Mercaptoalkoxy-thioxanthones as novel photoinitiators for free radical polymerization – mechanistic study

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DOI: dx.doi.org/10.14314/polimery.2019.3.4

Abstract: Three mercaptoalkoxy-thioxanthones were developed as new photoinitiators for radical polymerization. These compounds can act as either one- or two-component photoinitiating systems. The quenching of the excited triplet states of thioxanthone derivatives by aromatic amines was investigated in dimethyl sulfoxide (DMSO). Based on the mechanism of the intermolecular electron-transfer process, we proposed sequence of reactions leading to the formation of radicals that are capable of initiating the polymerization reaction.

Keywords: free radical polymerization, photoinitiators, mercaptoalkoxy-thioxanthones, laser flash photolysis.

Merkaptoalkoksy-tioksantony jako nowe fotoinicjatory polimeryzacji rodnikowej

Streszczenie: Zsyntetyzowano trzy alkoksypochodne tioksantonu i oceniono możliwość ich zastosowania jako nowych fotoinicjatorów polimeryzacji rodnikowej. Na podstawie wyników badań stwierdzono, że związki te mogą działać zarówno jako jednoskładnikowe układy fotoinicjujące, jak i układy dwuskładnikowe w kompozycji z donorem elektronu. Fotoliza i badania kinetyczne stanów wzbudzonych zsyntetyzowanych pochodnych tioksantonu w obecności amin aromatycznych w środowisku dimetylosulfotlenku (DMSO) pozwoliły na zaproponowanie sekwencji reakcji prowadzących do powstania rodników zdolnych do zainicjowania reakcji polimeryzacji.

Słowa kluczowe: polimeryzacja wolnorodnikowa, fotoinicjatory, merkaptoalkoksy-tioksantony, laserowa fotoliza błyskowa.

Photoinitiated polymerization may be initiated by direct photolysis of a precursor providing free radicals by bond dissociation. The radicals may be also formed in bimolecular processes that involves electron or proton transfer reactions [1, 2]. Most commonly, the components of such initiating systems act as classical a single-phase solution in which the composition is uniform on a molecular scale (solutes are present as single molecules). Second approach applies a polymer chain as an initiator carrier. This includes both types of initiators, *i.e.*, photoinitiators that form free radicals by photo-cleavage reaction [3–5] as well as in bimolecular processes [6–8].

Previously, we reported on free-radical polymerization systems, based on sulfur containing benzophenones [9], xanthene dyes [10, 11], and xanthone and thioxanthone derivatives [12] constituting the absorbing chromophore. Photolysis of these groups of compounds in the presence of hydrogen donors, such as amines and amino acids leads to free radical formation followed by intermolecular electron transfer (PET) process between an excited acceptor (A) and an electron donor (D) (aromatic amines). Then, a proton transfer from the electron donor radical cation to the dye radical anion yields a neutral radical-initiated polymerization and the reduced radical of the dye. The most important processes finally giving as an intermediate free radical able to initiate polymerization chain reaction are illustrated in Scheme A [13].

In our previous paper [14], we revealed that aromatic ketones generating radicals by an electron and hydrogen transfer required an electron donor (HD) as a second component in the polymerizing formulation. The most commonly employed co-initiators are tertiary amines.

Also known are thioxanthonethiols used as one-component photoinitiators developed by the research groups of Yagci and Arsu [15–18]. A good example is the 2-mercapto-thioxanthone (TX-SH) [15] which acts as both a triplet photosensitizer and a hydrogen donor.

The mechanism of the polymerization is based on the intermolecular reaction between the excited triplet state of

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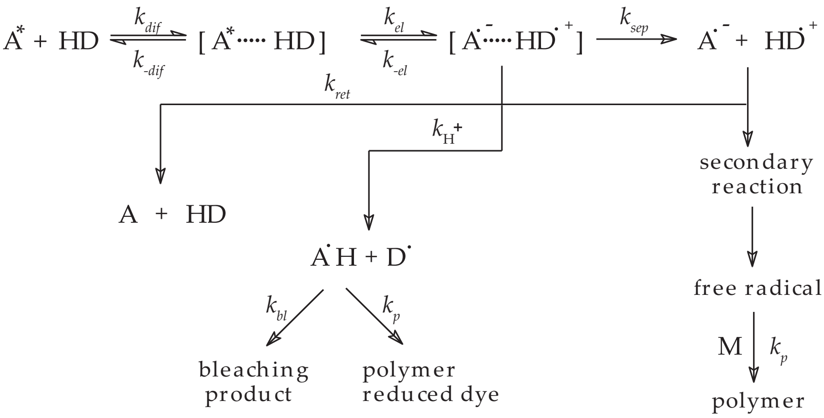
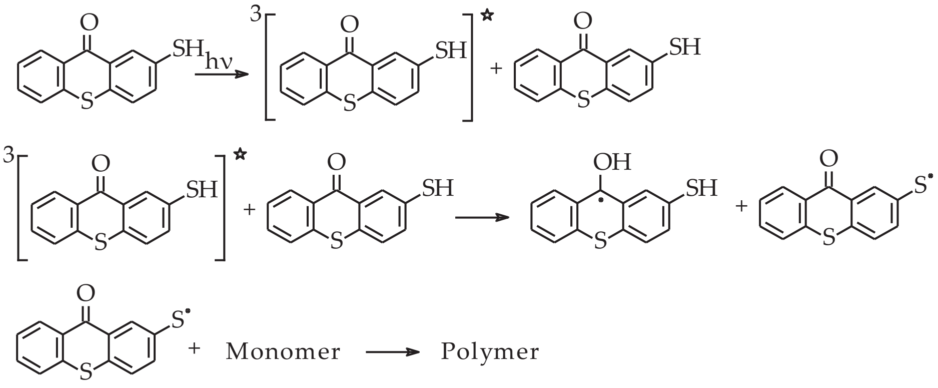


