



## Preparation of novel thioxanthone based polymeric photoinitiator for flexographic varnish and determination of their migration behaviour

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### ABSTRACT

Today, polymeric photoinitiators are good choice for initiation mechanism of UV-curable printing inks with their low migration potential. In this study, new thioxanthone-styrene polymeric photoinitiators were synthesized. Polystyrene that was synthesized by atom transfer radical polymerization (ATRP) was functionalized by cyclohexeneoxide and then reacted with thioxanthone-thioacetic acid. Piperazine was reacted with bromine chain end of polystyrene and final polymeric photoinitiator was obtained. Proton Nuclear Magnetic Resonance (<sup>1</sup>H NMR), Attenuated Total Reflectance- Fourier Transform Infrared Spectroscopy (ATR-FTIR), Gel Permeation Chromatography (GPC) and Ultraviolet-Visible Spectroscopy (UV-vis) analyses were confirmed the expected structures. The curing property of new polymeric photoinitiator was compared with a conventional thioxanthone printing formulation that is used in flexographic varnish. The photopolymerization kinetics were determined by Photo Differential Scanning Calorimetry (Photo-DSC) and the results showed that 83% of conversion was reached for thioxanthone-styrene polymeric photoinitiator with MW = 4200. The migration behavior was identified with Liquid Chromatography–Mass Spectrometry LC–MS. It was shown that thioxanthone based polymeric photoinitiator is usable in flexographic varnish and thioxanthone migration level is reduced with macrophotoinitiation.

### 1. Introduction

Photoinitiated polymerization have drawn great scientific and industrial interest due to their applications involving coating on various material, printing inks, adhesives, printing plates etc. [1–5]. Initiators are the most important component of coating formulation, which are used to generate radicals. Thioxanthone and its derivatives are commonly preferred initiator because of their near UV range absorption characteristics [6–13]. They have been used as Type II initiators in printing inks, dental materials, surface coating, microelectronics, nanocoatings etc. [14–16]. Hence the excitation energy of thioxanthone derivatives is not high enough for fragmentation, it can produce initiating radical by interacting with a coinitiator [17–22]. Recently, a new thiol derivative of thioxanthone having the advantage of one component system was reported by Arsu et al. [23]. It can provide both triplet photosensitizer and a hydrogen donor so it doesn't need a co-initiator.

Although photoinitiators have a key function in the drying process of printing inks and varnish due to their “high migration” properties, they are not intended for food packaging. In 2005, 2-

isopropylthioxanthone (ITX) migration from ink, created a confusion in the packaging industry [24] since the ITX concentrations in the babies milk powder were found very high. Molecular weight, polarity, volatility and lipophilicity are considered as the main physicochemical properties of the photoinitiators acting in migration [25].

Due to the advantages of macromolecules in comparison to low molecular weight analogues, significant developments are described in the synthesis of macrophotoinitiator. It is known that the activity of macroinitiators is higher than low molecular weight analogs due to having more effective excitement mechanism [26]. Moreover they undergoes less migration due to their high molecular structures. There have been many reports on the synthesis of end-functional macromonomers with controllable structure by applying controlled radical polymerization (CRP) technique [27–31]. Atom transfer radical polymerization which is a type of a CRP, is the most effective and versatile method because of reaction condition, usable monomers, initiators, catalysts. ATRP gives low polydispersity, functionality, and controllable molecular weight properties to macromolecules [32–34].

In this study we synthesized new thioxanthone-styrene polymeric photoinitiator by using ATRP and characterized with ATR-FTIR, UV-vis,

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**Table 1**  
Varnish formulations.

Formulation code	UV flexo varnish (wt.%)	Photoinitiator (wt.%)	Co-initiator (wt.%)	
F1	96.8	Thioxanthone	3	Triethylamine 0.2
F2	96.8	ITX-PSt 2100	3	Triethylamine 0.2
F3	96.8	ITX-PSt 4200	3	Triethylamine 0.2

$^1\text{H}$  NMR, GPC and thermal gravimetric analysis (TGA). Initiation characteristic of polymeric photoinitiator was determined with Photo-DSC experiments. They were also used to prepare UV-Flexo varnish. The printing properties of varnish were also determined. The photoinitiator migrations were analyzed by liquid chromatography–mass spectrometry (LC–MS).

## 2. Experimental

### 2.1. Materials

Piperazine, dimethylformamide, sulfuric acid (95–97% wt.), thio-salicylic acid, cyclohexene oxide, 3-cyclohexene-1-methanol, 2-bromopropanoyl bromide, 3-chloroperoxybenzoic acid, CuBr, Thiophenoxyacetic acid were obtained from Aldrich. Styrene (Fluka), sodium bicarbonate (Merck), dichloromethane (Lab-scan), pyridine (Lab-scan), 2,2-bipyridine (Merck) and all other solvents and chemicals were used as received. High gloss UV Flexo Varnish (14HC121) formulated without photoinitiator was kindly obtained from Sun Chemical (Turkey).

