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# Study of the Polymerization of Methyl Methacrylate Initiated by Thioxanthone Derivatives: A Magnetic Field Effect

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Free radical photopolymerization of methyl methacrylate (MMA) initiated by 2-mercaptothioxanthone (TX-SH), thioxanthone-thioacetic acid (TXSCH<sub>2</sub>COOH), and thioxanthone-carboxymethoxy acetic acid (TXOCH<sub>2</sub>COOH) as so called one-component initiators was performed with and without an external magnetic field (MF). These initiators contain light-absorbing and electron/hydrogen-donating fragments in one molecule and do not require an additional hydrogen donor, and initiate the polymerization of MMA in the air. Polymerization experiments were performed in solutions with 3 different optical densities at  $\lambda$  365 nm, where the photoinitiator absorbs. It was observed that application of MF leads to both larger conversion and higher molecular weight of the prepared PMMA, other conditions being equal. The effect of MF on the photopolymerization of MMA is discussed.

**Key Words:** Magnetic field effect, polymerization, photoinitiator, thioxanthone, one-component initiator.

## Introduction

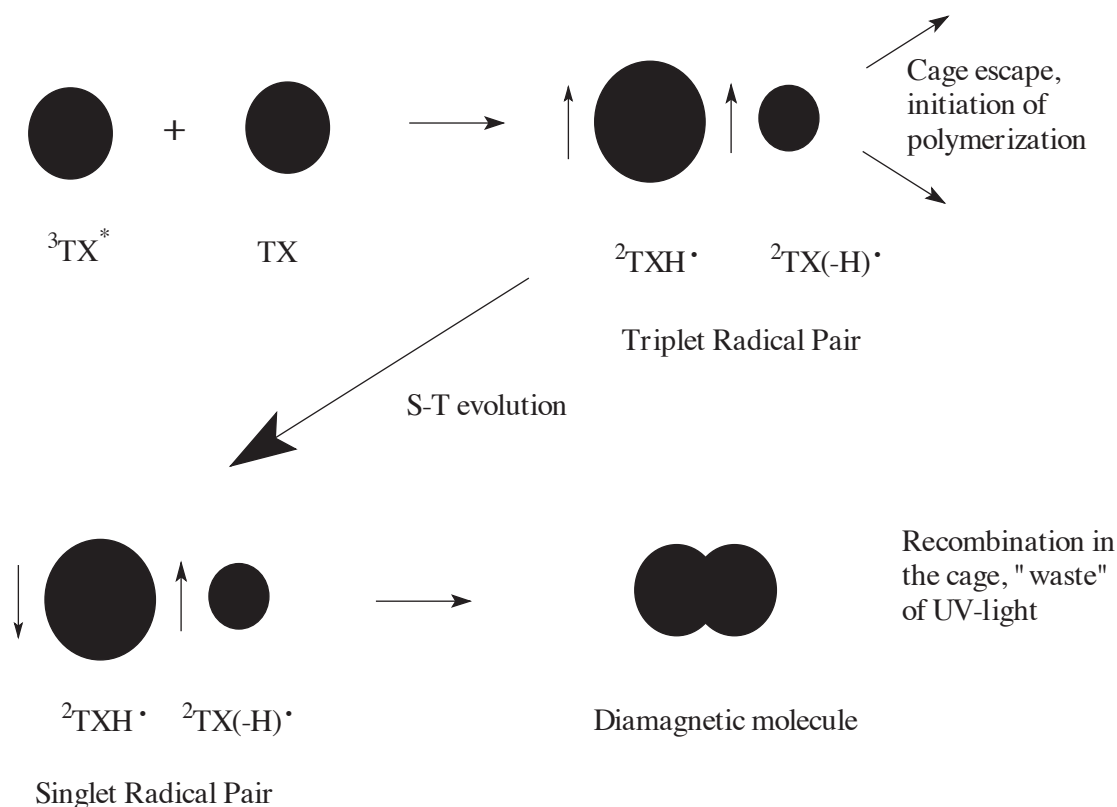
The application of a moderate external magnetic field (MF) affects dark- and photopolymerization.<sup>1–5</sup> Photopolymerization initiated by molecules reacting in the triplet state is usually accelerated by the application of MF.<sup>1–4</sup> To the best of our knowledge, MF effect (MFE) was studied only on Type I photoinitiators (PIs),<sup>6</sup> i.e.

