



An effective method to prepare sucrose polymers by Thiol-Ene photopolymerization

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ABSTRACT

A facile method to obtain novel sucrose polymers is reported. These polymers were obtained by means of the Thiol-Ene photopolymerization technique. The sucrose was functionalized with allyl groups by etherification with allyl bromide and then photopolymerized by the step-growth mechanism with multifunctional thiols. The kinetics of photopolymerization were determined by optical pyrometry and Real-Time FT-IR. It was found that this photocurable system was highly reactive obtaining solid crosslinked polymers that displayed high uniformity in the crosslink density. A T_g of 58 °C was determined by means of DMA for the polymer derived from A2S and PETKMP. The prepared polymers displayed thermal stability up to 230 °C.

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1. Introduction

Thiol-Ene photopolymerizations have gained considerable importance in the technological and scientific ambits of radiation curing because of the inherent advantages of these systems. For instance, these reactions proceed with high regioselectivity under mild conditions, even in the presence of oxygen, reaching high conversions (Killops, Campos, & Hawker, 2008; Service, 2008). These characteristics make them very attractive for certain applications where other systems like radical or cationic photopolymerizations are less suitable. One of the areas where this kind of polymerization may have impact is in the development of biomaterials. Nowadays, the research for novel biocompatible materials for medical applications has acquired increasing importance (Opsteen, Ayres, & Van Hest, 2008). There are reports where the Thiol-Ene photopolymerizations have been used to prepare materials with potential applications as restorative dental resins (Carioscia, 2005; Lu, Carioscia, Stansbury, and Bowman, 2005) and scaffolds for biomaterials (Rydholm, Reddy, Bowman, & Anseth, 2004). The polymers intended to be applied in these applications need to fulfill certain characteristics such as non-toxicity, cell-adhesiveness and controlled biodegradability (Baroli, 2006).

Thiol-Ene photopolymerizations require that the monomers involved must have two or more functional groups. In (Scheme 1), the radical-step-growth mechanism for the photoinitiated Thiol-Ene polymerization is shown (Cramer & Bowman, 2001; Jacobine, 1993). The primary radicals produced in the photolysis of the photoinitiator can abstract the hydrogen atom of the thiol group, producing a thiyl radical (Eq. (1)). This thiyl radical would

then react with the double bond of the unsaturated monomer to generate a secondary free radical (Eq. (2)), which in turn can abstract the hydrogen atom of a second molecule of the thiol, generating a new thiyl radical to repeat the cycle (Eq. (3)). Termination occurs by the reaction of two radical species (Eqs. (4)–(6)).

On the other hand, polymers derived from sucrose and other carbohydrates have attracted increasing attention due to the multiple applications where they are involved (Gruber & Knaus, 2000; Spain, Gibson, & Cameron, 2007). Among others the following applications can be mentioned: preparation of stationary phases for chromatography (Liu & Dordick, 1999), biocatalytic (Novick & Dordick, 1998) and biosensible hydrogels (Miyata, Uragami, & Nakamae, 2002) and controlled release of drugs (Yun, Goetz, Yellen, & Chen, 2004).

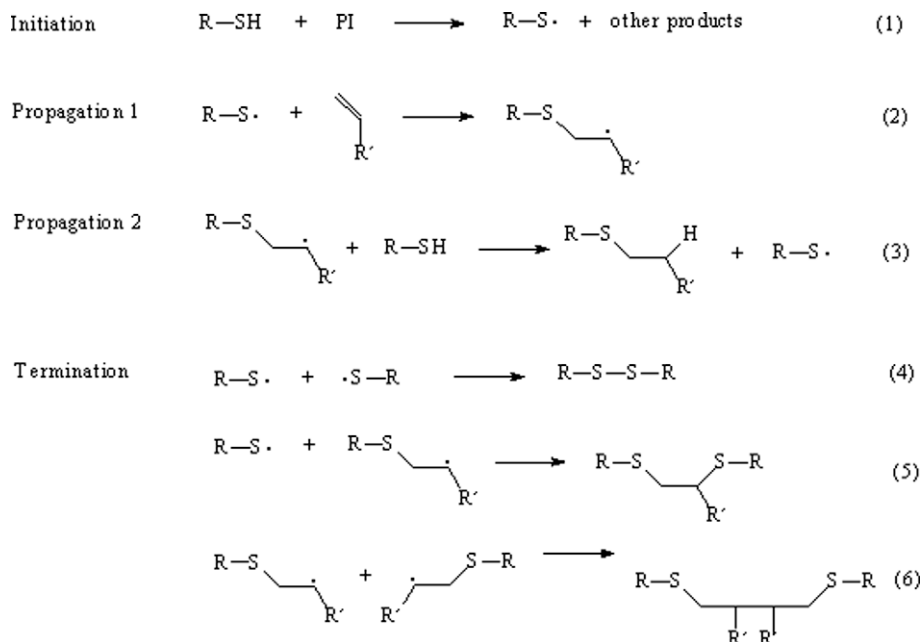
The preparation of sucrose polymers via Thiol-Ene photopolymerization is of interest to our research group in using this technique to prepare different biocompatible materials. This paper deals with the preparation of the diallyl sucrose monomer and its photopolymerization with multifunctional thiols. The kinetics as well as the mechanical and thermal properties of the obtained polymers were determined.