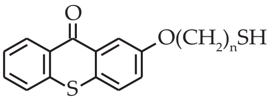
Scheme A



Scheme B

the photoinitiator $^3(TX\text{-}SH)^*$ and the TX-SH molecule being in the ground state to yield thiyl radical. The radical efficiently initiates an acrylate polymerization (Scheme B).

In this paper, we report on the application of mercaptoalkoxy-thioxanthones [Formula (I)] as one- and two-component photoinitiating systems for free radical polymerization. Mechanism of the photoreductive sensibilization of the polymerization reaction was proposed based on the laser flash photolysis experiments. The kinetic and thermodynamic rate constants of the PET process were determined as well.



(I)

TX-O-$(CH_2)_n$-SH (n = 3, 6, 12)

EXPERIMENTAL PART

Materials

All solvents, monomer: 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA), *N*-phenyl-glycine (NPG), diphenylamine (DPA), diethylamine (DEA) and reagents for preparation of the thioxanthone derivatives were purchased from Aldrich Chemical Co. They were the best available purity grades and were used without further purification.

Syntheses

Synthesis of 2-hydroxy-thioxanthone

The 2-hydroxy-thioxanthone was synthesized based on the method described by Catalina [19] and co-workers. The procedure was as follows.

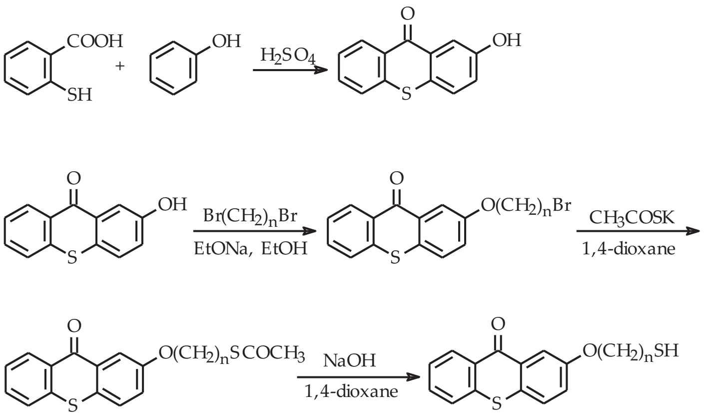
Thiosalicylic acid (3.2 g, 0.0208 M) was slowly added to the concentrated sulfuric acid (76 cm^3). The mixture was stirred for 5 min, then phenol (6 g, 0.064 M) was added within 60 min. The reagents were stirred at room temperature for 1 h and then at 80 °C for 2 h. The resulting mixture was left to stand at room temperature overnight. Then, it was carefully poured with stirring into 10 times its volume of boiling water and boiled for 5 min. The solution was cooled and filtrated. The residue was recrystallized from water : 1,4-dioxane (20 : 80 v/v) to give 2-hydroxy-thioxanthone.

m.p. 151 °C.

UV-Vis (DMSO), λ_{max} = 394 nm, ε_{max} = 1780 [$M^{-1} \cdot cm^{-1}$].

IR (KBr, cm^{-1}): 3063 (C=C), 1683 (C=O), 1580 (C=C), 1067 (C-S), 755 (Ar-SH).

^{1}H-NMR (DMSO-d_6); δ [ppm]: 8.466–8.418 (d, 1H, aromatic), 7.854–7.753 (m, 2H, aromatic), 7.713–7.669 (m, 2H,



Scheme C

aromatic), 7.586–7.504 (m, 1H, aromatic), 7.295–7.237 (m, 1H, aromatic), 10.1171 (s, 1H, -OH).

Synthesis of 2-mercaptoalkoxy-thioxanthones (MAlc-TX)

Our approach to the thioxanthones with different alkyl chain separating the thiol group from the chromophore was based on modification of the 2-hydroxy-thioxanthone. Our intention was to synthesize compounds containing a mercaptoalkoxy moiety in position 2 relative to the carbonyl group [see Formula (I)].

The sequence of reactions leading to the mercaptoalkoxy-thioxanthones was elaborated based on the method described by Richardson [20]. A general route for the synthesis is shown in Scheme C.

A detailed description of the synthesis and spectral characteristics of the obtained compounds is presented in our previous paper [14]. The synthesized 2-mercapto-alkoxy-thioxanthones were applied as photoinitiators for TMPTA polymerization.