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PIs that undergo photodissociation via a triplet state into 2 reactive radicals, which initiate polymerization of a vinyl monomer.<sup>1,3,4</sup> In the present work, we studied MFE on the Type II PIs.<sup>6</sup> Type II PIs abstract hydrogen/electron in triple state from a donor. Thioxanthen-9-one and its derivatives (TX) are typical Type II PIs.<sup>6</sup> The peculiarity of TX studied in the present work is that they are so-called one-component PIs, which abstract labile hydrogen from itself.<sup>7-9</sup> Radical pairs (RPs) are important intermediates, and their self-reactivity (cage effect) affects the efficiency of polymerization.

Free radical photopolymerization is accompanied by the formation of transients with a non-zero spin angular momentum: free radicals, RPs, triplet states of photoinitiators, and a stable molecule in a triplet state, which is molecular oxygen. All these species play a role in photopolymerization. Magnetic and spin effects can be observed in free-radical photopolymerization. The outcome of a photochemical reaction depends to a significant extent on the spin-state dynamics of the RP (see Scheme 1).



**Scheme 1.** Pictorial presentation of photolysis of TX. Radicals of TX recombine or disproportionate with regeneration of starting TX.

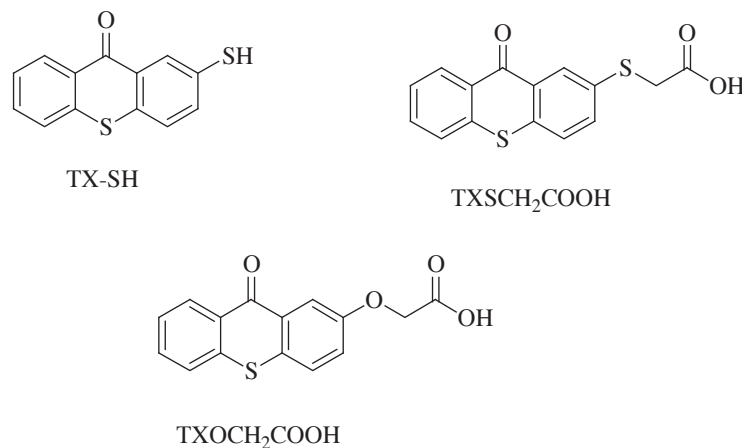
The reactivity of a radical pair is thus the rate of polymerization initiation sensitive to the application of MF.<sup>1-4</sup>

In this study, we used previously synthesized one-component TX-based photoinitiators<sup>7-9</sup> for the polymerization of MMA and the MFE on this polymerization.

## Experimental

### Synthesis of photoinitiators

Thioxanthone based novel one-component initiators were synthesized as given in the literature<sup>7,8</sup> (Chart 1).



**Chart 1.** Chemical structures of TX-based one-component PIs.

### Materials

Dimethylformamide (DMF) was obtained from Aldrich. Methyl methacrylate (MMA) was washed with NaOH (5%), dried with Na<sub>2</sub>SO<sub>4</sub>, and used for polymerization after vacuum distillation.

### Photopolymerization

Solutions were prepared in dimethylformamide (DMF) in the presence of MMA (2 mL) with appropriate optical densities. The magnetic flux density of 640 mT was provided by an electromagnet. A reaction cell was placed between the poles of the electromagnet. The electromagnet was removed for experiments in the Earth's magnetic field. Solutions of MMA (2 mL) and photoinitiator in DMF were prepared in quartz (1 × 1 × 3 cm rectangular) cuvettes. The solutions were irradiated with a filtered light of medium pressure Hg lamp with a band around λ 365 nm. Light intensity was 1.1 × 10<sup>-7</sup> (einstein/(L.s)). The optical density (OD) of the initiator in the studied solutions was determined as 0.5, 1.0 and 1.5 at λ 365 nm.

