

Furan–chitosan hydrogels based on click chemistry

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Received: 10 October 2014 / Accepted: 6 March 2015 / Published online: 25 March 2015
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Abstract The modification of polymers by click chemistry has increased abruptly over the past years. In this study, furan groups were attached onto chitosan chain via reaction of 6-azido-6-deoxy chitosan and furfuryl propargyl ether. With this purpose, 6-azido-6-deoxy chitosan was synthesized by bromination and the subsequent nucleophilic substitution with sodium azide on the C6 hydroxyl groups of a previously amino-protected *N*-phthaloyl chitosan. Then, 6-azido-6-deoxy chitosan was reacted with furfuryl propargyl ether by the Cu(I)-catalyzed Huisgen 1,3-dipolar cycloaddition reaction, resulting in an *o*-substituted furan–chitosan derivative with a degree of substitution of 10 %. The structure of all derivatives was analyzed and confirmed by means of infrared and nuclear magnetic resonance spectroscopies. Clicked chitosan with

furan side groups was cross-linked with a bismaleimide to produce a polymer network via Diels–Alder reaction at 75 °C. The system presented a sol–gel transition with some syneresis. The gelation process was monitored by the evolution of the viscoelastic properties of the reaction mixture. The generated chitosan–furan–maleimide polymer network exhibited the typical pattern of a soft polymer hydrogel, in which both moduli were almost frequency independent with values lower than 10 Pa. These weak mechanical properties were interpreted as a consequence of the polymer degradation, which took place during the *N*-phthaloyl deprotection procedure.

Keywords Chitosan · Furan · Click chemistry · Diels–Alder · Hydrogels · Maleimide

Electronic supplementary material The online version of this article (doi:10.1007/s13726-015-0325-4) contains supplementary material, which is available to authorized users.

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Introduction

The search for novel properties in polymers is of great interest for the development of new technologies. Nowadays, click chemistry is used to generate new physical and chemical properties in polymers. The concept “click chemistry” involves at least eight chemical reactions described in the literature that fit accurately within its criteria [1]: that is, simple experimental conditions, stereospecificity, high yields, rapidity, insensitive to oxygen or water, high thermodynamic driving force, simple product recovery and absence of toxic byproducts [2–4]. One of those eight reactions, the Huisgen 1,3-dipolar cycloaddition, involves an azide that reacts with a terminal alkyne to give 1,4- or 1,5-regioisomers whose stereoselectivity could be directed using copper or ruthenium salts, respectively [5, 6]. Another reaction is known as Diels–Alder cycloaddition. The latter comprises a conjugated diene and a substituted alkene (dienophile) that gives a substituted cyclohexene. For example, furan and maleimide compounds