Methods of testing

Spectroscopic and the voltamperometric measurements

Absorption spectra were obtained using a Shimadzu MultiSpec-1501 photodiode array spectrophotometer. The reduction potentials of thioxanthone derivatives were measured using cyclic voltammetry. An Electroanalitycal MTM System model EA9C-4z was used for the measurements. A platinum (1 mm) disk electrode was applied as the working electrode, a Pt wire constituted the counter electrode and an Ag-AgCl electrode served as a reference electrode. The measurements were carried out under argon in a 0.1 M solution of tetrabutylammonium perchlorate in dry acetonitrile.

Polymerization process

Measurements of the kinetics of polymerization were carried out by measuring the heat evolution of a sample irradiated with an Innova 90-4 argon-ion laser (351 and 361 nm lines). The measurements were performed in a homemade micro-calorimeter as described earlier [21–23]. The irradiation intensity was measured with a Coherent Power Meter Type 543–500 mA.

The kinetics of free radical polymerization was studied using a polymerization solution composed of either monomer [2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA)] and initiator (mercaptoalkoxy thioxanthones) for one-component photoinitiating system or monomer, initiator and co-initiator [*N*-phenyl-glycine (NPG), diethylamine (DEA) or diphenylamine (DPA)] for two-component photoinitiating system. The initiator concentration was prepared assuming that 2 mm thick formulation layer should have absorbance equal 2. An electron donor concentration was 0.1 M. Intensity of the laser beam was a 60 mW/0.196 cm^2. The polymerizing formulation was not deareated.

Laser flash photolysis

Nanosecond laser flash photolysis experiments were performed using a LKS.60 Laser Flash Photolysis apparatus (Applied Photophysics). Laser irradiation at 355 nm from the third harmonic of the Q-switched Nd:YAG laser from a Lambda Physic/model LPY 150 operating at 65 mJ/pulse (pulse width about 4–5 ns) was used for the excitation. Transient absorbances at preselected wavelengths were monitored by a detection system consisting of a monochromator, a photomultiplier tube (Hamamatsu R 955) and a pulsed xenon lamp (150 W) as a monitoring source. The signal from the photomultiplier was processed by a Hewlett-Packard/Agilent an Agilent Infiniium 54810A digital storage oscilloscope and an Acorn compatible computer. In all experiments, the thioxanthone derivative concentration was in the range of 0.0002–0.0005 M. All experiments were run in argon-purged solutions.

RESULTS AND DISCUSSION

Laser flash photolysis experiments were performed to identify and study products formed after photolysis

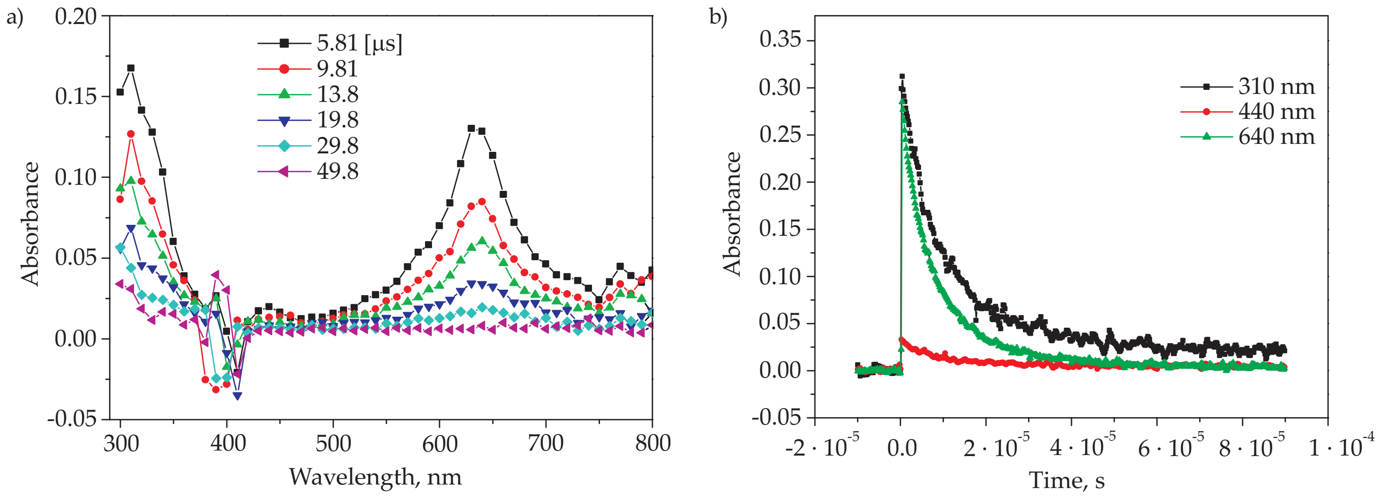


Fig. 1. a) The transient absorption spectra of a TX-O-$(CH_2)_3$-SH ($4.84 \cdot 10^{-4}$ M) in DMSO recorded after irradiation with laser pulses at 355 nm; the delay time is marked on the figure, b) the decay kinetics at 310 nm, 440 nm and 640 nm

