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Host/guest complex of β -cyclodextrin/5-thia pentacene-14-one for photoinitiated polymerization of acrylamide in water

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ABSTRACT

β -Cyclodextrin (β -CD) was used to complex the photoinitiator, 5-thia pentacene-14-one (TX-A), yielding a water-soluble host/guest complex. IR, UV-Vis and fluorescence spectroscopy were employed to characterize complexed β -CD/TX-A. Photoinitiated polymerization of acrylamide in water was achieved with β -CD/TX-A in the presence of *N*-methyl-diethanolamine (MDEA). Excellent polymerization yields were observed in air saturated solutions when MDEA was added.

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1. Introduction

Cyclodextrins (CDs) are cyclic oligosaccharides built from six, seven, eight or nine optically active glucopyranose units (α -CD, β -CD, γ -CD or δ -CD, respectively) with a hydrophobic cavity and hydrophilic exterior [1]. Because of their special molecular structure, these molecules have the capability to enclose small hydrophobic molecules into their cavity and consequently to form host/guest compounds in aqueous solution and in emulsion [2–5].

Photoinitiated free radical polymerization is a well-accepted technology which finds industrial application in coatings on various materials, adhesives, printing inks and photoresists [6–10]. Environmental issues involving conventional organic solvents are one of the major concerns in such applications. Photopolymerization in aqueous solution is a highly effective approach using water instead of organic solvents. Pioneering work by Ritter demonstrated that hydrophobic vinyl monomers became water soluble due to the inclusion/complexation of CD and can easily be polymerized in aqueous solution in the presence of a water-soluble thermal free radical initiator [11]. During polymerization, the CD gradually slipped off from the growing chain and remained in an aqueous phase. The concomitantly precipitated polymer was obtained in high yields. Photoinitiators play a vital role in photopolymerization as they generate initiating species upon photolysis. The same

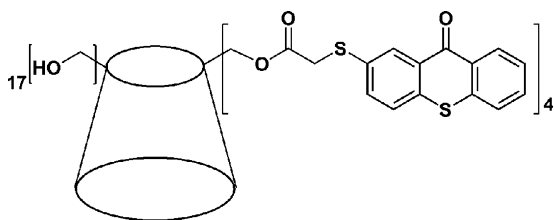
research group also showed that the complexation of a *Type I* (α -cleavage) photoinitiator, namely 2-hydroxy-1-phenylpropan-1-one, with methylated β -CD (Me- β -CD) results in the formation of a water-soluble host/guest complex [12]. Compared to the bare photoinitiator, this complex exhibited a much higher initiation efficiency in the polymerization of the water-soluble monomer, *N*-isopropylacrylamide [12]. In another study, Li et al. [13] demonstrated that the host/guest complexation of Me- β -CD with the more hydrophobic photoinitiator, 2,2-dimethoxy-2-phenyl acetophenone (DMPA), gave a stable water-soluble compound with high photoactivity and the same efficiency of polymerization. Yin et al. also prepared a similar water-soluble supramolecular-structured photoinitiator between Me- β -CD and DMPA. The efficiency of Me- β -CD/DMPA was found to be a more efficient photoinitiator than DMPA [14].

We reported previously the photoactivity of TX groups chemically attached to β -CD and their efficiency in the photopolymerization of methyl methacrylate (MMA) which can form a host/guest complex with these molecules [15] (see Scheme 1).

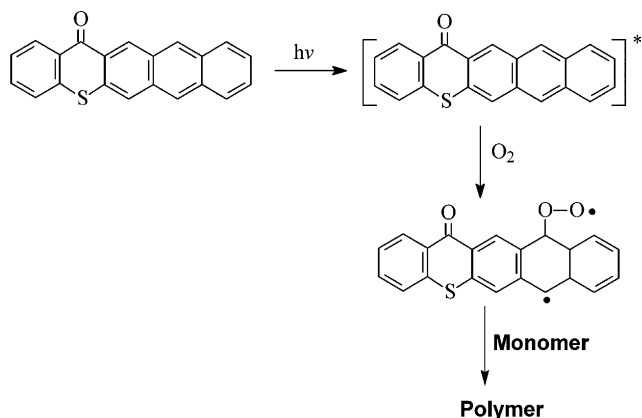
As a continuing interest in synthesizing novel photoinitiators, thioxanthone-anthracene (TX-A), namely 5-thia-pentacene-14-one, possessing respective photochromic groups was synthesized and it was found that TX-A is an efficient photoinitiator for free radical polymerization of acrylic and styrenic type monomers in the presence of oxygen (see Scheme 2) [16].

