

## Synthesis of a novel thiolated photopolymerizable monomer derived from soybean oil and its thiol-ene photopolymerization with unsaturated monomers

## Síntese de um novo monômero fotopolimerizável tiolado derivado de óleo de soja e da sua fotopolimerização tioleno com monômeros insaturados

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### ABSTRACT

In this study is presented a synthetic methodology to prepare a thiolated monomer derived from renewable natural products resources such as the soybean oil. This product was thiolated by a thiol-ene coupling reaction between the double bonds of the vegetable oil and thioacetic acid. The obtained intermediate was subsequently hydrolyzed to obtain a mixture of thiolated fatty methyl esters. The attained mixture was characterized by FTIR and NMR spectroscopies. The reactivity of this compound was tested as comonomer in a thiol-ene photopolymerization using different types of unsaturated compounds. It was found that the thiolated compound reacted readily under UV irradiation forming polythioethers. The nature of the obtained polymers depended on the characteristics of the unsaturated monomers.

**Keywords:** soybean oil, thioacetic acid, thiol-ene photopolymerization.

### RESUMO

Neste estudo é apresentada uma metodologia sintética para preparar um monômero tiolado derivado de recursos de produtos naturais renováveis, como o óleo de soja. Este produto foi tiolado por uma reação de acoplamento tiol-eno entre as ligações duplas do óleo vegetal e ácido tioacético. O produto intermediário obtido foi subsequentemente hidrolisado para obter uma mistura de ésteres metílicos de ácidos gordos tiolados. A mistura obtida foi caracterizada por espectroscopias FTIR e NMR. A reatividade deste composto foi testada como comonómero em uma fotopolimerização tiol-eno usando diferentes tipos de compostos insaturados. Verificou-se que o composto tiolado reagia prontamente sob irradiação UV formando politioéteres. A natureza dos polímeros obtidos dependia das características dos monômeros insaturados.

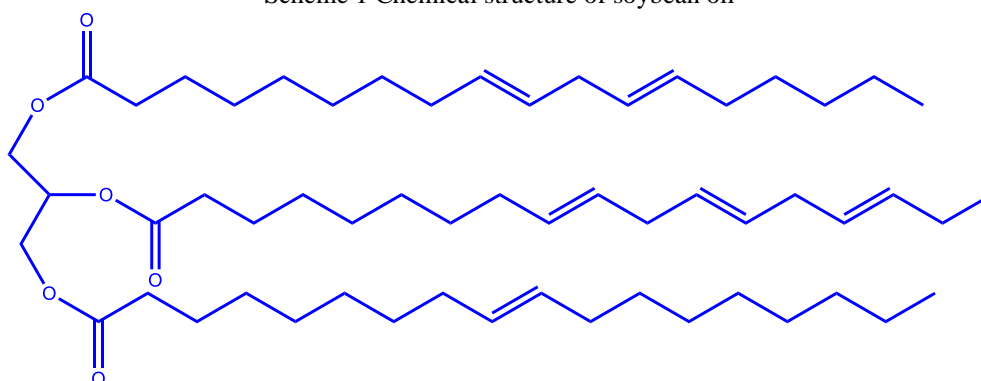
**Palavras-chave:** óleo de soja, ácido tioacético, fotopolimerização tiol-eno.

## 1 INTRODUCTION

Soybean oil is a vegetable oil that comes from the pressing of soybeans and refined to be edible. Beside its obvious use in the preparation of foods, this commodity compound has found multiple applications such as a component of eco-friendly pesticides, fungicides, paints and plastics. It can also be used to obtain biodiesel and lubricants, soaps and cosmetics <sup>1</sup>. The soybean oil is attractive as starting material to prepare different type of compounds because it is very cheap and highly available. In 2020 Brazil surpassed USA as the global leading producer of soybean oil with 138 million of metric tons <sup>2</sup>.

