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Mechanistic Study of Photoinitiated Free Radical Polymerization Using Thioxanthone Thioacetic Acid as One-Component Type II Photoinitiator

Meral Aydin,[†] Nergis Arsu,[†] Yusuf Yagci,[*,‡] Steffen Jockusch,[§] and Nicholas J. Turro[§]

Department of Chemistry, Davutpasa Campus, Yildiz Technical University, Istanbul 34210, Turkey, Department of Chemistry, Istanbul Technical University, Maslak, Istanbul 80626, Turkey, and Department of Chemistry, Columbia University, 3000 Broadway, New York, New York 10027

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ABSTRACT: A mechanistic study concerning photoinitiated free radical polymerization using thioxanthone thio-acetic acid (TX−S−CH_2−COOH) as one-component Type II photoinitiator was performed. Steady-state and time-resolved fluorescence and phosphorescence spectroscopy, as well as laser flash photolysis was employed to study the photophysics and photochemistry of TX−S−CH_2−COOH. The initiator undergoes efficient intersystem crossing into the triplet state and the lowest triplet state posseses $\pi-\pi^*$ configuration. In contrast to the unsubstituted thioxanthone, TX−S−CH_2−COOH shows an unusually short triplet lifetime (65 ns) indicating an intramolecular reaction. From fluoroscence, phosphorescence, and laser flash photolysis studies, in conjunction with photopolymerization experiments, we propose that TX−S−CH_2−COOH triplets undergo intramolecular electron transfer followed by hydrogen abstraction and decarboxylation producing alkyl radicals, which are the active initiator radicals in photoinduced polymerization. At low initiator concentrations (below 5×10^{-3} M) this intramolecular reaction is the dominant path. At concentrations above 5×10^{-3} M, however, the respective intermolecular reactions may be operative.

Introduction

Photoinitiated polymerization is a well-accepted technology that finds industrial application in coatings on various materials, adhesives, printing inks, and photoresists.[1−5] Although photoinitiated cationic polymerization has gained importance in recent years, the corresponding free radical polymerization is still the most widely employed route in such applications. Because of their vital role in photopolymerization, photoinitiators are the subject of particularly extensive research. Most of this research has focused on Type I photoinitiators, which upon irradiation undergoes an α-cleavage process to form two radical species. Type II photoinitiators are a second class of photoinitiators and are based on compounds whose triplet excited states are reacted with hydrogen donors thereby producing an initiating radical[6−8] (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.

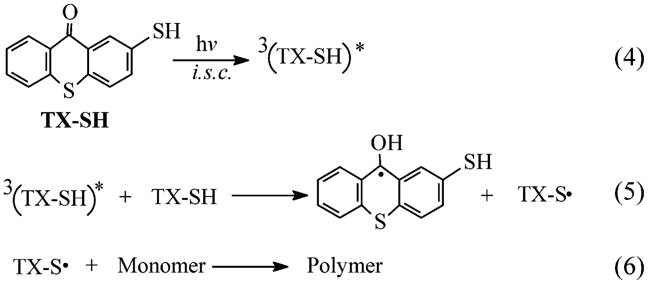
Scheme 1

$$Ar_2C{=}O \xrightarrow{h\nu} {}^3\left[Ar_2C{=}O\right]^* \tag{1}$$

$${}^3\left[Ar_2C{=}O\right]^* + R\text{-}H \longrightarrow Ar_2\dot{C}\text{-}OH + R^\bullet \tag{2}$$

$$R^\bullet + \text{Monomer} \longrightarrow \text{Polymer} \tag{3}$$

Scheme 2



Typical Type II photoinitiators include benzophenone and derivatives, thioxanthones, benzil, quionones, and organic dyes, 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.[9−13] We recently reported[14] the use of a thiol derivative of thioxanthone (TX−SH; Scheme 2) as photoinitiator for free radical polymerization. A great advantage of this initiator is related to its one component nature. It can serve as both triplet photosensitizer and a hydrogen donor. Thus, this photoinitiator does not require an additional co-initiator, i.e., a separate hydrogen donor. The mechanism of the photoinitiation is based on the intermolecular reaction of triplet, ^{3}TX−SH*, with the thiol moiety of ground-state TX−SH. The resulting thiyl radical initiates the polymerization (Scheme 2).

More recently, we reported[15] the synthesis and use of acetic acid derivatives of thioxanthone of the structure shown in Chart 1 as photoinitiators for free radical polymerization. The light aborbing and electron donating and consequently hydrogen donating sites are incorporated into the photoinitiator molecules.

