

Photoinitiated polymerization of β -cyclodextrin/methyl methacrylate host/guest complex in the presence of water soluble photoinitiator, thioxanthone-catechol-O,O'-diacetic acid

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Abstract β -Cyclodextrin (β -CD) was used to complex the monomer, methyl methacrylate (MMA), yielding a water-soluble host/guest complex. Photoinitiated polymerization of β -CD/MMA complex was achieved in the presence of thioxanthone-catechol-O,O'-diacetic acid (TX-Ct), a one component water soluble photoinitiator. Photodecarboxylation of TX-Ct in water seems to be an important reaction mechanism. Therefore, resulting alkyl radicals are able to initiate the polymerization of β -CD/MMA host/guest complex in water.

Keywords Photopolymerization · Free radical polymerization · β -Cyclodextrin · Thioxanthone · Water soluble photoinitiator

Introduction

Cyclodextrins (CDs), are macrocyclic oligosugars most commonly composed of 6, 7, or 8 glucosidic units bearing the names α -, β - and γ -CD, respectively [1–4]. CDs, which have an inner cavity with a defined diameter, recognize specific organic molecules (guests) by their sizes and accept them into the cavity to form the corresponding inclusion complexes in aqueous solution and in emulsion [2–9].

Photoinitiated free radical polymerization is of enormous commercial importance. Techniques such as curing of coatings on various materials, adhesives, printing inks, and photoresists are based on photoinitiated radical vinyl polymerization [10–14]. 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 the 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 [5]. During polymerization, the CD gradually slipped off from the growing chain and has remained in the aqueous phase. The concomitantly precipitated polymer has been obtained in high yields.

Ritter et al. 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 [15]. Compared to the bare photoinitiator, this complex exhibited much higher initiation efficiency in the polymerization of the water soluble monomer, *N*-isopropylacrylamide [15]. In another study, Li et al. [16] 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. Efficiency of Me- β -CD/DMPA was found to be a more efficient photoinitiator than DMPA [17]. The photoactivity of TX groups chemically attached to β -CD and their efficiency in the photopolymerization of methyl methacrylate

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(MMA) which can form a host/guest complex with these molecules were reported [18]. Complexation of a novel photoinitiator namely Thioxanthoneanthracene with β -CD was reported and photopolymerization of acrylamide was achieved with TX-A/ β -CD inclusion complex [19].

Photoinitiators are very important constituents of photopolymerizable formulations and among these initiators, thioxanthone (TX) derivatives have recently received a revitalized interest because of their absorption characteristics at near UV range.

The acetic acid derivatives of thioxanthone as a one component initiator (TXOCH₂COOH, TXSCH₂COOH) were reported in our previous study [20, 21]. The light absorbing and electron donating sites are contained in the photoinitiator molecules. The initiation mechanism of this one-component nature initiators involved intramolecular electron transfer followed by hydrogen abstraction and decarboxylation [20, 21] (see Scheme 1).

In our previous study, TXOCH₂COOH as the monofunctional initiator has been used for the photopolymerization of

MMA in DMF [20]. Unfortunately, the solubility of TXOCH₂COOH in water for this study is limited.

