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Phenothiazine-based oxime ester as a photobase generator for thiol-acrylate reactions

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Abstract:

In this work, a previously designed and synthesized phenothiazine-based oxime ester was investigated as a photobase generator for the formation of thiol-acrylate networks through the polymerization of thiol-acrylate reactions and more appealingly the base-catalyzed thiol-acrylate Michael addition reactions. This system accomplished a complete disappearance and a full conversion of the characteristic acrylate peak within 10 min of irradiation with a light-emitting diode ($\lambda = 405$ nm) or within 1 or 2 min of the same irradiation source and 24 hours of heat exposure ($T = 60$ °C). Photobase generation was evidenced using phenol red as a pH-indicator, enabling to confirm the production of methyl amine (CH_3NH_2) as initiating species. Photoinitiation mechanism through which base reactive species are produced and the reactions by which the thiol-acrylate polymerization proceeds were investigated according to the base detection experiments, the obtained real-time Fourier transform infrared spectroscopy results, and according to the general photochemical base-generation reactions of oxime-esters. Finally, differential scanning calorimetry scans and Shore A and Shore D hardness experiments have been performed on the polymers obtained to examine their thermal properties and surface hardness features.

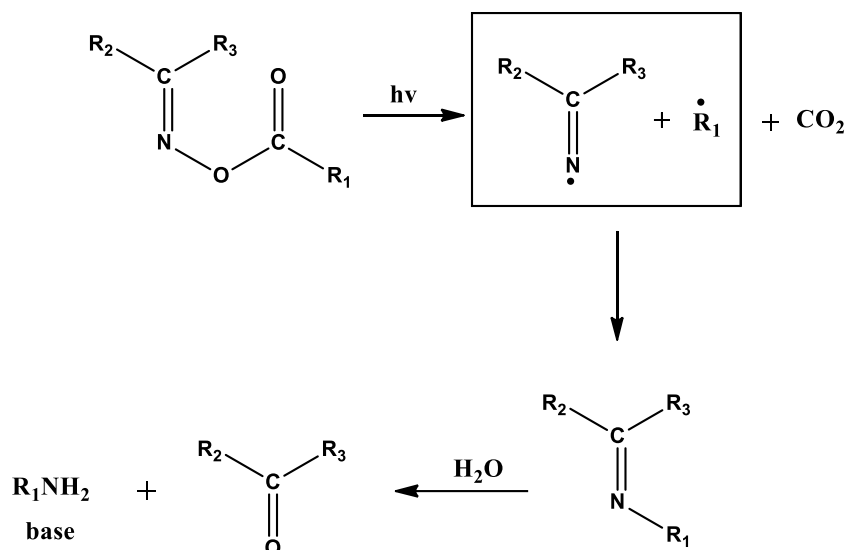
1. Introduction

Photochemical processes generating reactive species (free radicals, acids and bases) are considered nowadays as an appealing approach capable to compete with the purely chemical processes and more and more fundamental works are devoted to the photogeneration of reactive species. These fundamental processes are notably used in a wide range of applications including drugs, fragrances, dental materials, imaging, adhesives, coatings, and polymer synthesis.¹⁻⁵ In the domain of polymer technologies, photoradical generators (PRGs) have been broadly investigated and they are considered as the most prevailing photoinitiators utilized to induce the free radical polymerization reactions.^{1, 2} However, these reactions are hindered by the inactivation process prompted by the atmospheric oxygen (usually called the oxygen inhibition).^{6, 7} Moreover, photoacid generators (PAGs) through which cationic polymerization reactions proceed are commercially limited, they cause corrosion of metal substrates, and some of them are defectively soluble in solvents or monomers.^{2, 8} In this context, photobase generators (PBGs) through which anionic polymerization reactions are catalyzed are free from these disadvantages.^{9, 10}

The documentation of photochemical base-generating systems started in 1987 during which the first PBG system was reported¹¹, and investigations in this subject have been extended to include different classes of PBGs, such as carbamates^{12, 13}, *O*-acyloximes^{14, 15}, ammonium salts¹⁶, aminimides^{17, 18}, α -aminoketones¹⁹ and quaternary ammonium salts²⁰⁻²². These PBG systems are employed to be used in polythiourethane polymer formation²³, sol-gel hydrolysis-condensation processes²⁴, crosslinking reactions and application to photoresist industry²⁵, as catalysts for imidization reactions²⁶, for the photocuring of epoxy resins²⁷, and in base-catalyzed Michael reactions²⁸.

Recently, huge research efforts have been employed to overcome the drawbacks of the traditional UV irradiation sources which are harmful to human health and environment, unable to penetrate in depth in resins, and require high operating costs⁹. Nevertheless, many of the PBG systems remain restricted to UV light (rather short excitation wavelength) and they cannot function properly under the irradiation of near-UV or visible light-emitting diodes (LEDs). Attempts which have been reported in this aspect include combinations of PBGs with sensitizers which possess