UV-Vis, FT-IR and fluorescence spectroscopic and polymerization studies revealed that photoinitiation occurs through the anthracene chromophore. In contrast to thioxanthone based

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Scheme 1. Structure of thioxanthone- β -cyclodextrin (TX- β -CD).



Scheme 2. Photoinitiated free radical polymerization by using thioxanthone-anthracene (TX-A).

photoinitiators, TX-A does not require an additional hydrogen donor for the initiation.

In this study, TX-A was used as initiator and prepared as an inclusion complex with β -CD in water. The photoinitiated polymerization of acrylamide with β -CD/TX-A complex was achieved in an air atmosphere.

2. Experimental part

2.1. Materials

β -Cyclodextrin (Aldrich) and *N*-methyldiethanolamine (MDEA) (Aldrich), acrylamide (AAm, 97%, Merck) and methanol (Merck) were used as received. 5-Thia pentacene-14-one (TX-A) was prepared as indicated in literature [16]. Distilled water was used as solvent for acrylamide polymerization.

2.2. Complexation of photoinitiator

0.57 g (0.5 mmol) of β -CD was dissolved in 100 mL of distilled water in 50 °C and 0.0312 g (0.1 mmol) of photoinitiator was added. The colorless dispersion was sonicated for 30 min yielding a clear yellow solution of the complexed photoinitiator. The host/guest complex was prepared with β -CD/TX-A molar ratios of 5:1; 10:1; 50:1 and 100:1, respectively.

2.3. Photopolymerization in water

Appropriate solutions of the acrylamide (1.0 M) as monomer and the host/guest complex of β -CD/TX-A in water with MDEA were irradiated in an air atmosphere in a photoreactor consisting of a 400 W medium pressure mercury lamp and a water cooling system. Polymers were obtained after precipitation in methanol and drying *in vacuo*. Conversions for all samples were calculated gravimetrically.

2.4. Characterization

Gel permeation chromatography (GPC) measurements were performed at room temperature with a setup consisting of a pump (HP 1050), a refractive index detector (HP 1047 A), and three high resolution Waters columns (AQ3.0, AQ4.0 and AQ5.0). The effective molecular weight ranges were 1000–60,000, 10,000–400,000 and 50,000–4,000,000, respectively. Water was used as eluent at a flow rate of 0.5 mL/min at room temperature. Data analyses were performed with HP Chemstation Software. Calibration with linear polyethylene oxide standards (Polymer Laboratories) was used to estimate the molecular weights. UV–Vis spectra were taken on an Agilent 8453. Fluorescence spectra were recorded on a Jobin Yvon–Horiba Fluoromax-P.

3. Results and discussion

TX-A is a novel oil soluble photoinitiator and it turned out to be fully water soluble after complexation with β -CD. Several methods were applied to the characterization of β -CD/TX-A complex.

The IR spectrum indicated the formation of β -CD/TX-A complex. Comparing the spectra of TX-A with the complexed β -CD/TX-A it became obvious that the characteristic signal for the carbonyl group of TX-A had significantly shifted to higher frequencies (from 1630 to 1651) due to the influence of the β -CD host component [12].

The UV spectra of TX-A in DMF and the complexed β -CD/TX-A in water, are given in Fig. 1. UV–Vis absorption spectra of both uncomplexed TX-A and complexed β -CD/TX-A proved the inclusion complex (see Fig. 1).

As can be seen from Fig. 1, the absorption spectra had similar spectral shapes and lower intensity. Fluorescence spectroscopy was also employed to characterize the inclusion complex of β -CD/TX-A. The emission spectrum represents the characteristics of the anthracene moiety rather than thioxanthone (see Fig. 2).

We used Benesi–Hildebrand's method to obtain information on the stoichiometry of the β -CD/TX-A complex [17–19]. The enhancement of the fluorescence intensity was measured as a function of host concentration, while the total concentration of TX-A remained constant. It is interesting to note that the increase in fluorescence intensity of TX-A with increasing β -CD concentration is attributed to the incorporation of TX-A into the nonpolar cavity. The enhancement of fluorescence intensity was observed up to a certain concentration of CD; with further increases of host concentration, some errors occurred (see Fig. 3).

