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Chemical incorporation of thioxanthone into β-cyclodextrin and its use in aqueous photopolymerization of methyl methacrylate

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Abstract

Photoinitiated free radical polymerization of methyl methacrylate (MMA) in aqueous solution via hydrogen abstraction mechanism was described. For this purpose, thioxanthone (TX) chromophoric group was chemically incorporated into β-cyclodextrin (β-CD) by a simple esterification process. The resulting thioxanthone photoinitiator (TX–β-CD) exhibited similar spectral characteristics and photoactivity to that of the parent TX molecule. Host guest complexes of MMA with TX–β-CD in water, in the presence of *N*-methyldiethanol amine (NMDEA) as a hydrogen donor, facilitated photoinitiated free radical polymerization in aqueous medium. The postulated mechanism is based on the intermolecular reaction of photoexcited triplet TX moiety of TX–β-CD with NMDEA. The resulting amino alkyl radicals initiate the polymerization.

Keywords: Photopolymerization; Thioxanthone; Cyclodextrin; Host guest complexes; Aqueous polymerization

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 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 to use 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 [11]. During the polymerization, the CD gradually slipped off from the growing chain and remained in 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 water soluble host/guest complex[12]. Compare to the bare photoinitiator, this complex exhibited much higher initiation efficiency in the polymerization of water soluble monomer, *N*-isopropylacrylamide [12]. In another study, Li et al. demonstrated [13] that the host/guest complexation of Me–β-CD with more hydrophobic photoinitiator, 2,2-dimethoxy-2-phenyl acetophenone, gave stable water soluble compound with high photoactivity and efficiency of polymerization.

Type II photoinitiators are a second class of photoinitiators and based on compounds whose triplet excited states are reacted with hydrogen donors thereby producing an initiating radical [14–18] (Scheme 1). Because the initiation is based on bimolecular reaction, they are generally slower than Type I photoinitiators, which are based on unimolecular formation of radicals. On the

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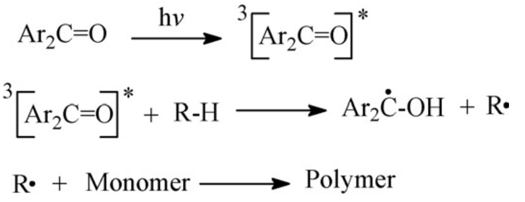


Scheme 1. Photoinitiated free radical polymerization by aromatic carbonyl compounds via Type II mechanism.

other hand, Type II photoinitiators in general possess better optical absorption properties in the near-UV spectral region.

Typical Type II photoinitiators include benzophenone and derivatives, thioxanthones, benzil and quionones while alcohols, ethers, amines and thiols are used as hydrogen donors. Among Type II photoinitiators, thioxanthone derivatives in conjunction with tertiary amines are efficient photoinitiators with absorption characteristics that compare favorably with benzophenones [15]. Therefore, recent research interest on Type II photoinitiators has mainly focused on the thioxanthone (TX)-based photoinitiators.

As an extension of our research on these photoinitiators, we investigate the photoactivity of TX groups chemically attached to β-CD and their efficiency in photopolymerization of methyl methacrylate (MMA) which can form host/guest complex with these molecules.

2. Experimental

2.1. Materials

β-Cyclodextrin (β-CD, 99%, Acros) and *N*-methylethanolamine (MDEA, 99%, Aldrich) were used as received. Thioxanthone–thioacetic acid was prepared according to the previously described procedure [19]. Methyl methacrylate (MMA, ≥99%, Fluka) were washed with 5% aq. NaOH solution, dried over $CaCl_2$ and distilled from CaH_2 in vacuo. Dichloromethane (DCM, 99.9%, HPLC grade, Aldrich) was distilled from CaH_2. Benzene (≥99.0%, Aldrich), petroleum–benzine (Aldrich) and ethylacetate (99.5%, HPLC grade, Acros) were used as received.

