

Photocuring of cinnamic carbohydrate esters: Controlling the reaction by monocinnamoylated derivatives

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Abstract

A monofunctional and a polyfunctional monomer were studied for use as potential co-photopolymers. The monomers were the totally cinnamoylated derivatives of *p*-nitrophenol (PNPCN) and D-manitol (MNTCN), and their structures were characterized by several spectroscopic techniques. The derivatives obtained were cross-linked by irradiation in the ultraviolet region, where the photosensitive monomers showed maximum sensitivity. The thermal properties of these photosensitive monomers and the mixtures prepared with different MNTCN:PNPCN ratios were investigated by differential scanning calorimetry under nitrogen atmosphere, and their photoreactivity was investigated in thin films. Photoreaction products were analyzed by gel permeation chromatography. The effect of PNPCN as a chain blocker in the MNTCN photocrosslinking reaction was evaluated by UV–visible spectroscopy and by ¹H NMR.
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1. Introduction

The crosslinking and subsequent insolubilization of photosensitive polymers is one of the oldest photochemical reactions (Delzenne, 1972; Delzenne, 1974). The first synthetic photopolymer used, which solved the problems associated with natural photopolymers (Delzenne, 1974; Egerton et al., 1981; Minsk, Smith, Van Deusen, & Wright, 1959; Tsuda, 1964), was polyvinyl cinnamate (PVCN) (Minsk et al., 1959), which, in turn, was replaced by a broad class of photopolymers based on cycloadditions (Delzenne, 1972; Williams, Laakso, & Borden, 1971). The polymers (olefins) are insolubilized by cyclodimerization of two cinnamoyl groups (excited chromophores) belonging to two different chains by means of a “four-centre” polymerization step (Wendell, 1983), involving the absorption of light energy (Ranby, 1998). This photoreaction

takes place in crystalline state, providing polyesters that contain units of cyclobutane. The carbonyl group provides the double reactive bond with the necessary polarization and the phenyl group increases the polarisability, thus increasing the chromophore’s power to absorb light (Williams, 1974). The presence of truxylic rather than truxinic acid in the crosslinked PVCN requires stereoregularity between chains (Reiser, 1980). The light-induced photoreaction and molecular reorientation of thin polymer films containing cinnamoyl groups depend on the regioisomerism of the these groups (Chae, Lee, Kim, Lee, & Ree, 2003a; Chae, Lee, Ree, Jung, & Kim, 2003b; Ichimura, Akita, Akiyama, Kudo, & Hayashi, 1997; Lee et al., 2003; Lin, Chu, Huang, & Reiser, 1992). In recent times, the synthesis of monomers and polymers that contain photoreactive groups has received fresh attention because of their potential use in emerging fields of microelectronics, liquid crystal screens, holographic head-up-displays, non-linear-optical materials, integrated circuits, etc. (Balaji, Grande, & Nanjundan, 2004; Chae et al., 2003a, 2003b; Lee et al., 2003). Monomers and polymers with

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α,β -unsaturated carbonyl groups, such as cinnamoyl groups, possess a high degree of photosensitivity, good pre-irradiation solubility, the potential to form thin films, resistance to solvents, plasmas and strong acids after crosslinking, and good thermal stability; they undergo crosslinking as a result of UV radiation and can be used as negative-type photoresists.

In previous studies we described the use of crosslinked cinnamic carbohydrate esters for immobilising different enzymes (García-Ruiz, 2000; Marín-Zamora, Rojas-Melgarejo, García-Cánovas, & García-Ruiz, 2005; Rojas-Melgarejo, Marín-Iniesta, Rodríguez-López, García-Cánovas, & García-Ruiz, 2006; Rojas-Melgarejo, Rodríguez-López, García-Cánovas, & García-Ruiz, 2004a, Rojas-Melgarejo, Rodríguez-López, García-Cánovas, & García-Ruiz, 2004b), and the dependence of the immobilized enzymatic activity on the crosslinking density (ρ) reached by the polymer during its irradiation (Rojas-Melgarejo, Rodríguez-López, García-Cánovas, & García-Ruiz, 2004c). After irradiation, the synthesized polymers that act as carriers of reactive groups (Fréchet, 1981) are insoluble in the aqueous medium used for enzyme reaction and/or storage.