The soybean oil is a triglyceride with fatty hydrocarbonated unsaturated chains as shown in Scheme 1. It contains double bonds that are susceptible to be functionalized. Crivello et.al. <sup>3</sup> carried out epoxidation reactions on the soybean oil to obtain a biobased epoxy resin, that was further cationically photopolymerized using triaryl sulfonium salts as photoinitiators and environmental solar irradiation

Scheme 1 Chemical structure of soybean oil



Dewasthale and collaborators <sup>4</sup> reacted the soybean oil with a silanol end-functionalized polydimethylsiloxane to obtain interpenetrated networks via a radical polymerization. In other study Chernikh et.al <sup>5</sup> reported a transesterification reaction between soybean oil and the 2-(vinylethoxy) ethanol that was performed to obtain a vinyl ether functionalized soybean oil. This compound was cationically polymerized in toluene. Acosta et.al <sup>6</sup> reported the use of epoxidized soybean oil as monomer for cationic photopolymerizations using benzyl alcohols as catalysts to accelerate the polymerization.

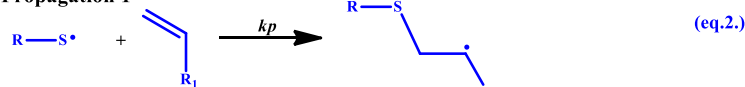
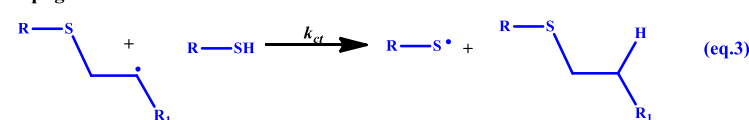
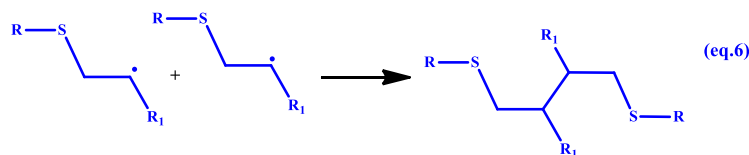
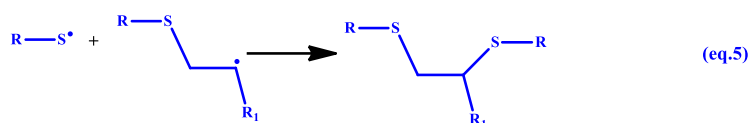
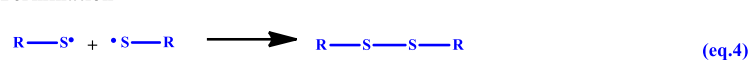
The thiol-ene photopolymerization is a versatile type of polymerization that involve a step-growth reaction between a multifunctional unsaturated compounds either with a three-functional or tetrafunctional thiol compound, to obtain polythioethers <sup>7</sup>. This type of photopolymerizations are not inhibited by oxygen, as most of radical

polymerizations, which represent a strong advantage in comparison with conventional radical polymerizations. These reactions proceed very rapidly at room temperature without the formation of sub-products. It was reported that any kind of compound with double bonds can react with a compound with a thiol group<sup>8</sup>. This type of polymerization are not inhibited by the humidity as in the case of cationic polymerization. The thiol-ene photopolymerization have found multiple applications in different areas such as materials for biomedical applications, in 3D printing, in the preparation of adhesives, hydrogels, dendrimers and enzymes inhibitors<sup>9</sup>. The main characteristic of this polymerizations is the weakness of the bond S-H, resulting in quantitative reactions with the unsaturated compounds, under mild conditions.

The mechanism of the thiol-ene photopolymerization is depicted in Scheme 2<sup>10</sup>. In the initiation step, the photoinitiator added to the photocurable formulation generates primary radicals when irradiated with UV light. These radicals can abstract the labile hydrogen atom of the thiol groups, to generate a thiyl radical (eq.1). These thiyl radicals can react with the double bond of the unsaturated compound to form a carbon-centered secondary radical (eq.2). To propagate the photo-polymerization the secondary radical can abstract the hydrogen atom of a new thiol group forming again a thiyl radical (eq.3). Two radical species of the same or different nature can react with themselves to terminate the polymerization (eqs 4,5 and 6)

Scheme 2. Mechanism of the thiol-ene photopolymerizations

**1. Initiation**

**2. Propagation 1**

**3. Propagation 2**

**4. Termination**


Therefore, considering the high availability of the soybean oil and its low cost, it was proposed its use to prepare a thiolated compound that can be used as comonomer in the thiol-ene photopolymerizations in conjunction with two unsaturated monomers such the 1,6-hexanediol diacrylate (HDDA) and the triallyl cyanurate (TAC).