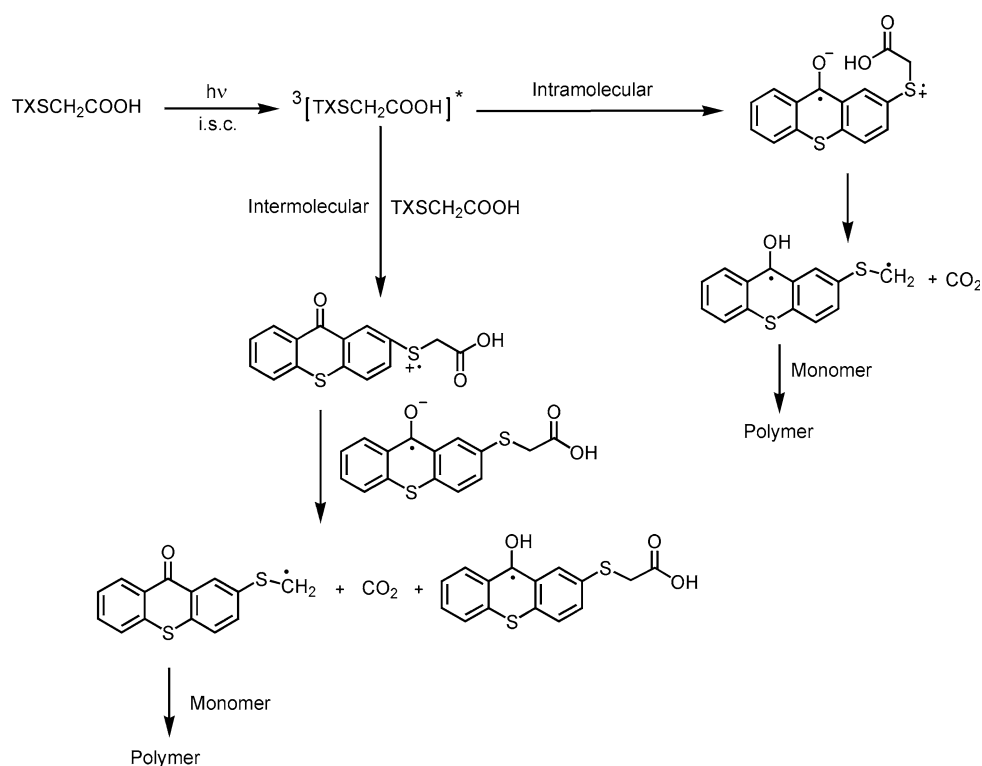
Therefore, a novel water soluble thioxanthone-based photoinitiator, namely, 3-carboxymethoxy-9-oxo-9H-thioxanthene-2-yloxy)-acetic acid (TX-Ct, thioxanthone O,O'-diacetic acid) was synthesized and used in the photoinitiated polymerization of a water soluble β -CD/MMA complex as photoinitiator.

Experimental part

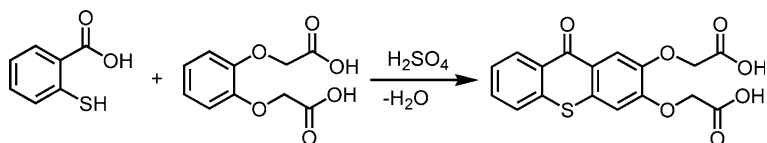
Materials

β -Cyclodextrin (Aldrich), *N*-methyl-diethanol amine (MDEA, Aldrich), and methanol (Merck) were used as received. Methyl methacrylate (MMA) was obtained from Merck and purified by conventional drying and distillation procedures.

Scheme 1 Intramolecular and intermolecular hydrogen abstraction mechanism of thioxanthone acetic acid derivatives as one component type II photoinitiator



Scheme 2 Synthesis of TX-Ct



Synthesis of thioxanthone-catechol-O,O'-diacetic acid (TX-Ct)

Thiosalicylic acid (0,32 g, 2.0 mmol) was slowly added to concentrated sulfuric acid (15 mL) in the ice bath, and the mixture was stirred for 5 min to ensure thorough mixing. Catechol-O,O'-diacetic acid (1.35 g, 6.0 mmol) was added slowly to the stirred mixture over a period of 30 min. After the addition, the reaction mixture was stirred at room temperature for 3 days, after which it was left to stand at room temperature overnight. The resulting mixture was poured carefully with stirring into cold water and a yellow colored product was obtained (see Scheme 2) [22].

Yield: 80%, m.p.: 210 °C. C₁₇H₁₂O₇S (360 g mol⁻¹): C, 56.66%; H, 3.36%; S, 8.90%. Found, C, 55.84%; H, 3.54%; S, 9.09%. ¹H NMR (DMSO, 250 MHz) δ ppm: 8.46-7.38 (m, 6H, aromatic), 4.96 (s, 2H, CH₂), 4.87 (s, 2H, CH₂); IR (KBr): 3413, 2923, 1732, 1717, 1593, 743 cm⁻¹. ¹³C NMR (DMSO, 50 MHz) δ ppm : 177.28 (C=O), 169.75 (C=O),

169.30 (C=O), 151.85-109.02 (m,aromatic), 65.05 (CH₂), 64.98 (CH₂).

Complexation of monomer

0.14 g (0.125 mmol) of β-CD was dissolved in 25 mL of distilled water and 0.125 g (1.25 mmol) of monomer was added. The colorless dispersion was sonicated for 30 min yielding a single phase solution of the complexed monomer.