Small variations in irradiation time provoke substantial changes in the crosslinking density and immobilized enzymatic activity attained, so that a method is needed to control the process and to provide more reproducible results. This problem can be solved by preparing mixtures of the immobilization support and an agent to limit the crosslinking density, regardless of the irradiation time and conditions used, thus controlling any increase in molecular weight and support branching. In this way, the physical-chemical characteristics (pore size and hydrophobic–hydrophilic ratio) of the final polymer obtained (Rojas-Melgarejo et al., 2004a) can be suited to the properties of the enzyme to be immobilized and to the specific application for which it is destined, and it will be possible to limit the cinnamoyl groups available to react in an uncontrolled way and thus modify the physical–chemical characteristics of the initial support obtained. For this reason, the principal aim of this study was to control the photocrosslinking process that takes place in monomers containing photoreactive cinnamoyl groups in an attempt to produce polymers for a specific application. In the present work, we used the totally cinnamoylated derivative of D-manitol (MNTCN) as monomer for crosslinking through the action of UV light, and *p*-nitrophenol (PNPCN) cinnamate as a chain blocker of the photocrosslinking reaction.

2. Materials and methods

2.1. Materials

D(-)-Manitol was supplied by Merck (Germany), while pure *p*-nitrophenol (PNP) and *trans*-cinnamic acid chloride were purchased from Sigma Chemical Co. (Spain). All other chemicals were of analytical grade and were supplied by Panreac Chemical, S.A. (Spain). Ultrapure water from a

Milli-Q system (Millipore Corp.) was used throughout this research.

2.2. Synthesis

2.2.1. Preparation of the totally cinnamoylated derivative of D-manitol (MNTCN)

The preparation followed a modified version of the method proposed by Van Cleve (Van Cleve, 1963), in which 0.02 mol (3.6 g) of D-manitol was dissolved in 100 ml of pyridine. The mixture was heated at 60 °C for 1 h to ensure complete dissolution. After cooling to room temperature, 0.15 mol (24.0 g) of cinnamic acid chloride was added. The reaction was allowed to proceed at room temperature for 4 h, after which the resulting mixture was poured into vigorously stirred cool water. The precipitate obtained, after decanting and filtering this mixture, was dissolved in chloroform and purified by adding, one drop at a time, to vigorously shaken hexane. The solid obtained was redissolved and reprecipitated before being dried on P₂O₅ at reduced pressure (yield: 76.4); mp = 98–99 °C (Fig. 1).

FT-IR (KBr, cm⁻¹): 1719 (C=O ester in the cinnamoyl groups); 1632 (vinylene C=C stretching vibration in the cinnamoyl groups); 1578, 1508, 1491 and 1449 (C=C stretching vibration of the benzene ring in the cinnamoyl groups); 1382; 1328; 1312; 1286; 1267; 1252; 1203, 1149 and 1069 (C–O ester stretching in the cinnamoyl groups); 1026; 984 (*trans*-vinylene C–H deformation vibration in the cinnamoyl groups), 870; 766 and 706 (=C–H out-of-plane bending of the benzene ring), 676. ¹H NMR (CDCl₃, δ in ppm): 4.39–4.73 (m, 2+2H, >CH–CH₂–O), 5.60–5.62 (m, 2H, >CH–CH–CH₂–), 5.91–5.93 (m, 2H, >CH–CH–CH<), 6.40–6.57 (m, 6H, Ar–CH=CH–), 7.24–7.59 (m, 30H, ArH), 7.67–7.88 (m, 6H, Ar–CH=). The integration signals corresponded to totally esterified derivatives. The absence of hydroxyl groups was confirmed by analysing samples to which deuterated water had been added; ¹³C NMR (CDCl₃, δ in ppm): 62.16 (>CH–CH₂–OOC–), 68.63 (>CH–CH₂–), 69.35 (>CH–CH–CH<), 116.67

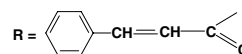
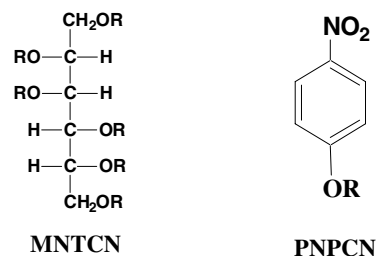


Fig. 1. Schematic representation of the structure of the photocrosslinkable monomers, MNTCN and PNPCN.

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