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ARTICLE

Thioxanthone−Fluorenes as Visible Light Photoinitiators for Free Radical Polymerization

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ABSTRACT: Two thioxanthone derivatives with fluorene additional chromophoric groups, namely thioxanthone−fluorenecarboxylic acid (TX-FLCOOH) and thioxanthone−fluorene sodium carboxylate (TX-FLCOONa), as visible light absorbing oil- and water-soluble photoinitiators, respectively, were synthesized and characterized. Their ability to initiate photopolymerization of methyl methacrylate (MMA), 2-(2-phosphonoethoxymethyl)acrylic acid ethyl ester (EAEPA), and a multifunctional monomer, trimethylolpropane triacrylate (TMPTA), were examined. The initiation efficiency of TX-FLCOOH was compared with the parent thioxantone (TX) both in the presence and in the absence of a co-initiator, and TX-FLCOOH was found to be more effective in all cases. Photopolymerization and laser flash photolysis studies revealed that depending on the concentration initiation by TX-FLCOOH occurs by intra- and intermolecular H-abstraction of the triplet ^{3}(TX-FLCOOH)*. No polymerization was observed when TX-FLCOONa was used as photoinitiator in the absence of a co-initiator. However, TX-FLCOONa acts as an efficient initiator in the visible range in the presence of H donors in water.

Introduction

Photoinitiated polymerization is a well-known technique exploited in many technologically important areas.[1,2] Both free radical and cationic polymerizations have been used, and the mechanisms of initiation have been studied in detail.[3−6] The free radical mode is in more advanced state due to its applicability to a wide range of formulations based on (meth)acrylates, unsaturated polyesters, and acrylated polyurethanes and the availability of photoinitiators having spectral sensitivity in the near-UV and visible range. The radical photopolymerization can be initiated either via bond α-cleavage (type I) or hydrogen abstaction type (type II) photoinitiators whose triplet states readily react with the H-donor compounds like tertiary amines, thiols, ethers, and alcohols to yield the initiating radicals (Scheme 1).[7−10] Because of the bimolecular radical generation process, they are generally slower than type I photoinitiators, which form radicals unimolecularly.

Scheme 1. Photoinitiated Free Radical Polymerization by Using Aromatic Carbonyl Compounds

$$\mathrm{Ar_2C{=}O} \xrightarrow{h\nu} {}^3\left(\mathrm{Ar_2C{=}O}\right)^*$$

$${}^3\left(\mathrm{Ar_2C{=}O}\right)^* + \mathrm{R\text{-}H} \longrightarrow \mathrm{Ar_2\dot{C}\text{-}OH} + \mathrm{R}\bullet$$

$$\mathrm{R}\bullet + \text{Monomer} \longrightarrow \text{Polymer}$$

Typical type II photoinitiators include benzophenone and derivatives, thioxanthones, benzil, and quinones. Among type II photoinitiators, thioxanthone (TX) derivatives in conjunction with tertiary amines are efficient photoinitiators with absorption characteristics that compare favorably with benzophenones.[11] Recently, thiol and carboxylic acid derivatives of thioxanthones have been reported to initiate photopolymerization without co-initiators as they contain functional groups with H-donating nature.[12−14] Alternative approach concerns the attachment of both chromophoric and hydrogen-donating groups into polymer chains.[15−26] This way, the odor and toxicity problems observed with the conventional photoinitiators and amine hydrogen donors were overcome. We have also developed a novel thioxanthone-based photoinitiator possesssing an anthracene group that does not require an additional hydrogen donor for radical (TX-A) formation and initiates the polymerization of both acrylate and styrene monomers in the presence of air.[15] In addition, TX-A possesses excellent optical absorption properties in the near-UV spectral region, ensuring efficient light absorption. In fact, photoinitiators with higher wavelength absorption characteristics are desired as they cost lower energy and are defined to be "green". Photoinitiators for visible light[27] have found particular interest because of their use in many targeted applications such as dental filling materials,[28−31] photoresists, printing plates, highly pigmented coatings, integrated circuits, laser-induced 3D curing, holographic recordings, and nanoscale micromechanics. The very well-known examples are the titanocene[28] and camphorquinone[32] in conjunction with an amine for the respective systems. More recently, organic ketones containing germanium were introduced as a new class of cleavable photoinitiators.[33,34] We have recently demonstrated that these type of photoinitiators can promote cationic polymerization under visible light.[35]

Another important issue in the practical application of photoinitiators is related to their water solubility. There is a clear shift from organic solvents toward water-borne formulations particularly in the paints and coatings industry. Water as a green solvent has several attractive properties such as nontoxicity, cheap cost,

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and readily availability for coatings technology. The water solubility is usually achieved by incorporation of hydrophilic substituents such as quarternary ammonium or sulfate to the main body of the photoinitiators. Direct substitution of such groups on the photoinitiator affects the nature of the chromophore and consequently its photoactivity. Generally, water-soluble photoinitiator have reduced photoactivity to that of its parent oil-soluble initiator. Examples of the typical structure of water-soluble photoinitiators are derivatives of benzophenones,[36] thioxanthones,[37] benzyl[38] and hydroxy alkyl ketones,[39] and phenyltrimethylbenzoyl phosphinates.[40] Recently, we also synthesized phenacylpyridinium oxalate as a water-soluble photoinitiator and investigated its initiating behavior with water-soluble monomers.[41]

As part of our continuous interest in developing new photoinitiating systems to prevail over the existing problems or enhance the efficiency of UV-curable formulations, herein we report synthesis, characterization, and photoinitiation capability of two different photoinitiators, namely thioxanthone-fluorene carboxylic acid (TX-FLCOOH) and its sodium salt (TX-FLCOONa). Interestingly, while the former photoinitiator is soluble in oil, the solubility of the latter in water makes it particularly useful in waterborne coatings. Notably both photoinitiators exhibit visible range absorption characteristics.