Photopolymerization in water

Various concentrations of the TX-Ct as photoinitiator and the host/guest complex of β-CD/MMA in water were irradiated for 15 min in the absence and presence of MDEA in air atmosphere in a photoreactor consisting of a 400 W medium pressure mercury lamp and a water cooling system (light intensity: 300 W/m²). Polymers precipitated during polymerization, but to complete this one drop of hydrochloric acid was added. After subsequent filtration the polymers were dried in vacuum. Conversions for all samples were calculated gravimetrically.

Analysis

Gel permeation chromatography (GPC) analyses of the polymers were performed at room temperature with a setup consisting of a pump (Agilent 1100), a refractive index detector (Agilent 1100 s), and three high-resolution Zorbax PSM columns (60S, 300S, and 1000S; size: 6.2 × 250 mm; particle size: 5 μm). The effective molecular weight ranges were 500–10,000, 3000–300,000, and 10,000–1,000,000 g/mol, respectively. Tetrahydrofuran (THF) was used as the eluent (flow rate 0.3 mL min⁻¹). The number-average molecular weights were determined using polystyrene standards. UV-Vis spectra were taken on an Agilent 8453. Fluorescence spectra were recorded on a Jobin Yvon-Horiba Fluoromax-P.

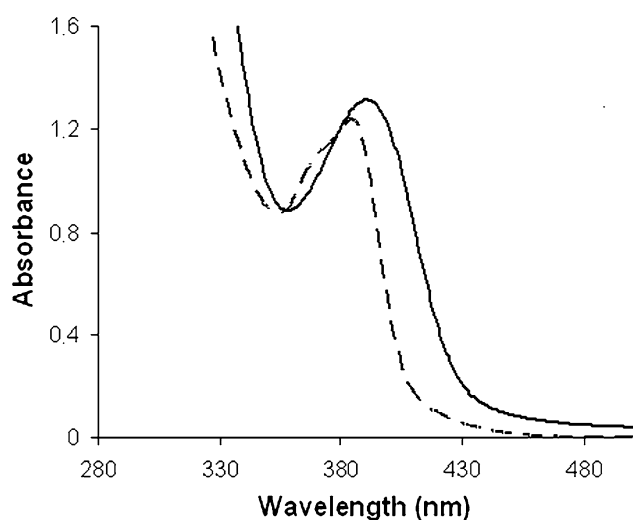


Fig. 1 Absorption spectra of TX-Ct [6×10^{-4} M] in water (solid line) and [2.5×10^{-4} M] in DMF (dotted line)

Table 1 Photoinitiated polymerization of MMA/β-CD complex in the presence of TX-Ct as photoinitiator in water

Run	TX-Ct (mol L ⁻¹)	MDEA (mol L ⁻¹)	Conversion (%)	R _p × 10 ⁵ (L mol ⁻¹ s ⁻¹)	M _n × 10 ⁻³ (g mol ⁻¹)
1	1 × 10 ⁻⁴	–	34	1.90	12.9
2		5 × 10 ⁻³	79	4.40	12.0
3	5 × 10 ⁻⁴	–	69	3.90	13.6
4		5 × 10 ⁻³	80	4.50	7.10
5	1 × 10 ⁻³	–	72	4.00	20.1
6		5 × 10 ⁻³	88	4.90	7.50

MMA: 5×10^{-2} mol L⁻¹

CD: 5×10^{-3} mol L⁻¹

Irradiation time: 15 min

Results and discussion

TX-Ct was synthesized as given in the literature and characterized [22] (see Scheme 2).

The optical absorption properties of TX-Ct in DMF and in water are given in Fig. 1.

TX-Ct possesses similar absorption characteristics to thioxanthone with a maximum at 390 nm (ϵ : 2,108 L mol⁻¹ cm⁻¹) in water. However, in contrast to thioxanthone itself, TX-Ct is rather a lot water soluble. As shown in Fig. 1, increasing the solvent polarity shifted the emission spectrum to the red. As n - π^* transitions have generally the opposite shift and due to the high extinction coefficient, this transition should be assigned to a π - π^* transition. A slight shift to longer wavelengths by polar solvents can be explained by the effect that the excited state may form stronger hydrogen bonds than the corresponding ground state.