longer wavelength absorption properties (e.g. derivatives of isopropylthioxanthone (ITX)) allowing the generation of base under the exposure of light with wavelengths that PBGs formerly could not absorb.²⁹⁻³¹ However, these combinations are easily affected by the efficiency of energy transfer and the viscosity of the resins used to prepare the formulations besides the complexity in understanding the mechanism of polymerization due to the presence of different initiating species. In this regard, *O*-acyloximes or oxime-esters (OXEs) (carrying R₁, R₂, and R₃ groups) are known as efficient photobase generators which can produce primary amines (R₁NH₂) upon irradiation (See Scheme 1)^{14, 15}. These molecules can undergo a homolytic cleavage of the N-O bond from their excited states followed by a decarboxylation step to generate iminyl and alkyl free radicals which recombine together to form the intended primary amines. R₂ and R₃ groups by which the excitation step is accomplished could be modified to a chromophore that absorbs light in the near UV or visible region without being involved in an unfavorable combination with other sensitizers. In this study, we have used our previously synthesized free radical photoinitiator based on phenothiazine-based oxime ester (denoted as **PTZ** in **Figure 1**)³² which has absorption properties in the near UV-Visible region and can be originally employed here as a PBG system for the polymerization of thiol-acrylate reactions and more interestingly for the initiation of the thiol-Michael addition reaction which is considered as a robust, highly efficient “click” reaction and an influential tool in the domain of polymer chemistry, **most often in polymer functionalization, surface modification and bioconjugation**³³⁻³⁵. Generation of methyl amine base active species (CH₃NH₂) upon irradiation of a **PTZ** system by a 375 nm LED was proved using phenol red as a pH-indicator. Mechanisms governing the photochemical base generation reaction and the thiol-acrylate polymerization reactions have been investigated using different complementary techniques. Moreover, thermal properties of the polymers obtained along with the surface hardness tests have been examined. **It is important to mention that the methyl amine base active species which we have obtained and employed in our experiments could be acquired commercially or through the Schiff's base reaction, whereas the use of light-induced polymerization processes is: environmentally propitious (solvent free and reduced waste), economically favorable (fast curing, high productivity, and low energy consumption), in addition to the high spatial and temporal control.**



Scheme 1. Photochemical base-generation reaction of *O*-acyloximes or oxime-esters.

2. Experimental part

2.1. Synthesis of the studied phenothiazine-based PBG

Synthesis of the investigated phenothiazine-based PBG (**PTZ**) is described in detail in the supporting information related to the published paper by our group (Reference [32]).

2.2. Other chemical compounds

The different monomers used i.e. pentaerythritol tetrakis(3-mercaptopropionate) (PETMP) and di(trimethylolpropane)tetraacrylate (TA) were obtained from Bruno-Bock GmbH Marschacht, Germany and Sartomer-Europe respectively and their chemical structures are presented in **Figure 1**. Phenol red indicator (Phenolsulfonphthalein) (3*H*-2,1-Benzoxathiole 1,1-dioxide) was obtained from Tokyo Chemical Industry, Japan.

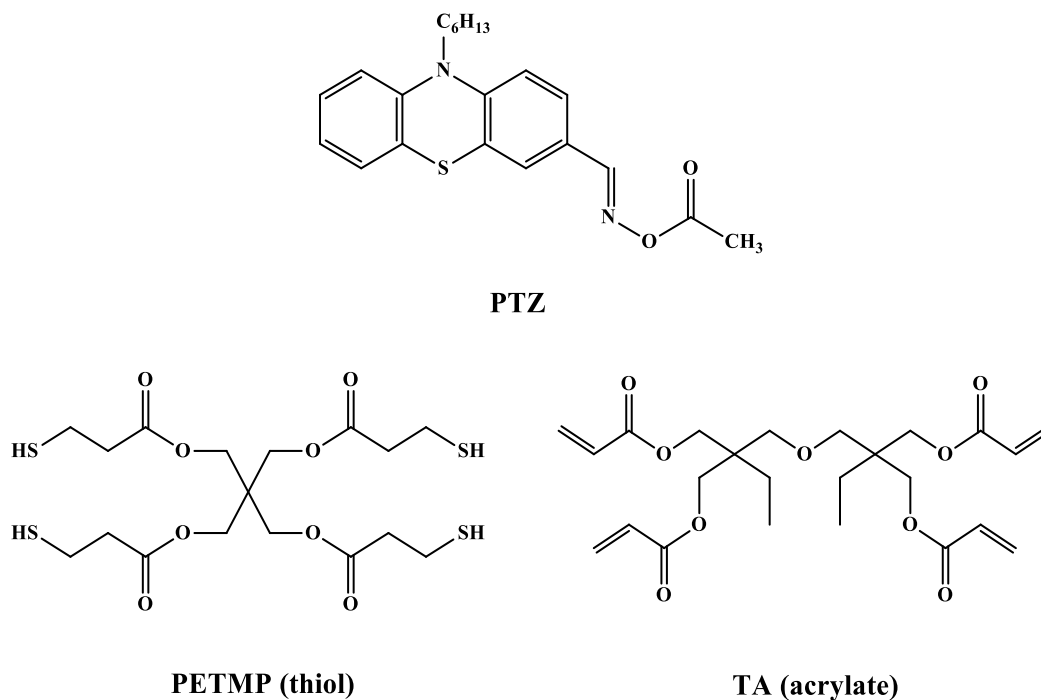


Figure 1. Chemical structures and abbreviations of the phenothiazine-based PBG (**PTZ**) and the benchmark monomers PETMP and TA.

2.3. Irradiation Sources

Different light-emitting diodes (LEDs) were used as irradiation sources: (1) LED@375 nm with an incident light intensity at the sample surface $I_0 = 40 \text{ mW} \cdot \text{cm}^{-2}$, and (2) LED@405 nm with an incident light intensity at the sample surface $I_0 = 110 \text{ mW} \cdot \text{cm}^{-2}$.

2.4. UV-Visible absorption and base detection experiments

UV-Visible absorption experiments used for the detection of the generated base were performed using a JASCO V730 spectrometer. Base detection experiments carried out for the prepared formulation (**PTZ** in acetonitrile) (10^{-5} M) were performed upon exposure to a LED@375 nm, and their associated UV-visible absorption spectra at different irradiation times were measured by means of the JASCO V730 spectrometer after the addition of 0.3 ml of the prepared phenol red solution (10^{-2} M).