Experimental Section

Materials. Thiosalicylic acid (97%, Sigma-Aldrich) and fluorene-4-carboxylic acid (96%, ethyl 4-dimethylaminobenzoate, 99% Alfa Aesar) were used without further purification. *N,N*-Dimethylaniline (DMA, g 99.5%, Fluka) was distilled over CaH_2 before use. Methyl methacrylate (MMA, 99%, Aldrich) was passed through basic alumina column before use to remove the inhibitor. Trimethylolpropane triacrylate (TMPTA, 95%, Aldrich) was used as received. *p*-Dioxane (99.9%, J.T. Baker), sulfuric acid (H_2SO_4, 95−97%, Fluka), dimethylformamide (DMF, 99%, Aldrich), and sodium hydroxide (NaOH, Carlos Erba) were used as received. The adhesive monomer 2-(2-phosphonoethoxymethyl)acrylic acid ethyl ester (EAEPA) and the cross-linker *N,N*-diethyl-1,3-bis(acrylamido)propane (DEBAAP) were provided by IVOCLAR VIVADENT AG (FL-9494 Schaan).

Synthesis of Thioxanthone−Fluorenecarboxylic Acid (TX-FLCOOH). Thiosalicylic acid (0.2 g, 1.3 mmol) was slowly added to concentrated sulfuric acid (10 mL), and the mixture was stirred for 5 min to ensure through mixing. Fluorene-4-carboxylic acid (0.85 g, 3.9 mmol) was added slowly to the stirred mixture over a period of 30 min. After the addition, the reaction mixture was stirred at 75 °C for 2 h, and later it was left to stand at room temparature overnight. Afterward, the resulting mixture was poured carefully with stirring into a 10-fold excess of boiling water, and it was then boiled further for 5 min. The solution was cooled and filtered. The residue was recrystallized from dioxane/water mixture to give the pure bright yellow solid. Yield: 52%, $\lambda_{393\,\mathrm{nm}}$ (ε) = 3512 L mol^{-1} cm^{-1}, $\lambda_{\mathrm{cutoff}}$ = 550 nm. ^1H NMR (d_6-DMSO, 250 MHz): δ = 9.01−7.51 (m, 9H, aromatic), 4.03 (s, 2H, CH_2), 13.5 (s, 1H, COOH). ^{13}C NMR (d_6-DMSO, 500 MHz): δ = 179.5 (C=O), 169.6 (C=O), 149.7−125.2 (aromatic), 36.9 (CH_2). FT-IR (ATR): 3420, 2883, 1703, 1584, 1438, 1395, 1256, 1175, 1082, 873, 762 cm^{-1}.

Synthesis of Sodium Fluorenecarboxylate−Thioxanthone (TX-FLCOONa). TX-FLCOOH (0.2 g, 0.58 mmol) was added into 50 mL of NaOH solution (2.9×10^{-5} mol L^{-1}). The suspension was refluxed at 100 °C overnight. The mixture was filtered, and the resulting orange-brown solid was dried at vacuum owen for 2 days. Yield: 98%, $\lambda_{375\,\mathrm{nm}}$ (ε) = 2015 L mol^{-1} cm^{-1}, $\lambda_{\mathrm{cutoff}}$ = 565.5 nm. ^1H NMR (D_2O, 250 MHz): δ = 8.42−6.85 (m, 9H, aromatic), 3.15 (s, 2H, CH2). ^{13}C NMR (D_2O, 500 MHz): δ = 179.3 (C=O), 169.4 (C=O), 149.5−125.3 (aromatic), 36.2 (CH_2). FT-IR (ATR): 2888, 1772, 1713, 1588, 1424, 993, 878, 737 cm^{-1}.

Photopolymerization. Appropriate solutions of the monomer and TX-FLCOOH were irradiated with a Polilight PL400 universal forensic light source at 415 nm in a nitrogen atmosphere. Polymers were obtained after precipitation in methanol and drying under vacuum. Conversions were calculated for all samples gravimetrically.