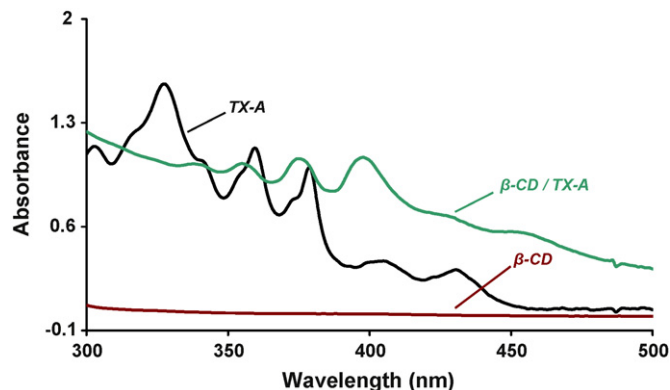


Fig. 1. Absorption spectra of TX-A [1×10^{-4} mol L $^{-1}$] in DMF and β -CD/TX-A complex [2×10^{-4} mol L $^{-1}$] and β -CD [1×10^{-3} mol L $^{-1}$] in water.

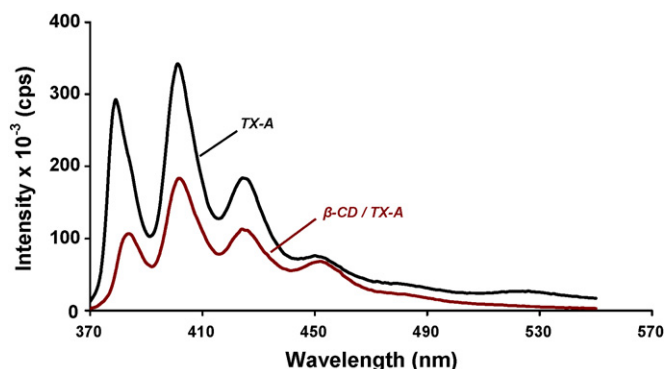


Fig. 2. Fluorescence spectra of TX-A [1×10^{-4} mol L $^{-1}$] in DMF and β -CD/TX-A [2×10^{-4} mol L $^{-1}$] complex in water $\lambda_{\text{exc}} = 360$ nm.

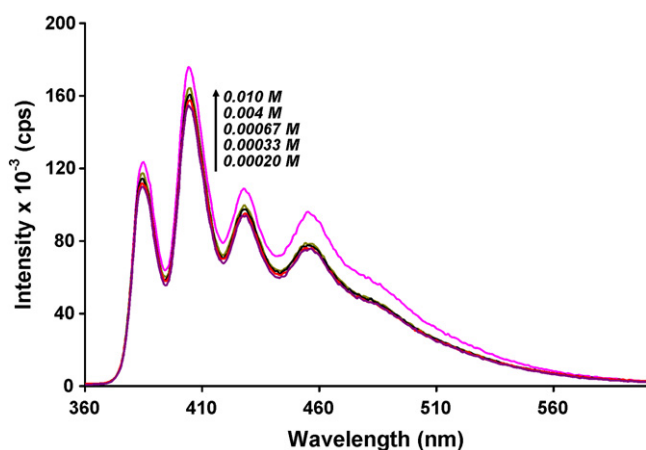


Fig. 3. Effect of β -CD on the fluorescence spectrum of TX-A [1×10^{-3} mol L $^{-1}$] in DMSO.

The data in Fig. 4 can be treated using the Benesi–Hildebrand equation for 1:1 (Eq. (1)) binding model or 2:1 model (Eq. (2)).

$$\frac{1}{I - I_0} = \frac{1}{I_1 - I_0} + \frac{1}{(I_1 - I_0)K[\beta - \text{CD}]} \quad (1)$$

$$\frac{1}{I - I_0} = \frac{1}{I_1 - I_0} + \frac{1}{(I_1 - I_0)K[\beta - \text{CD}]^2} \quad (2)$$