2.2. Synthesis of thioxantone–cyclodextrin (TX–β-CD)

β-CD·H_2O (0.60 g, 5.2×10^{-4} mol) and $TXSCH_2COOH$ (0.16 g, 5.2×10^{-4} mol) were dissolved as a suspension in benzene:ethyl acetate solution (15:2, 15 mL) and 96% sulfuric acid was added drop-wise in excess. The mixture was heated at the reflux temperature for 7 h. The suspension was filtered and the solvent was removed by evaporation. The resulting black oil was washed with petroleum–benzine twice then air dried to afford the desired compound. Yield: 0.53 g, 77.5%.

R_f: 0.71 (benzene:ethyl acetate (v/v); 15:2).

Anal. Calcd. for $C_{102}H_{102}O_{43}S_8$ (2270 g mol^{-1}): C, 53.92%; H, 4.49%; S, 11.27% found, C, 54.64%; H, 4.01%; S, 11.98%.

IR (KBr): 3411 (OH), 3054 (aromatic), 2928 and 2906 (CH_2), 1742 and 1709 (C=O), 1633 (C=C), 1285 and 1171 (C–O), 577 (C–S) cm^{-1}.

^{1}H NMR ($CDCl_3$, 250 MHz) δ ppm: 2.53–2.64 (m, 21H; 14H, CHOH and 7H, $CHCH_2OH$); 2.71–2.77 (m, 14H, O–CHO); 3.68–3.77 (m, 14H, CH_2OH and –S–CH_2CO–); 4.07 (s, –$COOCH_2$, 2H); 4.10 (s, –$COOCH_2$, 2H); 4.11 (s, –$COOCH_2$, 2H); 4.13 (s, –$COOCH_2$, 2H); 4.58–5.00 (m, 17H, –OH, changing with D_2O); 7.45–7.66 (m, 16H, aromatic); 8.58–8.62 (m, 12H, aromatic).

2.3. Analysis

The photolyzing light was generated by a medium pressure mercury lamp (Flexi-cure UV system) and was conducted through flexible fiber optic for the photolysis of sample solution. Gel permeation chromatography (GPC) measurements were performed at room temperature with a setup consisting of a pump (Agilent 1100), a refractive index detector (Agilent 1100S) and three high resolution Zorbax PSM columns (60S, 300S and 1000S). The effective molecular weight ranges were 500–10,000, 3000–300,000 and 10,000–1,000,000, respectively. THF was used as eluent at a flow rate of 0.3 mL/min at room temperature. Data analyses were performed with Polymer Laboratories Caliber Software Calibration with linear polystyrene 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. A PerkinElmer Spectrum-One FTIR spectrophotometer was used for recording IR spectra.