Instrumentation. ^1H NMR measurements were recorded in $CDCl_3$ with $Si(CH_3)_4$ as internal standard, using a Bruker AC250 (250.133 MHz) instrument. ^{13}C NMR measurements were recorded in d_6-DMSO and D_2O with $Si(CH_3)_4$ as internal standard, using a Bruker AVANCE-500 (500 MHz) instrument. FT-IR spectra were recorded on a Perkin-Elmer FT-IR Spectrum One-B spectrometer. UV spectra were recorded on a Shimadzu UV-1601 spectrometer. Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer Diamond DSC. Molecular weights were determined by gel permeation chromatography (GPC) instrument, Viscotek GPCmax Autosampler system, consisting of a pump, three ViscoGEL GPC columns (G2000H_{HR}, G3000H_{HR}, and G4000H_{HR}), a Viscotek UV detector, and a Viscotek differential refractive index (RI) detector with a THF flow rate of 1.0 mL min^{-1} at 30 °C. Both detectors were calibrated with PS standards having narrow molecular weight distribution. Data were analyzed using Viscotek OmniSEC Omni-01 software. Laser flash photolysis experiments employed the pulses from a Applied Photophysics with YAG laser (355 nm, pulse, 5 ns) and a computer-controlled system. Gas chromatography−mass spectroscopy (GC-MS) was performed using an Agilent 6890/5973 inert gas chromatograph/mass selective detector system in electrospray ionization mode (70 eV), through an HP-5MS capillary column using helium as carrier gas at a flow rate of 1.6 mL/min.

Photocalorimetry (Photo-DSC). The photodifferential scanning calorimetry (photo-DSC) measurements were carried out by means of a modified Perkin-Elmer Diamond DSC equipped with a high-pressure mercury arc lamp (320−500 nm). A uniform UV light intensity is delivered across the DSC cell to the sample and reference pans. The intensity of the light was measured as 58 mW cm^{-2} by a UV radiometer capable of broad UV range coverage. The mass of the sample was 3 mg, and the measurements were carried out in an isothermal mode at 30 °C under a nitrogen flow of 20 mL min^{-1}. The reaction heat liberated in the polymerization was directly proportional to the number of acrylate groups reacted in the system. By integrating the area under the exothermic peak, the conversion of the acrylate groups (*C*) or the extent of the reaction was determined according to eq 1

$$C = \Delta H_t / \Delta H_0^{\mathrm{theory}} \qquad (1)$$

where ΔH_t is the reaction heat evolved at time *t* and $\Delta H_0^{\mathrm{theory}}$ is the theoretical heat for complete conversion. $\Delta H_0^{\mathrm{theory}}$ = 86 kJ mol^{-1} for an acrylic double bond.[42] The rate of polymerization (R_p) is directly related to the heat flow (d*H*/d*t*) by eq 2:

$$R_p = dC/dt = (dH/dt)/\Delta H_0^{\mathrm{theory}} \qquad (2)$$

Results and Discussion

Synthesis and Characterization of the Photoinitiators. Thioxanthone−fluorenecarboxylic acid (TX-FLCOOH), 13-oxo-7,13-dihydroindeno[1,2-*b*]thioxanthene-11-carboxylic acid, was synthesized according to the modified literature procedure.[43] The sodium derivative, sodium 13-oxo-7,13-dihydroindeno[1,2-*b*]thioxanthene-11-carboxylate (TX-FLCOONa), was simply formed by the treatment of suspension of aqueous TX-FLCOOH with sodium hydroxide (Scheme 2).

The structures of the photoinitiators were confirmed by spectroscopic analysis (see Experimental Section). As can be seen from Figure 1 both compounds exhibit characteristic protons of both thioxanthone and fluorene structures. The disappearance of the carboxylic acid proton at around 13.5 ppm clearly evidences the complete neutralization of the carboxylic acid function with the sodium hydroxide (Figure 1).

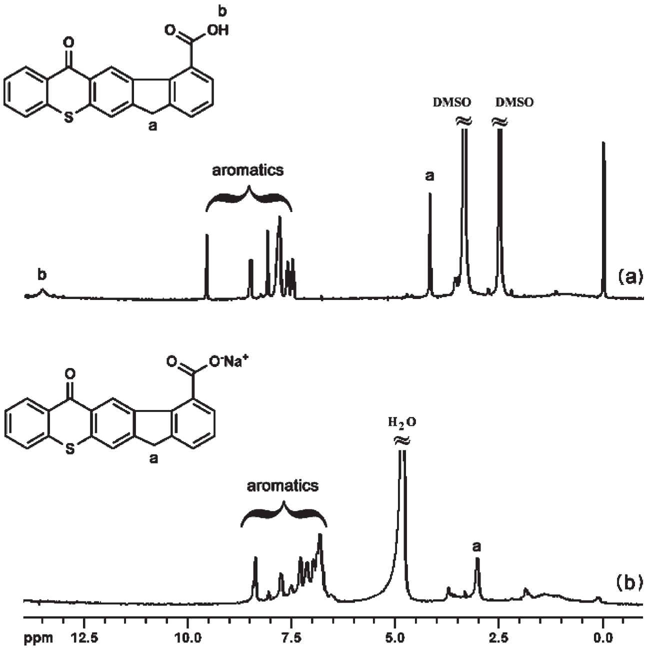


Figure 1. ^{1}H NMR spectra of thioxanthone−fluorenecarboxylic acid (TX-FLCOOH) (a) in d_6-DMSO and thioxanthone−fluorene sodium carboxylate (TX-FLCOONa) (b) in D_2O.