2.5. Photopolymerization kinetics (RT-FTIR)

Detailed experimental conditions for each formulation have been noted in the caption of the different figures. The prepared formulations were stirred in the dark for 24 h. All polymerization experiments were performed using a LED@405 nm at room temperature and the irradiation was initiated after $t = 10$ s. The weight of the system was calculated from the monomer content. In our experiments, we used 0.02 g (2% phr, parts per 100 g resin) PI in 1 g of monomers (PETMP/TA) or in 1 g of TA monomer. The conversion of the acrylate function of TA was continuously followed by real-time Fourier transform infrared spectroscopy (JASCO FTIR 6600). The formulations were deposited inside 2.3 mm thickness molds under air and the acrylate group band was continuously followed from 6117 cm^{-1} to 6221 cm^{-1} . The final acrylate function conversion of TA was obtained by using the following equation:

$$\text{FC (\%)} = \frac{A_0 - A_t}{A_0} \times 100$$

Where FC is the final function conversion, A_0 is the proportion of the peak area at 0 sec, and A_t is the portion of the peak area at t s. The procedure has been already described by our group in Reference [32].

2.6. Differential scanning calorimetry (DSC)

Thermal properties of the obtained polymers were characterized by differential scanning calorimetry (Mettler Toledo DSC). About 10 mg of each obtained polymer was inserted into a 100 μL aluminum crucible. Two-cycle DSC scans were conducted from $-50\text{ }^{\circ}\text{C}$ to 250°C using a $10\text{ }^{\circ}\text{C min}^{-1}$ heating and cooling rate, and all the experiments were carried out under nitrogen with a flow rate of 100 mL.min^{-1} .

2.7. Shore A and Shore D hardness tests

Shore hardness is a measure of the resistance of material to indentation by a spring-loaded indenter. There are several scales of durometer used for materials with different properties. The two most common scales are type A (used for soft materials) and type D scales (for harder ones).

Hardness of our obtained polymers was measured by using Shore A and Shore D hardness tests from SAUTER.

3. Results and discussion

3.1. UV-Visible absorption and base detection experiments

Generation of base active species induced by the photochemical base-generation reactions of the studied PBG system is a key crucial step for the initiation of the anionic polymerization reactions. The generation of these active species could be confirmed by using phenol red which is a pH-indicator dye that exhibits a gradual transition from yellow to red over a pH range of 6.2 to 8.2.

In our work, the generation of methyl amine base active species (CH_3NH_2) triggered by the irradiation of the PBG system used (**PTZ**) by a 375 nm LED was proved by measuring the UV-visible absorption spectra of **PTZ** (10^{-5} M) in acetonitrile upon exposure to different irradiation times and after the addition of 0.3 ml of the prepared phenol red solution in acetonitrile (10^{-2} M). No spectral change was observed without irradiation, whereas a new band clearly appeared at 578 nm whose intensity increased with the irradiation time (**Figure 2 (B)**). This new band corresponds to the characteristic absorption band of the deprotonated form of phenol red. These results prove that there is no premature base release in the absence of light and there is an increasing release of base under irradiation. Moreover, in addition to the formation of the characteristic band at 578 nm, we have noticed a visual change in the color of **PTZ** solution upon exposure to irradiation and after the addition of phenol red solution from yellow to red (See **Figure 2 (A)**) which is also related to the deprotonated form of phenol red. These experiments clearly support the generation of methyl amine (CH_3NH_2) upon irradiation of the PBG system used (**PTZ**) by a 375 nm LED.

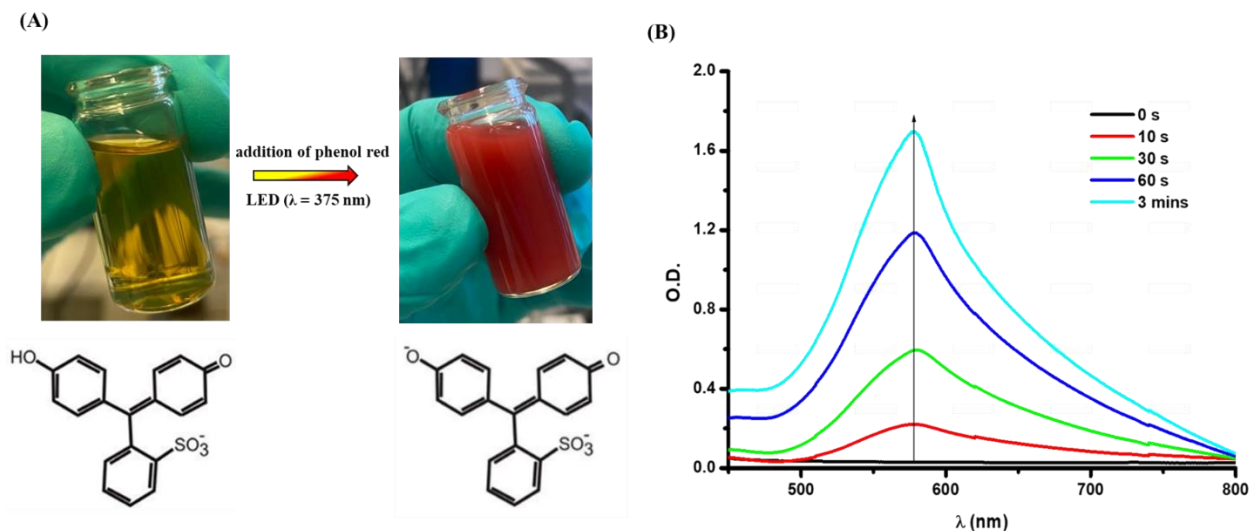


Figure 2. (A) Color change, and (B) UV-visible absorption spectra of **PTZ** (10^{-5} M) in acetonitrile upon exposure to a LED ($\lambda = 375$ nm) and after the addition of 0.3 ml of phenol red solution (10^{-2} M).