of the tested compounds. Upon laser excitation of the mercaptoalkoxy-thioxanthones in Ar-saturated DMSO a transient absorption having three peaks was observed as shown in Fig. 1. The spectrum contains two intense absorption bands with the maximum at 310 nm and 640 nm and one, low-intensity at 440 nm. Based on similarities to the transient spectra of TX-SH and thioxanthone derivatives [12], the observed band at 640 nm was assigned to the triplet-triplet (T-T) absorption of MAlc-TX. It decays mono-exponentially with lifetimes in the range from 4.6 μs to 8.5 μs depending on the tested MAlc-TXs (see Table 1). Similar results were obtained for xanthone (0.75 μs), and thioxanthone derivative (1.65–2.98 μs) in acetonitrile [12, 15, 24]. In contrast, the absorption transients at 310 nm and 440 nm were fitted to a biexponential function with τ_1 = 7.73 μs and τ_2 = 160 μs at 440 nm, and τ_1 = 7.87 μs and τ_2 = 74.9 μs at 310 nm for TX-O-$(CH_2)_3$-SH. The data clearly showed that the absorption transient signals at 310 nm and 440 nm decay on time scales ranging from a few microseconds (τ_1) to a dozens (or hundred) of microseconds (τ_2). It is worth notice that the τ_1 at both 310 nm and 440 nm is similar to the lifetime of the T-T absorption. The absorption transients are shown in Fig. 1.

The triplet lifetime of the MAlc-TXs tested depends on their concentration (Fig. 2). The obtained results for TX-O-$(CH_2)_6$-SH clearly indicate that an increase of the

T a b l e 1. Spectral and electrochemical characteristics of the tested MAlc-TX and their photolysis products

	TX-O-$(CH_2)_3$-SH	TX-O-$(CH_2)_6$-SH	TX-O-$(CH_2)_{12}$-SH
λ^{Ab}_{max} [nm], [DMF]	400	399	399
log ε	2.99	3.01	2.99
$\lambda_{T\text{-}T}$ [nm], [DMSO]	640	640	640
log $\varepsilon_{T\text{–}T}$	2.82	2.97	2.54
$\tau_{T\text{–}T}$ [μs]	8.5	4.6	5.3
$\tau_{1\ 310\ nm}$ [μs]	7.87	5.28	2.6
$\tau_{2\ 310\ nm}$ [μs]	74.9	22.6	7.84
$\tau_{1\ 440\ nm}$ [μs]	7.73	4.84	1.97
$\tau_{2\ 440\ nm}$ [μs]	160	51.4	39.0
λ^{Fl}_{max} [nm], [DMSO]	454	451	455
E_{00} [eV]	2.73	2.75	2.72
E_{red} [eV]	-0.766	-0.743	-0.766
$k_q \cdot 10^{-8}$ [s^{-1}], [DEA]	2.88	1.83	3.09
[DPA]	6.88	5.02	5.49
[NPG]	6.42	4.67	4.74
ΔG_{el} [eV], [DEA]	-0.748	-0.772	-0.748
[DPA]	-0.334	-0.357	-0.334
[NPG]	-0.034	-0.057	-0.034

τ_i – lifetimes of photolysis products, E_{00} – energy of the 0→0 transition, E_{red} – reduction potential, ΔG_{el} – the standard free energy change for electron transfer process, k_q – the primary reaction rate constants.