These one-component photoinitiators initiate the polymerization much more efficiently than two-component systems in which light-absorbing and electron donating sites are in different molecules. Regarding the initiation mechanism, it could not be definitely concluded whether

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[†] Yildiz Technical University.
[‡] Istanbul Technical University.
[§] Columbia University.

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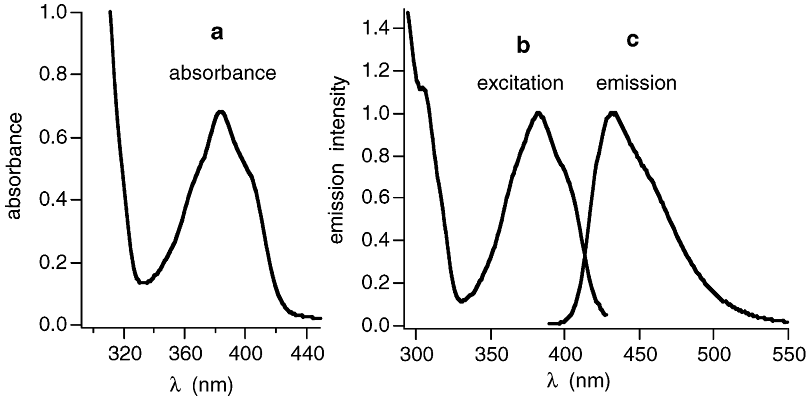

Figure 1. Optical absorption (a), fluorescence excitation (b), and fluorescence emission spectrum (c) of TX−S−CH_2−COOH (1.7 × 10^{-4} M (a); 5 × 10^{-5} M (b, c)) in 2-methyltetrahydrofuran at 23°C.

Scheme 3

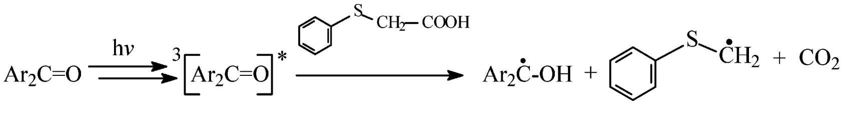

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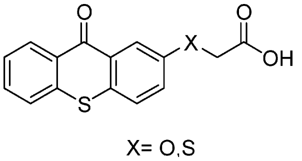
Chart 1. Structure of Thioxanthone Acetic Acid Derivatives



the initiating radicals are generated by intra- or intermolecular hydrogen abstraction reaction followed by decarboxylation process. To resolve this issue, the present paper reports laser flash photolysis, fluorescence and polymerization studies in order to gain more insight on the mechanism of photoinitiation of free radical polymerization by using thioxanthone thioacetic acid as a one-component Type II photoinitiator.

Experimental Section

Materials. 2-Thioxanthone−thioacetic acid (TX−S−CH_2−COOH) was synthesized as described previously.[15] Thiophenoxyacetic acid (Ph−S−CH_2−COOH), was obtained from Aldrich (97%) and used as received. Methyl methacrylate (MMA) (≥99%, Fluka) was washed with 5% aqueous NaOH solution, dried over $CaCl_2$, and distilled over CaH_2 in vacuo. Dimethylformamide (DMF) (99.5%, Fluka) was dried over $MgSO_4$ and then distilled under reduced pressure. Acetonitrile (99.8%, Merck) and 2-methyltetrahydrofuran (>98%, Merck) were used as received.

Photopolymerization. Typical polymerization procedure: A solution of MMA (0.5 mL, 4.7 M) and TX−S−CH_2-COOH (4.5 mg, 1.5 × 10^{-2} M) in 0.5 mL DMF was irradiated in a photoreactor consisting of a 400 W medium-pressure mercury lamp and a water cooling system, in air atmosphere for 15 min. The light intensity of the photoreactor was 7.12 × 10^{16} photon s^{-1} as measured by potassiumferrioxalate actinometer. At the end of irradiation, polymer was obtained after precipitation in methanol and drying in vacuo. Conversion: 14.4%. M_n: 22400 g mol^{-1}.