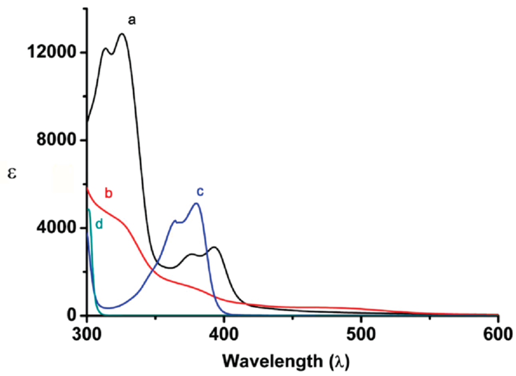


Figure 2. UV spectra of thioxanthone−fluorenecarboxylic acid (TX-FLCOOH) (a), thioxanthone−fluorene sodium carboxylate (TX-FLCOONa) (b), thioxanthone (TX) (c), and fluorene (F) (d).

Photophysical characteristics of the obtained thioxanthone compounds were investigated by UV and fluorescence spectroscopy. Figure 2 demonstrates the comparison of UV spectra of TX-FLCOOH and TX-FLCOONa, with the parent compounds, thioxanthone (TX) and fluorene (F). As can be seen, both new photoinitiators exhibit absorption characteristics very similar to TX, except a tail absorption in the visible wavelength region ($\lambda > 400$ nm), where TX chromophore is transparent. Although F itself does not absorb the light at above 310 nm, it has a dramatic effect on the absorption characteristics particularly at high wavelengths due to the extended conjugation.

Figure 3 demonstrates the comparison of UV spectra of both of the photoinitiators with camphorquinone (CQ), which is widely used in conjunction with hydrogen donors as visible light free-radical photoinitiator particularly in dental applications. Both TX-FLCOOH and TX-FLCOONa have greater molar absorbencies in the visible region compared to that of CQ.

Fluorescence spectra of the photoinitiators may also provide information on the nature of the excited states involved. As can be seen from Figure 4, excitation and

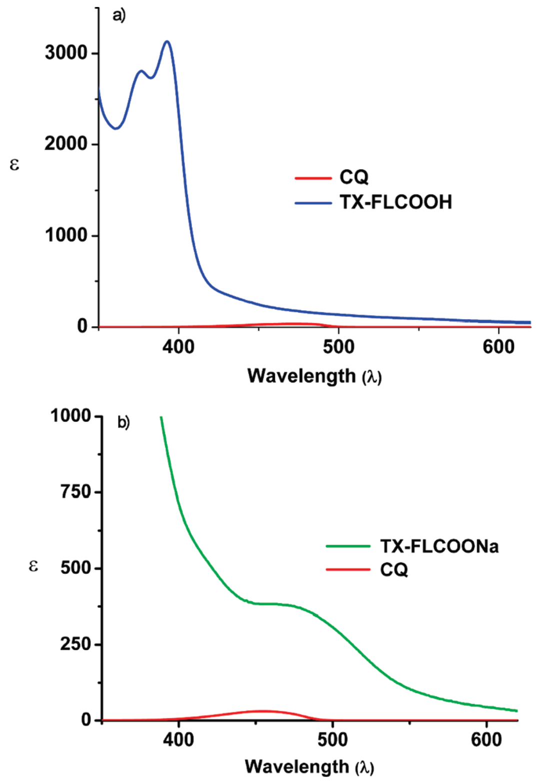
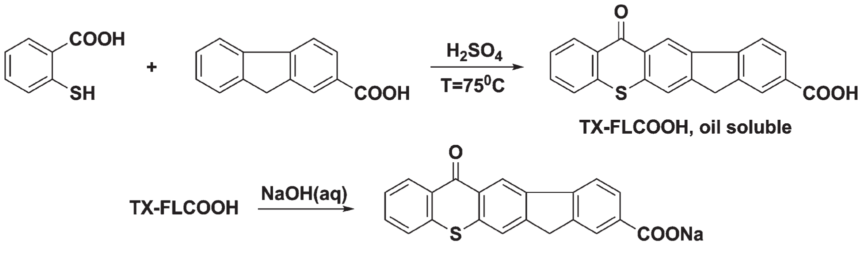


Figure 3. UV spectra of (a) TX-FLCOOH and CQ in CH_2Cl_2 and (b) TX-FLCOONa and CQ in water.

Scheme 2. Synthesis of Fluorenecarboxylic Acid−Thioxanthone (TX-FLCOOH) and Sodium Fluorene Carboxylate−Thioxanthone (TX-FLCOONa)



TX-FLCOOH, oil soluble

TX-FLCOONa, water soluble

emission fluorescence spectra in THF and water of TX-FLCOOH and TX-FLCOONa, respectively, are almost the same. Both spectra show a nearly mirror-image-like relation between absorption and emission again similar to bare TX, indicating its dominant photoexcited (singlet) state in the photoinitiator.

Photopolymerizations Using Thioxanthone−Fluorenecarboxylic Acid (TX-FLCOOH). TX-FLCOOH was used as photoinitiator for the polymerization of methyl methacrylate (MMA) at 415 nm under a nitrogen atmosphere. The results obtained in the presence or absence of a hydrogen donor are compiled in Table 1. For comparison, photopolymerizations with TX were also included. As can be seen, TX is not an efficient photoinitiator when the irradiation is performed at the visible light ($\lambda > 415$ nm). Interestingly, TX-FLCOOH was found to initiate photopolymerization at this region even in the absence of an additional hydrogen donor. Notably, the addition of a hydrogen donor such as *N*,*N*-dimethylaniline (DMA) accelerates the polymerization.