## 2 EXPERIMENTAL METHODS

### 2.1 MATERIALS

The soybean oil was purchased from a local supermarket. The thioacetic acid, benzoyl peroxide, sodium hydroxide, toluene, methanol, and 37 % hydrochloric acid, 1,6-hexanediol diacrylate (HDDA), 2,4,6-Triallyloxy-1,3,5-triazine (TAC) and 2,2-dimethoxy, 2-phenyl acetophenone (DMPA) were purchased from Sigma-Aldrich Mexico (Toluca).

### 2.2 PREPARATION OF THIOLATED SOYBEAN OIL (TSO)

In a 250 mL three-necked round-bottom flask provided with condenser, thermometer and magnetic stirring, were added 10 g (0.011337 moles) of soybean oil and 3.0 g (0.03941) of thioacetic acid. Thereafter, it was added 0.2744 g (0.001133 moles) of benzoyl peroxide and finally 50 mL of toluene. The reaction mixture was heated at 95 °C

for 5 h. After this time the mixture was allowed to cool down and then it was washed thrice with 30 mL of 10% w/v of an aqueous solution of NaOH. Then the resulting mixture was washed thrice with 20 mL of distilled water and thereafter dried with 12 g of anhydrous sodium sulfate and filtered using Whatman paper #40. The reaction mixture was rotoevaporated and the crude product was weighed obtaining 9.8 g of the TSO in 80 yield %

### 2.3 HYDROLYSIS OF THE TSO

In a 250 mL three-necked round bottom flask provided with condenser, thermometer and magnetic stirring was added 50 mL of methanol, 10 g of TSO and 50 mg of NaOH as pellets. The reaction mixture was heated at 60 °C for 5 h in nitrogen atmosphere. After this time the mixture was allowed to cool down and then it was washed thrice with 30 mL of a 10 % HCL aqueous solution, to eliminate the basic residues. Then it was washed thrice with 30 mL of distilled water and subsequently dried with 5 g of anhydrous sodium sulfate. The suspension was filtered and the filtrated methanolic solution was rotoevaporated to obtain 9.68 g of the crude product, which represent a yield of 96.2 %.

### 2.4 THIOL-ENE PHOTOPOLYMERIZATION OF THE THIOLATED METHYLIC ESTERS OF SOYBEAN OIL (METSO) WITH UNSATURATED MONOMERS

The obtained METSO was photopolymerized in conjunction with two unsaturated monomers: the 1,6-hexanediol diacrylate (HDDA) and the triallyl cyanurate (TAC). The average molecular weight of METSO was considered as 363 g/mol with two thiol groups in its structure. The molar relationship of METSO with HDDA and TAC was 1:1 and 1:1.5, respectively. The thiolated monomer was mixed separately with each unsaturated monomer and then it was added 1.0 mol % of the radical photoinitiator DMPA. The resulting photocurable formulations were irradiated in a UV chamber provided with a 300 W Fusion UV lamp, for 15 min.

## 3 RESULTS AND DISCUSSION

### 3.1 SYNTHESIS OF METSO

This study was aimed to obtain a biobased thiolated compound derived from soybean oil that can be used as comonomer in a thiol-ene photopolymerization. The

soybean oil was subjected to a thiol-ene coupling between its double bonds and thioacetic acid. This reaction proceeded thermally in the presence of benzoyl peroxide. The chemical reaction is depicted in Scheme 4. The reaction proceeded in 5 h obtaining the thioester functionalized soybean oil. This compound was obtained in 80 % yield. It was characterized by FTIR spectroscopy. Figure 1 display a comparison of the FTIR spectra of the pristine soybean oil and of the TSO. It can be observed that the peak at  $3006\text{ cm}^{-1}$  characteristic of the double bonds of soybean oil, disappeared and a new band at  $1687\text{ cm}^{-1}$  corresponding to the carbonyl group of the thioester, is visible. This confirms the functionalization of the vegetable oil.