### 2.2. Characterization techniques

Spectrophotometric investigation was performed using a Shimadzu UV–vis spectrophotometer 2450 (Kyoto Jap). The chemical structures of synthesized oligomers were identified by using a Perkin–Elmer Spectrum 100 ATR-FTIR spectrophotometer (WA).  $^1\text{H}$  NMR spectra were performed with using a Varian Unity Inova Spectrometer (CAL USA) operated at 400 MHz frequency.

Gel permeation chromatography (GPC) was used to analyze the molecular weight of polymeric photoinitiators. GPC was carried out on a Waters system, with a Waters 1515 pump, a Waters 2414 Refractive Index detector and Waters Styragel columns placed in series (HR 5, HR 4E, and HR3). THF was used as eluent at a flow rate of 1 mL/min and calibration was done with polystyrene standards. All measurements were performed at 40 °C.

UV Varnish formulations were applied on plexiglass panels and cured in a bench type UV Processor, which is equipped with 120 W/cm medium pressure mercury UV-lamps (EMA-Turkey). The IGT-F1 Printability Tester (IGT Testing Systems, Amsterdam, NL) was used for the laboratory printing trials.

The photo-DSC experiments were carried out with Pyris Diamond DSC equipped with a UV curing system (EXFO Omni-Cure™ 2000). Photo-DSC samples were placed in an aluminum pan and covered with quartz disc. The lamp intensity is 20 W/cm<sup>2</sup>.

### 2.3. Synthesis of 2-thioxanthone-thioacetic acid (TX-SCH<sub>2</sub>COOH)

2-Thioxanthone-thioacetic acid was synthesized according to literature [35]. Thio-salicylic acid (1.6 g, 10.3 mmol) was charged into a two-neck flask equipped with a magnetic stirrer at 250 rpm and under nitrogen atm. at room temperature. 15 mL of concentrated sulfuric acid (95–97%wt.) was added drop by drop and the mixture was stirred for 5 min. Thiophenoxyacetic acid (7.4 g, 44 mmol) was then added drop by drop and the mixture stirred at room temperature for an hour. After, the temperature raised to 80 °C and the mixture stirred at this temperature for additionally two hours. The mixture was further stirred at room temperature for overnight. Tenfold excess boiling water was carefully added to mixture and boiled for 5 min. Solution was cooled, filtered and recrystallized from dioxane/water. Yield: 78%, m.p.:194–197 °C.  $^1\text{H}$  NMR (DMSO-*d*<sub>6</sub>, ppm): 8.46–7.29 (m, 7H, aromatic), 3.94 (s, 2H,CH<sub>2</sub>); ATR-FTIR (cm<sup>-1</sup>): 3470 (–OH), 2927 (CH<sub>3</sub>), 1707(C=O carboxylic acid), 1637 (C=O ketone), 1603 (C=C), 747 cm<sup>-1</sup> (aromatic C–H).

### 2.4. Synthesis of 3-cyclohexenylmethyl-2-bromopropanoate (CH–Br)

3-cyclohexenylmethyl-2-bromopropanoate was synthesized as

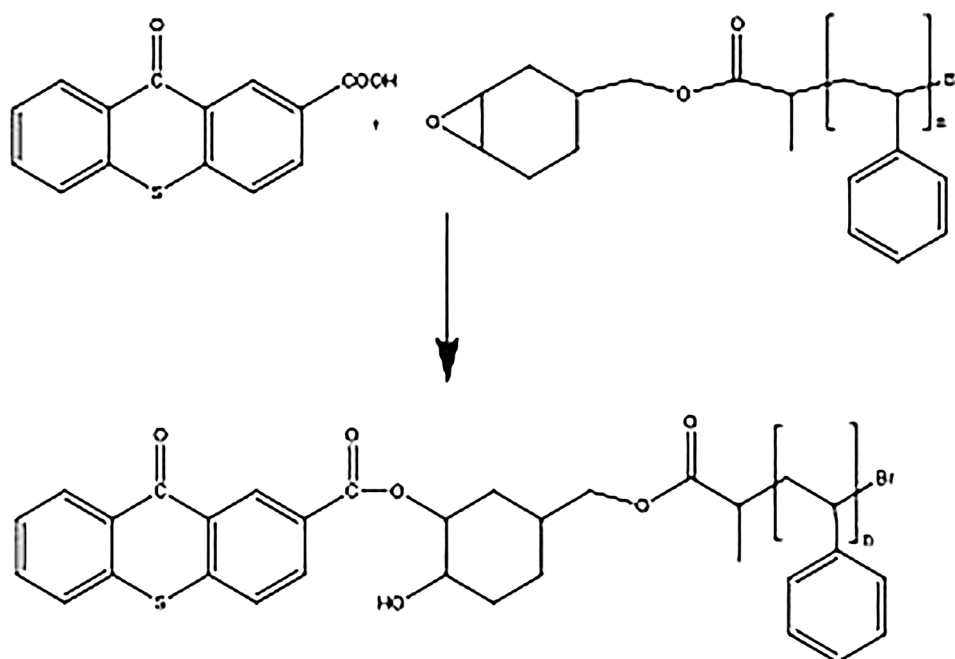


Fig. 1. The synthesis of ITX-PSt 2100.

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