

Recently, Ritter et al. have reported that some hydrophobic vinyl monomers including a series of commercial monomers and some monomers with long hydrocarbonic side chain became water-soluble due to the inclusion/complexation of cyclodextrin [12,13,21–23]. These complexes can be easily polymerized in water by thermal initiator via a free radical mechanism. They found that during the homopolymerization the cyclodextrin slipped off step by step from the growing chain and the polymer precipitated in high yields while the cyclodextrin remained in the aqueous phase. The unthreaded cyclodextrin is soluble in water and thus can be reused to entrap new monomer [12,15]. All these investigations showed that CD-mediated polymerization reactions in aqueous solution opened up a new way to decrease the use of the organic solvents.

As is well known, 2,2-dimethoxy-2-phenyl acetophenone (DMPA) is an efficient commercial photoinitiator and is widely used in a variety of UV-curable materials, however, it is nearly water-insoluble. So it is reasonable to develop DMPA to be a water-soluble initiator. The research of Ritter's group on the photopolymerization of *N*-isopropylacrylamide in water initiated by the complex of Me-β-CD/2-hydroxyl-2-methyl-1-phenylpropan-1-one gave a preliminarily result and a feasibility [24]. However, the influence of cyclodextrin complex on

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the kinetic and mechanism of polymerization have not been addressed. In this paper, we report our results of the kinetic investigation on the host/guest complex of Me-β-CD/DMPA used as photoinitiator to initiate AM photopolym-erization in aqueous solution.

2. Experimental section

2.1. Materials

β-Cyclodextrin (β-CD) (Shanghai Chemical Reagent Co.) was purified by recrystallization from water, acrylamide (AM), (Jiangxi Changjiu Biochemical Engineering Co.) and 2, 2-dimethoxy-2-phenyl acetophenone (DMPA), (Ciba-Geigy Co.) was used as received. Randomly methylated-β-cyclodextrin (Me-β-CD) was synthesized according to the literature [25], and it is a mixture with an average degree of methylation of about 1.8 per glucose unit. All other chemicals were commercially available products of reagent grade.

2.2. Complexation of photoinitiator

The host/guest complexes 1a and 2a were prepared at Me-β-CD/DMPA molar ratio of 1:1 and 2:1 respectively. 1.55 g of Me-β-CD (1.2 mmol) and 0.30 g of (1.2 mmol) DMPA were dissolved in 9 mL of ethanol and then 1 mL of distilled water was added gradually to the ethanol solution with stirring. The mixture solution was shaken for 3 h at room temperature and then placed in dark for another 3 h. After solvent evaporation the solid complex 1a was dried under vacuum at 40 °C for 12 h. The inclusion complex 2a was prepared in the same way.

2.3. Photolysis and photopolymerization

The photolysis reaction of uncomplexed DMPA and Me-β-CD complexed DMPA were carried out at 30 °C in ethanol solution and aqueous solution respectively. The photolysis process was monitored with the UV spectra. A high-pressure mercury lamp (300 W) was used as the UV light source (light below 300 nm was filtered out with thick pyrex glass). The light intensity of irradiation was measured to be 5.0 mW/cm^2.

The photopolymerization kinetic measurement was performed by the dilatometer method at the conversion less than 15%. The prepared aqueous solutions including the monomer and the initiator were deaerated by bubbling with nitrogen in the dilatometer for 10 min in an ice bath, then adding the toluene into the capillary section of the dilatometer. The experimental data were treated by a least-squares method and the correlation coefficients were between 0.975 and 0.999.

Polymerization products were purified by reprecipitation in acetone and then dried in vacuum at 40 °C. The average molecular weight was estimated according to the equation [26] $[\eta] = 6.8 \times 10^{-4} M_n^{0.66}$.

2.4. Measurement

The ^{1}H NMR spectra were recorded on a Bruker DPX 400 in D_2O. Chemical shifts were referred to the internal standards TMS. UV/vis spectra were recorded on a JASCO V-530 instrument. IR spectra were recorded on a Bio-Rad FTS 165 instrument.

