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Preparation of a crosslinked sucrose polymer by thiol–ene photopolymerization using dithiothreitol as comonomer

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ABSTRACT

The thiol–ene photopolymerization technique was used to prepare a crosslinked sucrose polymer. Sucrose was chemically modified to introduce two allyl groups, however, in the synthesis were also produced mono and triallyl derivatives. After purification by column chromatography, a fraction (F2A2S) with 94% diallyl sucrose (A2S), 4% of triallyl sucrose (A3S) and 2% of monoallyl sucrose (A1S) was obtained. This fraction was subsequently photopolymerized with dithiothreitol (DTT) which is a difunctional thiol. The presence of small concentration of A3S in F2A2S helped to crosslink *in situ* the obtained polythioether. Photopolymerization kinetics were determined using the Real-Time Infrared technique. It was found that photopolymerization can proceed in the absence of photoinitiators but the rate of photopolymerization and conversion increased considerably when different photoinitiators at 1 mol% were used and when the intensity of UV light was increased. The analysis by DMA of probes of the obtained sucrose polythioether revealed that the difunctionality of both comonomers, A2S and DTT, resulted in flexible materials with a T_g of 30 °C and high storage modulus values. The sucrose polythioether was completely degraded in 2 h in strongly acidic medium. Additionally, the ability of water to absorb the prepared material was tested. We found that it was pH dependent with the maximum absorption at pH = 14. The biopolymer displayed high thermal stability up to 230 °C.

1. Introduction

In recent years sucrose has been considered to be a feasible starting material for preparing biopolymers because of its low cost and wide availability. It has been used as monomer after chemical (Barros & Sineriz, 2002; Crucho, Petrova, Pinto, & Barros, 2008; Sachinvala, Niemczura, & Litt, 1991) or enzymatic modification (Patil, Li, Retwitsch, & Dordick, 1997) to prepare polymers, and also as comonomer to modify the properties of polyurethanes (Brown-Gomez, Alba-Gutierrez, Gregori-Valdez, Reyna-Hernandez, & Vazquez-Torres, 2007; Brown-Gomez, Vazquez, et al., 2007; Hernandez et al., 2005) and polyesters (Park, Chang, & Dordick, 2001). The resulting polymers may be used in biomedical applications because they are generally nontoxic, biodegradable and highly absorbent materials (Patil, Dordick, & Rethwisch, 1996; Dordick, Martin, & Linhardt, 1994); Poschalko et al., 2003; Strumia, Zamora, & Bertorello, 1991). These biopolymers can also be used as plant growth regulators (He, Yao, & Wei, 2005), as additives for water treatment (Patil, Rethwisch, & Dordick, 1991), as surfactants (Sanders, 1969), in drug delivery (Shantha & Harding, 2002) and as sequestering agents in textile bleaching (Lund, 1999).

Thiol–ene photopolymerizations have become a valuable synthetic tool in the preparation of biopolymers. The orthogonality and high efficiency of these reactions have prompted many research groups to utilize this technique to produce well defined polymers. Moreover, thiol–ene systems display other advantages. They require mild polymerization conditions, lack oxygen inhibition, do not need toxic transition-metals as catalyst, and have the ability to polymerize with small amounts of photoinitiators or even in the absence of them. Several applications using this polymerization technique have been reported. These applications include among others, development of protein biochips (Lin, Weinrich, & Waldmann, 2010), cellular microarrays (Gupta et al., 2010), hydrogels (Aimetti, Machen, & Anseth, 2009; Rydholm, Bowman, & Anseth, 2005), injectable intraocular lenses (Niu et al., 2010) and dental restorative materials (Cramer et al., 2010).

Thiol–ene photopolymerizations require that both comonomers, thiols and alkenes, must be bifunctional or multifunctional. Scheme 1 shows the radical step-growth mechanism for photoinitiated thiol–ene polymerization (Jacobine, 1993). The primary radicals produced in the photolysis of the photoinitiator can abstract the hydrogen atom of the thiol group, producing a