Measurements. UV−vis spectra were recorded on an Agilent 8453 spectrometer. Steady-state luminescence spectra were recorded on a SPEX Fluorolog 2T2 1680 0.22 m double spectrometer (Jobin Yvon Inc.). For room-temperature experiments 1 × 1 cm Suprasil quartz cells were used and for low-temperature experimets (77 K) 3 mm Suprasil quartz tubes in conjunction with a liquid nitrogen dewar were used. Time-resolved phosphorescence measurements were performed by multichannel scaling on a OB900 fluorimeter (Edinburgh Analytical Instruments) using a pulsed xenon lamp μF 900, Edinburgh Analytical Instruments). Laser flash photolysis experiments employed the pulses from a Spectra Physics GCR-150−30 Nd:YAG laser (355 nm, ca. 5 mJ/pulse, 5 ns) and a computer-controlled system that has been described elsewhere.[16] Solutions of the thioxanthone derivatives were prepared at concentrations such that the absorbance was ∼0.3 at the excition wavelength (355 nm).

Results and Discussion

As stated in the previous article[15] and shown in Figure 1a, TX−S−CH_2−COOH has an excellent optical absorption in the near UV (ϵ_{290} = 20 490 mol^{-1} L cm^{-1} and ϵ_{384} = 3900 mol^{-1} L cm^{-1}), and may therefore find practical application in UV-curing of pigmented systems as a free radical photoinitiator.

In view of the decarboxylation behavior[17−20] of the sulfur containing carboxylic acids upon reaction with photoexcited aromatic carbonyl compounds (e.g., benzophenone; see Scheme 3), photolysis of TX−S−CH_2−COOH results in the formation of free radicals. The decarboxylation nature of the photoinitiation was demonstrated by concomitant evolution of carbon dioxide. To clarify the mechanistic details, we have performed steady state and time-resolved fluoroscence and laser flash photolysis measurements together with polymerization experiments.

Figure 1b,c shows that a nearly mirror-image-like relation exists between excitation and emissionof TX−S−CH_2COOH. The quantum yield for fluoroscence emission (ϕ_f) in 2-methyltetrahydrofuran at 23 °C was found to be 0.06, which is similar to that of unsubstituted thioxthone.[21]

Steady-state and time-resolved excitation and emission spectra of TX−S−CH_2−COOH were also measured at 77 K in 2-methyltetrahydrofuran (Figure 2a−c). The two emission bands (Figure 2) at 430 and 508 nm are attributed to fluorescence and phosphorescence, respectively. Phosphorescence measurements are useful to gain information on the triplet energy and electron configuration of TX−S−CH_2−COOH. Phosphorescence spectra of ketones with n−π^* nature of the lowest triplet state are usually structured, due to the vibrational progression of the C=O vibration, and π−π^* triplets are mostly unstructured.[22, 23] In addition, the phosphores-

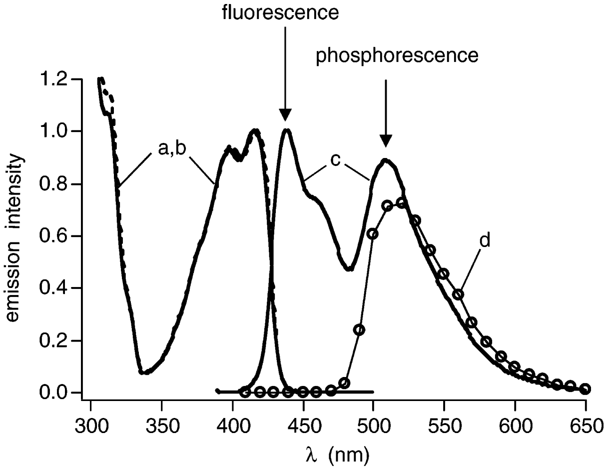


Figure 2. Steady-state luminescence excitation (a, $\lambda_{em} = 438$ nm; b, $\lambda_{em} = 508$ nm) and emission (c; $\lambda_{ex} = 384$ nm) spectra of TX−S−CH$_2$−COOH (5×10^{-5} M) in 2-methyltetrahydrofuran at 77 K. Time-resolved emission spectrum (d) 10−80 ms after the excitation pulse ($\lambda_{ex} = 384$ nm) at 77 K.