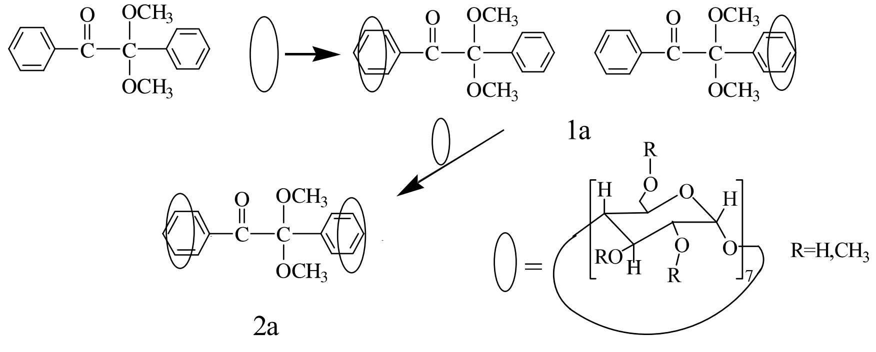
3. Results and discussion

3.1. Complex of Me-β-CD/DMPA

DMPA is a kind of water-insoluble photoinitiator, and becomes water-soluble in the Me-β-CD complexed form. Since there is a dynamic equilibrium in solution, it is possible to form 1:1 and 2:1 host/guest complex between the cyclodextrin and DMPA with varying molar ratio of Me-β-CD/DMPA. As shown in Scheme 1, the 1:1 complex may have two inclusion forms. Me-β-CD located at the benzoyl side or on the other side ring of DMPA, while in the case of 2:1 complex both phenyl rings were included into the CD cavity. The experimental results indicated that 1a was slightly soluble, so the good water-soluble complex of 2a was used to the following study.

Several methods were applied to the characterization of CD inclusion complex 2a. ^{1}H NMR spectroscopy was used to verify the existence of CD complexes. Fig. 1 shows the characteristic of ^{1}H NMR shifts of 2a in comparison with free Me-β-CD in D_2O. The spectrum of 2a showed a high resolution of the signals. The signals of the CD protons changed obviously and the shifts were induced by the guest molecule. From the integral ratio it was indicated the ratio of host/guest is 2:1.

The ^{13}C NMR also gave the structure information about the CD inclusion complex 2a. The chemical shifts of the carbonyl



Scheme 1. Formation of the Me-β-CD/DMPA inclusion complex in mixed solution.

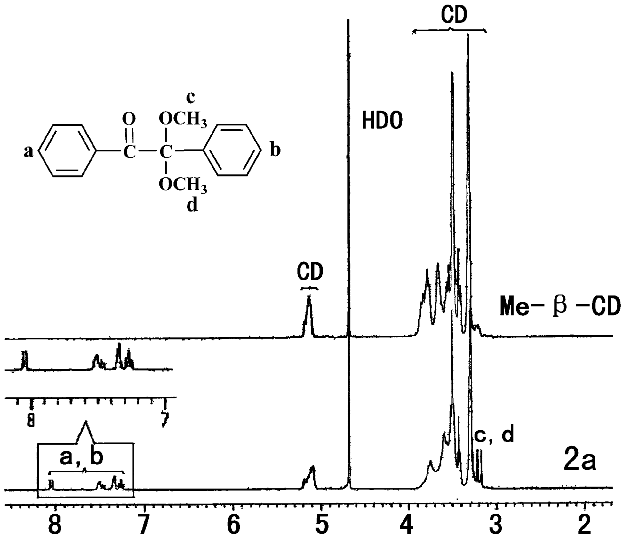


Fig. 1. 400 MHz ^{1}H NMR spectra of Me-β-CD/DMPA complex 2a (bottom) and uncomplexed Me-β-CD (top) in D_2O.

group and its neighboring carbon atoms of 2a shifted to higher field in comparison with the uncomplexed DMPA, while the chemical shifts of the other carbon atoms shifted to lower field, which indicated the phenyl part within the cavity and the carbonyl part projecting outside [27].