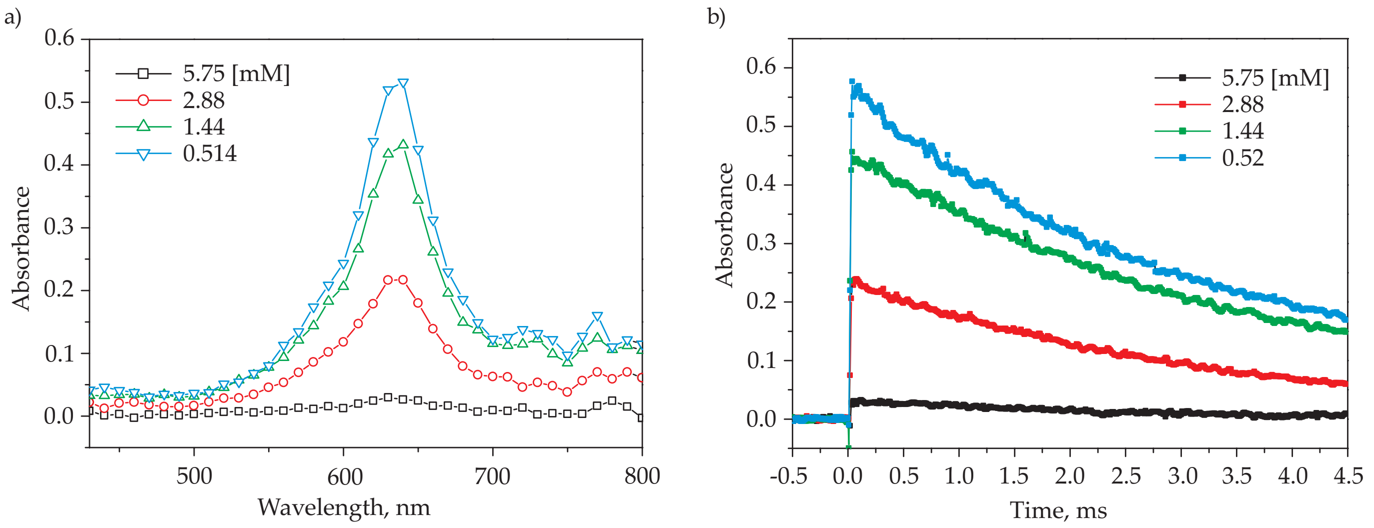


Fig. 2. a) The transient absorption spectra of TX-O-(CH$_2$)$_6$-SH recorded after the delay time τ = 0.29 μs, b) decay kinetics at 640 nm at various concentrations of the 2-mercaptoalkoxy-thioxanthone; the concentration of the TX-O-(CH$_2$)$_6$-SH is marked in the figure

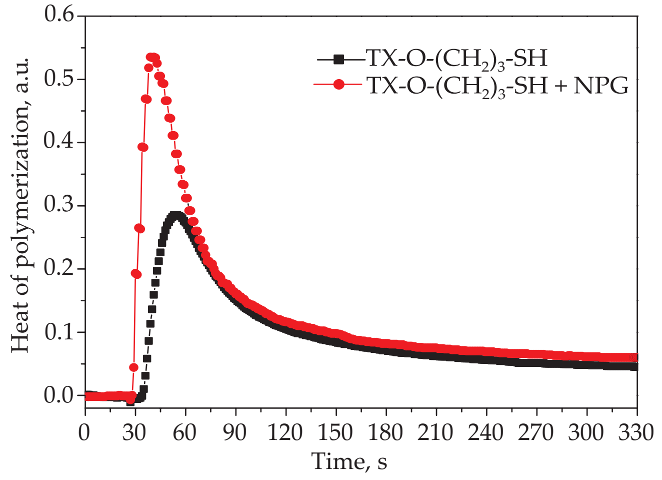


Fig. 3. Kinetic curves for polymerization of TMPTA initiated by TX-O-(CH$_2$)$_3$-SH and in the presence of NPG as electron donor; description of the curves in the legend

2-mercaptoalkoxy-thioxanthone concentration significantly decreases the intensity of the triplet absorption band at 640 nm. Changes in the amount of the 2-mercaptoalkoxy-thioxanthone from *ca*. 0.5 mM to 5 mM decreases the absorption intensity from about 0.5 to almost 0. The observed lowering of the extinction coefficient of the triplet state absorption is probably due to a reaction between the molecule in the excited triplet state and the one in the ground state. This observation is in a good agreement with the intramolecular electron and/or a proton transfer mechanism proposed by Turro *et al*. [17].

The obtained results and our previous studies [14] revealed that there are two different routes leading to free radicals starting a chain reaction for 2-mercaptoalkoxy-thioxanthone one-component photoinitiators. In the first case, the radicals are formed as a result of intramolecular electron transfer from the sulfur atom followed by the proton transfer. In the second one, the electron transfer