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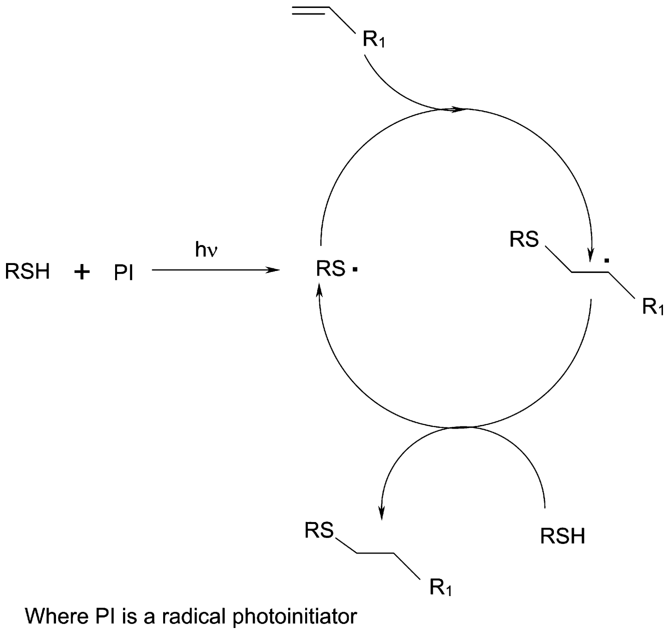


Scheme 1. Mechanism of thiol–ene photopolymerizations.

thiyl radical. This thiyl radical would then react with the double bond of the unsaturated monomer to generate a secondary free radical, which in turn can abstract the hydrogen atom of a second molecule of the thiol, generating a new thiyl radical to repeat the cycle. Termination occurs by the reaction of two radical species.

The aim of this work was to prepare degradable biocompatible materials based on renewable source materials using the thiol–ene photopolymerization technique. By reacting a difunctional thiol with diallyl sucrose in the presence of small concentrations of triallylsucrose as crosslinking agent, it was possible to obtain a more flexible crosslinked polymer. The kinetics of photopolymerization as well as the viscoelastic properties and water absorbency properties of the polymer are discussed.

2. Experimental

2.1. Materials and equipment

Sucrose, allyl bromide, sodium hydroxide, tetrabutyl ammonium bromide, 1,4-dimercapto-2,3-butanediol, also known as dithiothreitol (DTT), 2,2-dimethoxy-2-phenylacetophenone (DMPA) and benzophenone (BP), were all reagent grade and purchased from Aldrich Co (Toluca, Mexico). 2-Hydroxy-1-[4-(2-hydroxyethoxy) phenyl]-2-methyl-1-propanone (Irgacure 2959) was kindly donated by CIBA Geigy Mexico. Routine infrared spectra and photopolymerization kinetics were performed on a Magna Nicolet 550 Infrared spectrometer (Middleton, WI). NMR spectra were obtained using a 300 MHz Jeol NMR spectrometer.

2.2. Synthesis of diallylsucrose A2S

The synthesis of A2S was carried out according to a previously reported method (Acosta Ortiz, Garcia Valdez, Martinez Aguilar, & Berlanga Duarte, 2009). Typically, 20 mL of water and 5 g (0.0146 mol) of reagent grade sucrose were placed in a 100 mL three-necked round-bottom flask fitted with a condenser, thermometer and magnetic stirrer. Then, 1.75 g (0.4382 mol) of powdered sodium hydroxide and 2.52 mL (2.92×10^{-2} mol) of allyl bromide were added. The reaction mixture was stirred for 15 min, and then 0.047 mg (1.4×10^{-4} mol) of tetrabutylammonium bromide was added as a phase transfer catalyst. Then, the mixture was heated to 70 °C and stirred for 24 h. After this time, the reaction mixture was extracted with four 30 mL portions of chloroform. The organic phase was dried with anhydrous sodium sulfate and then rotoevaporated to eliminate the solvent. The residue was purified by column chromatography using silica gel and hexane:ethyl acetate (7:3) as the eluent. Slight differences in polarity between the diallyl sucrose (A2S), the monoallyl sucrose (A1S) and triallyl sucrose (A3S), made difficult the complete separation of the three derivatives. The analysis by HPLC revealed that the fraction that we used in this study contained 94% of A2S, 4% of A3S and 2% A1S. This fraction will be defined as F2A2S in the rest of the paper. The overall yield of F2A2S was 50%.