Photopolymerization

Some of the host/guest studies with CD in the literature were performed via the complex formation of methyl methacrylate with CD [5]. Because of effective complexation of MMA with CD, the host/guest complex of β -CD/MMA was also employed for our study. To an aqueous solution of CD, a known amount of MMA was dispersed to give a clear and homogenous solution of the β -CD/MMA host/guest complex, simply by stirring. The photoinitiated polymerization of the β -CD/MMA complex was conducted with TX-Ct as the water soluble difunctional initiator in the

presence and absence of MDEA. Due to the good solubility of TX-Ct in water, various initiator concentrations were used and rapid precipitation of the corresponding water insoluble polymers was observed during the polymerization reaction. The polymers were separated by filtration, washed, dried and characterized by GPC. The gravimetrically determined conversions of monomer (MMA) into polymer for these experiments are shown in Table 1. As expected, when polymerization of the β -CD/MMA complex was performed with and without MDEA in the

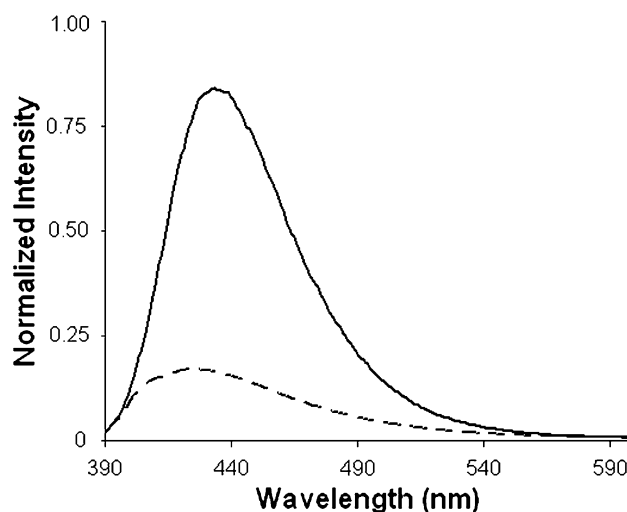


Fig. 3 Fluorescence spectra of TX-Ct (solid line) in water and poly(methylmethacrylate) (dotted line) obtained ([PI]: 1×10^{-3} M) in CH₂Cl₂ (λ_{exc} : 380 nm)

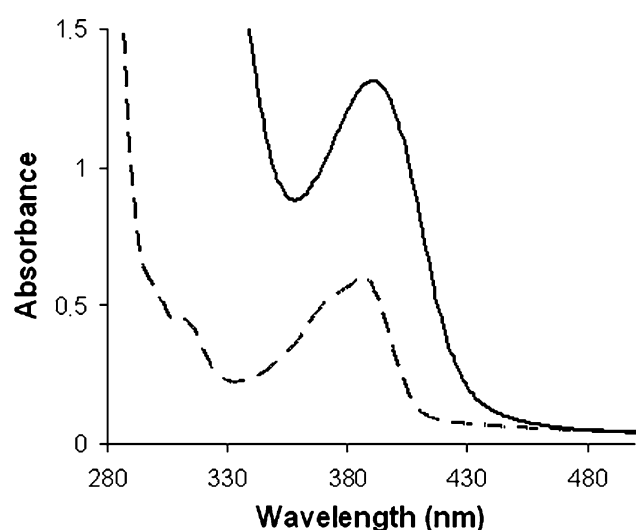


Fig. 2 Absorption spectra of TX-Ct (solid line) in water and poly(methylmethacrylate) (dotted line) obtained ([PI]: 1×10^{-3} M) in CH₂Cl₂