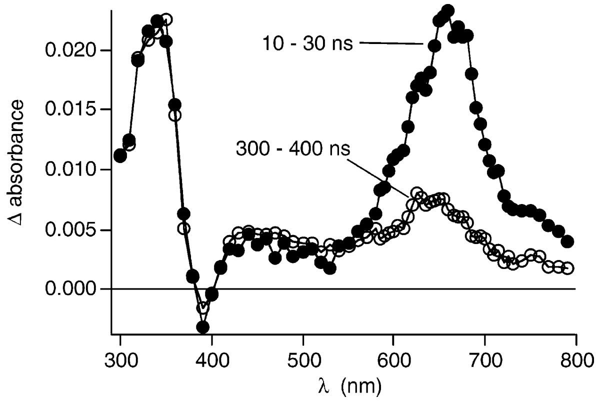


Figure 3. Transient optical absorption spectrum recorded 10−30 ns and 300−400 ns following laser excitation (355 nm, 5 ns) of TX−S−CH$_2$−COOH (5×10^{-5} M) in argon saturated acetonitrile solution at 23 °C.

cence lifetime for n−π* triplets are significantly shorter (in the order of several milliseconds) compared to π−π* triplets (more than 100 ms).[23,24] Thus, the broad structureless phosphorescence of TX−S−CH$_2$−COOH, together with the long phosphorescence lifetime, i.e., 127 ms in a matrix at 77 K, indicates a π−π* nature of the lowest triplet state. This is in agreement with the π−π* nature of the lowest triplet state of unsubstituted TX[21] and also with TX−SH.[14]

To investigate the triplet state of TX−S−CH$_2$−COOH further, laser flash photolysis was performed. Figure 3 shows the transient absorption spectra of a deoxygenated acetonitrile solution conatining TX−S−CH$_2$−COOH recorded 10−30 ns and 300−400 ns after irradiation with laser pulses of 355 nm. The spectrum shows two peaks at 660 and 340 nm. The peak at 660 nm was assigned to the triplet−triplet absorption of TX−S−CH$_2$−COOH based on similarities with the triplet−triplet spectra of TX[25] and TX−SH.[14] Figure 4 (right) shows the decay kinetic of the transient absorption at 660 nm. The triplet−triplet absorption at 660 nm decayed in a first-order kinetic corresponding to a lifetime of 65 ns. In contrast, the transient absorption at 340 nm decayed orders of magnitude slower (12 μs) (Figure 4, left). Notably, both transients were quenched by oxygen with rate constants close to the diffusion limit ($k_{O_2}{}^{340\ nm} = 5 \times 10^9$ M^{-1} s^{-1} and $k_{O_2}{}^{660\ nm} = 4 \times 10^9$ M^{-1} s^{-1}) suggesting a radical or triplet nature of the transients.

The assignment of transient absorption at 340 nm is more difficult. We tentatively assigned the absorption at 340 nm to an overlap of triplet−triplet absorbance of TX−S−CH$_2$−COOH and absorbance of the corresponding thioxanthone ketyl radical. Thioxanthone triples[14,25] and thioxantone ketyl radicals[26] are known to have some absorption between 300 and 400 nm. The fast rise time of the signal (within the laser pulse) is consistent with the assignment to the triplet absorption and the slower decay (12 μs) and the oxygen quenching is consistent with the assignment to the ketyl radical. In addition, TX−S−CH$_2$−COOH possesses an absorption between 340 and 420 nm. Excitation of TX−S−CH$_2$−COOH will bleach this absorption, which complicates the assignment of transient absorptions below 420 nm.

Typically, triplet states of TX derivatives, such as TX or TX−SH possess triplet lifetimes longer than 10 μs (TX−SH: $\tau_T = 21$ μs).[14] In contrast, TX−S−CH$_2$−COOH showed a triplet lifetime of only 65 ns (observed at 660 nm), which indicates the involvement of a fast intramolecular quenching process. We propose that the fast intramolecular quenching proces is a fragmentation reaction leading to carbon centered radicals (see below), which than can initiate the polymerization. Previously, we have shown that TX−S−CH$_2$−COOH is a good photoinitiator to initiate free radical polymerization of acrylates, indicating that TX−S−CH$_2$−COOH generates radicals efficiently.[15] To test if triplet quenching occurs in an intramolecular process or intermolecular process, laser flash photolysis experiments were performed at two different concentrations of TX−S−CH$_2$−COOH, 2.5×10^{-5} M and 5×10^{-5} M. At both concentrations, an identical triplet lifetime (65 ns) was observed, showing that at these low photoinitiator concentrations no intermolecular reaction occurs, where the triplet of TX−S−CH$_2$−COOH gets quenched by another molecule of TX−S−CH$_2$−COOH in the ground state. Furthermore, such a bimolecular quenching proces is unlikely at these low concentrations of TX−S−CH$_2$−COOH (5×10^{-5} M), because of the short triplet lifetime (65 ns).

