



A water-soluble supramolecular structured photosensitive initiation system: Me- β -CD complex of xanthene dye/aryliodonium salt

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ABSTRACT

A water-soluble supramolecular structured photosensitive initiator (SSPI) was developed by the supramolecular self-assembling between the photosensitizer (xanthene dye) and the initiator (Complex A). The structure of SSPI was characterized by static and dynamic fluorescence quenching method. The photolysis properties of SSPI in the film were evaluated. The photopolymerization of AM and bis-AM in the film using the SSPI as the photoinitiator was also carried out. The results indicated that the SSPI formation played an important role in the photolysis and photopolymerization process. The SSPI was an efficient water-soluble photosensitive initiator.

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1. Introduction

Photopolymerization utilizes the light as the energy source to initiate the polymerization of various monomers, oligomers, and prepolymers, it has been found in many important industrial processes with a wide range of applications [1–3]. Due to the organic solvent pollution in conventional photopolymerization the nonorganic solvent processes, such as aqueous dispersed coatings, water-developable resins have received increasing attention [4,5]. Photoinitiators play an important role in the photopolymerization. Great attention has been paid to synthesize new water-soluble photoinitiators in recent years [6–10]. In general, new water-soluble photoinitiators can be developed by introducing the ionic groups such as quaternary ammonium salts, sulphonic acid, and carboxylic acids [11,12] or hydrophilic groups [13] into the oil-soluble initiators which are known to exhibit high activities in solvents. The possible disadvantage of this method is that it is always included the complicated synthesis and the direct substitution on the photoinitiator affects its photoactivity. Recently, Ritter and our group [8,9] developed a new method to get the water-soluble photoinitiators through the complexed initiator by cyclodextrin. This way is rapid and effective to get the water-soluble initiator.

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 [14–16]. Due to the special

molecular structure they are able to encapsulate the hydrophobic molecules or hydrophobic side groups of polymer as guests into their cavities to form host/guest compounds in aqueous solution and in emulsion [17–23]. This inclusion complex leads to a significant change of the solution properties and reactivities of the guest molecule, but without any chemical modification [24–34].

Aryliodonium salt is another kind of important photoinitiators in industrial applications. Several papers have reported that ion pairing and chemical bonding of the dye and onium salt can eliminate the influence by the diffusion. Thus the initiating efficiency was increased, especially in highly viscous and rigid polymeric systems [35,36]. However the ion pairing complexation cannot be used in aqueous solution because it will disassociate in the polar medium [37,38]. Recently we have found a promising approach to solve this problem by using methylated- β -cyclodextrin (Me- β -CD) to bind the dye and cointiator together to form a supramolecular complex [39]. This method has several advantages. This photoactive supramolecular complex can be easily obtained by using Me- β -CD to encapsulate the hydrophobic initiator. Then the electron transfer between dye and initiator is possible to occur in the intramolecular complex without the limitation of diffusion rate for the common bimolecular reaction. This allows for the fast photoinduced electron transfer between the dye and the initiator within the short lifetime of the dye. At the meantime the supramolecular complex eliminated the dosage of the cointiator, thus significantly reduced the material damage and toxicity from the residual photo reagents.

In this paper we reported the preparation of the water-soluble supramolecular structured photosensitive initiator (SSPI). And the

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structure of SSPI was characterized by static and dynamic fluorescence quenching method. The photochemical properties and the photoinitiation in the film for the SSPI were studied in detail. The SSPI formation can eliminate the influence of the diffusion, so it can be used as the photoinitiator in the viscous water-soluble photopolymerization resin system. It demonstrated that the SSPI was an efficient water-soluble photosensitive initiator.

2. Experimental section

2.1. Materials

Randomly methylated- β -cyclodextrin (Me- β -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), eosin (EO), rose Bengal (RB) (Beijing Chemical Reagent Co.), acrylamide (AM, Jiangxi Changjiu Biochemical Engineering Co.), bisacrylamide (bis-AM, The Institute of JinKe Fine Chemicals), hydroxypropyl methyl cellulose (HPMC, 60RT50, Repon Chemical Co., Shanghai).

2.2. Complex of Me- β -CD with DMDPI

1.56 g of Me- β -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 was dried under vacuum at 40 °C for 6 h.