2.3. Determination of kinetics of thiol–ene photopolymerizations by RT-FT-IR

A Nicolet Magna 550 FT-IR spectrometer equipped with a DTGS detector and fitted with a UVEXS model SCU 110 mercury lamp was used to monitor the kinetics of the photocurable system, A2S/DTT, during photopolymerization. The UV lamp produces peaks at 365 and 440 nm. The intensity of the UV irradiation was measured with a UV Process Supply Inc. Control cure radiometer. All kinetics experiments were conducted at 25 °C with various light intensities. The course of the photopolymerization was followed by simultaneous monitoring decreases in the peaks of the corresponding functional groups. For instance, the thiol was monitored following the infrared absorption band at 2567 cm^{-1}, which is due to its S–H group. Allyl group conversion was monitored using the carbon–carbon double bond absorption peak at 1646 cm^{-1}. Each kinetic run was carried out a minimum of five times. Data were collected at a rate of one spectrum per second and processed with the OMNIC Series software. Conversions were calculated using the ratios of the peak areas before and after photopolymerization.

2.4. Study by DMA

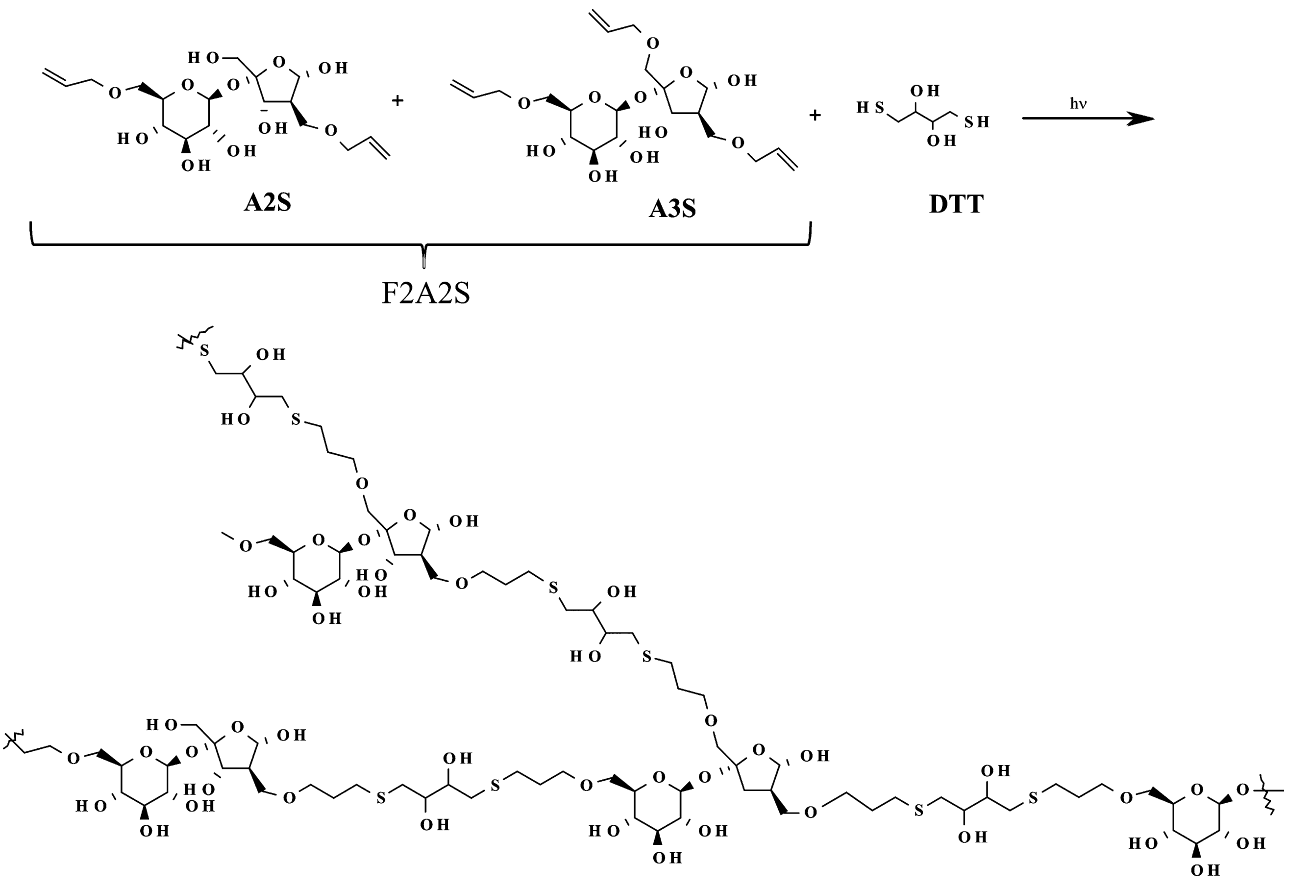
The DMA technique provides useful and accessible information. It enables us to determine the modulus of the material at any temperature and identifies the glass transition region. The DMA provides a picture of those temperature regions where material properties are very stable and rapid changes may occur that could render the product useless. In this study, the viscoelastic properties were determined with a Dynamic Mechanical Analyzer (DMA Rheometrics Scientific) with a frequency of 1 Hz and a heating rate of 5 °C/min over a range of −100 to 100 °C in nitrogen. The probe geometry was 10 mm × 40 mm with a thickness of 2 mm. The probes were produced by irradiating the formulation with both comonomers and the photoinitiator for 15 min in a UV chamber with a 300 W Fusion lamp. The formulation was contained in an aluminum mold.