3.2. Thiol-acrylate polymerization reactions

In order to discuss the experimental results obtained by real-time FTIR of the thiol-acrylate polymerization reactions, it is fundamental first to explain how these reactions proceed. The formation of thiol-acrylate networks could be attained either by radical-mediated thiol-acrylate reactions or through base-catalyzed thiol-acrylate Michael addition reactions (**Scheme 2 (B)**). Therefore, and in the aim of studying the efficiency of our PBG system (**PTZ**) in the polymerization of thiol-acrylate reactions and its ability in activating specifically the base-catalyzed thiol-acrylate polymerization reactions, two approaches have been developed.

The first attempt includes the preparation of two formulations, the first one containing a mixture of PETMP/TA (thiol/acrylate) (50/50 w/w), and the second one containing TA (acrylate) alone. The two formulations were prepared in thick samples (2.3 mm, under air) in the presence of **PTZ** (2% phr) and exposed to 10 min of irradiation with a LED ($\lambda = 405$ nm). Characteristic acrylate peaks before and after photopolymerization for both formulations are shown in **Figures 3 (A) and (B)**, and the associated acrylate conversions versus irradiation time profiles with their final acrylate conversions are shown in **Figure 3 (C)**. The first formulation carrying 2% phr **PTZ** in the PETMP/TA mixture achieved an absolute disappearance of the characteristic acrylate peak (See

Figure 3 (A)) with a 98% conversion of this peak, whereas the second formulation bearing 2% phr **PTZ** in TA alone attains an incomplete disappearance with a 65% conversion of the acrylate peak. This significant increase in the percentage of acrylate conversion from 65% (in the presence of acrylate alone) to 98% (in the presence of thiol-acrylate) clearly demonstrates the efficient role of **PTZ** system in the polymerization of thiol-acrylate reactions. It is essential to mention that an inner filter effect is observed due to the high light absorption properties of **PTZ** i.e. the performance of **PTZ** in the FRP of acrylate group is altered negatively for thick samples (here 2.3 mm – **Figure 3**), while this effect is not detected in thin samples (See Figure S1; thickness ~ 25 μ m) where the performance of **PTZ** is much more better (81% of acrylate conversion within 150 secs of irradiation of a LED ($\lambda = 405$ nm); Reference [32]).