2.3. Characterization of SSPI

The fluorescence measurements were carried out on a Hitachi F-4500 fluorescence spectrophotometer. Fluorescence lifetime measurements were made on a multiplexed time-correlated single-photo counting fluorometer FL900 Edinburgh Instruments Spectrometer. UV-vis spectra were recorded on a JASCOV-530 instrument.

2.4. Photolysis

The light source for photolysis was 400 W Xenon lamp (a filter was used to cut off the light with $\lambda < 300$ nm) and the intensity of irradiation was 4.82 mW/cm². In the photobleaching experiment, the film forming material was 10% HPMC aqueous solution, adding the Dye/Complex A into the solution and then poured onto the glass substrates. The film thickness was controlled to be about 47 μ m by the scraper. The samples were dried in vacuum oven for 2 h at 45 °C. The photobleaching rate was expressed by the relative change in the maximum optical density of the absorption peak at long wavelength as a function of irradiation time $R_b = (OD_0 - OD)/OD_0t$, OD_0 is the absorption of the dye before photoirradiation, OD is the absorption of the dye at time t .

2.5. Photopolymerization

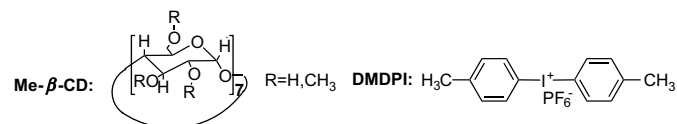
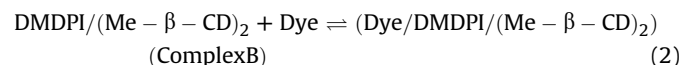
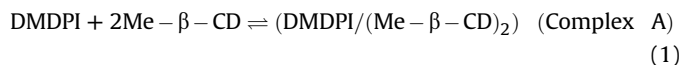
FTIR spectra were recorded on a Nicolet 5700 instrument (Nicolet Instrument, Thermo Company, USA). Series RTIR were used to determine the conversion of the one-photon polymerization. The mixture of film forming material (HPMC), monomer AM, (bis-AM), photosensitizer (xanthene dye) and initiator (Complex A) were poured onto the glass substrates. The film thickness was controlled to be about 47 μ m by the scraper. The samples dried in vacuum oven for 1 h at 30 °C and irradiated with a visible light source (CHF-XM-500W). The light intensity on the surface of samples was 30 mW/cm², which was detected by Visible Light Radiometer (400–

1000 nm, Beijing Normal University, China). The double bond conversion of the mixtures was monitored using near IR spectroscopy with the resolution of 4 cm⁻¹. The absorbance change of the =C–H peak area from 6103.69 to 6192.40 cm⁻¹ was correlated to the extent of polymerization. For each sample, the series RTIR runs were repeated three times.

3. Results and discussion

3.1. Formation and characterization of SSPI

The new supramolecular structured photosensitive initiator (SSPI) is a photoactive supramolecular complex (Complex B). Its formation includes two steps as depicted in Eqs. (1) and (2). Complex B consists of xanthene dye and arylidonium salt (DMDPI) in which xanthene dye acts as photosensitizer and DMDPI as initiator. Firstly the water insoluble DMDPI was complexed by Me- β -CD to become the water-soluble compound (Eq. (1)). Then the obtained compound (Complex A) associated with water-soluble xanthene dye via molecular reorganization to form a stable binary compound (Complex B, Eq. (2)). In previous work, we have reported that the formation Complex A through the encapsulation of Me- β -CD. The stoichiometry of host to guest is 2:1 [39]. It means that one molecule of DMDPI associates with two molecules of Me- β -CD to form a stable host/guest complex (Complex A).



The Complex B formation is examined in aqueous solution by fluorescence spectra. FL is one typical compound of xanthene dyes and is a well-known efficient fluorophore. The interaction between the excited FL dye and DMDPI is easily detected by fluorescence quenching. Fig. 1 shows the emission spectra changes of FL dye observed upon addition of Complex A and uncomplexed DMDPI for comparison. A remarkable fluorescence quenching occurs with addition of Complex A and become more significantly in range of higher concentration. But it was not observed in the case of uncomplexed DMDPI where the fluorescence intensity decreases stepwisely (Fig. 1B). Apparently this difference in spectral changes provides important evidence that the supramolecular structured complex between the photosensitizer FL and the initiator Complex A is indeed formed. And the quenching of photosensitizer FL is accelerated by the formed supramolecular complex.