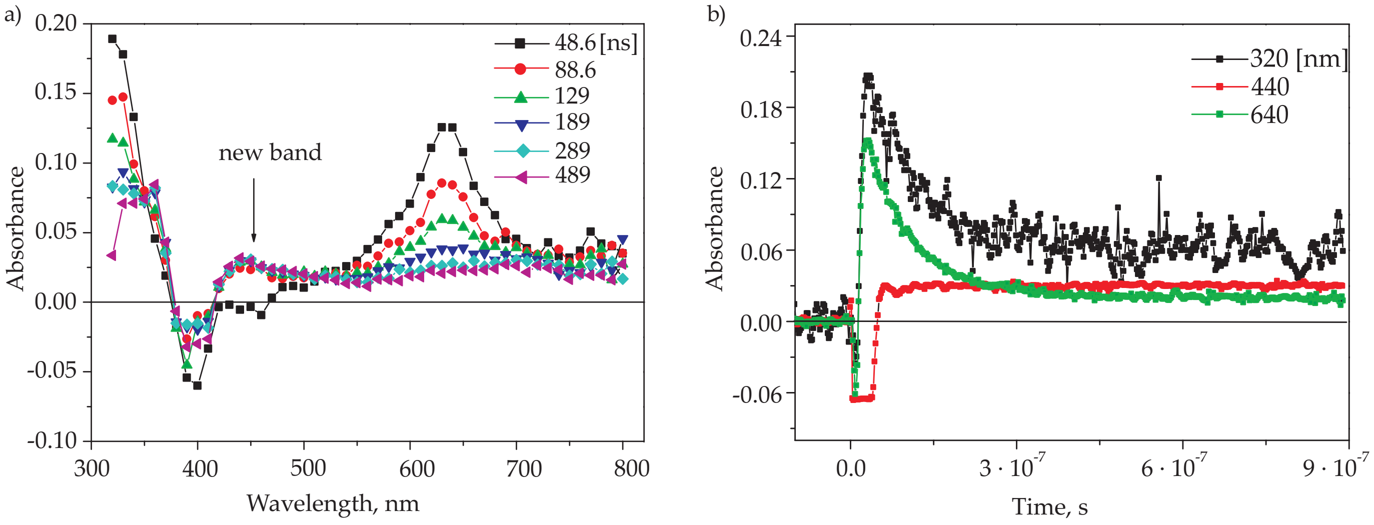


Fig. 4. a) Transient absorption spectrum of TX-O-(CH$_2$)$_6$-SH in DMSO in the presence of 300 μl DEA (3.4 · 10^{-4} M); delay times are shown in figure, b) decay kinetics of TX-O-(CH$_2$)$_6$-SH at 320 nm, 440 nm, and 640 nm

process competes with the intermolecular electron transfer from the excited triplet states ^{3}[TX-O-$(CH_2)_n$-SH]* to the ground state of this molecule. The resulting radical ion pair creates free radicals by proton transfer process. In both cases, the forming thiyl radical efficiently initiates polymerization of acrylates.

However, the polymerization kinetic data showed that the addition of an electron donor to the polymerizing composition containing 2-mercaptoalkoxy-thioxanthones increases the rate of polymerization several times (Fig. 3). Thus, the photolysis study were performed in the presence of electron donors such as NPG (E_{ox} = 0.426 eV) [9], DPA (E_{ox} = 0.84 eV) and DEA (E_{ox} = 1.14 eV) [25] which are able to quench the triplet state of the 2-mercaptoalkoxy-thioxanthones (see Table 1).

Figure 4 illustrates the transition absorption spectrum of the TX-O-$(CH_2)_6$-SH in the presence of DEA as an electron donor (a triplet state quencher).

In principle, only one major reaction product was detected by the observation of the transient absorption curves. Based on the previous results regarding the sulfonic derivatives of TX [12], the newly formed absorption band at 440 nm may be attributed to the ketyl radical of thioxanthone derivative (TXH$^\bullet$).

Further information on the quenching mechanism of the triplet absorption spectra of MAlc-TX come from the study of an influence of DPA on TX-O-$(CH_2)_{12}$-SH T-T absorption spectra. Besides the bands characteristic for the triplet excited state (λ = 640 nm) and radical-cation DPA$^{+\bullet}$ (λ = 720 nm), the absorption bands with a maximum at 680 nm and 440 nm are observed (Fig. 5). The individual peaks are assigned to the thioxanthone anion-radical (TX$^{-\bullet}$) and ketyl radical of thioxanthone derivative (TXH$^\bullet$), respectively. They are formed according to the intermolecular electron transfer (PET) mechanism.

Furthermore, it was found that the increase of the amine concentration in the tested solution, causes gradual decreases in the intensity of the absorption triplet band followed by a long-wavelength shift. This means that the triplet state of the 2-mercaptoalkoxy-thioxanthones is effectively quenched by amines.

However, the electron donors have no significant effect on the population of the other two intermediates formed upon photolysis process. But both of the absorption bands (at 310 nm and 440 nm) disappear in the presence of the MAlc-TXs and their absorption bands (at 320 nm and 440 nm) disappear in the presence of oxygen. The results suggest the radical nature of the transient products. Thus, the peak at 440 nm was assigned to the mixture of the thioxantyl ketyl radical (AlcTXH$^\bullet$) resulting from an H-transfer to the excited triplet [12, 25–28]. The transient absorption at 310 nm was attributed to the absorption of a mixture [25] of radical centered on S atom (thiyl radical) and thioxantyl ketyl radical [29].

Triplet lifetimes and quenching rate constants of MAlc-TXs studied by nanosecond laser flash photolysis are summarized in Table 1. The observed rate constants, k_{obs}, were determined by monitoring the transient decays at maximum of the triplet-triplet absorption at various quencher concentrations. The resulting pseudo-first-order rate constants, k_{obs}, were then correlated with the quencher concentration [Q] which was found to obey Stern-Volmer equation (1):

$$k_{obs} = k^0 + k_q\,[Q] \qquad (1)$$

where: k^0 – quenching rate constant of the 2-mercaptoalkoxy-thioxanthones triplet in the absence an electron donor, k_q – bimolecular reaction rate constant of the excited state, [Q] – concentration of the quencher.

The Stern-Volmer plots for the quenching of the 2-mercaptoalkoxy-thioxanthones triplet by selected amines and the decay of TX-O-$(CH_2)_3$-SH triplet at 640 nm monitored for various concentrations of *N*-phenylglycine (NPG) are presented in Fig. 6.

Based on the linear Stern-Volmer relationship, the primary reaction rate constants, k_q, was determined from the slopes according to equation (1).