To investigate if bimolecular quenching can occur at higher concentrations, a model compound was used, thiophenoxyacetic acid (Ph−S−CH$_2$−COOH), as quencher of triplet states of TX−S−CH$_2$−COOH (analogue reaction in Scheme 3). Laser flash photolysis experiments were performed with deoxygenated acetonitrile solutions of TX−S−CH$_2$−COOH (5×10^{-5} M) and different concentrations of Ph−S−CH$_2$−COOH ($0-2.5 \times 10^{-2}$ M). Pseudo-first-order treatment of the decay kinetics of the TX−S−CH$_2$−COOH triplet states observed at 660 nm gave a quenching rate constant of 8×10^8 M^{-1} s^{-1}. This shows that a bimolecular quenching process, where the triplet of TX−S−CH$_2$−COOH gets quenched by another molecule of TX−S−CH$_2$−COOH in the ground state, can only compete with the intramolecular quenching at concentrations in the order of several millimolar.

We have also performed polymerization experiments. The dependence of conversion of methyl methacrylate to polymer upon irradiating in DMF in air, on the concentration of the initiator, TX−S−CH$_2$−COOH, is shown in Figure 5.

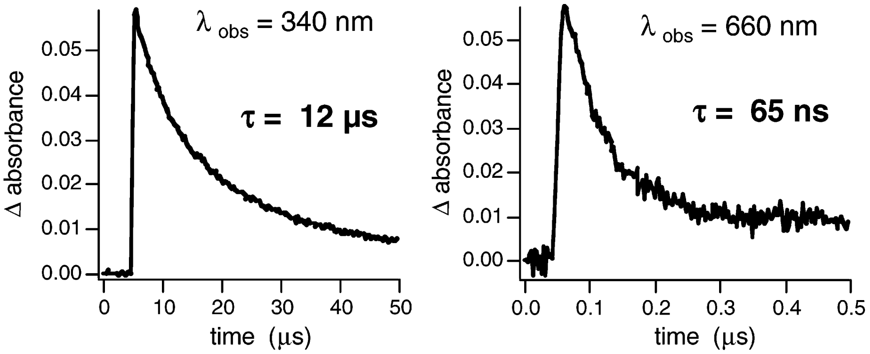


Figure 4. Transient absorption kinetics observed at 340 nm (left) and 660 nm (right) following laser excitation (355 nm, 5 ns) of TX−S−CH_2−COOH (5 × 10^{-5} M) in argon saturated acetonitrile solution at 23 °C.

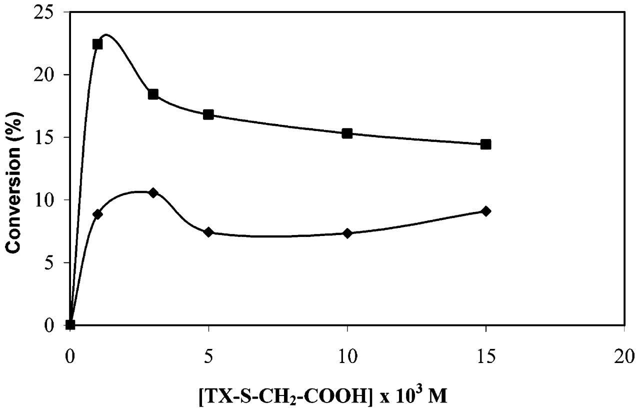


Figure 5. Photopolymerization of methyl methacrylate by using TX−S−CH_2−COOH in DMF for 10 min (◆) and 15 min (■).

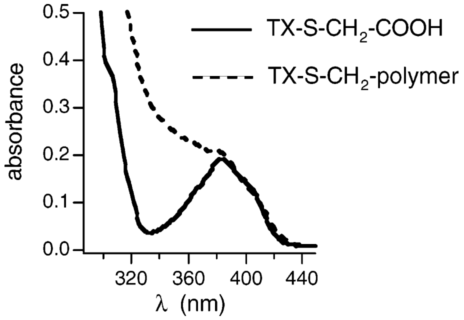


Figure 6. Dashed line: Optical absorption spectrum of a 2-methyltetrahydrofuran solution of the purified polymer (2% w/w) (purified by several percipitations) obtained by photopolymerization of methyl methacrylate initiated by TX−S−CH_2−COOH (5 × 10^{-3} M). For comparison, the absorption spectrum of pure TX−S−CH_2−COOH (5 × 10^{-5} M) is also shown (solid line).