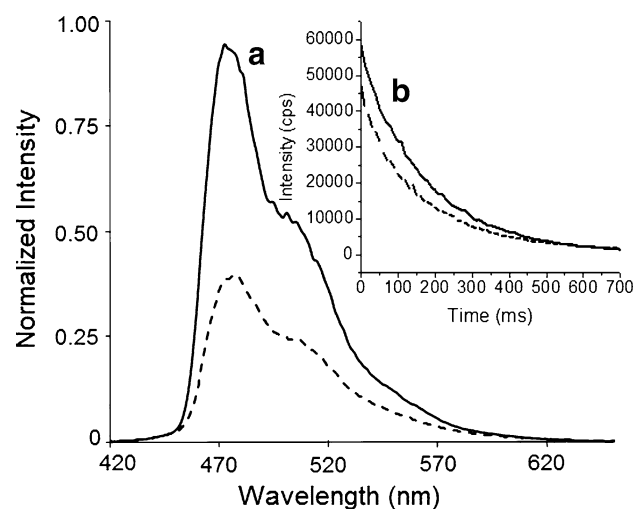
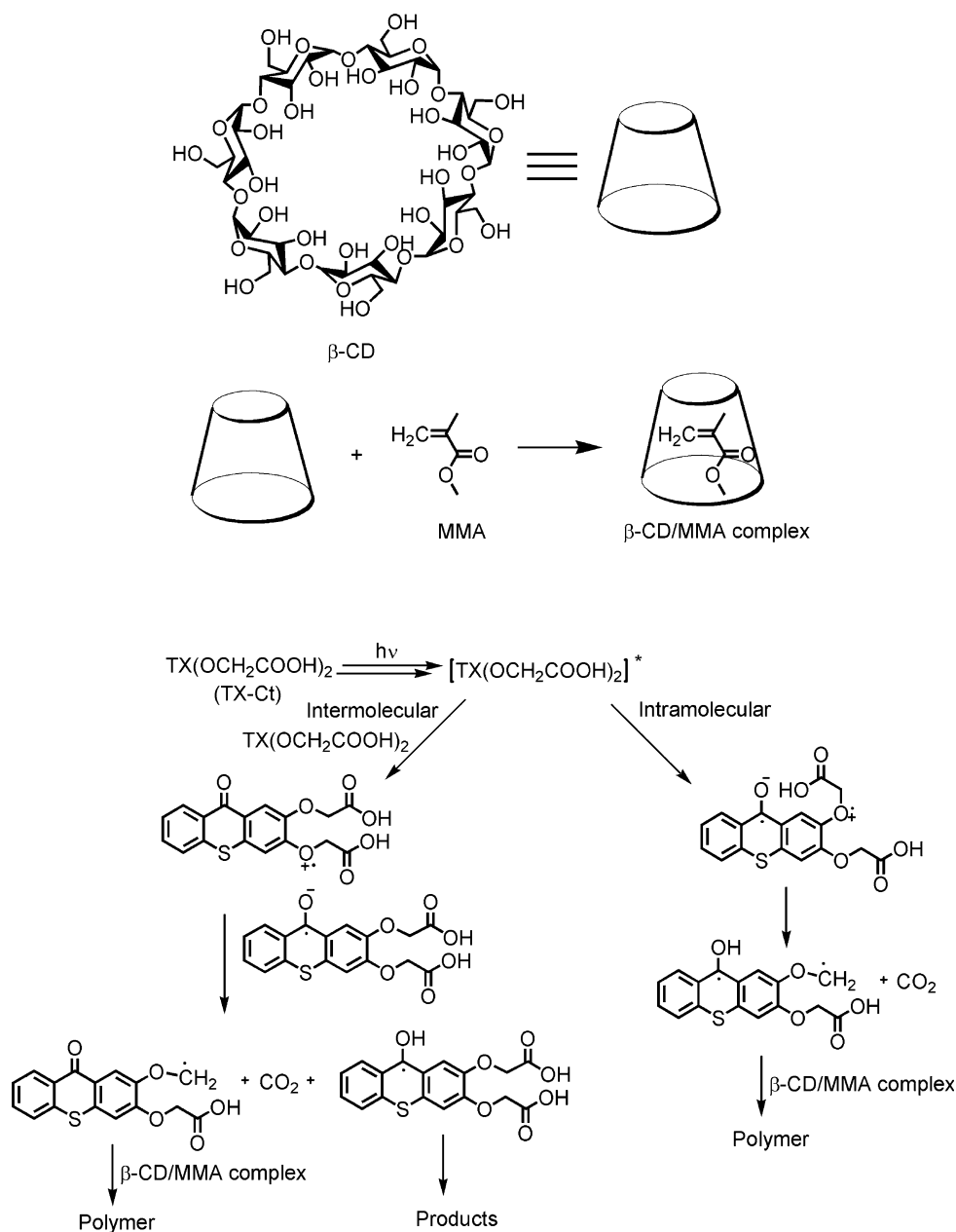


Fig. 4 Phosphorescence emission spectra (a) and kinetic decay (b) of TX-Ct (solid line) and poly(methylmethacrylate) (dotted line) obtained by photoinitiated polymerization by using TX-Ct ([PI]: 1×10^{-3} M) in 2-methyltetrahydrofuran at 77 K (λ_{exc} : 380 nm)