2.5. Analysis of polymers by TGA

Thermal stability of the sucrose polymers was measured on a thermogravimetric analyzer TGA U 500 (TA Instruments, Inc) with a heating rate of 10 °C/min in air. The average weight of the test samples was 3–5 mg.

2.6. Swelling capacity

The swelling capacity of the sucrose polythioether was determined either in double distilled water at pH = 7, or in basic aqueous solutions of sodium hydroxide with pHs of 8, 10, 12 and 14. All the experiments were performed in triplicates. The polymer was dried in a vacuum oven for about 48 h before being submerged



Scheme 2. Photopolymerization of F2A2S and DTT.

in water and allowed to swell for about 48 h at room temperature. The swollen hydrogels were then removed from the medium and excess liquid was wiped off the surface using filter paper. The swollen hydrogel was weighed carefully. The equilibrium water content was determined from the following equation:

$$\%\,\text{swelling} = \left(\frac{W_t - W_0}{W_0}\right) \times 100$$

where W_0 is the weight of the dried polymer and W_t is the weight of the swollen polymer.

2.7. Degradation of the polymer in acid media

The rate of degradation of the sucrose polythioether in acid was determined by placing it in 10, 1 and 0.1 N HCl aqueous solutions. The time it took the solid sample to completely dissolve was measured.

3. Results and discussion

In a previous work (Acosta Ortiz et al., 2009), we reported the preparation of sucrose polythioethers using the monomer A2S and pentaerythritol tetrakis mercapto propionate (PETKMP). It was found that these two comonomers photopolymerized rapidly when irradiated in the presence of the photoinitiator DMPA. However, the polymers obtained were highly crosslinked because of the tetrafunctionality of the thiol. In this work, we decided to change the PETKMP, replacing it with difunctional DTT. This monomer is quite attractive to use, because it is a small molecule with two hydroxyl groups that in conjunction with the free hydroxyl groups of the sucrose, could render a water absorbing polymer. Although a linear polymer should be produced as both monomers are difunctional (A2S and DTT), the presence of a small concentration of A3S in F2A2S yielded a crosslinked sucrose polymer.

3.1. Synthesis of A2S and A3S

A2S was obtained at 50% yield, by reacting sucrose with allyl bromide in the presence of sodium hydroxide, using water as the solvent. A phase transfer catalyst, tetrabutyl ammonium bromide was added to the reaction mixture to improve the yield. In the synthesis, mono and triallylated by-products were also produced and separated by column chromatography. As it was mentioned in Section 2, a fraction of F2A2S with 94% of A2S, 4% of A3S and 2% A1S was obtained. We decided to use this fraction in our experiments as our main objective was to obtain a polymer with lower crosslink density. By using this fraction, a linear polymer should be obtained when copolymerizing A2S with DTT, as both comonomers are difunctional, but the presence of small amounts of A3S would help to crosslink the polythioether (see Scheme 2). It is well known that only small concentrations of crosslinking agents are needed to crosslink linear polymers (Patil et al., 1997). Thus, it was a happy state of affairs to use the mixed fraction, as the contaminant A3S could act as crosslinking agent and A1S would not affect the properties of the polymer. Fig. 1 shows the ^{1}H NMR spectrum of F2A2S that correspond mainly to A2S. The vinyl signals of the allyl groups are located at 5.2 and 5.9 ppm while the protons of hydroxyl groups, the methylenes of allyl groups and the hydrogen of the carbons adjacent to hydroxyl groups, are all overlapped in the range of 3.2–4.5 ppm. The proton of the anomeric carbon in sucrose is at 5.4 ppm.