2. Experimental

2.1. Materials and equipment

Sucrose, allyl bromide, sodium hydroxide, tetrabutyl ammonium perchlorate, pentaerythritol tetrakis (3-mercaptopropionate) [PETKMP], trimethylol propane tris (3-mercaptopropionate) [TMPTMP], 2,2-dimethoxy-2-phenylacetophenone (DMPA), benzophenone (BP), were all reagent grade and purchased from Aldrich Co (Milwaukee). Routine infrared spectra and photopolymerization

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Scheme 1. Step-growth mechanism of Thiol-Ene photopolymerizations.

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 diallyl sucrose monomer (A2S)

In a three necked 500 mL round bottom flask provided with a thermometer, a condenser and a magnetic stirrer, were placed 80 g (0.233 mol) of sucrose, followed by the addition of 250 mL of water. Then were added 28.04 g (0.701 mol) of sodium hydroxide and 0.8 g of tetrabutyl ammonium perchlorate. Thereafter, 40.5 mL (0.467 mol) of the allyl bromide were added dropwise to the reaction mixture by means of an addition funnel. The reaction mixture was heated at 70 °C and left at this temperature for 24 h. After this time, the reaction mixture was allowed to cool to room temperature and subsequently extracted with chloroform (4 × 100 mL). Then the organic phase was washed with water to remove the phase transfer catalyst. The chloroform extracts were combined together and dried with sodium sulphate anhydrous. The solvent was rotoevaporated and the residue was purified by column chromatography using a gradient of hexane:ethyl acetate as eluent. A viscous liquid was obtained at 61% yield.

FT-IR (film, cm^{-1}): 3413 (ν O—H), 2923 (ν C—H), 1647 (ν C=C), 1422 (ν C—C) 1077 (ν C—O—C), 925 (ν CH=CH).

RMN ^1H (300 MHz, CDCl_3 , δ ppm): 3.3–3.7 (m, 13H, C—H cycle, O—H), 3.8–4.3 (m, 10H, CH_2 —O), 5.1 (m, 5H, CH=CH $_2$), 5.8 (m, 2H, CH=CH $_2$).

2.3. Determination of kinetics of Thiol-Ene photopolymerizations

2.3.1. By optical pyrometry (OP)

Falk, Vallinas, and Crivello (2003) designed a rather simple and reliable method to monitor the course of the photopolymerizations by measuring the increase in temperature as a result of the heat released during the highly exothermic photopolymerizations. The configuration of the system used in this study and the preparation of the samples are described therein. The photopolymerization studies were conducted at ambient temperatures. An unmodified Omega OS552-V1-6 Industrial Infrared Thermometer (Omega Engineering, Inc. Stamford, CT) equipped with a laser-sighting

device was used in the studies of optical pyrometry. This instrument has a sensitivity of 1 °C with an operating temperature range of −18 to 538 °C. In all cases the samples were allowed to equilibrate and establish a flat baseline for 20 s before the start of the UV irradiation. Temperature data were collected at a rate of one measurement per second and directly recorded to a computer.

