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Mechanistic studies of thioxanthone–carbazole as a one-component type II photoinitiator

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ABSTRACT

A mechanistic study concerning photoinitiated free radical polymerization using Thioxanthone–Carbazole (TX–Cz) as a one-component Type II photoinitiator was performed. TX–Cz presented visible initiator characteristics with absorptions at 434 and 414 nm where the molar absorption coefficients were 2014 and 1754 L mol^{-1} cm^{-1}, respectively. Fluorescence and phosphorescence spectroscopy, as well as laser flash photolysis was employed to study the photophysical properties of TX–Cz. In addition, photopolymerization of methyl methacrylate (MMA) showed that TX–Cz is efficient photoinitiator. To explain the initiation mechanism of TX–Cz, fluorescence and phosphorescence emission spectra of poly (methyl methacrylate) (PMMA) were also taken to see whether the initiator covalently bonded to the polymer. The postulated mechanism is based on inter- molecular reaction of the triplet, ^{3}(TX–Cz)* with the carbazole moiety at ground state, TX–Cz. The photoinitiation efficiency of TX–Cz during gelation of multifunctional acrylates was also investigated by Photo-Differential Scanning Calorimetry (Photo-DSC) technique and high polymerization rates were obtained.

1. Introduction

Photoinitiators are one of the important constituents of photopolymerizable formulations since photopolymerization has a wide range of applications such as for coatings, microelectronics, printing plates, adhesives and inks. Generally Type I and Type II photoinitiators are used for industrial applications [1–5].

Recently, mercapto thioxanthone and carboxylic acid derivatives of thioxanthone were used for the polymerization of acrylates and methacrylates without a co-initiator [6–8]. However, oxygen is a big problem, especially for the curing of formulations in air atmosphere. Thioxanthone–Anthracene (TX–A) was suitable for these kinds of applications because oxygen is needed to form endoperoxide, and then to produce the initiating alkoxy or peroxy radicals [9,10]. With respect to the migration problems of photoinitiators, thioxanthone-containing initiators, either oil-soluble or water-soluble, were synthesized. Due to the requirements of the water soluble system, water soluble photoinitiators were synthesized and their efficiency in the formulation was reported [11,12]. Another approach was undertaken and thioxanthone–benzotriazole was synthesized, which presented stabilizer and initiator properties in one component [13].

Carbazole-based compounds are excellent optical and electronic materials with respect to their photorefractivity and photoconductivity, and their derivatives show interesting and unique chemical and physical properties and possess good thermal stability. Much attention has been paid to carbazole-based compounds because of the following reasons: 9H-carbazole is a very cheap material; it has a fully aromatic unit providing better chemical and environmental stability; and the nitrogen atom can be easily substituted with a wide variety of functional groups to fine tune the optical and electrical properties. There have been many studies of carbazole-based compounds in devices, but fewer studies of their photophysical properties in fluids and in the solid state [14–16].

TX–Carbazole was previously synthesized by Yagci et al. (see Chart 1) [17,18]. In this study we report the detailed photophysical characteristics of the singlet and the triplet excited states of TX–Cz using absorption, fluorescence, phosphorescence and laser flash photolysis techniques. This will help us to elucidate the initiation mechanism of TX–Cz which was used as an initiator for the polymerization of mono and multifunctional monomers. The polymerization kinetics of the acrylates were recorded by Photo-DSC.

2. Experimental

2.1. Materials

Thiosalicylic acid (Aldrich), sulfuric acid (99.8%, Aldrich), and N-methyldiethanolamine (MDEA, 99%, Aldrich) were used as received. 9H-Carbazole (Fluka), was used after crystallization with ethanol. 1,6-Hexandiolediacrylate (HDDA) and lauryl acrylate (LA)

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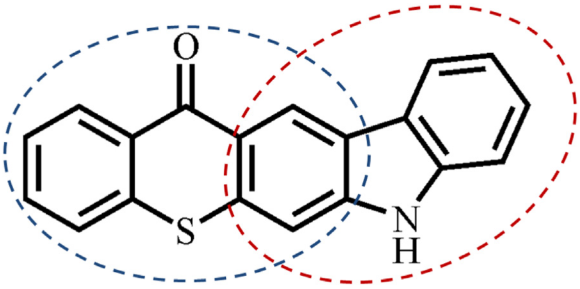


Chart 1. Structure of Thioxanthone–Carbazole (TX–Cz). .

were obtained from Aldrich and used as received. Solvents were supplied by Merck and purified by conventional drying and distillation procedures. Methyl methacrylate (MMA) was washed with NaOH (5%), dried with sodium sulfate (Na_2SO_4), and distilled under vacuum.

2.2. Instruments

^{1}H NMR measurements were recorded in d^6-DMSO with $Si(CH_3)_4$ as the internal standard using a Bruker AC250 (250.133 MHz) instrument. FTIR spectra were recorded on a Perkin-Elmer. UV spectra were recorded on a Varian Spectrometer. Differential Scanning Calorimetry (DSC) was performed on TA Instruments DSC (Q-100). Fluorescence and phosphorescence spectra were recorded on a Jobin Yvon-Horiba Fluoromax-P. Laser flash photolysis experiments employed the pulses from Applied Photophysics with a YAG laser (355 nm, pulse, 5 ns) and a computer-controlled system. The light intensity of the photoreactor was measured with Macam UV203 ultraviolet radiometer.