The efficiency of the TX-FLCOOH in the photocuring of formulations containing multifunctional monomers was also studied. The heat released during the photocuring of the formulations was followed by photo-DSC. In Figures 5 and 6, kinetic profiles referring to the polymerization of trimethylolpropane triacrylate (TMPTA) under polychromatic light emitting at $\lambda = 315-450$ nm are shown. TX-FLCOOH and TX and DMA served as photoinitiators and hydrogen donor, respectively. The shape of the curves indicates the existence of two stages: a rapid first stage followed by a slow stage. It can be seen that at low and sufficiently high concentrations polymerization takes place more rapidly with TX-FLCOOH than with TX. In the absence of a hydrogen donor DMA, TX does not initiate the polymerization.

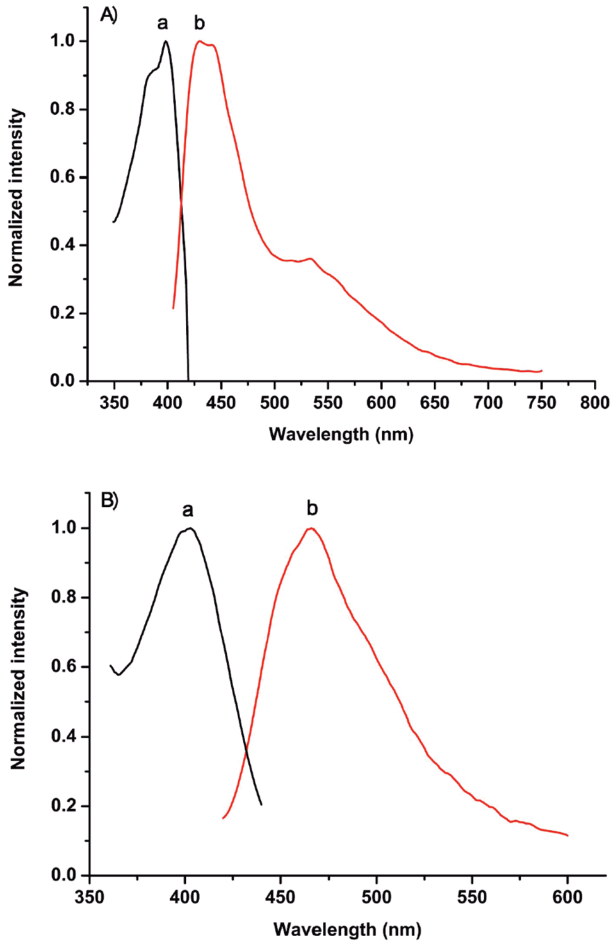


Figure 4. (A) Normalized excitation (a) and emission (b) fluorescence spectra of fluorenecarboxylic acid−thioxanthone (TX-FLCOOH) in THF at room temperature. (B) Normalized excitation (a) and emission (b) fluorescence spectra of sodium fluorene carboxylate−thioxanthone (TX-FLCOONa) in H_2O at room temperature.

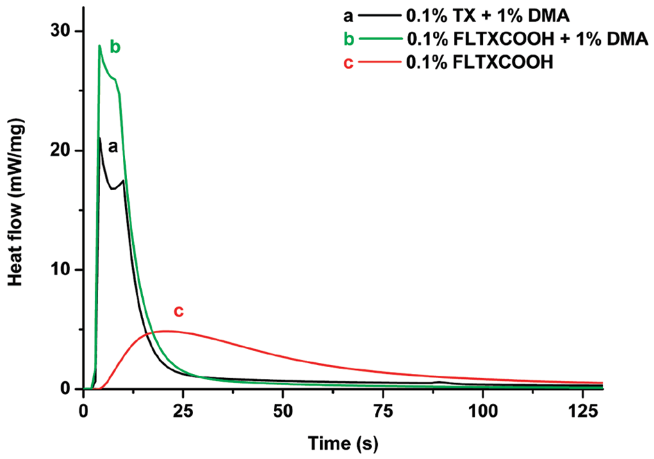


Figure 5. Photo-DSC profiles for photopolymerization of TMPTA irradiated at 30 °C by UV light with an intensity of 58 mW cm^{-2}.

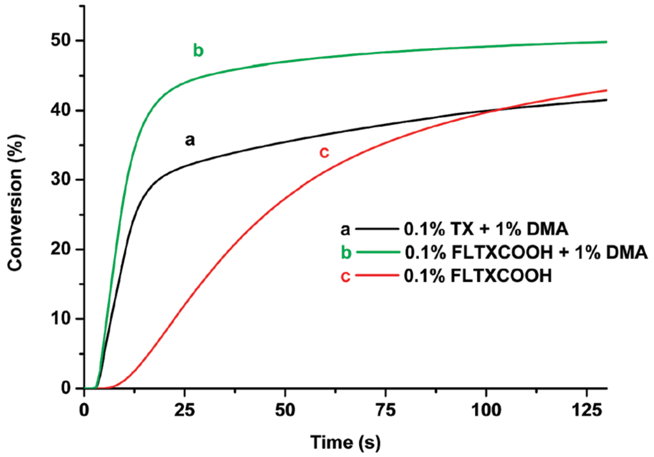


Figure 6. Conversion vs time curves for photopolymerization of TMPTA irradiated at 30 °C by UV light with an intensity of 58 mW cm^{-2}.