2.3.2. By Real-Time FT-IR (RT-FTIR)

RT-FTIR was also used to monitor the kinetics of photopolymerization of the synthesized monomers with a Nicolet Magna 550 FT-IR spectrometer equipped with a DTGS detector fitted with a UVEXS model SCU 110 mercury lamp. 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 RT-FTIR experimental setup was described in detail elsewhere (Crivello & Ortiz, 2002). The course of the photopolymerization was followed by simultaneously monitoring the decrease of the peaks of the corresponding functional groups. For instance, the thiol was monitored following the infrared absorption band at 2567 cm^{-1} due to its S—H group. Allyl group conversion was monitored using the carbon–carbon double bond absorption peak at 1647 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 ratio of peak areas to the peak area prior to photopolymerization. The kinetic parameter R_p/M_0 for selected kinetics runs was determined from the initial slopes of the irradiation time-conversion curves according to this equation:

$$R_p/M_0 = ([\text{conversion}]t_2 - [\text{conversion}]t_1)/(t_2 - t_1) \quad (7)$$

where R_p and M_0 are, respectively, the rate of photopolymerization and the initial monomer concentration as well as the conversions are as determined from the curves at irradiation times t_1 and t_2 .

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 of interest and identifies the glass transition region. DMA provides a picture of those temperature regions where materials properties are very stable with temperature and those regions where rapid changes may occur that could render the product useless. In this study the viscoelastic properties were determined on 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 –70 to 100 °C in nitrogen. The probe geometry was 10 × 40 mm with a thickness of 2 mm

2.5. Study by TGA

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

3. Results and discussion

3.1. Synthesis of monomer A2S

Scheme 2 shows the methodology of synthesis of the A2S monomer. The method used was straightforward using water as solvent and a phase transfer catalyst. After purification by column chromatography, the degree of substitution of the sucrose was determined by ¹H NMR considering the integral of the peak at 5.8 ppm that is not overlapped by any other peak and represents one vinylic proton. The integral of this peak is compared against the integral of the peaks in the range 3.3–4.3 ppm that includes all the other protons of the sucrose backbone and the protons of the methylene of the allylic group. The exact position of the allyl groups was not determined as our main interest was to have a bifunctional monomer. Nonetheless, previous studies had determined that the primary hydroxyl groups in the position 6 and 6' reacted preferentially over the secondary groups when sucrose is subjected to chemical reactions (Khan, 1984).

3.2. Determination of the kinetics of Thiol-Ene photopolymerizations

The overall behaviour of the Thiol-Ene photopolymerizations was monitored by optical pyrometry. The formulation with two equivalents of the monomer A2S and one equivalent of PETKMP in the presence of DMPA as the photoinitiator, displayed high reactivity when it was irradiated with UV light. Fig. 1 shows the thermal profiles of the experiments that were run at different light intensities. It can be observed that even at intensity as low as 1 mW cm^{−2} the photopolymerization took place reaching a maximum temperature of 57 °C at about 60 s after the lamp was turned on. When the intensity was set at 15 and 30 mW cm^{−2} there was a remarkable increase in the peak temperature at a relatively shorter time. In the former case the maximum temperature was 67 °C at about 30 s while the latter reached 87 °C at about 20 s. It can also be seen that when the intensity was 30 mW cm^{−2} the increase in

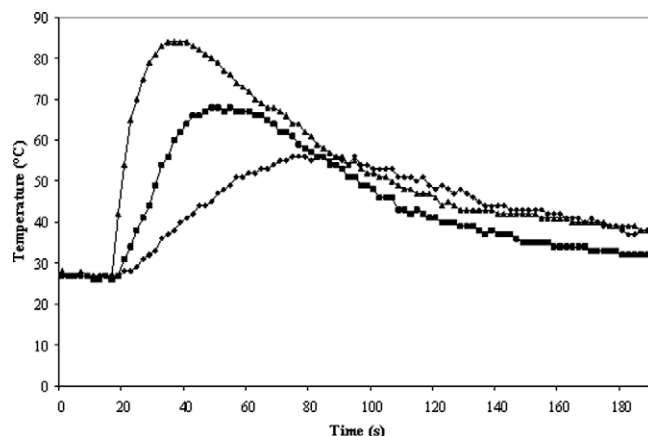


Fig. 1. Effect of light intensity (in mW cm^{−2}) on the thermal profiles of the photopolymerization of A2S with PETKMP (2:1 molar mixture), using 2 mol% of DMPA: 1 (◆), 15 (■), 30 (▲).

the temperature was observed almost immediately after turning on the UV lamp.