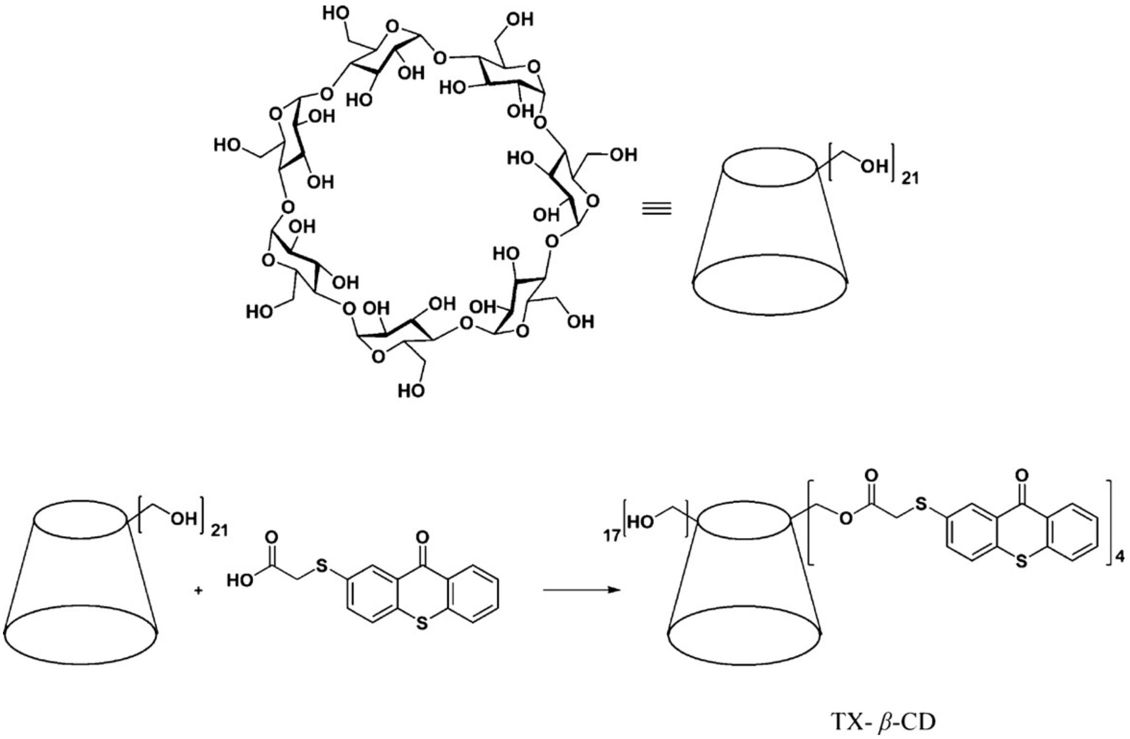
^{1}HNMR spectra were recorded on a Bruker 250 instrument with $CDCl_3$ as solvent and tetramethylsilane (TMS) as the internal standard.

2.4. Photopolymerization

Typical procedure: 0.23 g (1.0×10^{-3} M) of TX–β-CD was dissolved in 100 mL of water and 0.2 mL (2.0×10^{-2} M) of MMA was added. The colorless dispersion was sonicated for 10 min yielding a clear colorless solution of the complexed monomer. TX–β-CD complex containing 6 g of MDEA (5×10^{-2} M) was put into a Pyrex flask and irradiated in a photoreactor consisting of a 400 W medium pressure mercury lamp and a water cooling system for 15 min in air atmosphere. Poly(methyl methacrylate) formed was precipitated in water during irradiation and dried in vacuo (conversion: 41.5 ± 0.2%; Mn = 52 120 g mol^{-1}). The other polymerization experiments were performed in the same manner and conversions were calculated for all samples gravimetrically.

3. Results and discussion

As stated in the introduction section, for the CD-mediated aqueous polymerizations two main strategies were followed. In the first strategy, the hydrophobic monomer complexed with CD was polymerized in water by using a water soluble initiator. Alternatively, complexation of a hydrophobic initiator facilitated its solubility in water, which was used to polymerize a



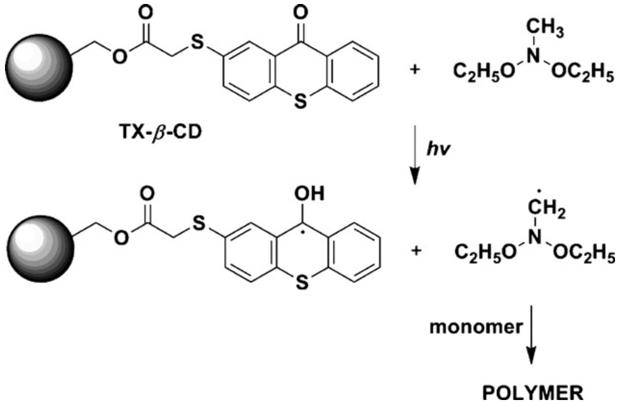
Scheme 2. Synthesis of thioxanthone–β-cyclodextrin (TX–β-CD).