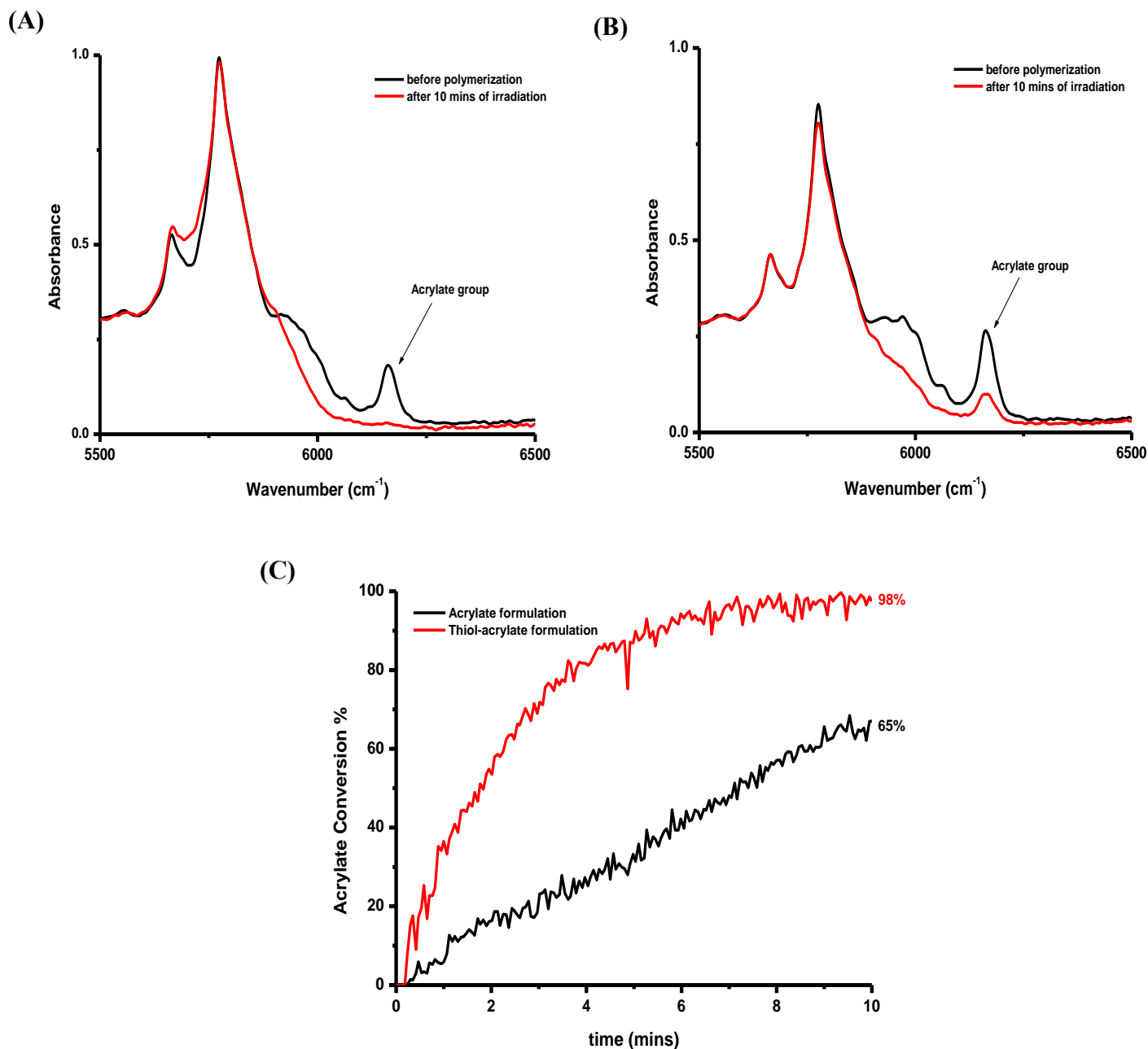


Figure 3. Characteristic acrylate peaks before and after photopolymerization of a PETMP/TA mixture (50/50 w/w) (A) and in TA alone (B) in the presence of **PTZ** (2% phr) upon exposure to 10 mins of a LED ($\lambda = 405$ nm); (C) Photopolymerization profiles (acrylate function conversion vs. irradiation time) under air (thickness = 2.3 mm) of the above formulations (A) and (B).

The second attempt comprises three formulations containing a mixture of PETMP/TA (thiol/acrylate) (50/50 w/w) prepared in thick samples (2.3 mm, under air) in the presence of **PTZ** (2% phr) but these formulations were exposed to different experimental conditions. Characteristic

acrylate peaks before and after polymerization for the three formulations are shown in Figures 4 (A) to (C), and the associated percentages of the acrylate conversion along with the visual changes observed according to the experimental conditions used are recapped in Table 1. The idea from this trial was to stop the radical-mediated thiol-acrylate reactions by turning off the light after one or two minutes of irradiation and then investigate the ability of the generated base in catalyzing the thiol-acrylate polymerization reactions in the presence of heat exposure.

The percentage of acrylate conversion reached 47% after 2 min of irradiation ($\lambda = 405$ nm) then 95% after one day in oven ($T = 60^{\circ}\text{C}$) in the first formulation (See Figure 4(A) and Table 1). The same successive trend has been observed in the second formulation where the percentage of conversion increased from 30% after 1 min. of irradiation to 98% after one day in oven (See Figure 4(B) and Table 1), whereas the acrylate peak remained the same without any conversion if the formulation was left one day in oven ($T = 60^{\circ}\text{C}$) without irradiation (See Figure 4(C) and Table 1). This behavior of the acrylate group according to the experimental conditions used is consistent with the observed visual changes, where we noticed a transformation from the liquid solutions to more gel-like ones after irradiation ($\lambda = 405$ nm) and we have got tacky-free samples after one day in oven ($T = 60^{\circ}\text{C}$) in the first two formulations, on the other hand the solution stays the same without any visual changes after one day in oven ($T = 60^{\circ}\text{C}$) in the third formulation. Results obtained clearly show that the generated base is able to catalyze the thiol-acrylate polymerization reactions in the presence of heat exposure without the integration of the radical-mediated thiol-acrylate reactions, and that the polymerization reactions cannot proceed in the presence of heat exposure only without the interference of the visible light exposure ($\lambda = 405$ nm) because no active species (i.e. base) will be generated. It is essential to note that the PTZ compound has absorption properties in the near UV-Visible range (Reference 32). Therefore, the photoinitiation ability of the PTZ system was examined upon exposure to a LED@405 nm, whereas the base detection experiments were investigated upon exposure to a LED@375 nm. This is the same absorption band and therefore the same photochemistry.