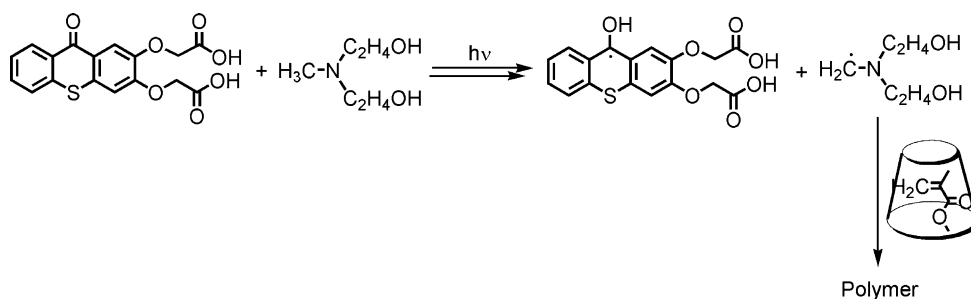
absence of an initiator in water as a control experiment, no polymer was obtained. Even at very low initiator concentrations and without MDEA, the conversion percentage of monomer to polymer was found to be 34. The highest conversion was achieved at a concentration of 1×10^{-3} M of TX-Ct in water (run 5, 72%). From these results the low photoinitiator concentration and/or oxygen inhibition might be responsible for the low double bond conversion in run 1. As can be seen from Table 1, although TX-Ct was an efficient photoinitiator in the absence of a co-initiator, the addition of MDEA to the β -CD/MMA host/guest complex in the presence of TX-Ct helped to increase the conversion

percentage values (run 2, 79%). The presence of an amine such as MDEA is important for effective photoreduction and photopolymerization. MDEA plays a dual action in the polymerization. Besides hydrogen donation by electron and proton transfer, MDEA can react with oxygen thereby reducing the retarding effect of oxygen on the polymerization [11, 23]. In the absence of any amine, the molecular weight is increased with increasing photoinitiator concentration. Addition of MDEA to the formulation reduced the molecular weight of polymer because amines act as chain transfer agents, which leads to the formation of polymers with a lower molecular weight (see Table 1).

Scheme 3 Complexation of the monomer(MMA) with CD and photopolymerization process



Scheme 4 Photoinitiated polymerization of β -CD/MMA complex with (TX-Ct) in the presence of MDEA



For the characterization of polymer obtained, absorption and fluorescence spectroscopy were used. In Fig. 2, the absorption spectra of TX-Ct and the polymer obtained from the β -CD/MMA host/guest complex with TX-Ct in the absence of MDEA are shown. UV absorption spectra of purified polymer produced from initiation with a high initiator concentration (1×10^{-3} M) showed absorbance at 390 nm, which indicates TX chromophores bound to polymers.

Indeed, besides the UV spectra, the fluorescence emission and phosphorescence spectra of TX-Ct and polymer (PMMA) were proof of the incorporation of TX to polymer, as shown in Figs. 3 and 4. From the kinetic decay of phosphorescence, it was found that the phosphorescence lifetimes of TX-Ct and PMMA are very similar (171 and 160 ms respectively). To explain the initiation mechanism of TX-Ct for β -CD/MMA, photodecarboxylation of the initiator in water was achieved. The photolysis in the absence of monomer was performed, as stated in our previous publications [20], and decarboxylation of the initiator resulted in concomitant CO_2 evolution which was determined [20]. The decarboxylation procedure was finished after 15 min of irradiation time (Light Intensity: 300 W/m^2).

The proposed mechanism is based on the intramolecular electron transfer followed by hydrogen abstraction and decarboxylation (see Scheme 3).

However, at high initiator concentrations, intermolecular electron transfer competes with intramolecular electron transfer. The resulting alkyl radical after decarboxylation of TX-Ct in water initiated the polymerization of the β -CD/MMA host/guest complex and as well as the alkyl radical produced from decarboxylation of the initiator, the α -aminoalkyl radical is another initiating radical for the polymerization of the β -CD/MMA host/guest complex in the presence of MDEA and therefore the yield of polymerization was higher (run 6, 88%) (see Scheme 4).

In conclusion, the β -CD/MMA host/guest complex was achieved and TX-Ct was employed as a water soluble initiator and successful polymerization was performed with and without MDEA in air atmosphere.

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