The IR spectra (not shown here) indicated the characteristic bands of the carbonyl group of the complexed 2a compared with the uncomplexed guest molecule DMPA slightly shifted to higher frequencies from 1691 to 1700 cm^{-1} due to the influence of Me-β-CD complex.

The UV spectra of the uncomplexed DMPA and the complexed 2a, as shown in Fig. 2, it could be found that they had a similar spectral shape with a maximum absorbance at 335 nm (C_2H_5OH) and 333 nm (H_2O), and the corresponding molar extinction coefficients were 287 L/mol/cm and 351 L/mol/cm, respectively. These results indicated that the complexation of Me-β-CD did not significant influence the n-π^* excitation state of DMPA. Based on the results of ^{1}H NMR, ^{13}C NMR, IR and UV, the structure of the complex 2a could be proposed, in which the phenyl ring of both sides is enclosed by the cyclodextrin, whereas the carbonyl group, photoactive sit, is situated in the exterior of the cavity of cyclodextrin. As a result, the complex 2a exhibited an identical photoreaction activity with the uncomplexed DMPA.

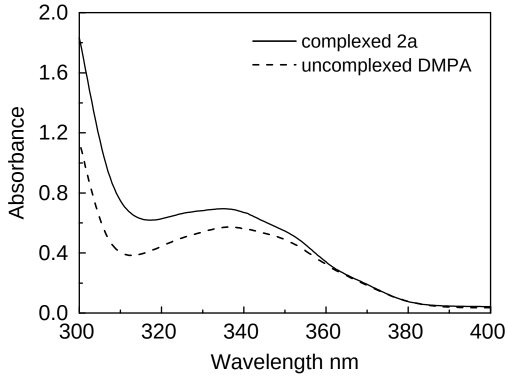


Fig. 2. The UV spectra of Me-β-CD/DMPA complex 2a in H_2O and uncomplexed DMPA in C_2H_5OH. [2a]$=2\times10^{-3}$ mol/L [DMPA]$=2\times10^{-3}$ mol/L.

3.2. Photolysis

DMPA is a high photoactive compound. Under the UV irradiation, it is easy to be excited to undergo fast α-cleavage reaction (Norrish I type, $k_d > 10^{12}$ s^{-1}), producing two radical species: benzoyl radical $R_1\cdot$ and dimethoxy benzyl radical $R_2\cdot$ [28]. The later $R_2\cdot$ is unstable and quickly proceeds subsequent cleavage to generate methyl radical $R_3\cdot$ and methyl benzoate. The radical products $R_1\cdot$ and $R_3\cdot$ possess high reactivity to initiate the radical polymerization of olefinic monomers. In certain applications, yellowness can be observed in coatings in which DMPA is used. The radical coupling products were found to be primarily responsible for the yellowing products [29].

The influence of CD complexation on the photodecomposition of DMPA was examined by monitoring the changes of UV spectra with irradiation. A new absorption peak was observed at the longer wavelength (λ_{max} 350 nm) which gradually increased with the irradiation time (Fig. 3), but this phenomenon didn't appear in the uncomplexed DMPA photoinitiator system. The absorbance of the uncomplexed DMPA (λ_{max} 335 nm) was decreasing monotonously with the irradiation time (Fig. 4). In order to prove the cage effect on

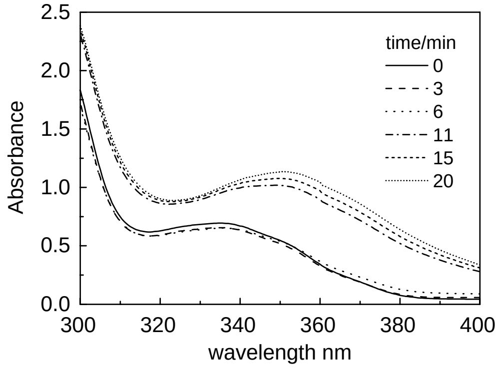


Fig. 3. UV spectra of 2a vs irradiation time in water [2a]$=2\times10^{-3}$ mol/L, $T=30$ °C.