The new complex formation (Complex B) between FL and Complex A means that the dynamic and static quench both existed in the solution. Systems that exhibit both types of quenching obeyed the Equation (3) [40].

$$\begin{aligned} I_0/I &= (1 + K_a[Q])(1 + K_{SV}[Q]) \\ &= 1 + (K_a + K_{SV})[Q] + K_aK_{SV}[Q]^2 \end{aligned} \quad (3)$$

Where I_0 and I are the emission intensities in the absence and presence of quencher $[Q]$, K_{SV} and K_a are the Stern–Volmer constant for dynamic quenching and static quenching. And K_a is also the association constant of the photosensitizer FL and the initiator Complex A.

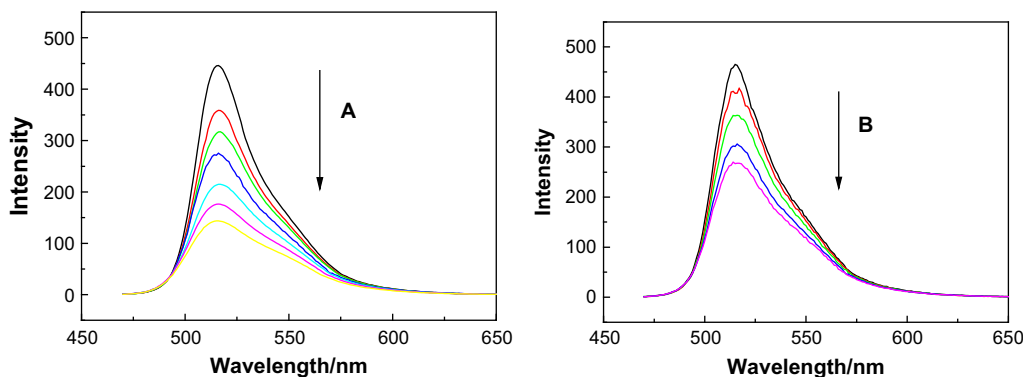


Fig. 1. Steady-state fluorescence spectra of FL dye in aqueous solution and mixed solution ($\text{CH}_3\text{OH}/\text{H}_2\text{O}=1:9$, v/v) at different concentrations of Complex A (A) and DMDPI (B). [Complex A] = 0, 3, 6, 9, 12, 14, 16×10^{-4} mol/L, [DMDPI] = 0, 3, 6, 9, 12×10^{-4} mol/L.

Based on the data K_{SV} , that was determined by using lifetime quenching measurements to be 174 M^{-1} . K_a value was obtained from the modified Stern–Volmer equation. The plot of $(I_0/I - 1)/[Q]$ versus $[Q]$ is shown in Fig. 2. Plotting $(I_0/I - 1)/[Q]$ versus $[Q]$ gives $(K_a + K_{SV})$ as the intercept and $K_a K_{SV}$ as the slope of the graph. A good linear relationship was observed confirming a complex formation between the photosensitizer FL and the initiator Complex A in ground state. The association constant K_a obtained from the plot is 145 M^{-1} in aqueous solution. From these results above it can be considered that the SSPI (Complex B) was obtained from the static charge interaction of the anionic FL dye and cationic onium DMDPI and further stabilization by Me- β -CD complexation.

3.2. Photochemical reaction of SSPI in film

Usually, the photosensitized reaction involves bimolecular electron transfer or energy transfer [38]; the reaction is controlled by diffusion so that, in solid and viscous media with low molecular mobility, it cannot occur effectively within the short lifetime of the excited state. In order to avoid this problem, the photosensitizer and initiator are pre-assembled by ion pairing and chemical bonding of the dye and onium salt. But this method is always included the complicated synthesis and always can be only used in the organic solvent system. Through the complexation of the cyclodextrin we got the water-soluble supramolecular structured photosensitive photoinitiator. In this section the photochemical property of SSPI in film was evaluated.

The SSPI is a photoactive compound in which the light absorber (the photosensitizer: xanthene dye) acts as electron donor and the

photoinitiator (DMDPI) acts as electron acceptor. The diffusion controlled intermolecular reaction hardly occurred within the very short lifetime of S_1 state ($<10^{-9}$ s). So the SSPI formation will decrease the diffusion effect and increase the initiating efficiency. Upon irradiation of visible light they easily undergo fast electron transfer from excited FL to onium DMDPI resulting in the aryl radical along with dye photobleaching. The photosensitized photolysis processes are illustrated in Scheme 2.