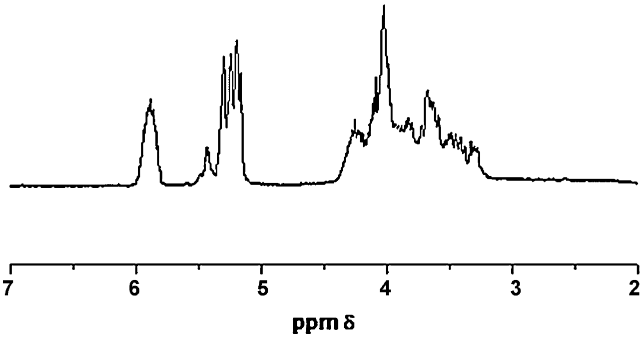


Fig. 1. ^{1}H NMR spectrum of F2A2S run in CDCl$_3$.

3.2. Photopolymerization studies

First, the ability of the photocurable formulation to polymerize in the absence of photoinitiators was tested. Fig. 2 shows the conversion versus times curves, where the reactivity of the system F2A2S/DTT in the presence and absence of a photoinitiator, under UV irradiation conditions is compared. It is clear that when F2A2S and DTT were irradiated with unfiltered 4.5 mW/cm^2 UV light, without a photoinitiator, the polymerization started as soon as the UV lamp was turned on. After 300 s there was a 33% conversion, as measured by the decrease in the absorbance of the DTT peak. It has been previously reported that thiol–ene photopolymerizations can proceed in the absence of photoinitiators (Cramer, Scott, & Bowman, 2002; Hoyle et al., 1984). The mechanism by which initiation occurs, has not been clearly elucidated. Charge-transfer complexes between the thiol and the ene (D'Souza, Nanjundiah, Baeza, & Szmant, 1987), the formation of thiyl radicals after absorption with 254 nm (Carlson & Knight, 1973) or the presence of disulfide impurities (Sayamol & Knight, 1968) has been proposed as the possible causes of the initiatorless thiol–ene photopolymerizations. In more recent studies realized by Cramer, Reddy, Cole, Hoyle, and Bowman (2004), it was found that the thiol–ene photopolymerization rate without photoinitiators, was highly dependent on the wavelength of the irradiating light, proceeding more readily when irradiated with light centered around 254 nm as compared to 365 nm light. The UV light of lower wavelengths is more easily absorbed by the photocurable system generating more free radicals. As a consequence, the photopolymerization rate using 254 nm UV light was four times faster than when 365 nm light was used. In our case, it was expected low photopolymerization rates because our UV lamp produces peaks at 365 and 440 nm.

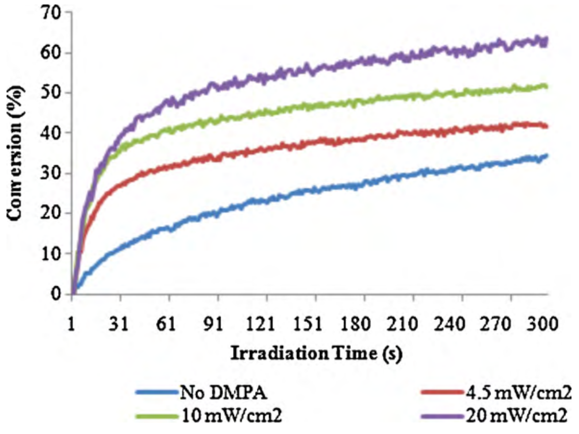


Fig. 2. Effect of the intensity of UV light and of the presence and absence of DMPA as photoinitiator. DMPA was used at 1 mol%. The peak analyzed was that of the thiol.

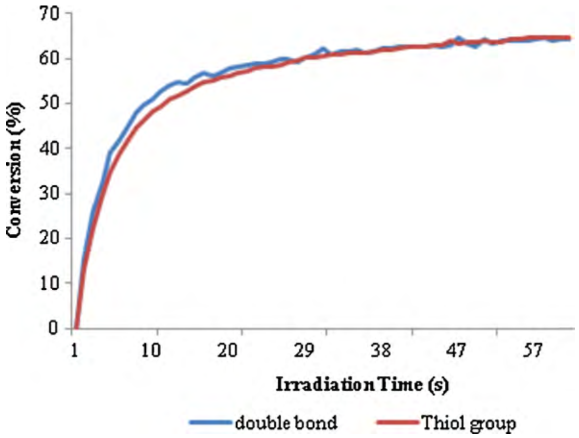


Fig. 3. Comparison of the reactivity of functional groups in the photopolymerization of F2A2S with DTT (1:1 molar mixture) using DMPA as photoinitiator at 1 mol% and irradiated with a UV light intensity of 10 mW/cm^2.

