Alkoxycarbonylation of ethylene with cellulose in ionic liquids†

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Alkoxycarbonylation of ethylene with carbon monoxide and cellulose in 1-*n*-butyl-3-methylimidazolium methanesulfonate affords cellulose propionate with a degree of substitution of 1–2.

Cellulose is the most abundant biopolymer, accounting for *ca.* 1.5×10^{12} tons of the annual biomass production.[1,2] Cellulose possesses excellent mechanical properties due to interchain hydrogen bonding between the β (1,4) linked linear chains. However, this also results in insolubility in water and organic solvents and intractability, which impedes processing of cellulose and restricts its utilization. To overcome these issues cellulose derivatives, such as cellulose esters, are employed.[3] Most prominently, cellulose acetate is produced by reaction of cellulose with acetic anhydride. A potentially useful direct route to higher esters, employing low cost basic chemicals, could be direct alkoxycarbonylation[4,5] of olefins with carbon monoxide and cellulose. This requires an appropriate reaction medium capable of solubilizing cellulose. To this end, ionic liquids[6] (ILs) have been found to be unique solvents.[7,8]

The solvent properties of ionic liquids for cellulose are due to the hydrogen bonding capability of their anions. It must be anticipated that the hydrogen bonding capability correlates to a certain degree with their tendency to coordinate to electrophilic metal cations, such as the active species in Pd(II) catalyzed carbonylation reactions. This will block coordination sites required for catalysis to proceed.[9] Screening of ethylene alkoxycarbonylation with *n* propanol by Pd(OAc)$_2$/PPh$_3$/methane sulfonic acid at 90 °C in 1 *n* butyl 3 methyl imidazolium (bmim) ionic liquids revealed that no reaction had occurred with [bmim][OAc] and [bmim][(MeO)$_2$PO$_2$][10] (both being good solvents for cellulose), while in [bmim][MeSO$_3$] essentially full conversion occurred, and a moderate conversion of 30% was observed in [bmim][N(SO$_2$CF$_3$)$_2$].‡ Notable in view of the primary and secondary OH moieties present in cellulose, *i* propanol was also converted completely to prop 2 yl propionate in [bmim][MeSO$_3$], though slightly longer reaction times were required.

Studies on the alkoxycarbonylation of ethylene with cellulose were therefore conducted in [bmim][MeSO$_3$], even though under reaction conditions the cellulose substrate is not dissolved completely in the initial reaction mixture. Screening of a range of mono and bidentate phosphines varying in bulk and electron donating properties, and optimization of reaction conditions, revealed that with triphenylphosphine and 9,9 dimethyl 2,7 disulfonato 4,5 bis(diphenylphosphino) xanthene disodium salt (sulfoxantphos)[11] cellulose propionate (Scheme 1) was formed at 90 °C and 55 bar, ethylene/CO 1:1.‡ Minor alkoxycarbonylation was observed with 1,2 bis (di *tert* butylphosphinomethyl)benzene. Optimum conditions for maximum substitution of cellulose were found to be 5 mol% Pd(OAc)$_2$ and 90 to 100 °C with PPh$_3$, at lower temperatures the reaction was prohibitively slow, and at 120 °C also low conversion was observed, presumably due to catalyst deactivation.

By contrast to the cellulose starting material, the alkoxycarbonylation products are soluble in DMSO, which evidences modification and facilitates characterization by solution methods. FT IR spectra of the solid polymer products feature an intense absorption peak at 1738 cm^{-1} which confirms the presence of a carboxylic acid ester. In ^{13}C NMR spectra (ESI†) of the propionylated cellulose recorded in DMSO d_6 at 100 °C characteristic signals at δ 171.6 172.8 ppm are observed in the carbonyl region, which suggest that modification has occurred at all three positions 2, 3 and 6. The methyl and methylene carbons of the propionate moieties resonate at 8.2 and 26.3 ppm, respectively. Moreover, the ^{13}C NMR spectra exhibit a shift of the resonances of C 6 (62.0 ppm) and C 2 (99.1 ppm) in the substituted cellulose by comparison to the unmodified starting material, C 6 (59.1 ppm) and C 2 (101.8 ppm). These FT IR and NMR spectroscopic data agree with reported spectroscopic properties of non catalytically prepared cellulose propionate,[12] and compare with reference compounds prepared for this purpose by classical esterification of cellulose with acid anhydrides (*cf.* ESI†). By diffusion ordered spectroscopy (DOSY; Fig. 1), identical rates of diffusion are observed for the propionate resonances and the cellulose backbone signals, which are slow by comparison to low molecular weight compounds present in the sample, such as residual non deuterated DMSO solvent (also *cf.* ESI†). This confirms the covalent linkage of the ester moieties to the cellulose backbone.