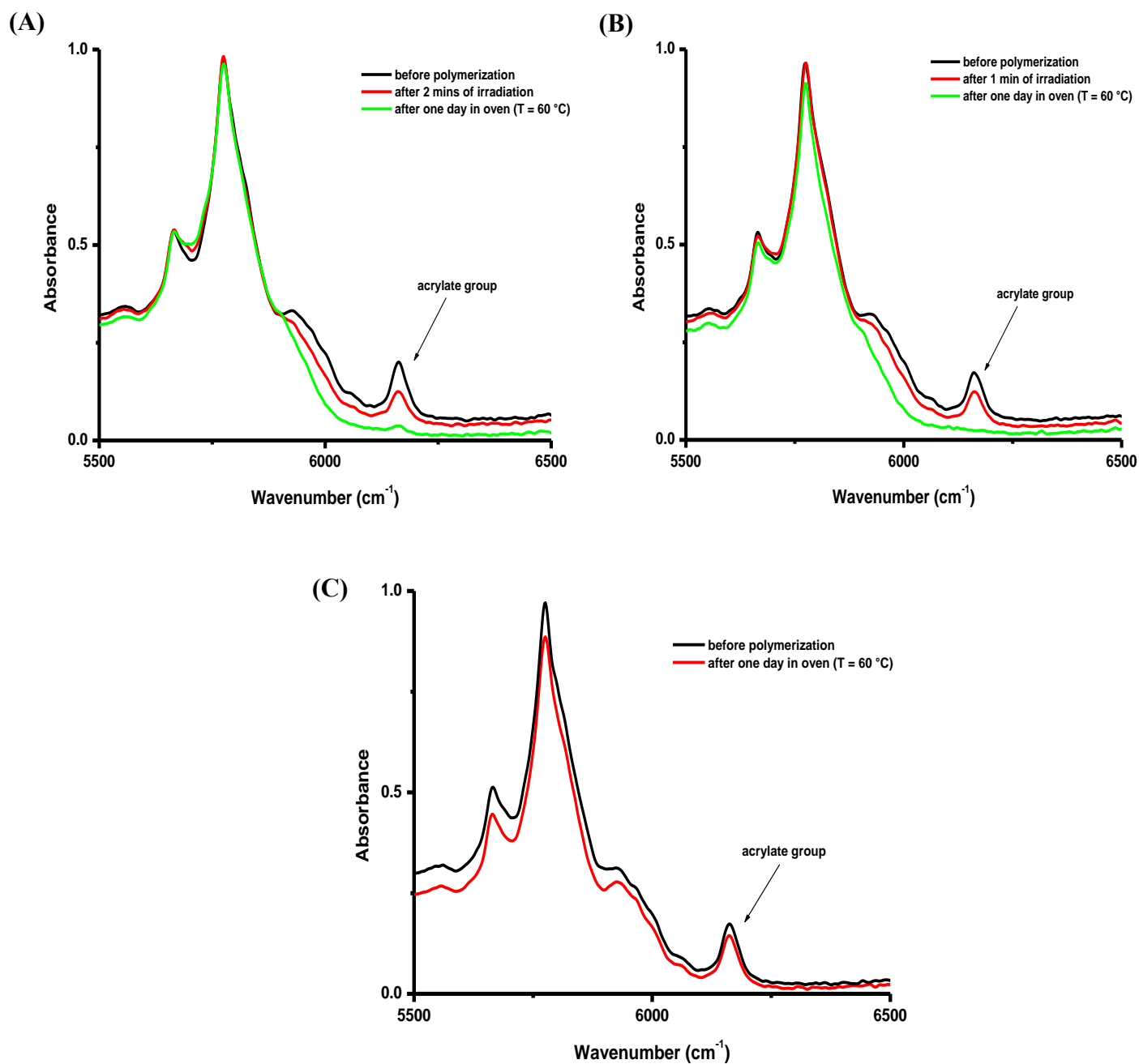
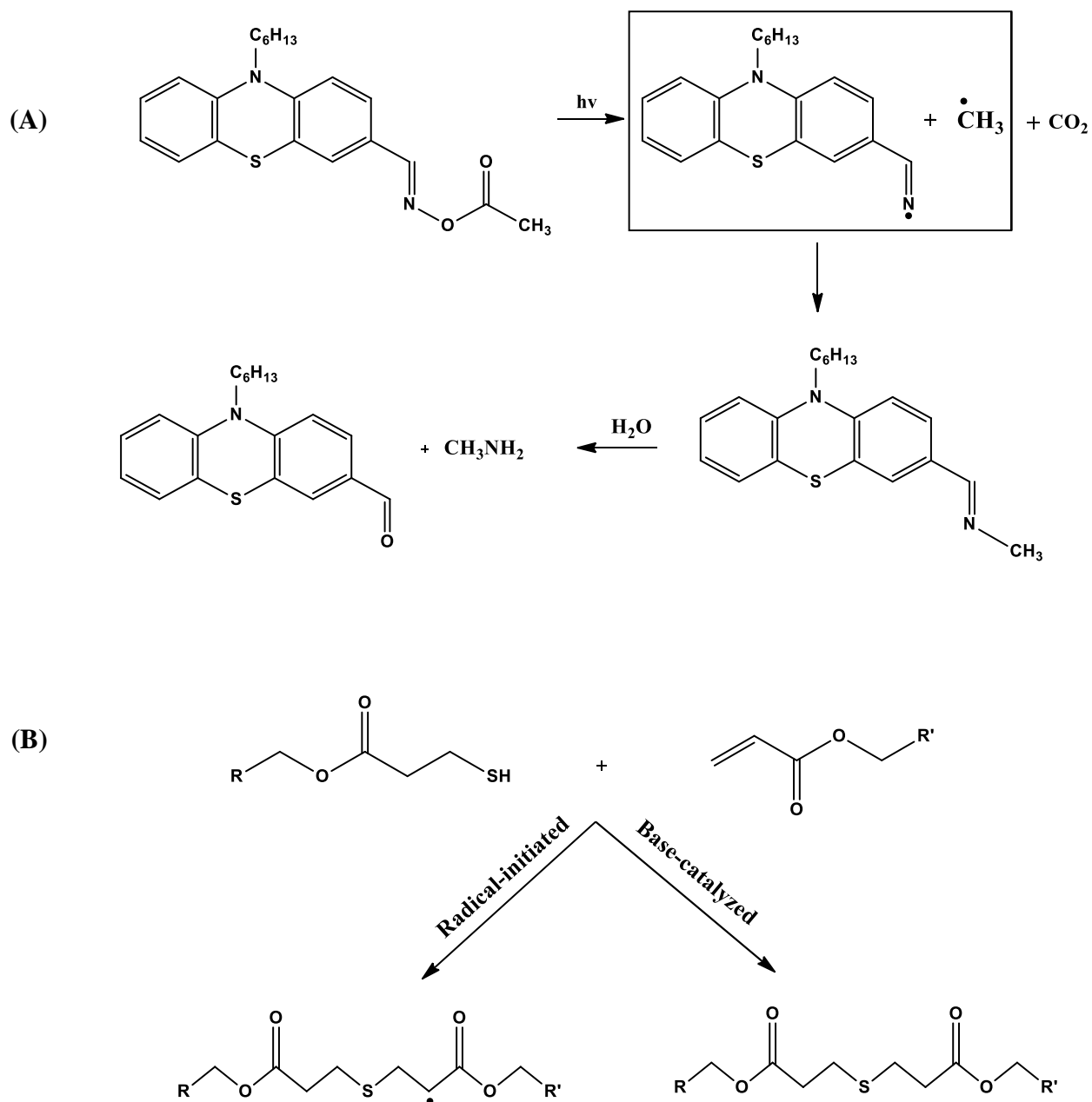


Figure 4. Characteristic acrylate peaks of a PETMP/TA mixture (50/50 w/w) in the presence of PTZ (2% phr) before photopolymerization and after 2 min of irradiation of a LED ($\lambda = 405 \text{ nm}$) then one day in oven ($T = 60^\circ\text{C}$) in (A); after 1 min of irradiation of a LED ($\lambda = 405 \text{ nm}$) then one day in oven ($T = 60^\circ\text{C}$) in (B); after one day in oven ($T = 60^\circ\text{C}$) in (C). All samples were prepared under air (thickness = 2.3 mm).