Scheme 3. Thiol-Ene coupling reaction to obtain TSO

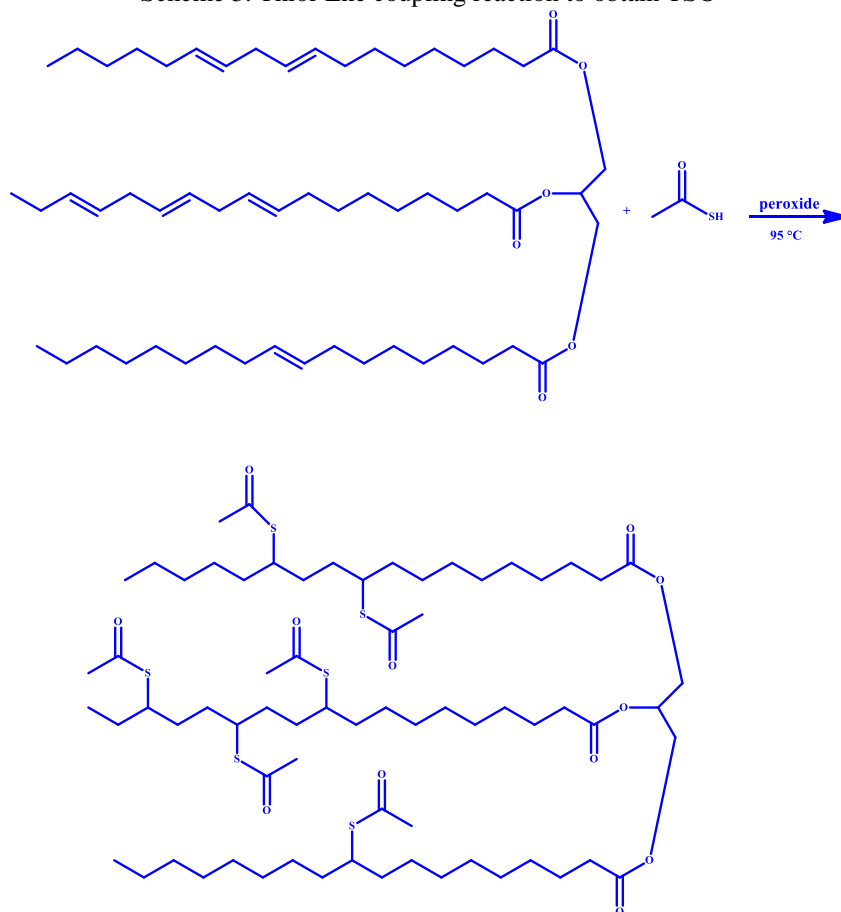


Figure 1. Comparison of FTIR spectra of: a) pristine soybean oil spectrum and b) thioester functionalized soybean oil (TSO).

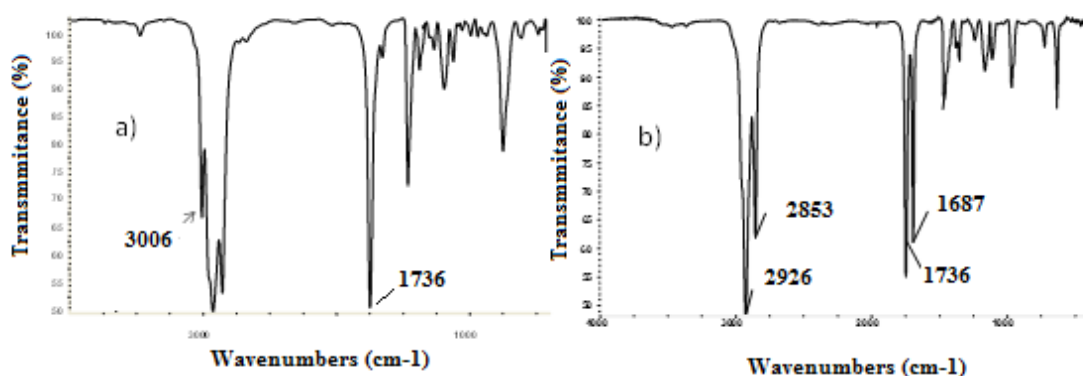


Figure 2. Comparison of the <sup>1</sup>H NMR spectra of pristine soybeanoil and TSO, run in CDCl<sub>3</sub>