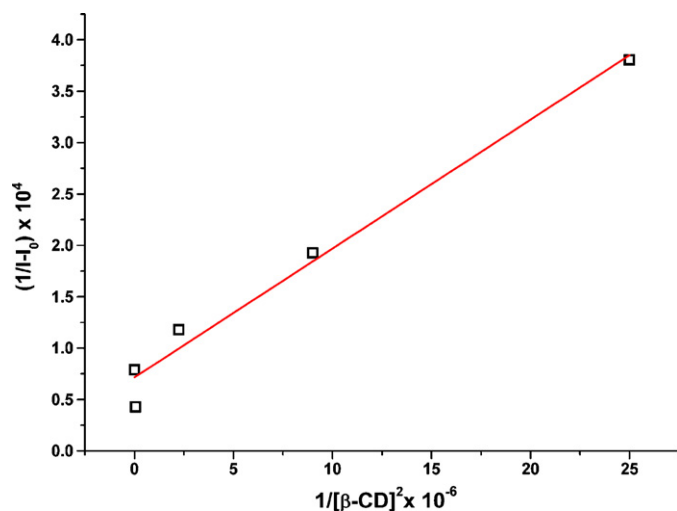


Fig. 4. The Benesi–Hildebrand plot of $1/(I - I_0)$ vs. $1/[\beta\text{-CD}]^2$.

Table 1

Photoinitiated polymerization of acrylamide with β -CD/TX-A complex in water

[TX-A] (mol L $^{-1}$)	$[\beta\text{-CD}]$ (mol L $^{-1}$)	Conversion (%)	$M_n^a \times 10^{-4}$ (g mol $^{-1}$)	M_w/M_n^a
5.0×10^{-5}	5×10^{-3}	50.9	18.9	2.44
1.0×10^{-4}	5×10^{-3}	24.8	12.7	3.75
5.0×10^{-4}	5×10^{-3}	24.8	11.5	4.02
1.0×10^{-3}	5×10^{-3}	14.0	9.6	4.25

t_{irr} : 15 min. [MDEA]: 5×10^{-3} mol L $^{-1}$.

^a Determined by GPC using polyethylene oxide standards. [Aam] = 1.0 M.

where I and I_0 are the initial fluorescence intensities of TX-A in the presence and absence of CD, respectively, and I_1 is the expected fluorescence intensity when all quest molecules are included in a complex. According to Eq. (2), a plot of $1/I - I_0$ versus $1/[\beta\text{-CD}]^2$, produces a good straight line (Fig. 4), from which K was calculated to be 5.6×10^6 M $^{-1}$. The linearity in the plot ($R^2 = 0.98$) reflects the formation of a 2:1 complex between β -CD and TX-A. The linearity of the plot obtained from Eq. (1) was not very satisfying, hence the possibility of a 1:1 complex formation is ruled out.

The resulting homogenous aqueous reaction mixture, included β -CD/TX-A complex and *N*-methyl diethanolamine as co-initiator for the polymerization of acrylamide in water, using a medium pressure mercury lamp as the polychromatic light source for irradiation (see Table 1).

Photoinitiated polymerization of AAm in water with β -CD/TX-A was not achieved in an air atmosphere compared to TX-A itself. There is no similarity in the polymerization results between uncomplexed TX-A and complexed β -CD/TX-A. Previously, it was found that TX-A is an efficient photoinitiator for the polymerization of methyl methacrylate and styrene in the presence of oxygen without a co-initiator such as MDEA [16], in contrast to thioxanthone types of photoinitiators.

According to the results obtained from IR, UV–Vis and fluorescence spectroscopy, the anthracene part seems to be included in the CD cavity and the phenyl group on the other side of the carbonyl was trapped with another CD, and the carbonyl group as a photoactive site is situated in the exterior of the cavity of cyclodextrin.

The highest conversion percentage values were obtained especially at low initiator concentrations of complex (see Table 1). The increase of the concentration of the photoinitiator led to a decrease in the conversion percentage. High concentrations of photoinitiator may lead to an absorption of light in the upper region of the film or solution, which decreases the rate of polymerization due to radical termination. Also if the light does not penetrate the whole film or solution, radical production will not occur in all of the polymerizable material [20–22]. Polymerization in water did not occur in air atmosphere without adding MDEA to the solution of complex. Therefore, additional photopolymerization studies using β -CD/TX-A complex in H $_2$ O and D $_2$ O were also performed in air atmosphere (see Table 2).

Anthracene derivatives are known to form instable endoperoxides upon irradiation. These endoperoxides decompose through

Table 2

Photoinitiated polymerization of acrylamide with β -CD/TX-A complex in H $_2$ O and D $_2$ O

Run	[AAm] (mol L $^{-1}$)	D $_2$ O Conv. %	H $_2$ O Conv. %	[MDEA] (mol L $^{-1}$)
1	1	1.2	–	–
2	1	67.5	50.9	5×10^{-3}
3	0.5	–	–	–
4	0.5	36.0	32.0	5×10^{-3}
5	0.25	–	–	–
6	0.25	10.3	<1	5×10^{-3}

t_{irr} : 15 min. [TX-A]: 5×10^{-5} M, $[\beta\text{-CD}]$: 5×10^{-3} M.