The primary electron transfer between excited FL dye and DMDPI was studied by using dynamic fluorescence quenching method. The Stern–Volmer plot obtained from the FL dye excited lifetime measurement, as is shown in Fig. 3, it is level over the whole concentration range of quencher Complex A. The results indicated that there is only the static quenching process via the Complex B in the film. The dynamic quenching via bimolecular collision controlled by diffusion process is excluded in the case of film. To evaluate the effect of electron transfer due to the formation Complex B we measured the quantum efficiency of electron transfer in film by using the dynamic fluorescence. In Table 1, the ratio of Complex B ($f_c = K_a[\text{Complex A}]$) and the quantum efficiency of electron transfer of Complex B (ϕ_c) in film were presented. From the result we can find with the increasing ratio of Complex B, the quantum efficiency of electron transfer also increased. It indicated the formation of Complex B played an important role for the electron transfer from the dye to initiator.

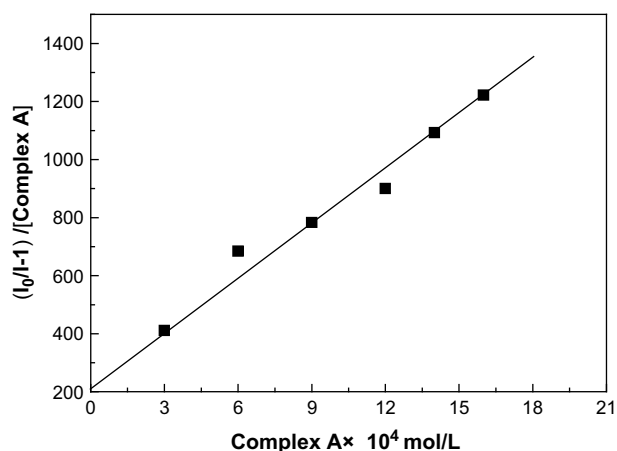


Fig. 2. Plot of $(I_0/I - 1)/[\text{Complex A}]$ versus $[\text{Complex A}]$.

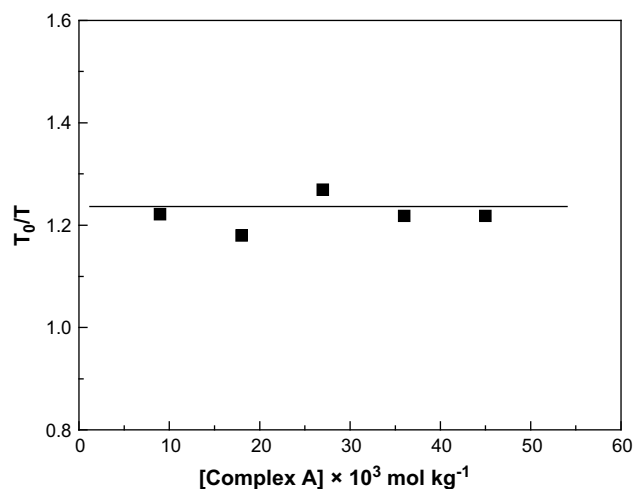


Fig. 3. Plot of τ_0/τ versus concentration of Complex A, $[\text{FL}] = 4.5 \times 10^{-3}$ mol/kg, $[\text{Complex A}] = 4.5 \times 10^{-3}$ mol/kg, 9×10^{-3} mol/kg, 13.5×10^{-3} mol/kg, 22.5×10^{-3} mol/kg, 45×10^{-3} mol/kg.

Table 1
The quantum efficiency of electron transfer of Complex B in film.

Complex A (mol/L)	1×10^{-3}	2×10^{-3}	3×10^{-3}	4×10^{-3}	5×10^{-3}
f_c	0.145	0.29	0.435	0.58	0.725
φ_c	0.345	0.455	0.490	0.555	0.584

f_c : The ratio of Complex B in film.

φ_c : The quantum efficiency of electron transfer of Complex B in film.

The photoreactions of SSPI were further studied by the photobleaching experiments. A series of photobleaching experiments were carried out in the HPMC film by monitoring the dye disappearance and some important influences are discussed.