A degree of substitution (DS) of 1 to 2 was estimated from ^{13}C NMR spectra. Intensities of the resonances of C 6 for the modified and unmodified moieties, respectively, were approximately equivalent, whereas for C 2 the resonance of the modified moieties predominated (*ca.* 1.7 fold). The degree of substitution of C 3 could not be quantified due to overlapping resonances.

The thermal properties of the modified cellulose were probed by light microscopy at various temperatures. At 180 200 °C the cellulose propionate turns rubbery, and deformation with a spatula is possible. Between 200 220 °C

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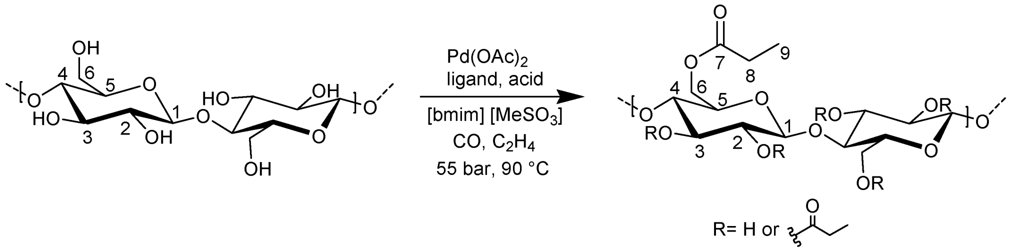

Scheme 1 Alkoxycarbonylation of ethylene with carbon monoxide and cellulose in [bmim][$MeSO_3$] to cellulose propionate.

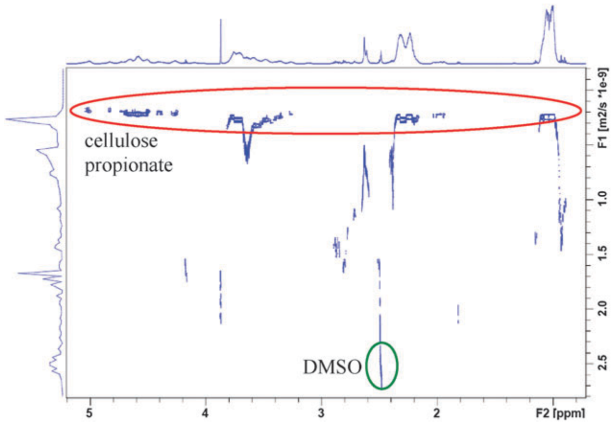

Fig. 1 DOSY spectrum of a cellulose propionate (DS 1 2) from catalytic alkoxycarbonylation, DMSO d_6, 600 MHz, 120 °C.

the cellulose propionate further softens, and streaks can be pulled. This qualitatively agrees with previous reports on the thermal behaviour of (non catalytically generated) cellulose propionate with comparable composition.[3]

In conclusion, catalytic alkoxycarbonylation is demonstrated to be a viable direct route to cellulose propionate. Degrees of substitution of 1 to 2 were observed in this work. If desired, the basic chemicals employed, ethylene and CO, are also accessible from renewable resources. The key to this reaction is the utilization of appropriate ionic liquids. For future developments of more efficient catalysts a detailed understanding of the interactions of the active sites with the IL reaction medium appears desirable.

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Notes and references

‡ Experimental conditions for propanol carbonylation: 1 mL (13 mmol) of *n* or *i* propanol in 4 g of IL, 107 μmol Pd(II), Pd:P 1:10, 3 equiv. CH_3SO_3H, 90 °C, 50 bar ethylene:CO 1:1 mixture, 30 h reaction time. For cellulose carbonylation: 150 mg (2.77 mmol OH) of cellulose in 3 g of IL, 135 μmol Pd(II), Pd:P 1:10, 3 equiv. CH_3SO_3H, 90 °C, 50 bar ethylene:CO 1:1 mixture, 30 h.

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