Thereafter, an RT-FTIR study was carried out to evaluate the reactivity of the Thiol-Ene system based on A2S and PETKMP using two different photoinitiators (see Fig. 2). When a formulation with a Type I photoinitiator, the DMPA, the sucrose monomer and the thiol was irradiated with UV light of 2 mW cm^{−2} it took about 20 s to get 80% conversion displaying a curve with a slope of 6.80 s^{−1}. This slope represents the parameter $R_p/[M_0]$ described in Eq. (7) and is directly proportional to the speed of the photopolymerization.

On the other hand when the Type II photoinitiator BP was used, the results shows that the photocurable system is considerably less reactive reaching 35% conversion in the same period of time with a slope of only 2.07 s^{−1}. Thus, comparing the values of the two slopes, it can be concluded that the photopolymerization of A2S with PETKMP proceeds 3.25 times faster with DMPA as the photoinitiator than with BP. This significant difference is due to the bimolecular nature of the photoinitiation mechanism. When BP is used, its efficiency is influenced by the viscosity of the medium. This situation was exacerbated due to the fact that the monomer A2S has six hydroxyl groups in its structure, whose hydrogen atoms are labile and can be very easily abstracted by the thiyl radical. Once the thiyl radical abstracts the hydrogen atom of the hydroxyl groups the thiol is regenerated. But the thiol can undergo again the hydrogen

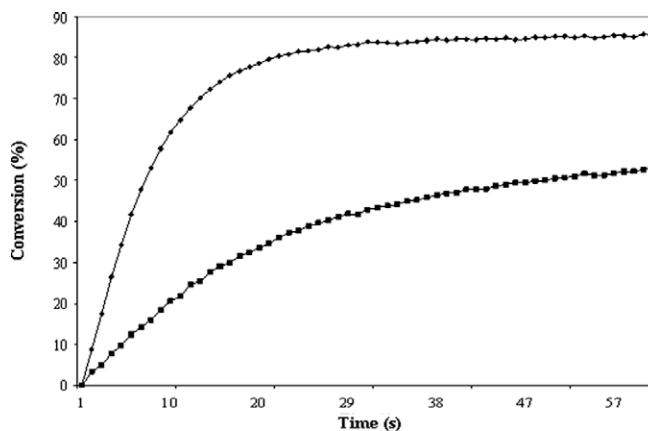
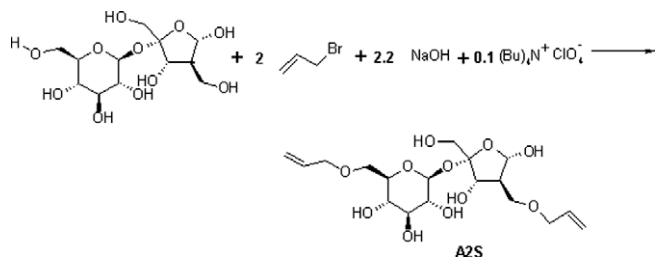


Fig. 2. Effect of the type of photoinitiator in the photopolymerization of A2S with PETKMP at a molar ratio of 2:1, photoinitiator at 2 mol% at 2 mW cm^{−2}: BP (■), DMPA (◆).



Scheme 2. Synthetic methodology to obtain A2S.

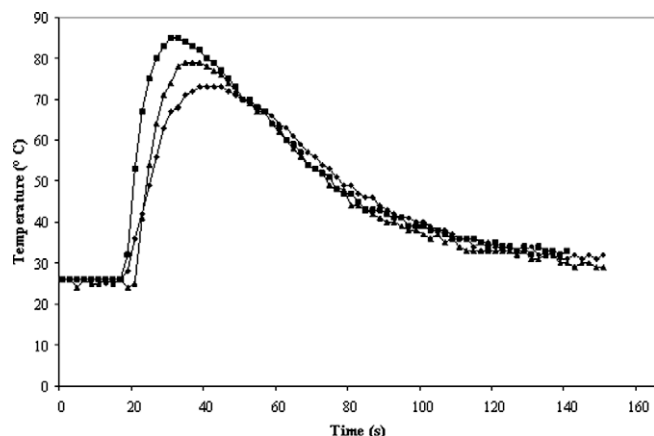


Fig. 3. Effect of the concentration of DMPA on the thermal profiles of the photopolymerization of A2S with PETKMP in a molar mixture of 2:1 using a light intensity of 15 mW cm^{-2} , 1% M (◆), 2% M (▲), 5% M (■).