Appropriate solutions of monomer and initiator in DMF were irradiated with a medium-pressure mercury lamp for 15 and 30 min in an air atmosphere. A polymer was obtained after precipitation in methanol and drying in vacuo. The conversion of MMA (Convand) polymerizations rates were calculated gravimetrically for all samples.

### Analysis

GPC analyses of the polymer were performed at room temperature with a setup consisting of a pump (Agilent 1100) and 3 columns (Zorbax PSM); THF was used as the eluent (flow rate 0.3 mL min<sup>-1</sup>), and the detection

was carried out with the aid of an Agilent 1100s differential refractometer. The number average molecular weights  $M_n$  were determined using Polymer Laboratories polystyrene standards. UV-Vis spectra were taken on an Agilent 8453.

## Results and Discussion

2-Mercapto-thioxanthone (TX-SH), thioxanthone-thio acetic acid (TXSCH<sub>2</sub>COOH), and thioxanthone-carboxymethoxy acetic acid (TXOCH<sub>2</sub>COOH) were previously synthesized and used as one-component initiators for the radical polymerization of acrylates and methacrylates.<sup>7,8</sup>

Polymerization experiments were performed at 3 different optical density values of initiator solution with and without an external magnetic field. The results of these experiments are presented in Tables 1-3.

**Table 1.** Photoinitiated polymerization of methyl methacrylate with 3 different PIs in the presence and absence of external MF during 2 different times of irradiation.

PI O.D.: 0.5	Conv (%) <sup>a</sup>		Conv (%) <sup>b</sup>	
	$t_{irr}$ (min)		$t_{irr}$ (min)	
	15	30	15	30
TX-SH	0.50	3.30	0.70	3.60
TX-SCH <sub>2</sub> COOH	0.70	4.60	1.30	4.20
TX-OCH <sub>2</sub> COOH	1.20	5.50	1.20	4.60

<sup>a</sup>No MF

<sup>b</sup>In the MF of 640 mT

These initiators contain light-absorbing and electron/hydrogen-donating fragments in one molecule. That made them different from the common Type II photoinitiators, which have co-initiator as another reagent. Therefore, proximity of reducing agents in thioxanthone based one-component initiators alleviates the inhibition effect of the molecular oxygen of air. Tables 1-3 show that an application of MF leads to faster photopolymerization, which manifests itself in higher conversion during the same time of irradiation in the Earth's MF and in an external MF. When the optical density value was held at 0.5, as can be seen in Table 1, the differences between conversion percentage values in the presence and absence of MF were determined as 40% for TX-SH, 86% for TXSCH<sub>2</sub>COOH, and 1.7% for TXOCH<sub>2</sub>COOH after 15 min of irradiation.

An application of MF leads to a decrease in the probability of intersystem crossing between triplet and singlet radical pairs (Scheme 1) predominantly due to the hyperfine coupling (HFC) mechanism.<sup>2,10</sup> More pairs stay in a triplet state in the MF, they cannot recombine, and radicals exit the cage and initiate polymerization (Scheme 1). Thus, the rate of initiation  $\omega_{in}$  increases in MF.

**Table 2.** Photoinitiated polymerization of methyl methacrylate with 3 different PIs in the presence and absence of external MF during 2 different times of irradiation.

PI O.D.: 1.0	Conv (%) <sup>a</sup>		Conv (%) <sup>b</sup>	
	t <sub>irr</sub> (min)		t <sub>irr</sub> (min)	
	15	30	15	30
TX-SH	0.60	5.20	1.40	5.50
TX-SCH <sub>2</sub> COOH	1.40	4.60	2.30	4.50
TX-OCH <sub>2</sub> COOH	1.25	4.50	1.90	5.60

<sup>a</sup>No MF<sup>b</sup>In the MF of 640 mT**Table 3.** Photoinitiated polymerization of methyl methacrylate with 3 different PIs in the presence and absence of external MF during 2 different times of irradiation.