Table 1. Summary of the photopolymerization profiles and visual changes obtained for PETMP/TA (50/50) blends under air (thickness = 2.3 mm) in the presence of 2% **PTZ** and with the exposure of different experimental conditions.

Samples experimental conditions	% of acrylate group conversion	Visual changes
After 10 min of irradiation of a LED ($\lambda = 405$ nm).	98%	Tacky-free samples are obtained.
After 2 min of irradiation of a LED ($\lambda = 405$ nm) then one day in oven ($T = 60^\circ\text{C}$).	47% \longrightarrow 95%	The liquid solution became more gel-like after irradiation then tacky-free samples are obtained after heat exposure.
After 1 min of irradiation of a LED ($\lambda = 405$ nm) then one day in oven ($T = 60^\circ\text{C}$).	30% \longrightarrow 98%	The liquid solution became more gel-like after irradiation then tacky-free samples are obtained after heat exposure.
After one day in oven ($T = 60^\circ\text{C}$).	No conversion	The solution remained the same without any visual changes observed.

Subsequently, and based on the performed base detection experiments along with the obtained real-time FTIR results and according to the photochemical base-generation reactions of Oxime-esters, a mechanism of the photochemical generation of methyl amine base upon irradiation of **PTZ** is illustrated in **Scheme 2(A)** and the thiol-acrylate polymerization reactions are shown in **Scheme 2(B)**.



Scheme 2. (A): Illustration of the photochemical generation of methyl amine base upon irradiation of **PTZ**; (B) thiol-acrylate photoinitiated polymerization (radical initiated and base catalyzed reactions).

3.3. DSC and surface hardness tests

In the purpose of studying the double bond conversion and the thermal properties of the polymers obtained by the polymerization of thiol-acrylate reactions and in order to compare them with that obtained through acrylate polymerization reactions, two-cycle DSC experiments have been performed and their associated curves (temperature vs heat flow) are presented in **Figure 5** (the second cycle of heating) and Figure S2 (the first cycle of heating). The onset temperature (T_{Onset}), the glass transition temperature (T_g), and the specific heat capacity (ΔC_p) along with the experimental conditions are summarized in Table 2. Markedly, the first three polymers obtained by thiol-acrylate polymerization reactions (A, B, and C) have nearly the same thermal properties (T_{Onset} , T_g , and ΔC_p) where low values of T_g were recorded ($-2\text{ }^{\circ}\text{C}$, $0\text{ }^{\circ}\text{C}$, $0\text{ }^{\circ}\text{C}$ for A, B, and C respectively) which render them usable as soft materials and there is an almost absence of residual monomers at high temperatures in the 1st cycle of DSC scans in agreement with the complete polymerization of the acrylate group obtained above. Conversely, polymers obtained through acrylate polymerization reactions (D) showed no glass transition temperature because it undergoes thermal polymerization of the residual monomers in accordance with the incomplete polymerization of the acrylate peak obtained above. Moreover, the surface hardness of the obtained polymers have been measured by performing the Shore A and Shore D hardness tests and the values obtained are presented in Table 2. We can clearly observe a notable increase in the Shore A average values for the polymers obtained by thiol acrylate polymerization (83, 82, 83 for A, B and C respectively) compared to the one obtained by acrylate polymerization (41). Jointly, a remarkable increase in the Shore D average values for the polymers was also obtained by the thiol acrylate polymerization (23, 21, 22 for A, B, and C respectively) compared to the one obtained by acrylate polymerization (5).