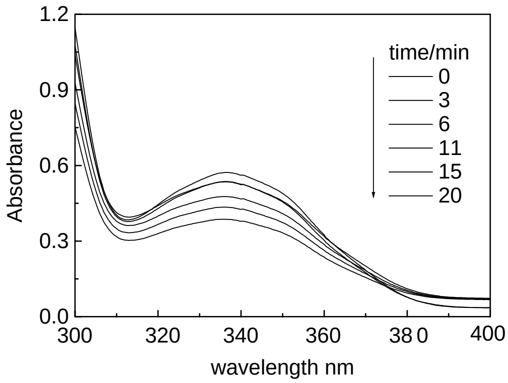
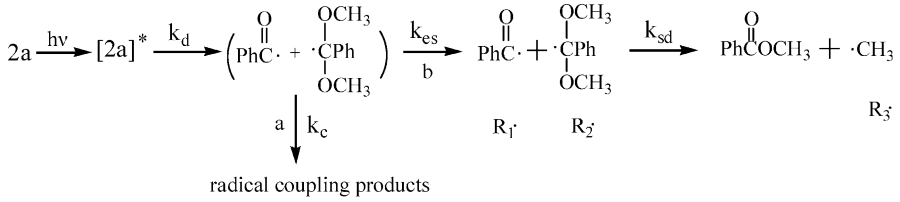


Fig. 4. UV spectra of DMPA vs irradiation time in ethanol [DMPA]$=2\times10^{-3}$ mol/L, $T=30$ °C.



* n-π* electron excited state ( ) solvent cage

k_c、k_{es}: rate constant for radical combination and escape from the cage respectively

Scheme 2. Photodecomposition mechanism of the complexed DMPA in solution.

the reaction product in the photolysis process for 2a, adding the monomer AM to the solution, the new absorption band at longer wavelength completely disappeared as a result of the radicals capture by AM. Based on these results, the photolysis process of DMPA in solution can be described in Scheme 2. The radicals R· produced by the photodecomposition of DMPA can undergo either cage combination to generate a product with longer wavelength (route a) or escape from the cage (route b). In the case of Me-*β*-CD complexed 2a the mobility of the radical was significantly reduced by the CD inclusion, leading to a greatly increase of the cage combination reaction. Therefore, a new absorbance of the radical coupling products appeared at longer wavelength, while in the case of the uncomplexed DMPA the radical fragments easily escaped from the cage, and the radical cage combination was eliminated. This phenomenon implicated that the complexation of Me-*β*-CD had a certain influence on the photoinitiation process of DMPA.

3.3. Photopolymerization kinetics

To evaluate the effect of Me-*β*-CD complexation on the initiation activity of DMPA, the complexed photoinitiator 2a and uncomplexed DMPA were used to initiate the polymerization of AM in the water and H_2O/DMF (9:1 v/v) mixed solution respectively. Conversion-time curves for polymerizations were performed at the same condition of [AM] = 2.0 mol/L, and [initiator] = 4×10^{-5} mol/L at 30 °C. As shown in Fig. 5, two identical conversation curves can be found, which indicated that the complexed photoinitiator 2a remained its own original high photoinitiation efficiency as uncomplexed DMPA.

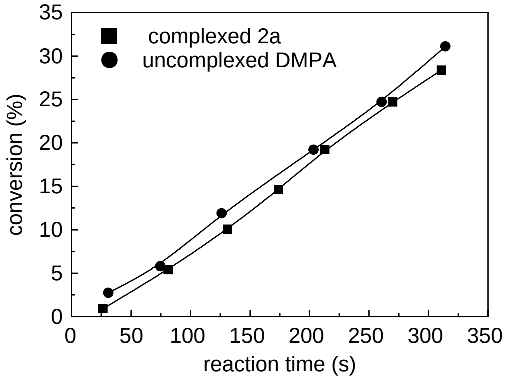


Fig. 5. AM conversion vs irradiation time for CD complexed 2a and uncomplexed DMPA.