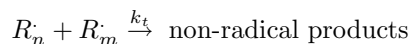
PI O.D.: 1.5	Conv (%) <sup>a</sup>		Conv (%) <sup>b</sup>	
	t <sub>irr</sub> (min)		t <sub>irr</sub> (min)	
	15	30	15	30
TX-SH	1.00	4.50	1.80	5.00
TX-SCH <sub>2</sub> COOH	1.40	5.60	1.20	4.80
TX-OCH <sub>2</sub> COOH	0.90	4.60	1.80	5.50

<sup>a</sup>No MF<sup>b</sup>In the MF of 640 mT

When the OD was increased to 1.0, the effect of an external MF was more significant: the difference in the conversion percentage values increased over 100% for TX-SH, 64% for TXSCH<sub>2</sub>COOH, and 52% for TXOCH<sub>2</sub>COOH in the presence of MF. From our previous studies, similar behavior was observed in the effect of the concentration of the initiator on the rate of polymerization of MMA in the Earth's field.<sup>1</sup> A further increase in OD to 1.5 changed the results for the benefit of TXOCH<sub>2</sub>COOH and the difference was found to be 100%. However, the MFE was more pronounced especially during the initial period of irradiation (Tables 1-3).<sup>11,12</sup> At longer times of irradiation and thus at larger conversions media viscosity essentially increases. Triplet radical pairs live too long, and MFE decreases due to relaxation of triplet sublevels in the MF.<sup>10</sup>

## Molecular Weights

If MF only increases the rate of initiation,  $\omega_{in}$ , then one should expect a decrease in the molecular weight of the polymer produced in MF,<sup>2-4</sup> because  $MW \sim \omega_{in}^{-1}$ .<sup>6</sup> However, the molecular weight of polymethyl methacrylate (PMMA) increased with the presence of an external magnetic field (Table 4). There is another MFE on photopolymerization: application of MF decelerates the reaction of termination of macroradicals due to the action of the same HFC mechanism.<sup>10</sup>



A decrease in the rate of termination (a decrease in  $k_t$ ) leads to an increase in the MW of polymer in the MF.<sup>6</sup> Thus, we have 2 opposite effects of MF on the MW of polymer: its decrease due to an increase in  $\omega_{in}$  and its increase due to a decrease in  $k_t^3$ , where an increase in the rate of polymerization was observed without a decrease in the MW of polymer. We have to assume that the MFE on  $k_t$  is more profound than the effect on  $\omega_{in}$ . Thus, MW increases in the MF.

**Table 4.** Molecular weight (Mn) of polymethyl methacrylate in the presence and absence of external magnetic field during 15 min of irradiation at 3 different optical densities of a solution at  $\lambda$  365 nm.

PI	Mn <sup>a</sup> (g mol <sup>-1</sup> )	Mn <sup>b</sup> (g mol <sup>-1</sup> )	Mn <sup>a</sup> (g mol <sup>-1</sup> )	Mn <sup>b</sup> (g mol <sup>-1</sup> )	Mn <sup>a</sup> (g mol <sup>-1</sup> )	Mn <sup>b</sup> (g mol <sup>-1</sup> )
	O.D.: 0.5		O.D.: 1.0		O.D.: 1.5	
TX-SH	50,700	59,100	52,350	66,890	38,700	47,000
TX-SCH <sub>2</sub> COOH	58,750	67,700	61,600	43,880	45,820	54,870
TX-OCH <sub>2</sub> COOH	59,650	69,450	53,560	57,400	47,510	48,460

<sup>a</sup>In the Earth's magnetic field

<sup>b</sup>In the external magnetic field

In conclusion, one-component thioxanthone based initiators lead to an increase in the conversion percentage values of polymerization of MMA with a magnetic field of 640 mT. Because the inhibition effect of oxygen is not as effective as Type II initiators, the initiating efficiency of these one-component initiators increased. The rate of polymerization of MMA essentially increases in MF due to acceleration of initiation and due to deceleration of termination stages. The values of observed MFE are high, and one may think of industrial applications for such MFEs. It was observed for the first time that the MW of polymer also increases in the MF.

At low optical densities, TXSCH<sub>2</sub>COOH is a more efficient initiator for the initiation of polymerization of MMA with a magnetic field, compared to the other 2 initiators, TXSH and TXOCH<sub>2</sub>COOH.

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