2.3. Photopolymerization

Typical Procedure: A solution of MMA (0.5 mL, 4.68 M) and TX–Cz 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.

For the experiments under argon atmosphere, the solutions inside the pyrex tube were flushed with dry argon prior to irradiation. Polymer was obtained after precipitation in methanol and drying in vacuum. Polymerization yields were calculated for all samples gravimetrically.

2.4. Photo differential scanning calorimetri (photo-DSC)

Photoinitiated polymerization of acrylate systems (HDDA and LA) with TX–Cz was carried out by TA-DSCQ100 equipped with a medium pressure mercury arc lamp. This unit emits radiation predominantly in the 220–400 nm range, and provides light intensity of 50 mWcm^2 as measured by a UV radiometer capable of broad UV range coverage. The mass of the samples was approximately 2 ± 0.1 mg and the measurements were carried out in an isothermal mode at room temperature under a nitrogen atmosphere (nitrogen flow 50 mL/min). The reaction heat liberated in the polymerization is directly proportional to the number of acrylate 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

$$C = \Delta H_t / \Delta H_0^{\text{theory}} \tag{1}$$

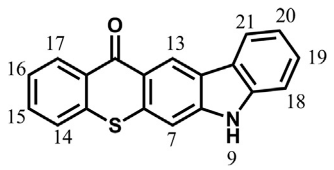
where ΔH_t is the reaction heat evolved at time t and $\Delta H_0{}^{\text{theory}}$ is the theoretical heat for complete conversion. A reaction heat for an acrylate double bond polymerization of $\Delta H_0{}^{\text{theory}} = 86$ kJ/mol was used [23]. The rate of polymerization (R_p) is directly related to the heat flow (dH/dt) by Eq. (2)

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

2.5. Synthesis of Thiochromeno[2,3–b] carbazol-13(7H)-one (TX–Cz)

Concentrated sulfuric acid (15 ml) was slowly added to thiosalicylic acid (0.309 mmol) at 0 °C and carbazole (0.103 mmol) was added to the solution in a two-necked round-bottomed flask. After the addition, the reaction mixture was left stirring at room temperature for fifteen minutes and then heated to 50 °C. The reaction mixture was then mixed for two days and the solution was precipitated in hot distilled water. The crude product which formed was collected by filtration, washed with dichloromethane (3 × 30 mL), and then the combined organic layers were separated, dried ($MgSO_4$), filtered, evaporated and TX–Cz was obtained as yellow crystals.

^{1}H NMR (250 MHz) in d^6-DMSO: 7.61–7.67 (m, 1H, H_{20}), 7.73–7.87 (m, 4H, H_7, H_{15}, H_{16}, H_{19}), 7.93–7.99 (m, 2 H, H_{13}, H_{14}), 8.13 (d, 1H, H_{17}), 8.51 (d, 1H, H_{18}), 8.67 (d, 1H, H_{21}), 13.74 (s, 1H, NH).



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IR (KBr) νs. (cm^{-1}): 3208 (s, N–H), 3059 (*w*, phenyl); 1708 vs (C=O); 1603, 1588 and 1587 (s, C=C).

3. Results and discussion

The absorption spectrum of TX–Cz shows characteristic absorption of the thioxanthone but absorption of the compound shifted more to the visible region, therefore camphorquinone (CQ) [1×10^{-2} M] was chosen as the visible initiator for comparison of the absorption properties of TX–Cz. As can clearly be seen from Fig. 1, the absorption properties of TX–Cz in the visible region are quite promising, since the molar absorption of TX–Cz [3.5×10^{-4} M] was 2014 and 1754 L. mol^{-1} cm^{-1} at 434 nm and 414 nm, respectively.

As reported earlier [17], irradiation of a degassed solution of TX–Cz in N, N-dimethylformamide (DMF) instead of aromatic amine in

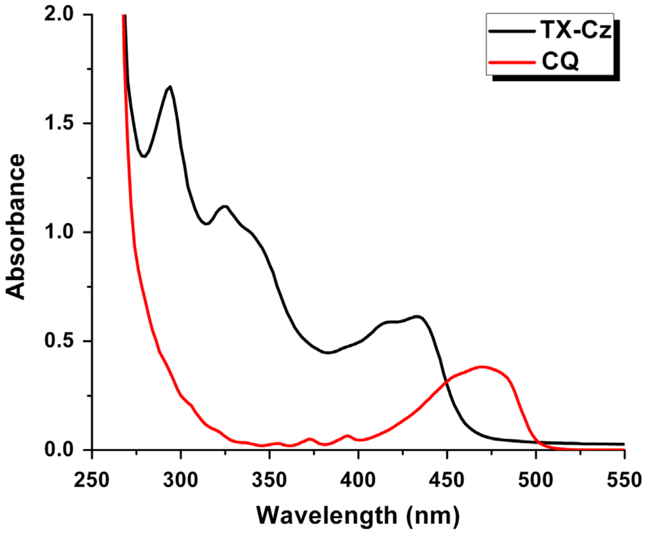

Fig. 1. Absorption spectra of Thioxanthone–Carbazole (TX–Cz) [3.5×10^{-4} M] and Camphorquinone (CQ) [1×10^{-2} M].