



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).

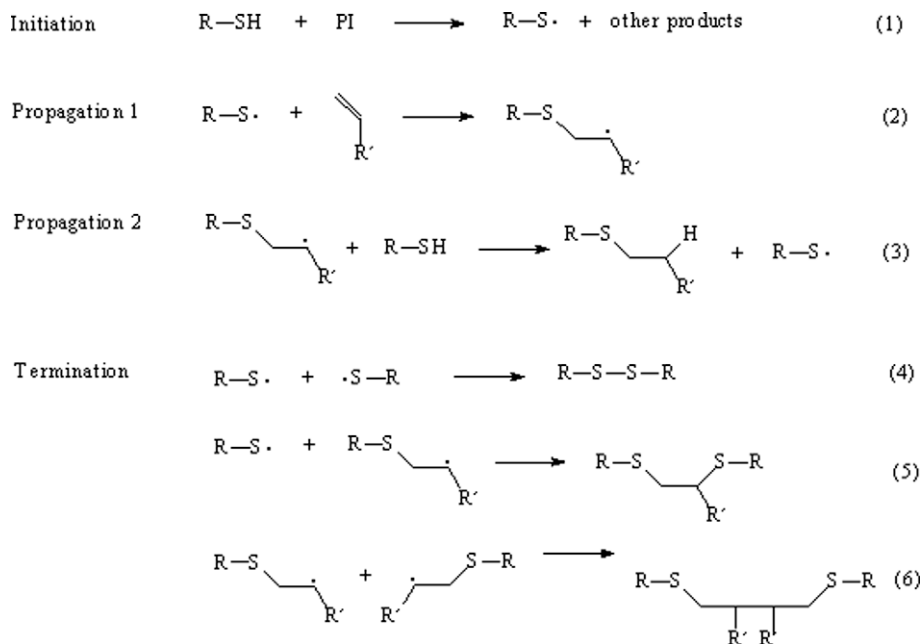
The preparation of sucrose polymers via Thiol-Ene photopolymerization is of interest to our research group in using this technique to prepare different biocompatible materials. This paper deals with the preparation of the diallyl sucrose monomer and its photopolymerization with multifunctional thiols. 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, $\text{CH}=\text{CH}_2$), 5.8 (m, 2H, $\text{CH}=\text{CH}_2$).

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

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