In the same figure are presented the conversion curves of the samples that were irradiated with different UV light intensities, but in the presence of DMPA at 1 mol% concentration. It was found that when the sample was irradiated with the same low intensity UV light (4.5 mW/cm^2), the photopolymerization rate was 6.6 times faster that when compared with the sample without a photoinitiator, reaching around 42% conversion after 300 s. When the UV light intensity was increased to 10 mW/cm^2, the slope of the curve was slightly higher than that of the intensity of 5 mW/cm^2 but final conversion reached 52% in the same time. Further increase in the intensity resulted in higher conversion (62%) although the photopolymerization rate remained the same as in the case of 10 mW/cm^2. The higher intensity of UV light induces a rapid increase in temperature as a result of the exothermic nature of the photopolymerizations, helping to drive the polymerizations to higher conversions. It can be concluded from these results that this photocurable system was rather reactive as only low intensity UV light is required to achieve moderate conversions, which can be improved by increasing the intensity of the UV light.

The nature of step-growth implies that both the thiols and double bonds must be consumed at the same rate if they react in stoichiometric ratios. This was confirmed when the decrease in the absorbance of both thiol and double bond functional groups were measured in the same run. Fig. 3 shows the conversion versus time curves for the DTT thiol group and the double bonds of F2A2S. Nearly identical curves were obtained because the comonomers are in a 1:1 molar relationship. Allylic double bonds are not very prone to homopolymerize. Therefore, they react almost solely with the thiol. This behavior has also been reported by other researchers for thiol–ene urethane (Senyurt, Hoyle, Wei, Piland, & Gould, 2007; Senyurt, Wei, et al., 2007) and for thiol–ene-acrylate systems (Cramer & Bowman, 2001).

Thereafter, the effect of the type of photoinitiator on the reactivity of the photocurable system F2A2S/DTT was studied. Fig. 4 depicts the results using both cleavage (Type I) and hydrogen abstraction (Type II) photoinitiators. As expected, the Type I photoinitiators, DMPA and Irgacure 2959, induced a faster polymerization with higher conversions than the Type II benzophenone initiator. It is well known that Type I photoinitiators are more efficient than Type II (Dietliker, 1991). The former undergo a rapid cleavage of their α-bond to carbonyl, forming two radicals. Either or both can abstract the hydrogen atom of the thiol (see Scheme 3a). Although Irgacure 2959 is slightly less reactive than DMPA is less cytotoxic than DMPA. Thus, for applications where is important to avoid DMPA, Irgacure 2959 could become a good choice as pho-

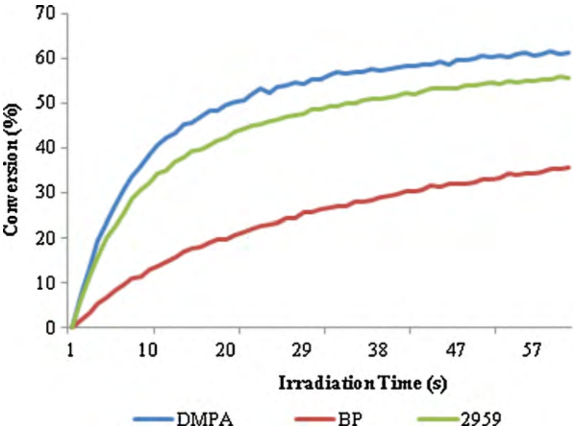


Fig. 4. Effect of the type of photoinitiator on the thiol–ene photopolymerization of F2A2S with DTT when used at 1 mol% concentration and irradiated with UV light intensity of 10 mW/cm^2.

toinitiator, because its activity is similar to that of DMPA, in this specific system.