The influence of molar ratio of FL dye to Complex A on the photobleaching rate at constant FL concentration of 4.5×10^{-4} mol% was examined in HPMC film in Fig. 4 and the inset. Remarkable rate enhancement was observed with increasing concentration of Complex A but no FL photobleaching occurred in the absence of DMDPI. These results demonstrated that the SSPI formation is a key factor that determines whether the fast electron transfer photosensitized reaction between FL and DMDPI is possible via intramolecular interaction route within very short lifetime of FL excited state. Therefore, the lower molar ratio of FL/Complex A the higher formation of Complex B and the larger photobleaching rate is observed. In the practical application a larger amount of residual initiator in the product is unfavorable. Thus a proper molar ratio of 1:2, which provide a satisfactory rate is proposed and used in following studies.

The influence of SSPI concentration on the photobleaching rate when the molar ratio of FL/Complex A is kept constant of 1:2 is depicted in Fig. 5. A remarkable rate enhancement was found in the lower concentration range then derives from the linear and drops as concentration increased. This phenomenon common observed in the photosensitization reaction system is attributed to the internal light screening effect as optical density of photosensitizer in higher level resulting in a reduction of photosensitization efficiency.

The influence of halogen substitution of fluorescein dye such as tetrabromofluorescein (eosin EO) and tetraiodo-tetrachlorido-fluorescein (rose Bengal RB), on the photobleaching rate is also studied in film. The chemical structure of the dyes is shown in Scheme 1. As shown in Fig. 6 the photobleaching rate R_b are in the order FL > EO > RB. Obviously the halogen atom substitutes in the skeleton of the fluorescein dye, especially in the *ortho* position of phenoxy group of FL, will play an important role in the electron transfer. The higher the electrophilic effect of the halogen atoms,

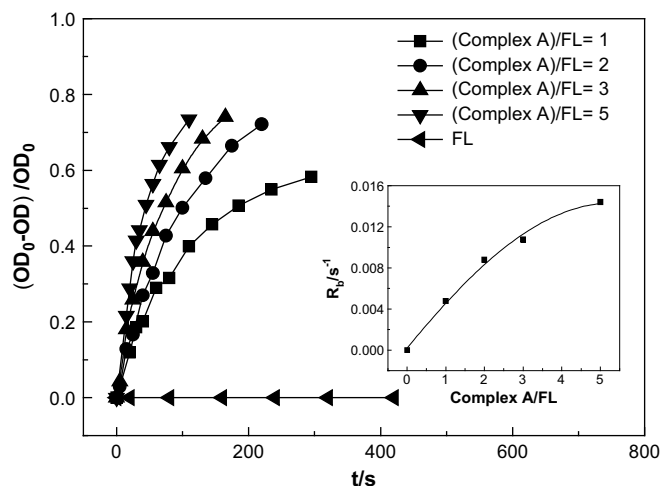


Fig. 4. Photobleaching rate as the function of Complex A/FL ratio. (Complex A)/FL = 1, 2, 3, 5.

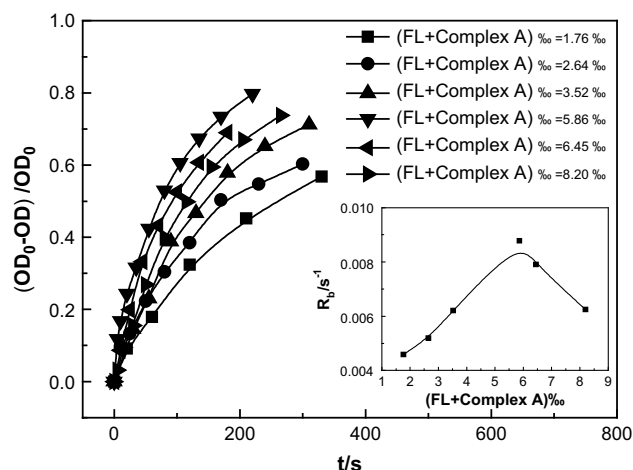
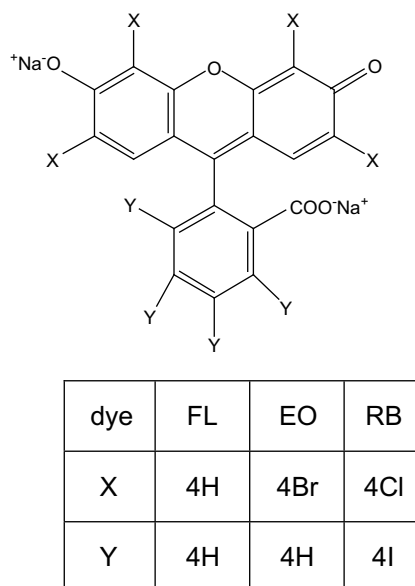


Fig. 5. Photobleaching rate as a function of total concentration of FL/Complex A at fixed molar ratio of 1:2.