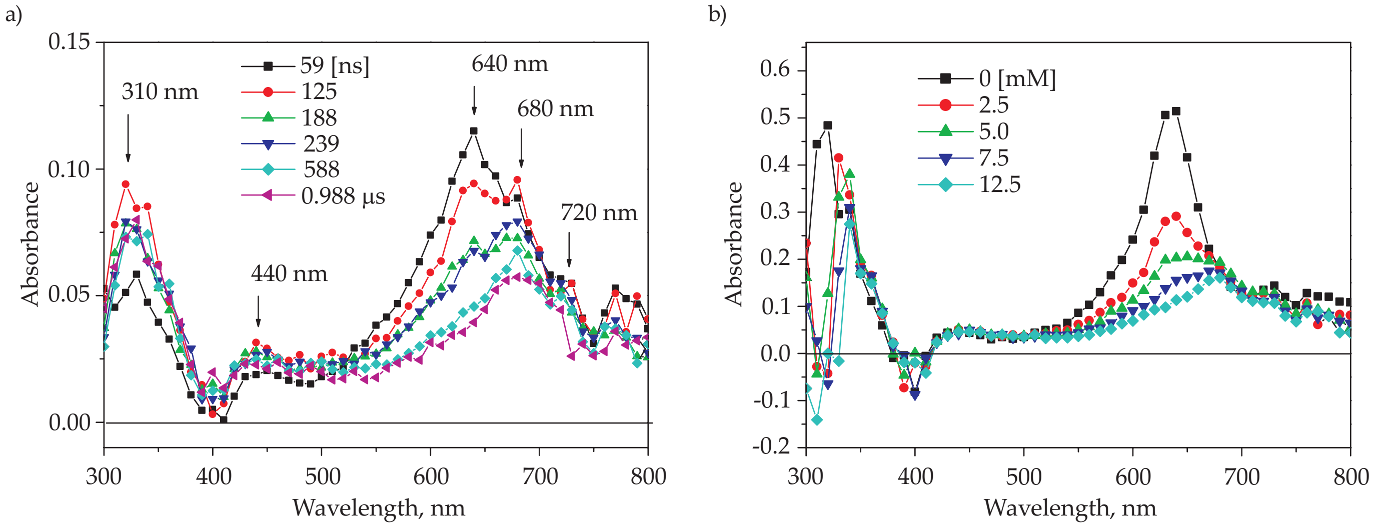


Fig. 5. Transient absorption spectra of TX-O-$(CH_2)_{12}$-SH: a) in DMSO in the presence of 300 µl ($7.6 \cdot 10^{-4}$ M) DPA; delay times shown in figure, b) in the presence of different concentrations of DPA; the delay time τ = 0.29 µs, the concentrations of DPA in the legend

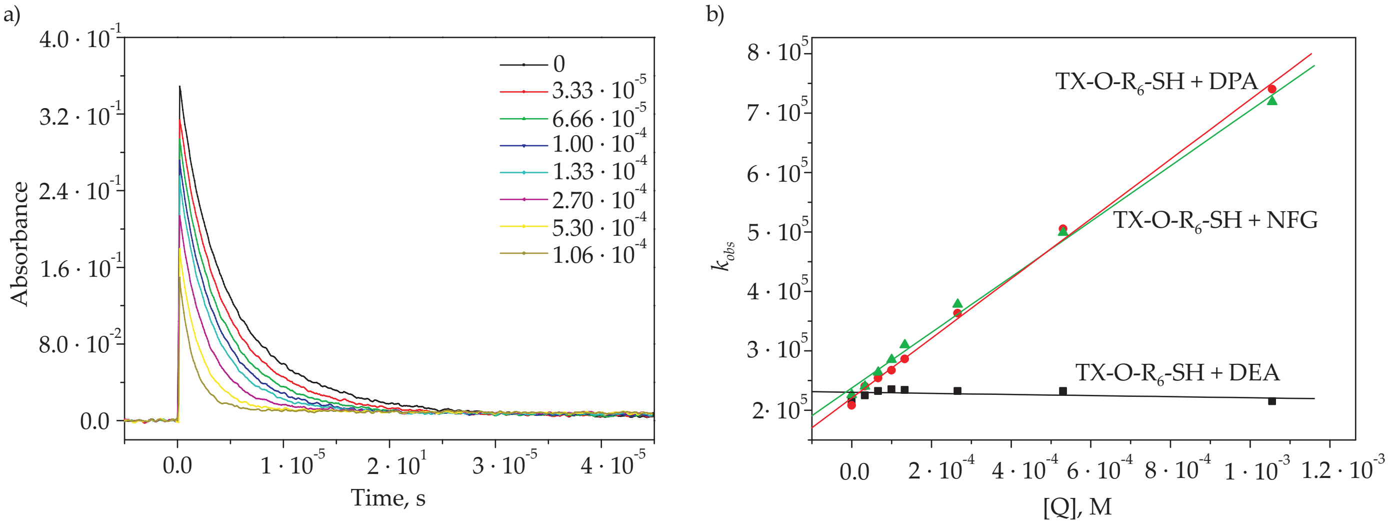


Fig. 6. a) The decay kinetics monitored at 640 nm for TX-O-$(CH_2)_3$-SH in the presence of NPG at different concentration, b) Stern-Volmer plots for the tested MAlc-TX triplet quenching by selected amines in DMSO