3.3.1. Influence of the photoinitiator concentration

The polymerization of AM was carried out in the condition of [AM] = 1.8 mol/L at 30 °C. The influence of the photoinitiator concentration on photopolymerization rate R_p was shown in Fig. 6. From its slope the concentration exponent of 2a was obtained to be 0.62, which means $R_p \propto [2a]^{0.62}$.

In the same condition, the photopolymerization of AM using the uncomplexed DMPA as initiator was carried out in the H_2O/DMF (9:1, v/v) mixed solution. From the Fig. 7 the concentration exponent was obtained to be 0.52, which means $R_p \propto [DMPA]^{0.52}$.

The higher concentration exponent of 2a comparative with the uncomplexed DMPA may attribute to the higher viscosity

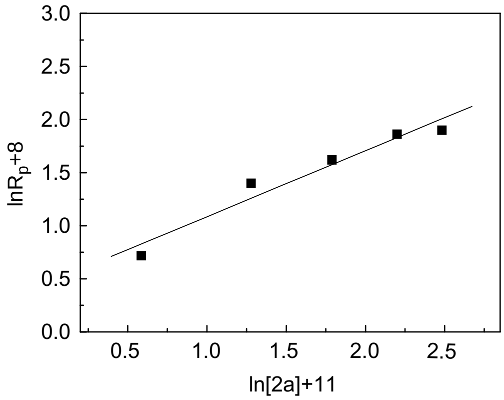


Fig. 6. Concentration influence of initiator 2a on polymerization rate R_p.

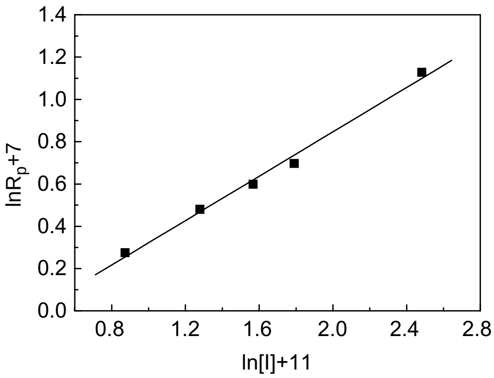


Fig. 7. Concentration influence of initiator on polymerization rate R_p.

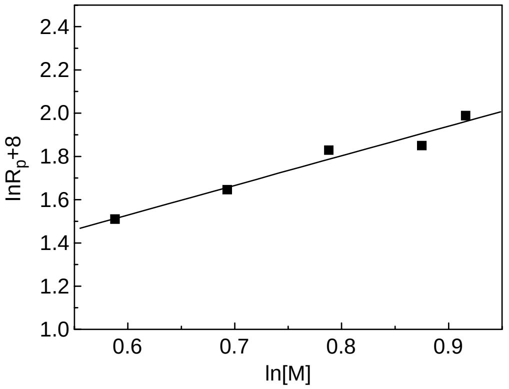


Fig. 8. Influence of monomer concentration [M] on polymerization rate R_p.

of aqueous solution than the mixed solution, which causes decrease of the diffusion rate of the polymer radical, resulting in a reduction of the bimolecular termination in the polymerization process.

3.3.2. *Influence of the monomer concentration*

The influence of the monomer concentration on photopolymerization rate R_p was carried out at constant concentration of $[2a]=4\times10^{-5}$ mol/L. As shown in Fig. 8, the polymerization rate is directly proportion to the concentration of monomer AM with order of 1.37, which means $R_p \propto [M]^{1.37}$. The higher index of the monomer concentration compared with normal value of 1.0 for conventional polymerization indicated that the monomers might participate the initiation process. The cage effect as mentioned for the photolysis of 2a becomes more important in the subsequent initiation process. The initiating mechanism of 2a was described in Scheme 3. Since the mobility of radical R• is restricted by steric effect of CD inclusion the radicals escape from the cage is weaken. In this case, the interaction between the radical and the monomer in cage becomes considerable. Therefore, the monomer concentration exponent was determined not only by the propagation rate but also by the initiation rate, which resulted in a higher order of [M].