abstraction in a chain reaction. The overall result is the observed photopolymerization rate. The DMPA can also undergo the same process, however, as the activity of benzophenone is influenced by the viscosity of the medium, the resultant polymerization rate is slower than when DMPA is used as photoinitiator.

Once the more effective photoinitiator was chosen, the effect of its concentration was analyzed by OP. Fig. 3 depicts the thermal profiles of the runs with different concentrations of DMPA showing that when the concentration of the photoinitiator is at 1 mol% the maximum temperature achieved is 72°C . When the concentration was doubled, there is an increase of only 6°C and when the concentration was augmented by 5-fold the maximum temperature is 85°C . Thus, the high reactivity of this Thiol-Ene system is not influenced greatly by the concentration of the photoinitiator.

The individual behavior of each monomer during the photopolymerization was monitored by RT-FTIR. Fig. 4 shows the curves of conversion versus time for the double bond peak of A2S and for the thiol group of PETKMP. It can be observed that practically identical curves are obtained confirming that the photopolymerization was proceeding by the step-growth mechanism. As the allyl monomer has a slight tendency to homopolymerize, it reacts very fast with the thyl radical forming a polysulfide. Here is worth to mention that despite the presence of six hydrogen atoms of the hydroxyl groups of the sucrose backbone that could inhibit the polymerization by inactivating the thyl radicals, the photopolymerization rate was high.

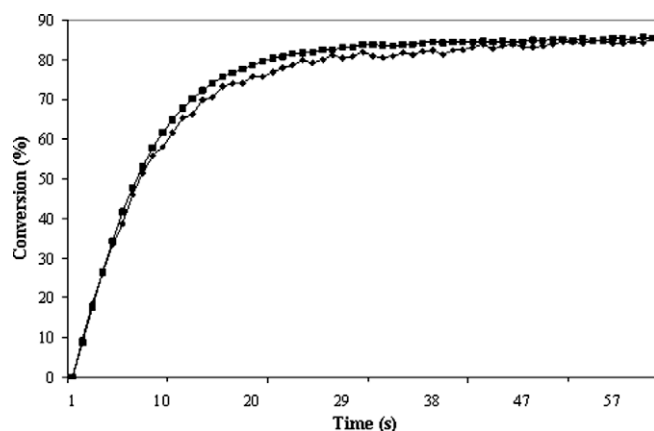


Fig. 4. Comparison of the reactivity of functional groups in the photopolymerization of A2S with PETKMP (2:1 molar mixture) with DMPA as photoinitiator at 2 mol% at 2 mW cm^{-2} : thiol (■), double bond (◆).

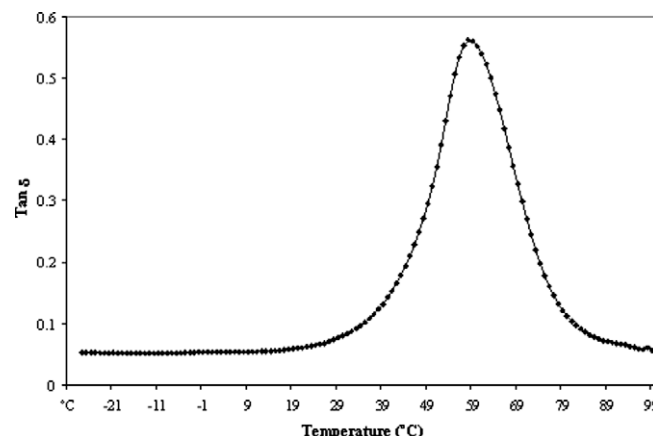


Fig. 5. $\tan \delta$ versus the temperature of a sample made from the photopolymerization of a 1:2 molar mixture of A2S and PETKMP with 2 mol% of DMPA.