BP is unable to undergo unimolecular cleavage and therefore upon the absorption of UV light, the carbonyl group goes to a triplet excited state forming a diradical species that can abstract the hydrogen atom from the thiol, forming concomitantly a ketyl radical and a thiyl radical, accelerating in this way the thiol–ene photopolymerization (Scheme 3b). Although BP has been used extensively as photoinitiator in thiol–ene photopolymerization, its activity is diffusion dependent. In our case, the decreased activity of BP was attributed to the high viscosity of our photocurable system.

3.3. DMA analysis

The viscoelastic properties of sucrose polythioether were determined by means of Dynamical Mechanical Analysis (DMA). The analysis was performed on the probes obtained by photopolymerizing the curable formulation F2A2S/DTT. After UV irradiation, flexible probes were produced. This flexibility could be attributed on the one hand to the reduced degree of crosslinking caused by using difunctional comonomers which result in the formation of linear polymeric chains that are *in situ* crosslinked by the action of A3S as crosslinking agent, and on the other hand, to the mobility induced by the thioether linkage. Fig. 5 shows both the storage modulus and tan δ versus temperature curves. The prepared polythioether displays a very high elastic modulus of 4900 MPa, with a markedly decreasing slope in the range of −100 to −10 °C. These high values may be attributed to hydrogen bonding induced by the presence of multiple hydroxyl groups. The rubbery region interval was found to be quite narrow. Additionally, it can be observed that the peak of the tan δ curve is quite symmetric which indicates high uniformity in the crosslink density. It peaks at 30 °C, which can be considered the T_g of the polymer. In our previous study (Acosta Ortiz et al., 2009) the reported value of T_g when the tetrafunctional PETKMP was photopolymerized with A2S was 58 °C. Thus, the lower network crosslink density derived from the use of a difunctional thiol instead of a tetrafunctional one, resulted in a more flexible material with a decrease in T_g of 28 °C.

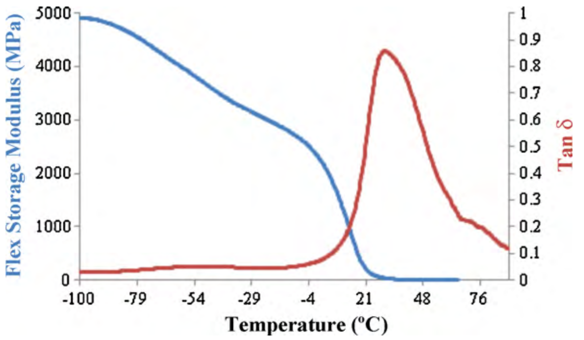
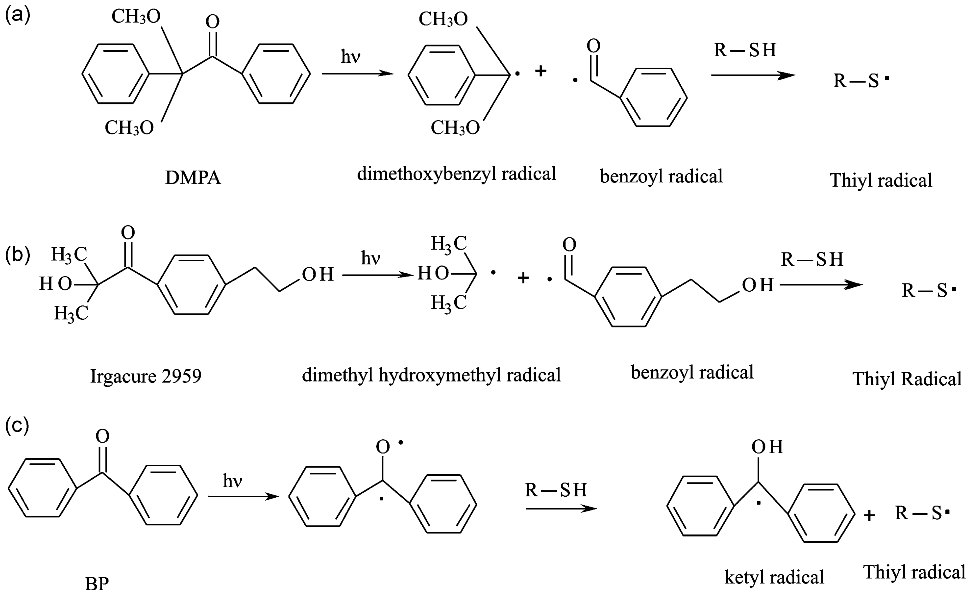


Fig. 5. Results of DMA analysis of the probe obtained by photopolymerizing stoichiometric amounts of F2A2S and DTT, with a 300 W Fusion lamp for 15 min using 1 mol% of DMPA.