Initially, the rate of initiation is proportional to the absorbed light and consequently the amount of initiator. However, when the concentration of the initiator is above a certain level the intermolecular hydrogen abstraction may become a dominant process. However, there should be no difference in polymerization efficiency since the monomer addition rate constants of the initiator radicals should be the same for intra- and intermolecular radical generation. The observed reduction in the conversion at high initiator concentration may be due to light absorption effects, where the light is absorbed completely within a small layer of the sample. This leads to a high local concentration of excited stated and radicals, and self-quenching processes could dominate. On the other hand, the formation of free radicals capable of initiating polymerization, is determined by the competion of intra- and intermolecular hydrogen abstraction processes. Indeed, the polymers obtained by using a low initiator concentration ([I] = 1 × 10^{-3} M) do not exhibit the characteristic absorption band of the thioxanthone moiety. On the contrary, the UV−vis spectra of the corresponding poly(methyl methacrylate) PMMA obtained by using a very high initiator concentration ([I] = 5 × 10^{-3} M) and purification by several precipitation presents an absorption band with a shoulder at 383 nm (Figure 6, dashed line) which is similar to the absorption spectrum of pure TX−S−CH_2−COOH (solid line).

The TX moiety, which is covalently attached to the polymer, is more clearly shown by luminescence spectroscopy. Figure 7 shows fluorescence and phosphorescence spectra of the same solutions of the UV−vis measurements (Figure 6). As can be seen from Figure 7, fluoroscence and phosporescence spectra in 2-methyltetrahydrofuran at 296 and 77 K, respectively, of the initiator and the corresponding polymer are very similar. The slight blue shift may be atributed to the slightly different structure of the polymer linked TX compared to the pure initiator. The excitation spectra for the emission signals (Figure 7, dashed lines) are in good agreement with the absorption spectrum of the precursor TX−S−CH_2−COOH (solid lines). In addition, the phosphorescence lifetimes at 77 K are also very similar; 127 and 123 ms, respectively.

On the basis of the above spectroscopic and flash photolysis studies of TX−S−CH_2−COOH, and polymerization studies, one can propose a scheme (see Scheme 4) illustrating major processes that may occur during photoinitiated polymerization.

Under low initiator concentrations, the dominant path of the reaction is intramolecular electron transfer followed by hydrogen abstraction and decarboxylation. The intramolecular reaction from the triplet excited state is supported by the short triplet lifetime (65 ns) observed by laser flash photolysis (Figure 4, right). The long-lived transient absorption at 340 nm (Fgure 4, left) suggest the formation of ketyl radicals (12 μs). At concentrations of TX−S−CH_2−COOH above 5 × 10^{-3} M, however, the respective intermolecular reactions may be operative, where the triplet excited state of of TX−S−CH_2−COOH reacts with another molecule of TX−S−CH_2−COOH in the ground state (Scheme 4). Kinetically, the intermolecular process should only be possible at concentrations of TX−S−CH_2−COOH above several millimolar, because at lower concentrations, the bimolecular reaction cannot compete with the fast intramolecular reaction. This is supported by laser flash photolysis experiments,