3.3.3. *Influence of the light intensity*

The polymerization experiment was performed in the constant condition of $[AM]=1.8$ mol/L, $[2a]=4\times10^{-5}$ mol/L, and the light intensity was adjusted by metal screen with different transmission. The relationship was shown in Fig. 9; a straight line with a slope of 0.5 was obtained via a log–log plot. This data indicated that the complexed photoinitiator 2a dissolves completely in water, and their optical density is not too high under the experimental condition. No intermolecular energy self-absorption occurs, and all the absorbed light energy can be reasonably assumed to excite 2a molecules. Therefore, when the light intensity increased the initiating rate increased with square root as the value of normal photopolymerization.

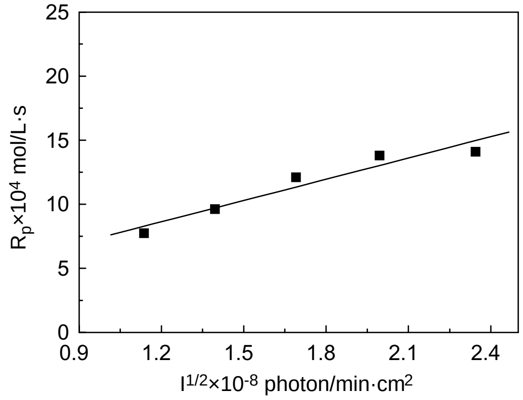
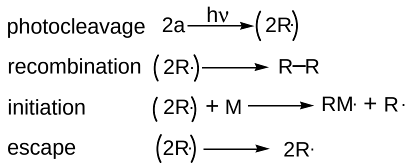


Fig. 9. Influence of light intensity on polymerization rate R_p.



Scheme 3. Photopolymerization process initiated by the complexed 2a ( ) represented the cage.

3.3.4. *Influence of the concentration of Me-β-CD*

The relationship between concentration of Me-β-CD and polymerization rate R_p was shown in Fig. 10. A level straight line was observed with varying the molar ratio of Me-β-CD/DMPA from 2:1 to 4.5:1. It was obvious that the excess of Me-β-CD in free state didn't influence the rate of the polymerization.

According to these obtained results, the kinetic equation of the polymerization of AM is $R_p=K[2a]^{0.62}[M]^{1.37}[I]^{0.5}[\text{Me-}\beta\text{-CD}]^{0}$, which quantitatively expresses the influence of complexation of Me-β-CD on the photopolymerization.

3.3.5. $k_p/k_t^{1/2}$

$k_p/k_t^{1/2}$ is a very important parameter to characterize the polymerization. For comparison, two $k_p/k_t^{1/2}$ values for the complexed photoinitiator 2a and the uncomplexed photoinitiator DMPA that were determined from the relationships of $1/P_n$ and the AM polymerization rate R_p as shown in Fig. 11 to be 4.43 and 4.75, respectively. The higher $k_p/k_t^{1/2}$ proved that the complexed 2a is a kind of efficient water-soluble photoinitiator, and is suitable for synthesizing high-molecule PAM and other polymers.

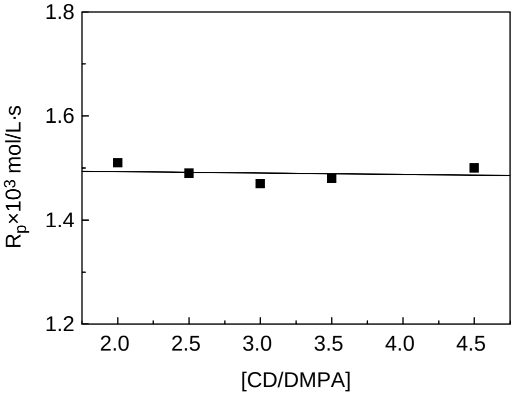


Fig. 10. Influence of Me-β-CD concentration on polymerization rate R_p.