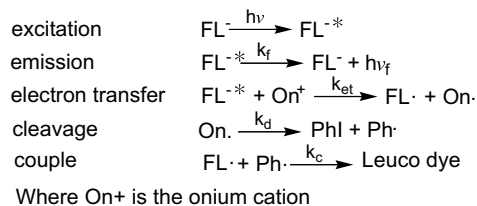
the lower the electron cloud density on the phenoxy anion, and thus the electrostatic attraction of the phenoxy anion to the DMDPI gradually decreases from FL to RB. In addition, the steric hindrance, depending on the size of the halogen substituent, increases the distance between cation and anion. The above two factors may decrease the degree of orbital overlap and weaken the interaction between donor and acceptor. As a result, xanthene dyes with halogen atom substituents have the slower photobleaching rates. These results were also observed in the ion-pair complex as reported by authors previously [37,38].

3.3. Photoinitiation of SSPI

As presented above the SSPI can occur efficiently the photoinduced electron transfer in film. So they could be utilized as an effective photoinitiator for water-soluble photopolymerization resin systems. The electron transfer from the photosensitizer FL dye to the photoinitiator DMDPI generates active radical initiating the polymerization. In this section photoinitiating effect of the SSPI in



Scheme 1. Chemical structure of FL, EO, RB.



Scheme 2. The main photosensitized photolysis process of FL/aryliodonium salt.

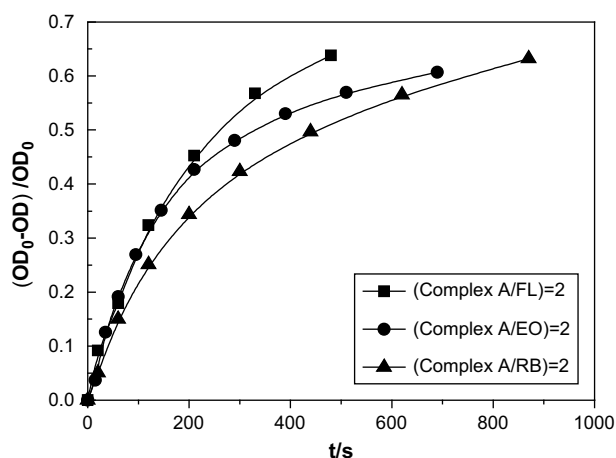


Fig. 6. Photobleaching rate of different halogen substituted xanthenes.

the film was evaluated. Fig. 7 shows the kinetic results recorded during the photoinitiated polymerization performed in film of HPMC consisted of acrylamide (AM)/bisacrylamide (bis-AM) in molar ratio of 9:1 in the presence of SSPI. FL/Complex A at fixed molar ratio of 1:2 employing FT-RTIR spectroscopy to monitor the kinetic of disappearance of the double bonds of the monomers under polymerization. The conversion of the monomer is lower than that is because the photopolymerization was carried out in the film at air. The movement of the monomer was restricted and the radicals can be easily quenched by the oxygen.

In order to confirm the important role of SSPI formation in the photoinitiated polymerization in film, the comparison study was accomplished by using Complex A and DMDPI as photoinitiator in

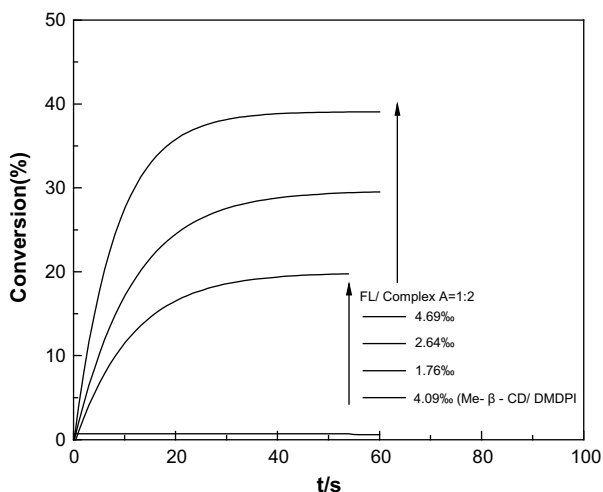


Fig. 7. Photopolymerization rate as a function of concentration of SSPI.