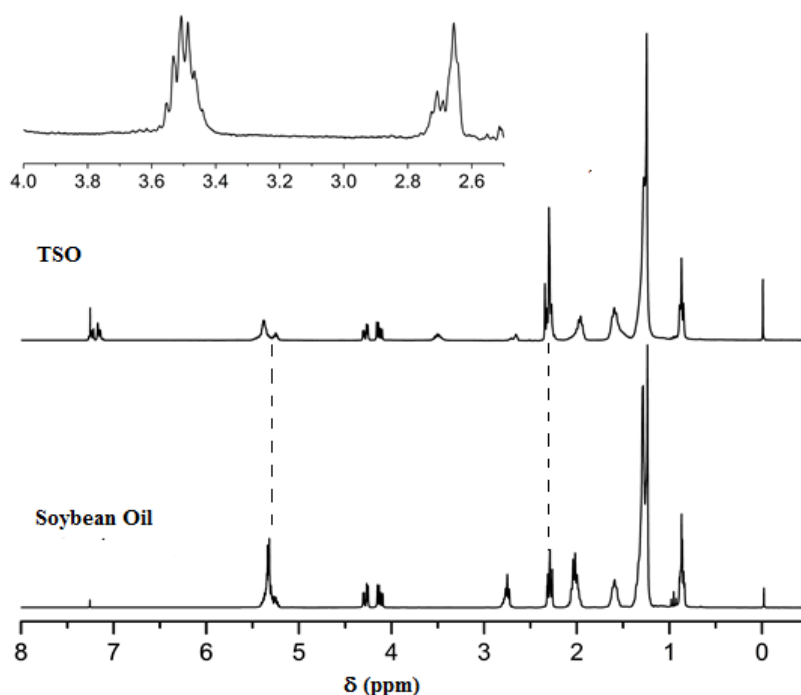


Figure 2 depict a comparison of the <sup>1</sup>H NMR spectra of soybean oil and TSO. The spectrum of soybean oil shows a multiplet at 5.45 ppm that correspond to the protons of the double bonds, and peaks in the range 4.0-4.5 ppm characteristic of the protons of the glycerol moiety. The allylic protons (adjacent to double bonds) are located in the 2.00-3.00 ppm interval, while the aliphatic protons are in the range 0.75-1.95 ppm. After functionalization with the thioacetic acid, the soybean oil was modified in such a way that thioester groups were introduced in the double bonds of the vegetable oil. The proton spectrum of TSO shows a decrease of the intensity of the peak at 5.45 ppm that reveals the introduction of the thioester groups, thus decreasing the amount of double bonds. It is

also observed the appearance of a new peak at 2.35 ppm corresponding to the protons of the methyl groups of the thioester. Other peaks appeared in the range of 2.60-2.70 characteristics of the protons of the carbons joined to the sulphur atom of the thioester groups. These characterization confirms the data obtain by FTIR spectroscopy regarding the functionalization of the soybean oil.

The TSO compound was subsequently hydrolyzed to release the thiol groups, obtaining a mixture of thiolated fatty methyl esters. (METSO). Scheme 4 shows the involved chemical reaction of hydrolysis of the thioester groups.