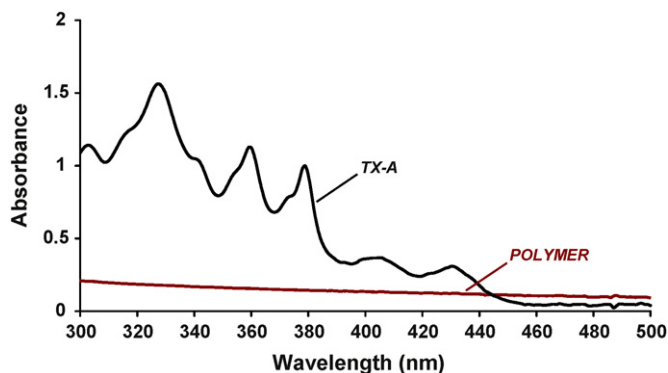
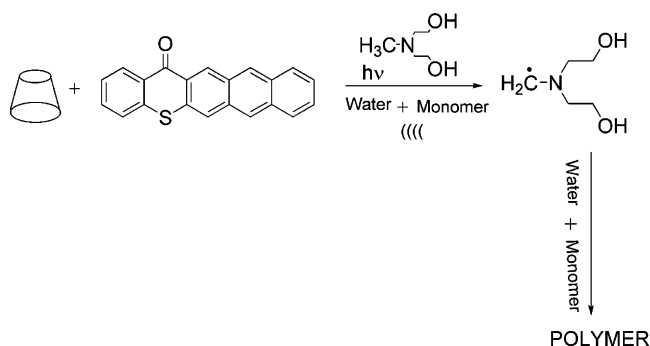


Fig. 5. Absorption spectra of TX-A [1×10^{-4} mol L $^{-1}$] in DMF and poly-(acrylamide) obtained by photoinitiated polymerization of AAm with β -CD/TX-A complex in water.



Scheme 3. Photoinitiated free radical polymerization of acrylamide with β -CD/TX-A complex in the presence of MDEA in water.

radical intermediates, which could initiate the polymerization of the monomers. It is known that singlet oxygen lives much longer in deuterated solvents (D_2O) [23,24]. As can be seen from Table 2, at 1 M concentration of AAm, polymerization occurred without adding MDEA to the D_2O solution. When amine was added to the formulation, a higher conversion percentage value was obtained compare to H_2O solution. When low monomer concentration was used, no polymer was obtained in the absence of MDEA. But higher conversion percentage values, for various monomer concentrations, were obtained for photopolymerization of complex in D_2O . The oxygen concentration in water is about one order of magnitude lower than in regular organic solvents so oxygen quenching should be slower, and less singlet oxygen is formed in water. In addition, the lifetime of singlet oxygen in water is much shorter than in most other organic solvents. Hence, the chance of reaction of singlet oxygen with the anthracene to form the endoperoxide is much lower. The obtained results confirmed this (see Table 2).

Furthermore, the 9,10 position of the anthracene could be shielded by the CD so that endoperoxide formation is hindered.

As a result, the complex β -CD/TX-A exhibited a different photoinitiation mechanism compared with the uncomplexed TX-A. Indeed, the UV-Vis spectrum of the resulting poly-(acrylamide) confirmed that the photoinitiator (TX-A) was not attached to the polymer and the possible initiating radical is an α -aminoalkyl radical (see Fig. 5).

The carbonyl group of complexed β -CD/TX-A abstracted hydrogen from the tertiary amine (MDEA) and resulted in α -aminoalkyl radical initiated polymerization of the acrylamide and the proposed mechanism is given in Scheme 3.

In conclusion, from the results, it was demonstrated that host/guest complexation of β -CD with hydrophobic photoinitiator TX-A gave a stable water-soluble complex with high photoinitiation reactivity. The initiation mechanisms, uncomplexed and complexed TX-A, were different from each other; complexed TX-A with β -CD initiates polymerization of acrylamide according to a Type II mechanism. In contrast, uncomplexed TX-A initiated polymerization of MMA in the presence of oxygen and possibly via endoperoxide formation.

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