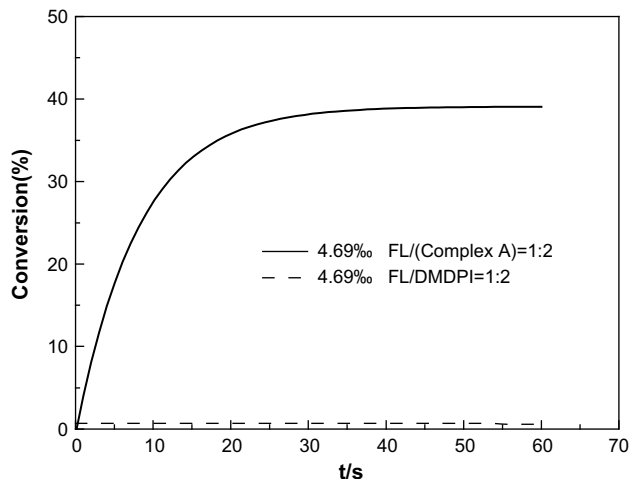


Fig. 8. Photopolymerization rate of FL/Complex A and FL/DMDPI system.

combination with the FL dye as photosensitizer. The data presented in Fig. 8 demonstrates that the polymerization occurs only in the case of utilizing Me- β -CD complexed DMDPI whereas no polymerization appeared as uncomplexed DMDPI used.

This result indicates SSPI is an effective photoinitiator for free radical polymerization. Within 20 s the photosensitized polymerization proceeds to their plateau conversion. The analysis of the kinetic curves indicates the photopolymerization rate and maximum conversion substantially increase as initiator concentration increased, but no polymerization takes place as photoinitiator DMDPI used solely. It is evident that FL dye displays very good electron transfer photosensitizing characteristics for onium DMDPI photoinitiator in the Me- β -CD complex form in which donor-acceptor pairing enhances the rate of free radical generation.

In Fig. 9 it is shown an evaluation of the photosensitizing abilities of three substituted fluorescein derivatives bearing different halogen atoms. It can be seen that these xanthenes dyes such as FL, EO and RB all display an effective photosensitizer for onium salt photoinitiator. The order of efficiency in photosensitive polymerization was obtained from values of R_p at some concentration $FL > EO > RB$. The substituted influences are consistent with the results described above due to the electron-withdrawing and steric negative effect.

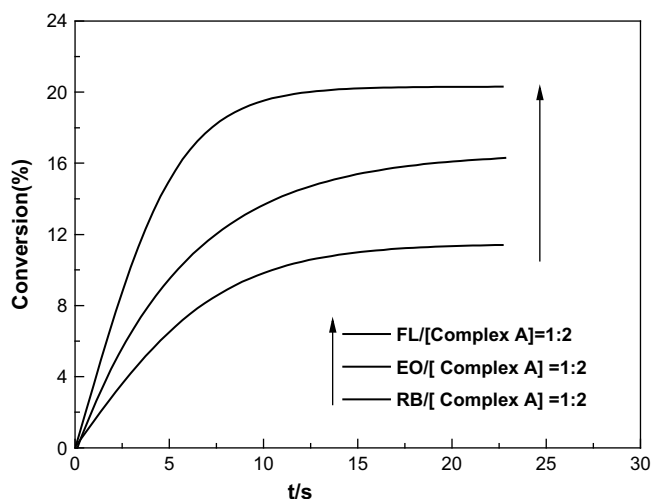


Fig. 9. Photopolymerization of AM and bis-AM initiated by xanthenes/Complex A. $[xanthenes] = 4.5 \times 10^{-3} \text{ mol kg}^{-1}$, $[Complex A] = 9 \times 10^{-3} \text{ mol kg}^{-1}$.

In conclusion we have developed a kind of water-soluble supramolecular structured photosensitive initiator (SSPI). In the initiation system we employed both commercial photosensitizer xanthene dye and photoinitiator DMDPI in which two functional components are assembled together with the help of Me- β -CD. The obtained SSPI can initiate the monomer AM and bis-AM photopolymerization in the film. The results indicated the SSPI can be used as the photoinitiator in the water-soluble photo resist system. This technique provides a new way to develop the water-soluble photosensitive initiator.

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