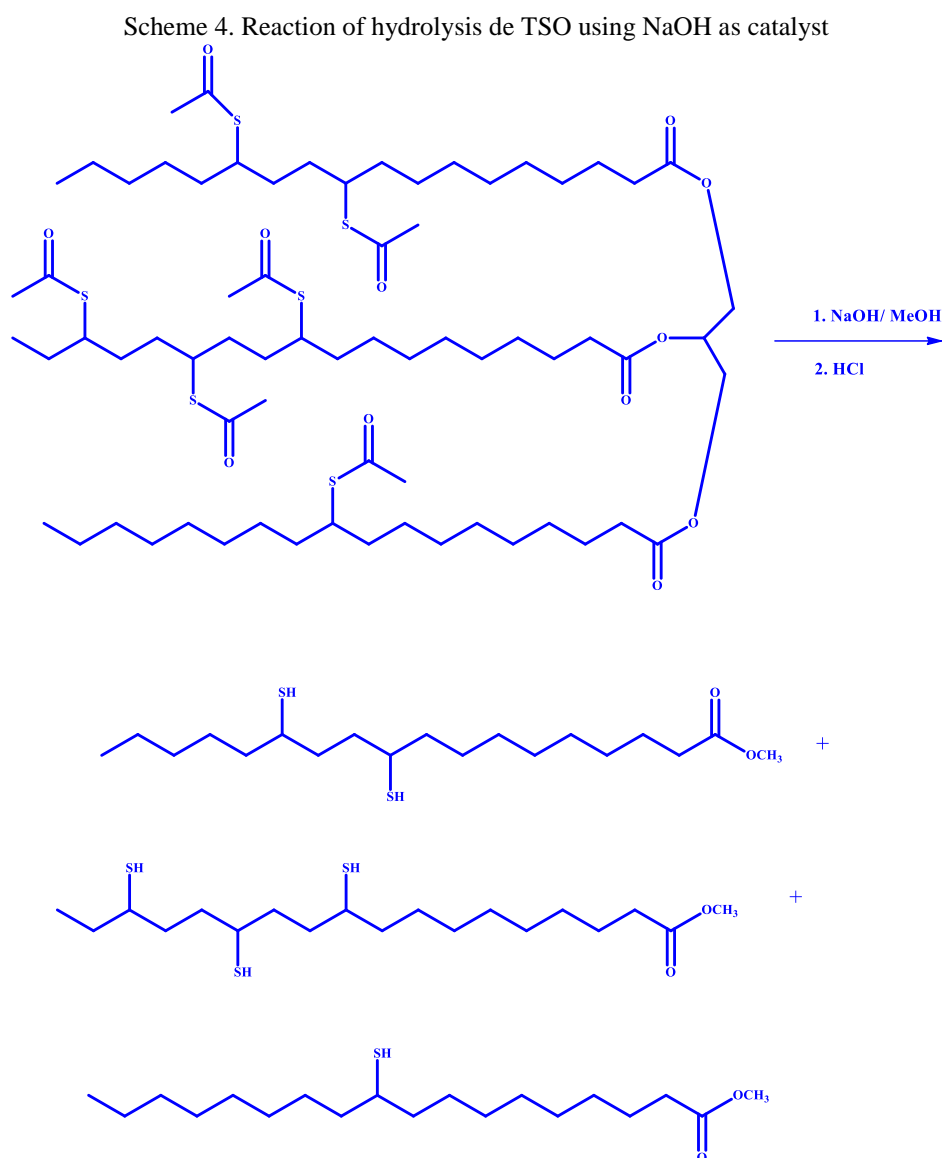


Figure 3 depicts the FTIR spectrum of METSO in which it is observed the appearance of a weak band at  $2100 \text{ cm}^{-1}$  that correspond to the S-H bonding, and the



disappearance of the band at  $1687\text{ cm}^{-1}$  of the carbonyl groups of the thioester in TSO. The band at  $1738\text{ cm}^{-1}$  corresponds to the carbonyl groups of METSO. The basic catalyst hydrolyzed not only the methyl thioester but also the glycidyl esters, releasing the methyl esters of METSO.