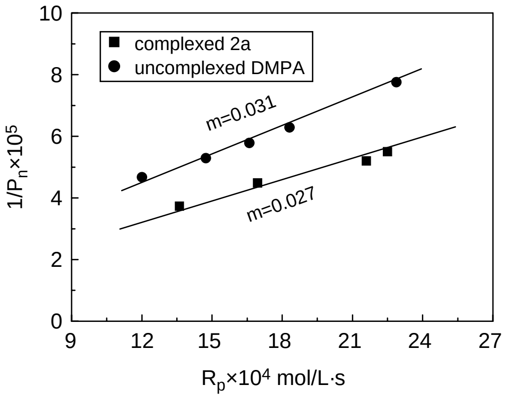


Fig. 11. The relationship between P_n and R_p.

Table 1
Data for AM photopolymerization induced by complexed initiator 2a

[2a]× 10^4 mol/L	$M_n \times 10^{-6}$	$R_i \times 10^8$ mol/L·s	$R_p \times 10^4$ mol/L·s	$\phi_p \times 10^{-4}$	ϕ_i
0.3	2.66	2.58	9.69	1.50	0.40
0.6	1.90	5.08	13.61	1.06	0.39
1.0	1.58	7.60	16.95	0.82	0.37
1.5	1.16	13.25	20.10	0.56	0.35
2.0	0.99	16.19	22.50	0.45	0.33

3.4. Quantum yield

The quantum yield ϕ was adopted to evaluate the efficiency of photopolymerization initiated by 2a. Table 1 listed the main parameters of AM photopolymerization at the different concentrations of the complexed photoinitiator 2a. For comparison Table 2 also listed the main parameters of photopolymerization for the uncomplexed photoinitiator DMPA. It can be found that the initiation quantum yield ϕ_i and the polymerization quantum yield ϕ_p were decreasing with the initiator concentration, which is a common characteristic frequently observed in the photopolymerization process, because self-quenching for excited photoinitiator molecular in solution increases with increasing concentration. Comparing the initiation quantum yield ϕ_i and the polymerization quantum yield ϕ_p for complexed 2a with uncomplexed DMPA it can be found that the quantum yield for 2a slight lower but molecular weight of product was somewhat higher. These observations were consistent with the hypothesis mentioned above that the mobility of radical was restricted by the steric effect of Me-β-CD complexation, which leaded to a decrease of the initiation rate as well as an increase of the molecular weight of products.

Table 2
Data for AM photopolymerization induced by uncomplexed initiator DMPA

[DMPA]× 10^4 mol/L	$M_n \times 10^{-6}$	$R_i \times 10^8$ mol/L·s	$R_p \times 10^4$ mol/L·s	$\phi_p \times 10^{-4}$	ϕ_i
0.4	1.52	5.61	12.01	1.39	0.65
0.6	1.34	7.69	14.54	1.20	0.64
0.8	1.23	9.60	16.60	1.08	0.62
1.0	1.13	11.52	18.31	0.96	0.61
1.5	0.92	16.78	21.65	0.72	0.56
2.0	0.73	23.40	24.71	0.57	0.55

ϕ_i, the kinetic chain numbers produced by per absorbed photon; ϕ_p, the monomer numbers participate in the photopolymerization per absorbed photon.

4. Conclusions

From the above results it was demonstrate that the host/guest complexation of Me-β-CD with hydrophobic photoinitiator DMPA gave a stable water soluble compound with high photo-reactivity and high efficiency of photopolymerization compared to the original uncomplexed DMPA. The comparative studies of photolysis and photo-polymerization kinetics for both complexed and uncomplexed photoinitiator DMPA revealed that the cage effect became important in the subsequent initiation reaction, which influences the resulting products and the kinetic process of polymerization. It is a valuable way to develop the water-soluble initiator for green chemistry.

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