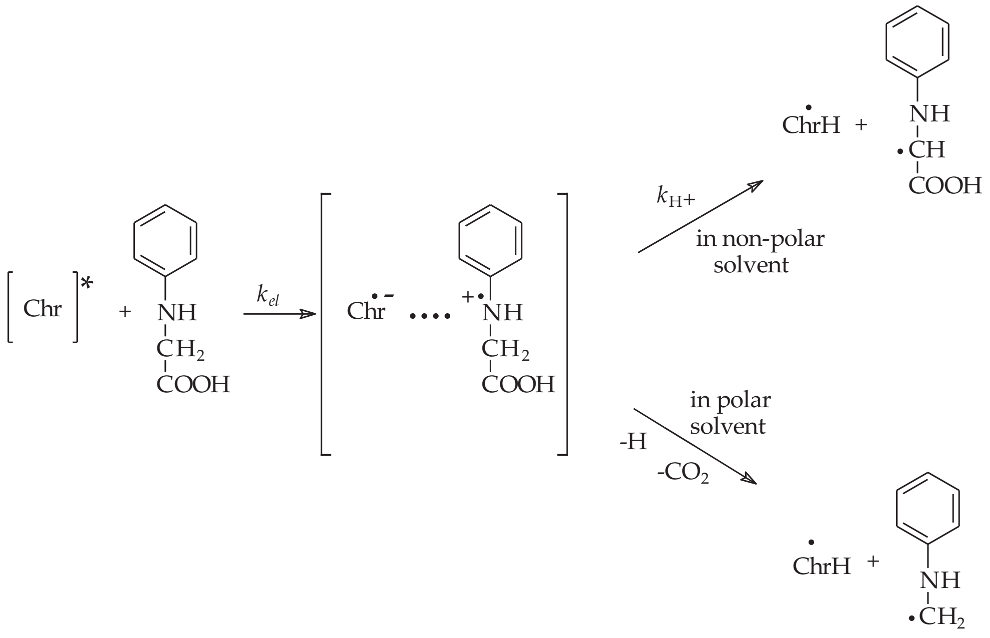
The calculated k_q values were compared to the standard free energy change for electron transfer process (ΔG_{el}), given by the Rehm-Weller equation [30, 31] [Eq. (2)]:

$$\Delta G_{el} = (E_{ox} - E_{red}) - E^T + C \qquad (2)$$

where: E_{ox} – potential of oxidation of the electron donor, E_{red} – potential of reducing of the electron acceptor, E^T – triplet energy, C – Coulombic energy; the free energy gained by bringing the radical ions formed to an encounter distance in a solvent with dielectric constant ε.

For the MAlc-TX the ΔG_{el}, values calculated from Eq. (2) are negative for all systems studied. This confirms that the photoinduced electron transfer process for the tested pairs is thermodynamically allowed.

Analysis of the obtained data allowed the mechanism of the radicals' formation to be established. The electron transfer from amine to the triplet excited state of the 2-mercaptoalkoxy-thioxanthones leads to a pair of ion-radicals. Then, two parallel paths may occur giving the final photolysis products. In high polarity solvent, the separation of the primary ion-radicals takes place. The isolated cation-radical of the amines has the character of a radical with N-H protons, which are acidic. This results in efficient deprotonation at α-carbon in respect to the nitrogen atom yielding α-aminoalkyl radical. In the case of NPG, decarboxylation additionally occurs giving an alkyl radical located on α-carbon the amine group. In a non-polar solvent, a pair of ion-radicals remains in the solvent cage because their separation is not possible. Thus, the secondary reaction occurring after PET is the proton transfer between the pair of the ion-radicals, which also results in the formation of a radical located on α-carbon related to the amino group. In the case of NPG used as a quencher



Scheme D

the carboxyl group remains in the molecule. Regardless of the reaction route, the α-aminoalkyl radicals effectively react with monomer molecules and start a chain reaction.

The proposed mechanism of α-aminoalkyl radical formation is presented on Scheme D where Chr depicts the 2-mercaptoalkoxy-thioxanthones that are a primary light absorbers.

CONCLUSIONS

Previous studies [14] have shown that the MAlc-TXs are good photoinitiators for acrylate polymerization. They operate as one-component systems or may be used as sensitizers in a pair with electron donors. In one-component systems, the light absorbing and electron donating and consequently hydrogen donating sites are incorporated into the photoinitiator molecules. The mechanism of photoinitiation is based on the intermolecular reaction of triplet, ^{3}MAlc-TX*, with the thiol moiety of the ground state MAlc-TX. The polymerization of acrylates is initiated by radicals located on the sulfur atom (thiyl radical). In the case of donor – acceptor pairs, the alkyl radical located on α-carbon in respect to the nitrogen atom starts the chain reaction. These radicals are formed in two parallel processes following electron transfer. The addition of an electron donor to the polymerizing composition increases the rate of polymerization because two different radicals can react effectively with monomer molecules.

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Received 15 V 2018.