Table 1. Photoinitiated Polymerization of Methyl Methacrylate (MMA) by TX-FLCOOH at 415 nm in DMF (Irradiation Time = 15 min)

run[a]	[TX-FLCOOH] (mol L^{-1})	[DMA] (mol L^{-1})	[TX] (mol L^{-1})	conversion (%)	M_n[b] × 10^{-3} (g mol^{-1})	M_w/M_n
1	1.0 × 10^{-3}	3.0 × 10^{-3}		11.1	33.7	1.24
2	5.0 × 10^{-3}	1.5 × 10^{-2}		29.6	13.6	1.38
3	1.0 × 10^{-2}	3.0 × 10^{-2}		8.1	11.8	1.35
4	5.0 × 10^{-3}			8.2	26.5	1.98
5		1.5 × 10^{-2}	5.0 × 10^{-3}	0		

[a] [MMA] = 4.68 mol L^{-1}; TX-FLCOOH = thioxanthone−fluorenecarboxylic acid; TX = thioxanthone, DMA = *N*,*N*-dimethylaniline. [b] Determined by gel permeation chromatography (GPC) using polystyrene standards.

For the evaluation of the potential use of TX-FLCOONa in dental formulations, photoinduced gelation of the water-borne primer formulation[29,44,45] consisting of a mixture of 2-(2-phosphonoethoxymethyl)acrylic acid ethyl ester (EAEPA), *N*,*N*-diethyl-1,3-bis(acrylamido)propane (DEBAAP), and water (2:1:2) was used. The photoinitiator/hydrogen donor (ethyl 4-(dimethylamino)benzoate) was in a concentration as usually applied under practical conditions. Although the same gel contents were attained, CQ appeared to be more convenient photoinitiator for dental applications, where shorter gelation times are desired.

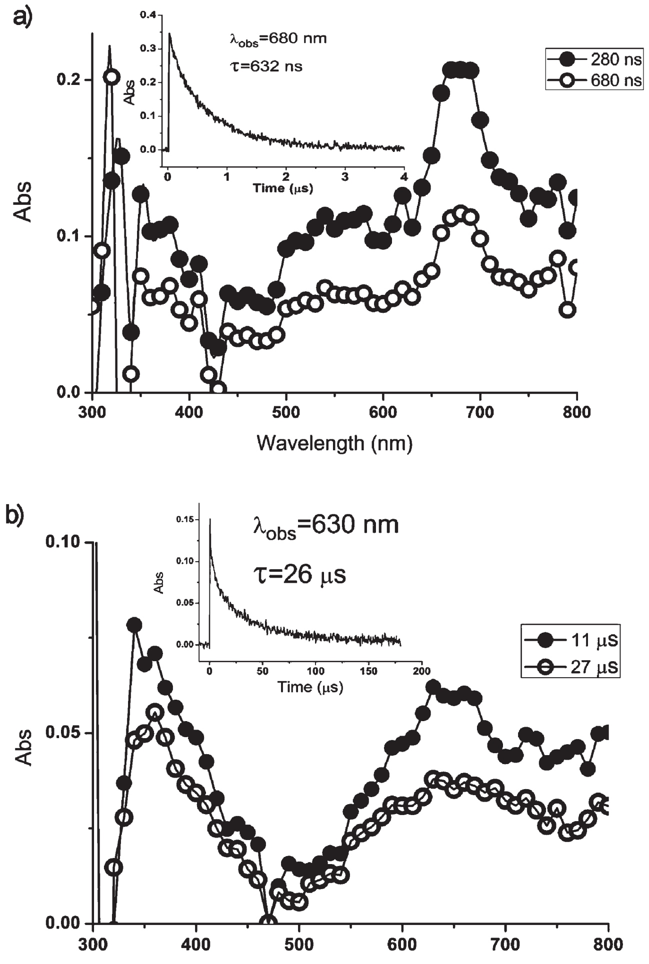


Figure 7. Transient optical absorption spectra recorded (a) at 280 and 680 ns following laser excitation (355 nm, 5 ns) of TX-FLCOOH in argon saturated acetonitrile solution and (b) at 11 and 27 μs following laser excitation (355 nm, 5 ns) of TX-FLCOONa in argon-saturated water solution.

We have studied the effect of pH on the photopolymerization by increasing acid concentration. The polymerization does not proceed in the acidic media when the hydrogen donor is present in the formulation. This is expected since amino compound is quarternized by the addition of acid which decreases hydrogen-donating efficiency. In the absence of hydrogen donor, the salt is converted to the oil-soluble acidic form and precipitates in water.

Laser Flash Photolysis Experiments. Laser flash photolysis studies were performed to investigate the triplet states of the photoinitiators. Figure 7a,b shows the transient absorption spectra of degassed acetonitrile solutions containing TX-FLCOOH and TX-FLCOONa after irradiation with laser pulses of 355 nm. The transients were recorded at 280 and 680 ns, and 11 and 27 μs, after the pulse for TX-FLCOOH and TX-FLCOONa, respectively.