3.4. TGA analysis

The thermal stability of the obtained sucrose polythioether was measured by TGA. Fig. 6 presents the results of this analysis. It was observed that 4% of the humidity was released in the range of 100–130 °C. The presence of multiple hydroxyl groups resulted in absorption of a small percentage of water. Increased heating of the sample resulted in a two step thermal degradation. The



Scheme 3. Mode of action of photoinitiators uses in this study.

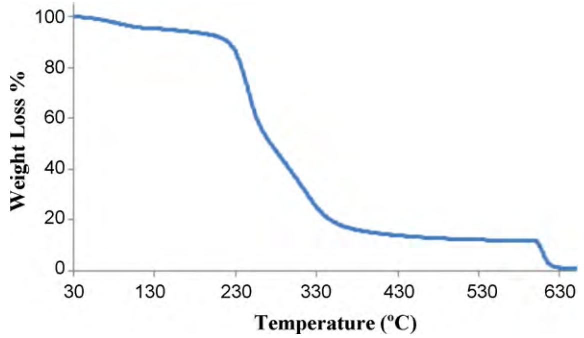


Fig. 6. Thermogram of the polythioether obtained from the photopolymerization of F2A2S and DTT in 1:1 molar mixture.

Table 1
Water absorption at different pHs.

pH	Percentage of absorbed water
7	33
8	40
10	25
12	32
14	88

first step started around 220 °C and continued until 350 °C with a weight loss of 82%. Then, the second step was observed as a plateau that extended until 600 °C and expelled 18–10% of the original mass. This residue may be from the formation of complex carbonaceous materials derived from the thermal degradation of the crosslinked polythioethers. Similar thermal behavior was reported by us for other sucrose polythioethers (Garcia Valdez et al., in press). Other groups presented the degradation of different polythioethers (Podkoscielny & Tarasiuk, 1996; Sundarrajan, Surianarayanan, Sabdham, & Srinivasan, 2004). Finally, at 600 °C, a stream of oxygen was introduced into the system that burned off the residue.

3.5. *Water absorbency of the sucrose polythioether*

The probes obtained were subjected to a water absorption test. The samples were immersed in deionized water for 48 h. Surprisingly, despite the presence of numerous hydroxyl groups in the polymeric chains, the samples only absorbed relatively small amounts of water. The degree of absorption varied with the pH of the aqueous solution (see Table 1). In the range of pH 7–12, the absorption varied from 25 to 40%, but when the pH of the water increased to 14, the absorption increased considerably, reaching 88%. Here, the ionization of the hydroxyl groups by effect of the strongly basic medium causes that formed alkoxy groups repel each other resulting in the swelling of the polymer.

3.6. *Hydrolysis of the sucrose polythioether*

It was observed that the sample degraded in acid media. For this reason, a study was carried out to determine the behavior of the sucrose polythioether in acid aqueous solutions.

The sample was placed in a 10 N HCl solution. It was observed that the solid polymer completely dissolved in 120 min. When the concentration of the acid was decreased to 1 and 0.1 N, the sample did not completely degrade. In the case of the sample immersed in 0.1 N HCl, there was a loss of 5% weight in 7 days, while in the case of the 1 N HCl solution, the loss in weight was 11% in the same time. Given that the polythioethers are very stable in acid media, the weakest point, which could be attacked by the acid is the glycosidic bond between the glucose and fructose, which results in breakage of the polymeric chain.

4. Conclusions

An easy method of preparing a sucrose polythioether was implemented. This method involves the use of fraction F2A2S containing 94% of A2S and 4% of A3S, and photopolymerizing it with DTT, a difunctional thiol. The presence of A3S crosslink the linear polymer derived from A2S and DTT. Kinetics of photopolymerization demonstrated that the thiol–ene photopolymerization of F2A2S and DTT proceeded very rapidly and with relatively high conversion. The obtained polymer displayed a high elastic modulus and a T_g of 30 °C. The presence of hydroxyl groups in the polymeric chain induced moderate water absorption ability, which was pH dependent. The sucrose polythioether rapidly degraded in a strong acid medium. This polymer has potential application in controlled drug delivery systems due to its properties of degradation in acid media and absorption of water.

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