



Synthesis of amide-functionalized cellulose esters by olefin cross-metathesis



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ABSTRACT

Cellulose esters with amide functionalities were synthesized by cross-metathesis (CM) reaction of terminally olefinic esters with different acrylamides, catalyzed by Hoveyda–Grubbs 2nd generation catalyst. Chelation by amides of the catalyst ruthenium center caused low conversions using conventional solvents. The effects of both solvent and structure of acrylamide on reaction conversion were investigated. While the inherent tendency of acrylamides to chelate Ru is governed by the acrylamide *N*-substituents, employing acetic acid as a solvent significantly improved the conversion of certain acrylamides, from 50% to up to 99%. Homogeneous hydrogenation using *p*-toluenesulfonyl hydrazide successfully eliminated the α,β -unsaturation of the CM products to give stable amide-functionalized cellulose esters. The amide-functionalized product showed higher T_g than its starting terminally olefinic counterpart, which may have resulted from strong hydrogen bonding interactions of the amide functional groups.

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1. Introduction

Amide functionality on the backbone or side chain of a polymer can not only affect physical, chemical, and mechanical properties (Kaczmarczyk & Danuta, 1995), but also polymer–polymer (Lin, Zhang, Dong, Dong, & Li, 2007) or polymer–small molecule (Yu & Mosbach, 1997) interaction by secondary forces like hydrogen bonding (Gellman, Dado, Liang, & Adams, 1991; Hagler, Huler, & Lifson, 1974; Lifson, Hagler, & Dauber, 1979). Although amide-containing synthetic polymers (e.g. nylons) as well as some natural polymers such as proteins have been well studied, to date relatively few studies have focused on the synthesis and properties of amide-functionalized cellulose and other polysaccharide derivatives. This is in part because of the limited number of synthetic approaches that have been described to prepare such derivatives. Amidation of carboxylic acid containing polysaccharides or their derivatives (e.g. carboxymethyl cellulose) with amines gives substituted amides; this method can be challenging since polysaccharide hydroxyl groups may also be reactive towards an activated carboxyl group (Benkaddour, Journoux-Lapp, Jradi, Robert, & Daneault, 2014; Zabivalova, Bochek, Kalyuzhnaya, Vlasova, & Volchek, 2003).

In a reversal of reactivity, amidation between amino-containing polysaccharides (e.g. chitosan) with carboxylic acids or acid chlorides has also been employed; the required amino substituted polysaccharide may not be readily available, and issues of N/O selectivity can also surface with this method (Ruiz Matute et al., 2013).

Olefin metathesis has been proven to be a powerful tool for synthesis of a variety of both small and polymeric molecules by scission and regeneration of carbon–carbon double bonds (Grubbs, 2004). Successful synthesis of small molecule amides through cross-metathesis (CM) has also been reported (Barrett et al., 2004; Choi, Chatterjee, & Grubbs, 2001; Formentin, Gimeno, Steinke, & Vilar, 2005; Streuff & Muñiz, 2005). In 2001, the Grubbs group investigated the synthesis of α,β -unsaturated amides by cross-coupling reaction of simple terminal olefins with corresponding amides (e.g. acrylamide) (Choi et al., 2001). Olefin CM chemistry has been adopted by the Edgar (Meng, Matson, & Edgar, 2014a; Meng, Matson, & Edgar, 2014b) and other groups (Joly, Granet, & Krausz, 2005; Malzahn et al., 2014) for polysaccharide modification towards discrete or cross-linked products. In our previous studies, cellulose esters with side-chain functionalities of carboxylic acid and a variety of carboxylate esters were synthesized by CM between ω -unsaturated cellulose esters (e.g. cellulose acetate undec-10-enoate) and CM partners including acrylic acid and the corresponding acrylates (Fig. 1). This synthetic pathway has been demonstrated to be a modular and efficient route to families of

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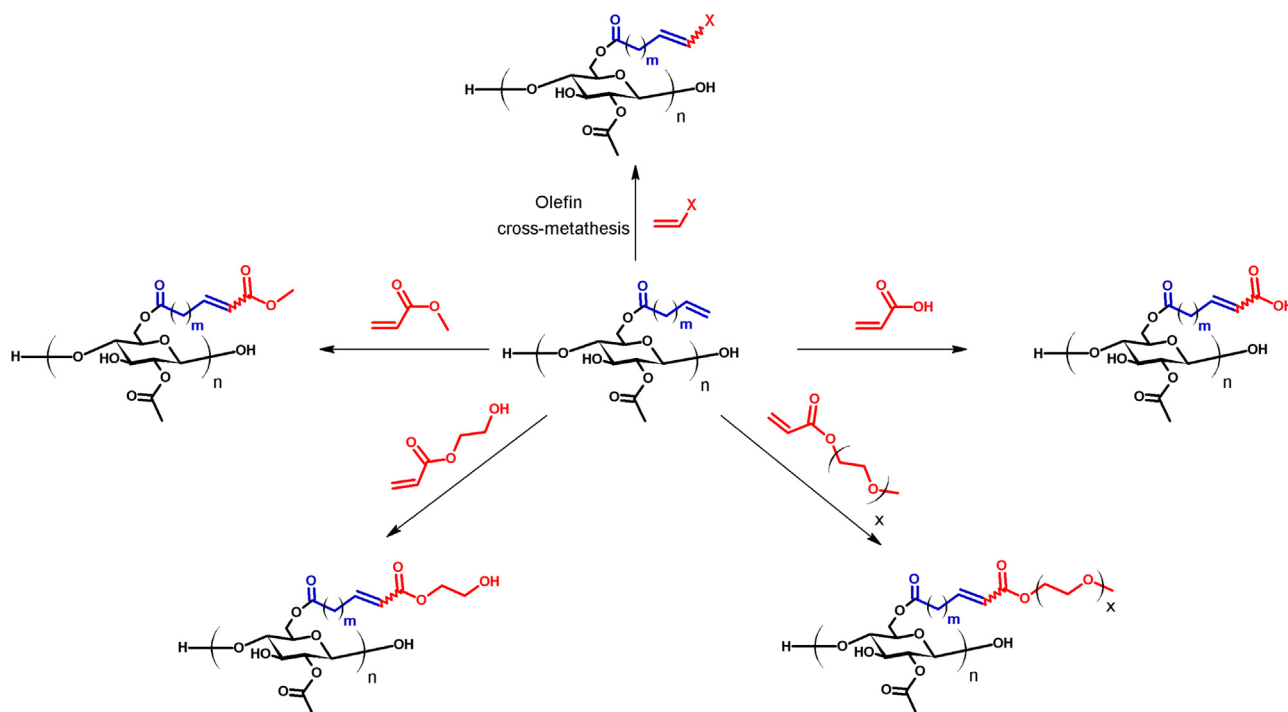