Both spectra show two peaks at around 340 and 650 nm. The peaks at longer wavelength, 680 and 630 nm for TX-FLCOOH and TX-FLCOONa, respectively, were assigned to the triplet−triplet absorption. The bare TX,[46] its thiol,[13] and thioacetic acid[14] derivatives also exhibit similar transient spectra. Apparently, the lifetimes of the triplet states of these TX compounds are quite close to that of TX-FLCOONa ($\tau = 26\ \mu$s at 630 nm) (Figure 7b). However, a much shorter triplet lifetime ($\tau = 632$ ns at 680 nm) observed in the case TX-FLCOOH indicates a fast quenching process. In contrast to the sodium derivative, the hydrogen abstraction reaction is facilitated by the carboxylic acid hydrogen present in the structure of TX-FLCOOH.

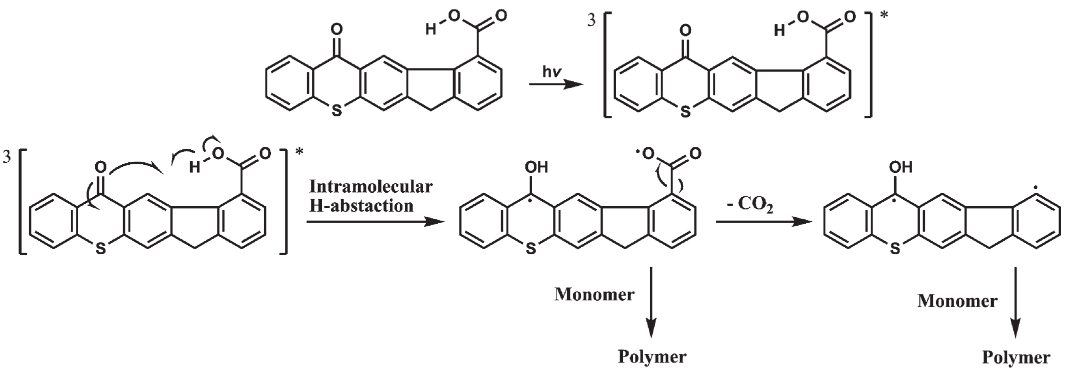
To test if triplet quenching occurs in an intramolecular process (Scheme 3) or intermolecular process (Scheme 4), laser flash photolysis experiments were performed at two different concentrations of TX-FLCOOH, 1.01×10^{-4} and 6.09×10^{-5} M. At low concentration very short triplet lifetime (163 ns) was observed, showing that at these low concentrations no intermolecular reaction occurs, where triplet of TX-FLCOOH gets quenched by another molecule of TX-FLCOOH in the ground state. Furthermore, such as bimolecular quenching process is unlikely at these low concentrations of TX-FLCOOH (6.09×10^{-5} M) because of the short triplet lifetime (163 ns). At concentrations of

Table 2. Gelation Time and Gel Content Comparison of Dental Formulations with the Photoinitiators TX-FLCOONa and CQ[a]

photoinitiators	gelation time (min)	gel content (%)
TX-FLCOONa	20	98
CQ	1	98

[a] Dental formulation: 40% EAEPA, 20% DEBAAP, and 40% water was used as a standard resin.

Scheme 3. Photopolymerization Mechanism in Lower Concentrations of TX-FLCOOH through Intramolecular H-Abstraction



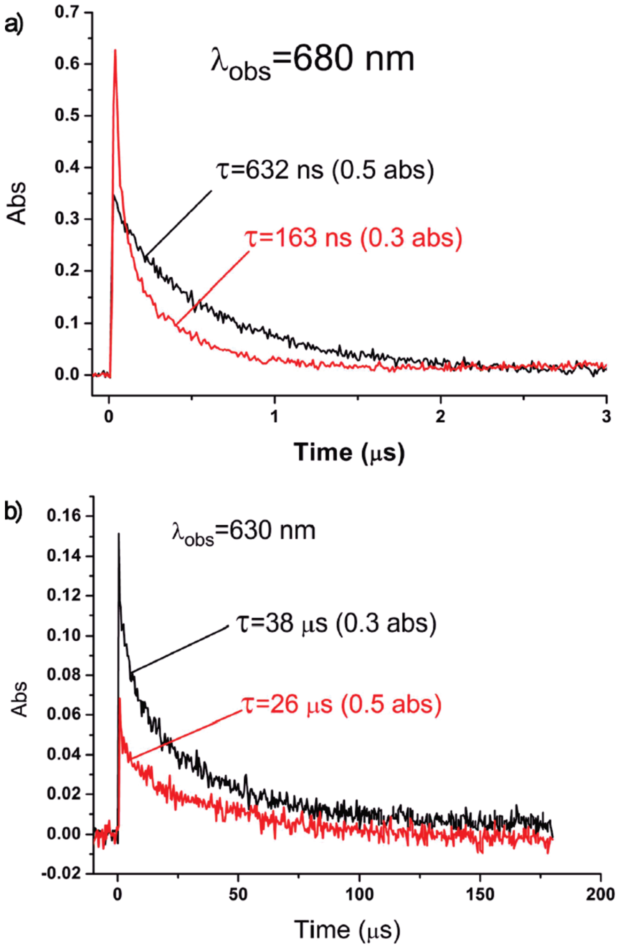
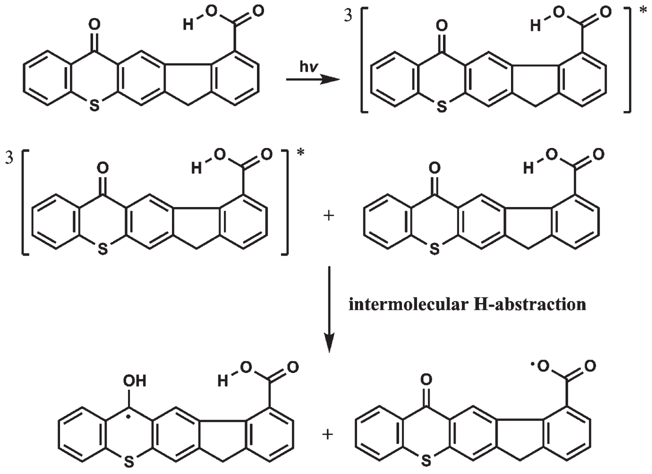