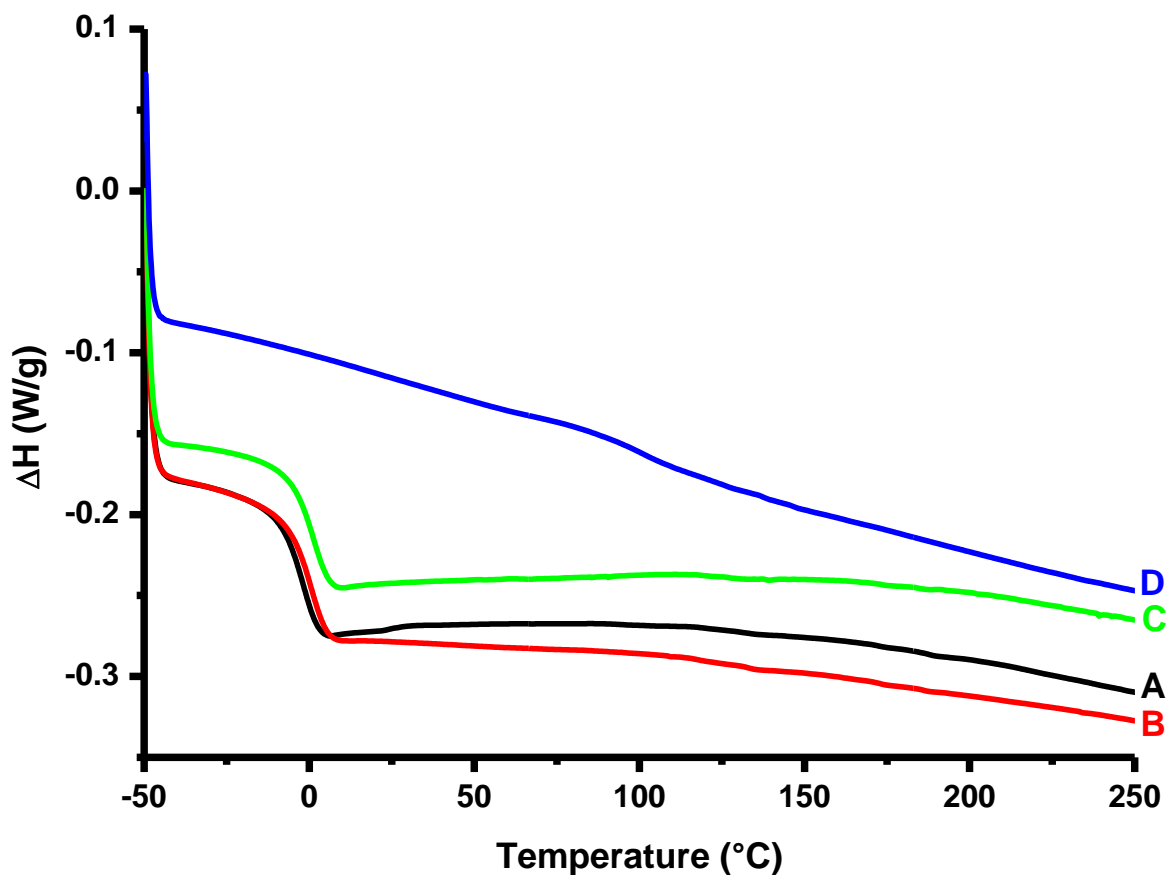


Figure 5. The second cycle of DSC scans of the different polymers obtained. (A) 2% phr **PTZ** in PETMP/TA (50/50) blends and 10 min of irradiation ($\lambda = 405$ nm), (B) 2% phr **PTZ** in PETMP/TA (50/50) blends and 2 min of irradiation ($\lambda = 405$ nm) then one day in oven ($T = 60^{\circ}\text{C}$), (C) 2% phr **PTZ** in PETMP/TA (50/50) blends and 1 min of irradiation ($\lambda = 405$ nm) then one day in oven ($T = 60^{\circ}\text{C}$), (D) 2% phr **PTZ** in TA and 10 min of irradiation ($\lambda = 405$ nm).

Table 2. The onset temperature (T_{onset}), the glass transition temperature (T_g), the specific heat capacity (ΔC_p), and the Shore A and Shore D average along with the experimental conditions for the four polymers (A to D).

Samples	Experimental Conditions	T_{onset} (°C)	T_g (°C)	ΔC_p (J.g ⁻¹ .k ⁻¹)	Shore A average	Shore D average
A	2% phr PTZ in PETMP/TA (50/50) blends and 10 min of irradiation ($\lambda = 405$ nm).	-9	-2	0.535	83	23
B	2% phr PTZ in PETMP/TA (50/50) blends and 2 min of irradiation ($\lambda = 405$ nm) then one day in oven ($T = 60$ °C).	-7	0	0.471	82	21
C	2% phr PTZ in PETMP/TA (50/50) blends and 1 min of irradiation ($\lambda = 405$ nm) then one day in oven ($T = 60$ °C).	-6	0	0.468	83	22
D	2% phr PTZ in TA and 10 min of irradiation ($\lambda = 405$ nm).		Not present		41	5

4. Conclusion

In this article, a new class of oxime-esters based on the phenothiazine chromophore has been used as a photo-base generating system for the polymerization of thiol-acrylate reactions and more intriguingly in the activation of the base-catalyzed thiol-Michael addition reaction. Base detection experiments based on phenol red indicator along with UV-visible absorption spectra were employed to confirm the generation of methyl amine base active species (CH_3NH_2) under the irradiation of a light-emitting diode ($\lambda = 375$ nm). The phenothiazine-based oxime ester compound could achieve a complete conversion of the acrylate group after 10 min of irradiation with a light-

emitting diode ($\lambda = 405$ nm) or after 1 or 2 min of the same irradiation source and 24 hours of heat exposure ($T = 60$ °C). Based on the general photo-base-generation reactions of oxime-esters, the experiments done to detect the formation of base, and the behavior of the acrylate conversion according to the experimental conditions used, the mechanism governing the photochemical generation of methyl amine upon irradiation of **PTZ** and the thiol-acrylate photoinitiated polymerization reactions have been depicted. Finally, thermal properties and surface hardness features of the obtained polymers have been examined by following the DSC scans and by performing the Shore A and Shore D experiments respectively. Future investigations of other photo-base generating systems that can be activated by using near UV-visible LEDs through which the polymerization of click reactions proceeds will be proposed in upcoming studies.

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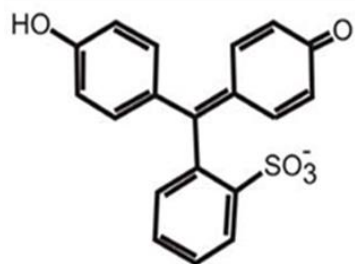
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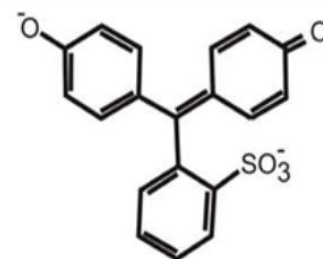
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TOC graphic

Detection of base generation



Addition of
phenol red



Photochemical generation mechanism of methyl amine base active species