water soluble monomer. However, no attempts were made to polymerize a hydrophobic monomer by using a hydrophobic initiator. This would be particularly important for UV curing applications of acrylate and methacrylate formulations in water by using photoinitiators with desired spectral sensitivity. Most of the free radical photoinitiators absorbing at far UV region are structurally hydrophobic. In principle, the simplest way would be to complex both monomer and photoinitiator with CD and irradiate the inclusion complexes in water at appropriate wavelength. However, it is known that the size and shape of the hydrophobic components should match with the cavity of CD and CDs exhibit selectivity for the molecules that carry alkyl groups [20]. It is, therefore, very likely that monomer and photoinitiator may form complexes at different rate and even in different CDs. Obviously, such complexes would lead to a limited interaction of the photochemically generated free radicals with monomer molecules and consequently it would result in lower polymerization efficiency. It seemed appropriate to attach chemically the photoinitiator molecule into CD, which can further be complexed with a hydrophobic monomer. TX was deliberately chosen as the photoinitiator, which generates initiating radicals via hydrogen abstraction mechanism and hydrogen donor molecules such as amines are highly soluble in water. Thus, thioxanthone incorporated β-cyclodextrin (TX–β-CD) was synthesized by the simple esterification process between $TXSCH_2COOH$ and β-CD according to Scheme 2. $TXSCH_2COOH$ is an oil soluble one-component photoinitiator [19], and became water soluble when chemically incorporated to β-CD.

The structure of TX–β-CD was confirmed by spectral and elemental analysis (see Section 2). The photoinitiator possesses signals corresponding to the protons of TX moiety as well as CD base unit. The degree of functionalization was also estimated using ^{1}H-NMR spectroscopy. ^{1}H NMR spectrum of TX–β-CD showed four oxymethylene signals at δ 4.07, 4.10, 4.11 and 4.13 ppm. In addition, *S*-methylene protons in TX–β-CD referring to 2H × 4 showed the shifts at 3.68–3.77 ppm as expected. The spectrum also exhibited 17 hydroxy protons at 4.58–5.00 ppm, which remained unreacted after the esterification reaction.

Upon photolysis in the presence of hydrogen donor such as *N*-methyldiethanol amine (NMDEA), TX–β-CD is expected to undergo fast hydrogen abstraction reaction producing two radicals, which results in the destruction of TX moiety (Scheme 3).

Such photobleaching was examined by monitoring the changes of UV spectra with irradiation. The absorbance of TX



Scheme 3. Photoinitiated free radical polymerization by using thioxanthone–β-cyclodextrin (TX–β-CD).

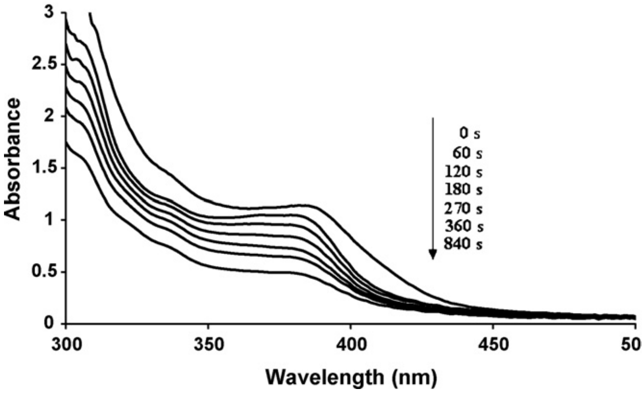


Fig. 1. Absorption spectra of TX–β-CD (9.0×10^{-4} mol L^{-1}) in air saturated dichloromethane solutions after irradiation at 366 nm for 0, 60, 120, 180, 270, 360 and 840 s.