Figure 8. Transient absorption kinetics observed (a) at 680 nm following laser excitation (355 nm, 5 ns) of TX-FLCOOH in argon-saturated acetonitrile solution and (b) at 630 nm following laser excitation (355 nm, 5 ns) of TX-FLCOONa in argon-saturated water solution.

Scheme 4. Photopolymerization Mechanism in Lower Concentrations of TX-FLCOOH through Intramolecular H-Abstraction



TX-FLCOOH above 10^{-4} M, however, the respective intermolecular reactions may be operative, where the triplet excited state of TX-FLCOOH reacts with another molecule of TX-FLCOOH in the ground state through various deactivation pathways.

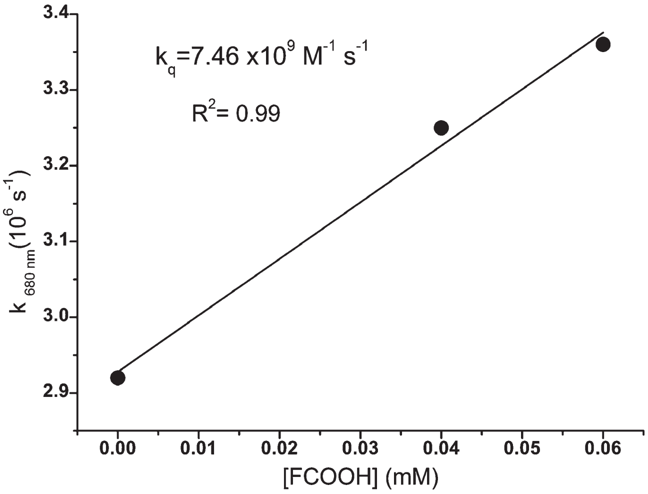


Figure 9. Quenching of TX-FLCOOH triplets by FLCOOH in acetonitrile; dependence of the pseudo-first-order rate constant of the decay at 680 nm on the concentration of FLCOOH.

A photolysis experiment was performed in the absence of monomer in order to clarify the initiation mechanism of TX-FLCOOH and to demonstrate the decarboxylation nature after hydrogen abstraction process (Scheme 3). Thus, 1 mL of a solution of TX-FLCOOH (6.25×10^{-2} M) in water was placed in a quartz tube and connected to another tube containing (3.40×10^{-3} M) aqueous Na_2CO_3 and one drop of phenolphthalein. The pink color of the solution completely disappeared at the end of 2 h irradiation. This effect is attributed to the decarboxylation of the initiator resulting in concomitant carbon dioxide evolution and consequently hydrogen carbonate formation.

In complete contrast, much longer triplet lifetimes were observed with the sodium derivative. In this case, the lifetime of triplet TX-FLCOONa was shorter at high concentration, again indicating bimolecular quenching as no hydrogen-donating site exists in the close proximity. Kinetically, the intermolecular process should only be possible above certain concentrations, as the bimolecular reaction cannot compete with the fast intramolecular reaction at lower concentrations. This is supported by laser flash photolysis experiments, where the model compound, fluorenecarboxylic acid (FLCOOH), was used as quencher (Figure 9). Pseudo-first-order treatment of the decay kinetics of the TX-FLCOOH triplet states observed at 680 nm gave a quenching rate constant of 7.46×10^9 M^{-1} s^{-1}. This shows that a bimolecular quenching process, where the triplet of TX-FLCOOH gets quenched by FLCOOH in the ground state, can only compete with the intramolecular quenching at concentrations in the order of several millimolar.

Conclusion

In this article, we synthesized two kinds of thioxanthone fluorene photoinitiators absorbing at visible range and then investigated the effect of structures of on photochemical behaviors in comparison with the parent thioxanthone compound. Fluorescence and laser flash photolysis studies in conjunction with photopolymerization experiments suggest that at low concentrations of TX-FLCOOH initiation occurs through intramolecular hydrogen abstraction. Above a concentration of 0.1 mM of TX-FLCOOH, intermolecular hydrogen abstraction probably dominates, which also generates radicals capable of initiating polymerization. The results also show that the sodium derivative, TX-FLCOONa, requires hydrogen donor such as amines for successful polymerization to occur as it does not possess abstractable hydrogen in the structure. It is clear that both photoinitiators possess excellent optical absorption properties in the visible region, ensuring efficient light absorption for many targeted applications such as dental filling materials, photoresists, printing plates, integrated circuits, laser-induced 3D curing, holographic recordings, and nanoscale micromechanics.

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