Fig. 1. General scheme of olefin CM between terminally olefinic cellulose ester and different CM partners.

novel polysaccharide derivatives, providing a valuable platform for structure–property relationship studies.

However, to the best of our knowledge, there have been no reports of synthesis of α,β -unsaturated amides using olefin CM to achieve either synthetic polymer or polysaccharide modification. This may be due to the fact that amides tend to chelate with the olefin metathesis catalyst, and thus the reaction could be expected to afford even lower conversion in a polymer system than the incomplete conversions previously observed for small molecules (Choi et al., 2001). We hypothesize that it may be possible to carry out olefin CM reactions between terminally unsaturated cellulose esters and acrylamides, so long as the proper solvents or additives are used to minimize deactivation of the metathesis catalyst by the amide groups. Herein, we report our approaches to synthesis of amide-functionalized cellulose esters by cross-metathesis reaction between terminally olefinic cellulose esters and acrylamides. We also describe the impact of using organic acids (i.e. acetic acid) as solvents for CM reactions with acrylamides, and try to rationalize the observed effects via a preliminary structure-activity relationship study. Furthermore, we propose a hydrogenation protocol to eliminate instability caused by labile γ -hydrogens in the initial α,β -unsaturated CM products. As mentioned earlier, intra- and intermolecular hydrogen bonding interaction via amide functionality may invest polymers with properties of interest for applications such as amorphous solid dispersion formulation (Taylor & Zografis, 1997) and molecular recognition (Yu & Mosbach, 1997). The current study focuses on our attempts to prove the concept of our hypothesis by developing a synthetic approach towards amide-functionalized cellulose derivatives, which may have great promise for these and other applications.

2. Experimental

2.1. Materials

Cellulose acetate (CA-320S, M_n 38.0 kDa, DS(Ac) 1.82) was from Eastman Chemical Company. The molecular weight information

was reported by the supplier and the DS value was previously measured by our group (Kar, Liu, & Edgar, 2011). Triethylamine (TEA) and 1,3-dimethyl-2-imidazolidinone (DMI) were purchased from Acros Organics. Dimethyl formamide (DMF), glacial acetic acid, ethyl acetate (EtOAc), methyl ethyl ketone (butanone, MEK) and ethyl ether were purchased from Fisher Scientific. Undec-10-enoyl chloride, Hoveyda–Grubbs 2nd generation catalyst, *p*-toluenesulfonyl hydrazide, acrylamide, *N*-phenylacrylamide, *N,N*-dimethylacrylamide, tetrahydrofuran (THF), butylated hydroxytoluene (BHT) and *N*-isopropylacrylamide were purchased from Sigma-Aldrich. DMI and DMF were dried over 4 Å molecular sieves before use. All other purchased reagents were used as received.

2.2. Measurements

^1H NMR spectra were acquired on a Bruker Avance 500 spectrometer operating at 500 MHz with 16 scans. Samples were analyzed as solutions in CDCl_3 or DMSO-d_6 (ca. 10 mg/mL) at 25 °C in standard 5 mm o.d. tubes. Three drops of trifluoroacetic acid were added to shift the water peak downfield from the spectral region of interest. ^{13}C NMR spectra were obtained on a Bruker Avance 500 spectrometer with a minimum of 5000 scans in DMSO-d_6 (ca. 50 mg/mL) at 25 °C. To obtain the T_g values of the cellulosic polymers, DSC was performed on a TA Instruments Q2000 apparatus using a heat/cool/heat cycle. Dry powders (ca. 5 mg) were loaded in TA hermetic aluminum pans. Each sample was equilibrated at -50 °C before heating to 160 °C at the rate of 20 °C/min, followed by quenching to -50 °C and heating to around 200 °C at a rate of 20 °C/min. FTIR spectra were obtained on a Nicolet 8700 instrument. Size exclusion chromatography (SEC), if not otherwise specified, was performed on an Agilent 1260 Infinity Multi-Detector SEC using DMAc with 0.1 M LiCl as the mobile phase (50 °C) with 3 PLgel 10 μm mixed-B 300 \times 7.5 mm columns in series. A system of multiple detectors connected in series was used for the analysis. A multi-angle laser light scattering (MALS) detector (DAWN-HELEOS II, Wyatt Technology Corporation, Goleta, CA),

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