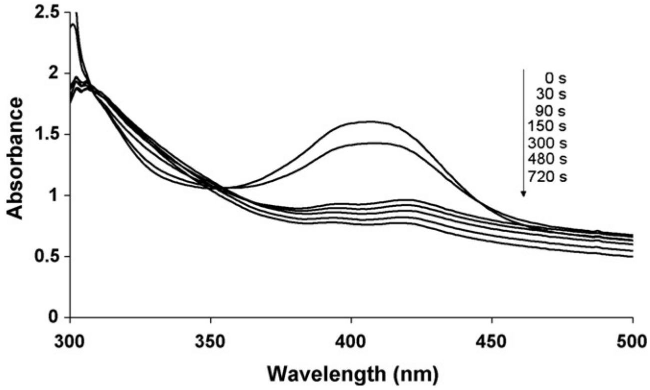


Fig. 2. Absorption spectra of TX–β-CD (7.0×10^{-3} mol L^{-1}) with MDEA (5.0×10^{-2} mol L^{-1}) in air saturated water solutions after irradiation at 366 nm for 0, 30, 90, 150, 300, 480 and 720 s.

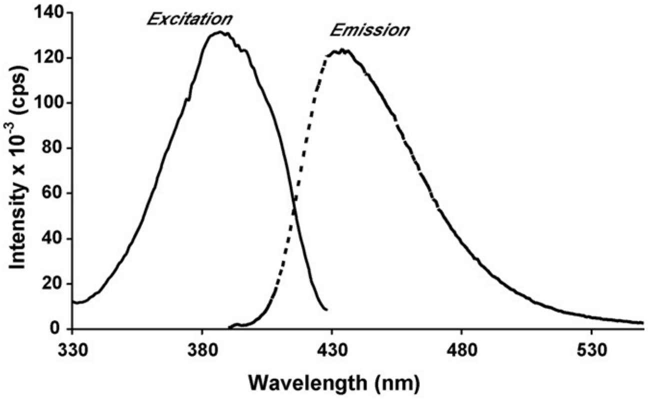


Fig. 3. Fluorescence excitation (—) and emission (- - -) spectra of TX–β-CD (1.0×10^{-5} M) in benzene; $\lambda_{exc} = 380$ nm.

chromophoric group was decreasing rapidly with the irradiation time (Figs. 1 and 2) during the photolysis in both aqueous and CH_2Cl_2 solutions. The absorbance characteristics and spectral changes are more significant in aqueous solution indicating better compatibility with the added amine and consequently more susceptibility to photoinduced reactions in water. Notably, the new absorption at shorter wavelength ($\lambda = 330$ nm), probably due to the coupling products, was observed.

Fig. 3 shows that a nearly mirror-image-like relation exists between absorption and emission of TX–β-CD. 9,10-Diphenyl anthracene was used as standard for the calculation of quantum yield for fluorescence emission (ϕ_f) fluorescence quantum yield of TX–TX–β-CD according to the following equation:

$$\phi_{\mathrm{f(sample)}} = \phi_{\mathrm{f(standard)}} \frac{\mathrm{Area}_{\mathrm{sample}}}{\mathrm{Area}_{\mathrm{standard}}}$$

$\mathrm{Area}_{\mathrm{sample}}$: area of emission spectrum of TX–β-CD, $\mathrm{Area}_{\mathrm{standard}}$: area of emission spectrum of 9,10-diphenyl anthracene, ϕ_f was found to be 0.06, which is similar to that of unsubstituted thioxanthone.

In order to demonstrate the possibility of the polymerization a hydrophobic monomer such as MMA in water by using TX–β-CD as a Type II photoinitiator several experiments were performed. The results presented in Table 1 are interesting to illustrate the effect of the photoinitiator and monomer concentration on the polymerization rate. Obviously, higher monomer conversions may be obtained by higher light intensity and prolonged irradiation times. The amine concentration was deliberately kept high so as to facilitate the interaction of excited CD–TX complex with hydrogen donor.

The results also indicate the crucial effect of hydrogen donors. In the absence of NMDEA polymerization was not initiated. This behavior indicates unfavorable intramolecular hydrogen abstraction from CD moiety.