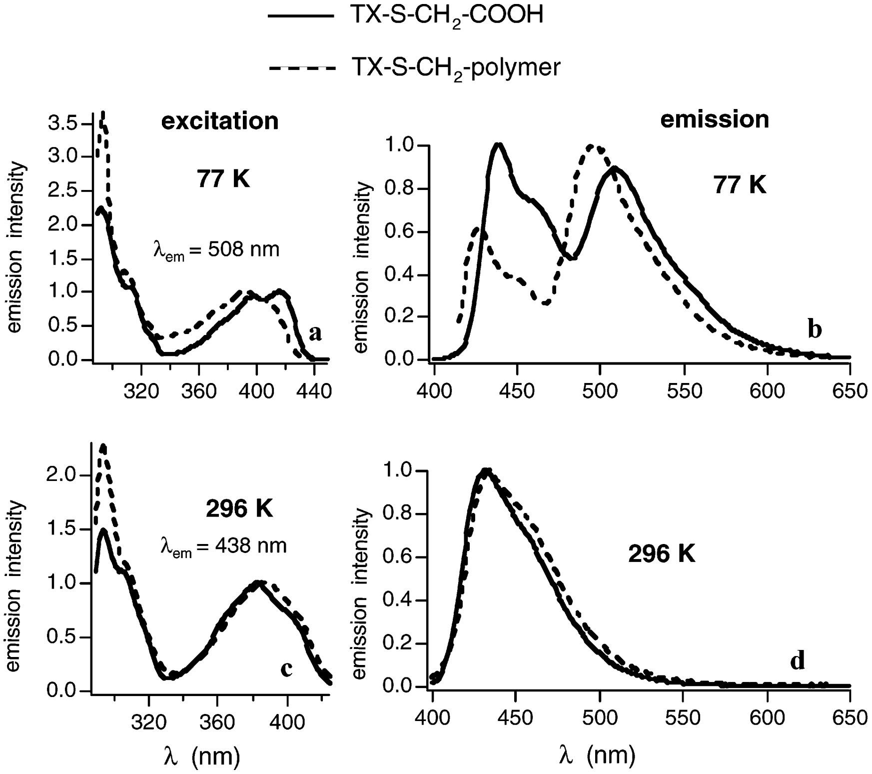
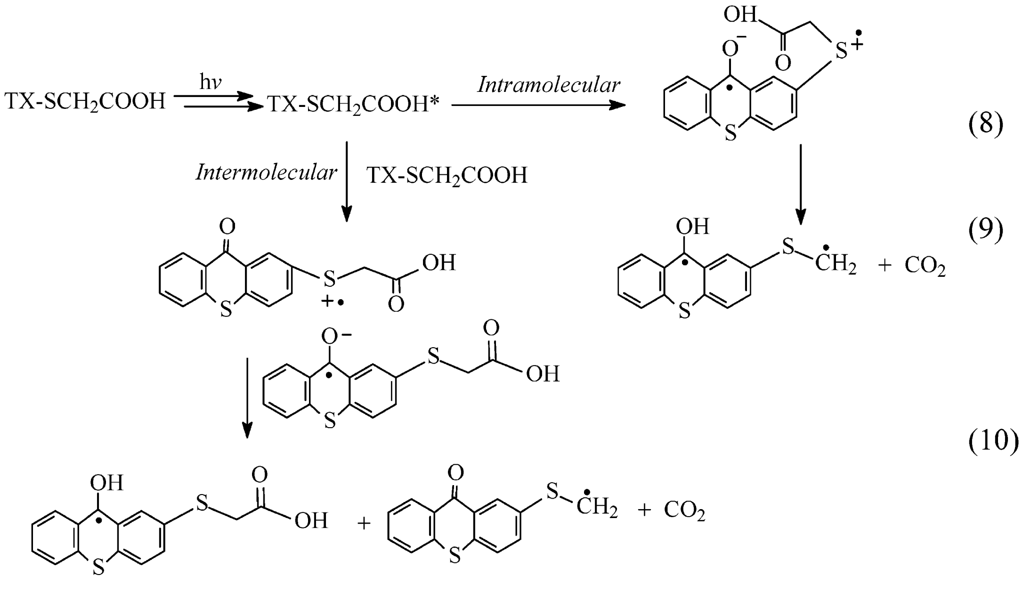


Figure 7. Dashed lines: luminescence excitation (left) and emission spectra (right) of 2-methyltetrahydrofuran solutions at room temperature (c, d) or frozen matrixes at 77 K (a, b) of the purified polymer (2% w/w) (purified by several percipitations) obtained by photopolymerization of methyl methacrylate initiated by TX−S−CH$_2$−COOH (5 × 10^{-3} M). For comparison, the luminescence spectra of pure TX−S−CH$_2$−COOH are also shown (solid lines).

Scheme 4



where the model compound Ph−S−CH$_2$−COOH was used as quencher (see above).

Conclusions

The one-component Type II photoinitiator TX−S−CH$_2$−COOH initiates free radical polymerization efficiently. Fluorescence, phosphorescence, and laser flash photolysis studies in conjunction with photopolymerization experiments suggest that at low concentrations of TX−S−CH$_2$−COOH (<5 mM) intramolecular electron transfer occurs, followed by hydrogen abstraction and decarbonylation to produce alkyl radicals, which initiate the polymerization. Above a concentration of 5 mM of TX−S−CH$_2$−COOH, intermolecular electron transfer probably dominates, which also generates alkyl radicals capable of initiating polymerization.

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