3.3. DMA studies of the viscoelastic properties of the prepared polymers

Fig. 5 presents the curve of $\tan \delta$ versus temperature of the polymer derived from A2S and PETKMP. The curve is symmetric which denotes high uniformity of the formed Thiol-Ene network. Again, this is a confirmation that the photopolymerization is proceeding by the step-growth mechanism, because as it was mentioned before, the uniformity of crosslinking is one of the characteristics of this sort of systems. It can also be observed that the $\tan \delta$ peak maximum is at 58°C which can be considered as the T_g of the polymer. The storage modulus of the sucrose polymer was determined in flexural mode (see Fig. 6). It is observed that the initial value of the elastic modulus is 2850 MPa at -30°C and as the temperature is increased, there is a continuous decline in the storage modulus until at 30°C where the slope is more pronounced. This is due to the flexibility of the chains of polysulfides that results in polymers with low T_g 's.

3.4. Thermal stability study by TGA

The thermal stability of the polymers obtained from A2S monomer and two different thiols was analyzed by means of TGA. Fig. 7 presents the results of this analysis. It can be observed that both polymers derived from PETKMP and TMPTMP show fairly the same behavior with the former displaying slightly higher stability. Both polymers are stable up to 230°C . After this temperature, the mass-temperature curve clearly shows a three step mass loss

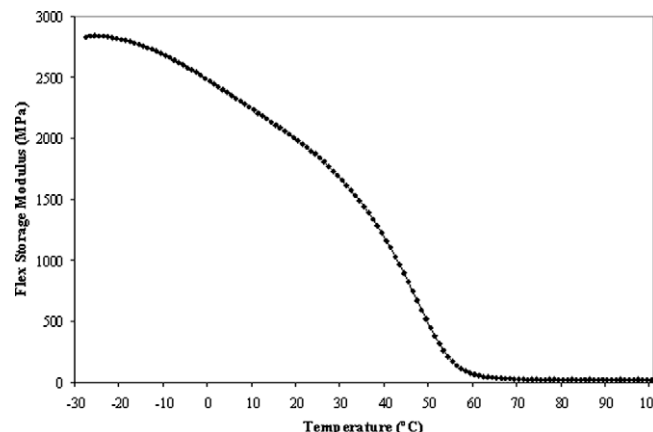


Fig. 6. Storage modulus of the polymer derived from the photopolymerization of A2S with PETKMP.

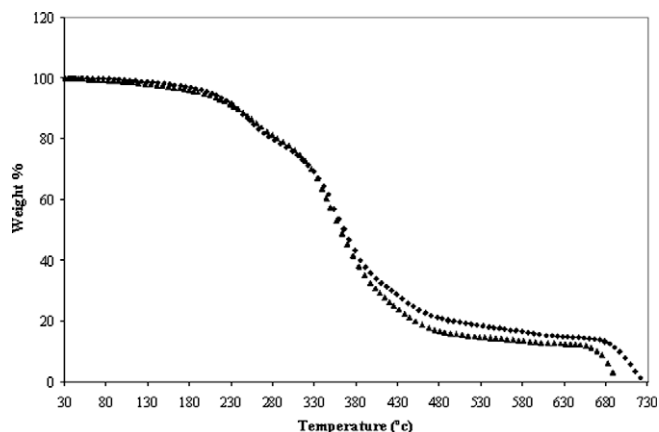


Fig. 7. Thermograms of samples obtained from A2S and PETKMP in a 1:2 molar mixture (♦); and from A2S and TMPTMP in a 1:1.5 molar ratio (▲), using DMPA as photoinitiator at 2 mol% and a light intensity of 15 mW cm^{-2} .

effect, the first starting at 230 °C (22.40 weight loss%), the second at 300 °C (68.50% weight loss%) and the third at 650 °C (8.38 weight loss%).

4. Conclusions

Novel sucrose polymers were prepared using the Thiol-Ene photopolymerization technique. It was demonstrated the high reactivity of the photocurable system that comprises the allyl sucrose monomer A2S with multifunctional thiols such as PETKMP and TMPTMP when they were irradiated with UV light. The obtained polymers displayed high uniformity of crosslinking as well as high thermal stability. These materials may have potential applications as biomaterials. The method described herein can be very useful to prepare biopolymers using biological molecules with thiol groups such as some peptides and aminoacids or by modifying chemically other molecules of interest.

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