In conclusion, chemical incorporation of a hydrogen abstraction type photoinitiator, TX into β-CD was successfully achieved. The complexation of the resulting photoinitiator, TX–β-CD with MMA makes it possible to perform photoinitiated polymerization in water. The aqueous solubility of both initiator and hydrophobic monomer is extremely valuable in preparing water-borne coatings based on acrylates and methacrylates. Further studies in this line are now in progress.

Table 1
Photoinitiated polymerization[a] of MMA with TX–β-CD complex in aqueous media

[TX–β-CD] (mol L^{-1})	[MMA] (mol L^{-1})	Conversion (%)	M_n[b] ($\times 10^{-4}$ g mol^{-1})	M_w/M_n[b]
8.0×10^{-4}	5.0×10^{-2}	25.0	0.49	1.65
1.0×10^{-3}	5.0×10^{-2}	27.0	4.03	1.19
2.4×10^{-3}	5.0×10^{-2}	37.0	0.56	1.57
8.0×10^{-4}	2.0×10^{-2}	<1.0	–	–
1.0×10^{-3}	2.0×10^{-2}	41.5	5.21	1.52

[a] Polymerization was performed by irradiating the solutions for 15 min in the presence of MDEA (5×10^{-2} M).

[b] Determined by GPC using polystyrene standards.

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References

[1] G. Wenz, Angew. Chem. 106 (1994) 851–870.

[2] A. Harada, Acta Polym. 49 (1998) 3–17.

[3] J. Jeromin, H. Ritter, Macromolecules 32 (1999) 5236–5239.

[4] H. Ritter, J. Storsberg, Macromol. Rapid Commun. 21 (2000) 236–241.

[5] J. Leyrer, W. Machtle, Macromol. Chem. Phys. 201 (2000) 1235–1243.

[6] S.P. Pappas, UV Curing Science and Technology, Technology Marketting Corp., Norwalk, CT, 1978.

[7] J.P. Fouassier, Photoinitiation, Photopolymerization and Photocuring, Hanser Verlag, Munich, 1995.

[8] K. Dietliker, Chemistry & Technology of UV & EB Formulation for Coatings, vol. III, Inks & Paints, SITA Technology Ltd., London, 1991.

[9] R.S. Davidson, Exploring the Science, Technology and Applications of UV and EB Curing, SITA Technology Ltd., London, 1999.

[10] M.K. Mishra, Y. Yagci, Handbook of Radical Vinyl Polymerization, Marcel Dekker Inc., New York, 1998 (Chapter 7).

[11] J. Storsberg, H. Ritter, Macromol. Rapid Commun. 21 (2000) 236–241.

[12] I.C. Alupei, V. Alupei, H. Ritter, Macromol. Rapid Commun. 23 (2002) 55–58.

[13] S.J. Li, F.P. Wu, M.Z. Li, E.J. Wang, Polymer 46 (2005) 11934–11939.

[14] A. Ledwith, M.D. Purbrick, Polymer 14 (1973) 521–522.

[15] R.S. Davidson, in: D. Bethel, V. Gold (Eds.), Advances in Physical Chemistry, Academic Press, London, 1983.

[16] A. Ledwith, J.A. Bosley, M.D. Purbrick, J. Oil Colour Chem. Assoc. 61 (1978) 95–104.

[17] T. Corrales, F. Catalina, C. Peinado, N.S. Allen, J. Photochem. Photobiol. A: Chem. 159 (2003) 103–114.

[18] M.G. Neumann, M.H. Gehlen, M.V. Encinas, N.S. Allen, T. Corrales, C. Peinado, F. Catalina, J. Chem. Soc., Faraday Trans. 93 (8) (1997) 1517–1521.

[19] M. Aydin, N. Arsu, Y. Yagci, Macromol. Rapid Commun. 24 (2003) 718–723.

[20] A. Harada, F. Ito, I. Tomatsu, K. Shimoda, A. Hashidzume, Y. Takashima, H. Yamaguchi, S. Kamitro, J. Photochem. Photobiol. A: Chem. 179 (2006) 13–19.