Figure 3. FTIR spectrum of METSO

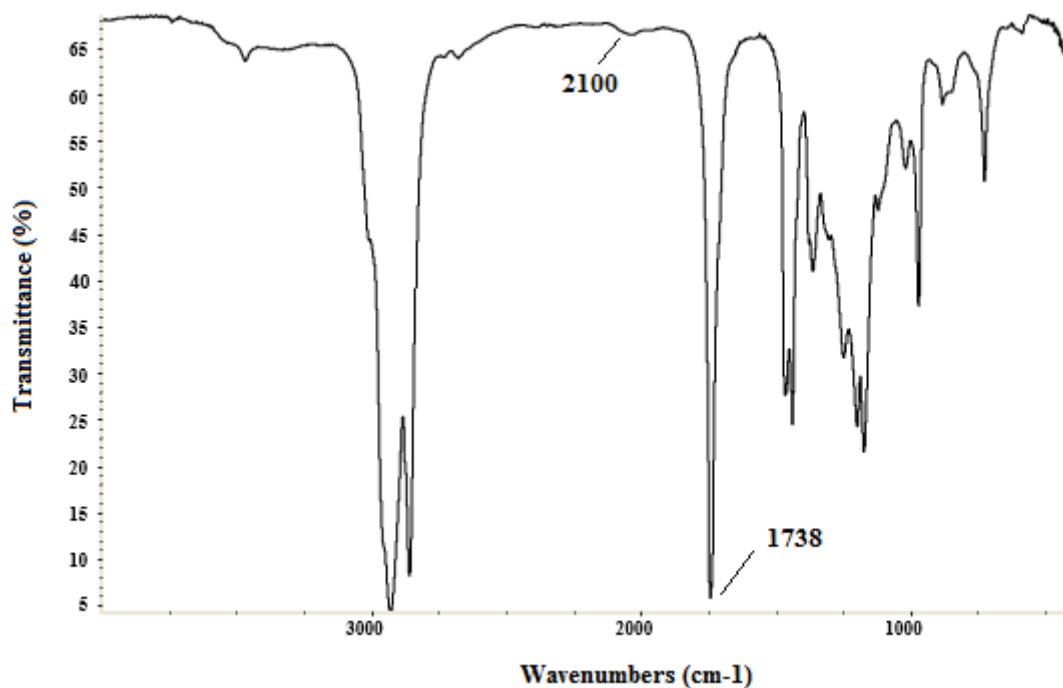
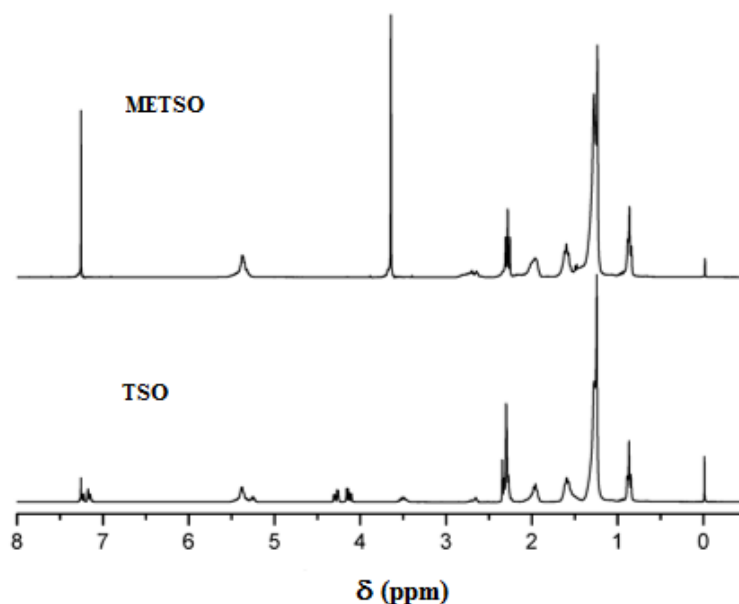


Figure 4 shows a comparison of the  $^1\text{H}$  NMR spectra of the produced METSO and of TSO. The appearance of a strong peak at 3.75 ppm, indicates the presence of methyl esters groups while the disappearance of the peaks in the range 4.0-4.5 ppm characteristic of the proton of the glycerol moiety of the triglyceride, confirms the hydrolysis of both the thioester and of the triglyceride, producing thiolated fatty methyl esters.

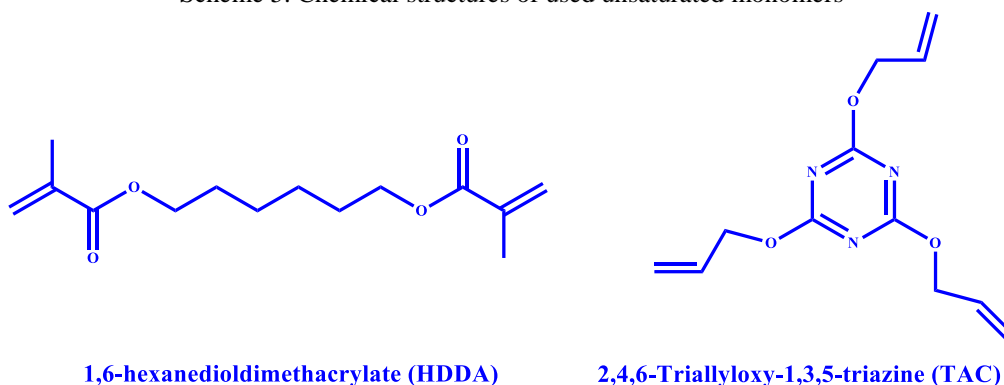
Figure 4. Comparison of the  $^1\text{H}$  NMR spectra of TSO and METSO run in  $\text{CDCl}_3$



### 3.2 THIOL-ENE PHOTOPOLYMERIZATION OF METSO WITH UNSATURATED COMPOUNDS

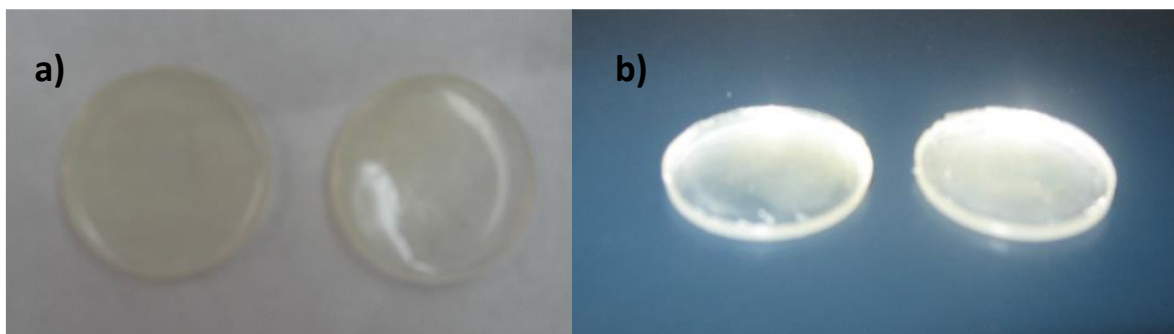
The produced METSO were reacted with two unsaturated monomers such as 1,6-hexanediol diacrylate (HDDA), and 2,4,6-triallyloxy-1,3,5-triazine (TAC) whose chemical structures are depicted in Scheme 5.

Scheme 5. Chemical structures of used unsaturated monomers



A bendable material was obtained in the case of the polymer derived from METSO and HDDA, due to the flexibility of the produced polythioethers and to the aliphatic chain of HDDA. The polymer produced in the reaction of METSO and TAC was more rigid due to the aromatic ring of the unsaturated compound. Figure 5 shows photographs of the corresponding polythioethers obtained.

Figure 5. Photographs of the produced polymers derived from METSO with: a) HDDA and b) TAC



#### 4 CONCLUSIONS

In this study it was synthesized a novel type of thiolated methyl fatty esters derived from soybean oil. The vegetable oil was subjected to a thiol-ene coupling with the thioacetic acid, producing the soybean oil functionalized with thioester groups that were subsequently hydrolyzed with a basic catalyst to produce the thiolated methyl fatty esters. These compounds were photopolymerized with HDDA and TAC. The obtained polythioethers derived from the latter were more rigid due to the aromatic nucleus of the triazine.

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