

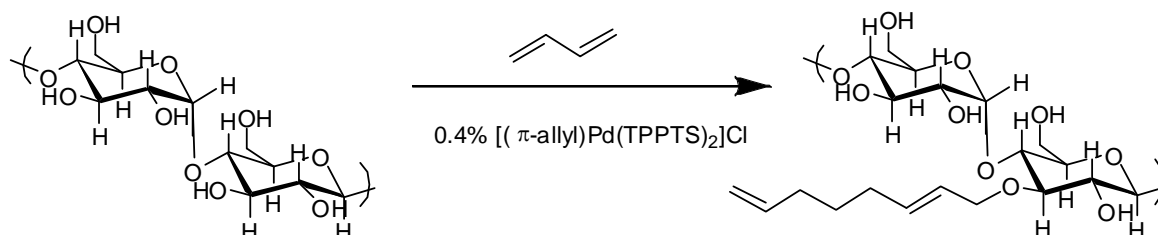
EFFICIENT TELOMERISATION OF BUTADIENE WITH STARCH

Julien Mesnager,^{a,b} Anne Lambin,^a Claude Quettier^a and Catherine Pinel^{b*}

^(a)Roquette Frères, F-62080 Lestrem, France,

^(b)Université de Lyon ; Institut de Recherches sur la Catalyse et l'Environnement de Lyon ; 2 avenue Albert Einstein F-69626 Villeurbanne, France, catherine.pinel@ircelyon.univ-lyon1.fr

Industrial use of the cheap and abundant native starch suffers from several drawbacks, such as readily thermal decomposition, retrogradation, and low shear stress resistance. Chemical, physical, or enzymatic treatment can provide useful modifications; in particular, esterification or etherification affords hydrophobic starch derivatives. We have developed a catalytic route based on the telomerization of a diene with native starch.¹ This palladium-catalyzed reaction allowed the formation of an octadienyl chain as the main product via dimerization of two molecules of the 1,3-diene with hydroxyl groups of the starch. 1,3-Butadiene, the simplest diene, is readily available at low cost. In our previous reports, we performed the reaction in the presence of a large excess of butadiene and using an in situ the Pd(OAc)₂/ 3TPPTS catalytic system. Here we describe a more efficient catalytic system, starting from a [(π -allyl)PdCl]₂ precursor.²



The catalytic system for the telomerisation of butadiene with MeOH in the presence of water was first optimized. The complex prepared from [(π -allyl)PdCl]₂ + 2 TPPTS was very stable and efficient in the reaction with MeOH in the presence of water, and was applied to the telomerization of butadiene with starch. After screening of several parameters (temperature, nature of solvent, reaction time, pH...), the conversion of butadiene reached 80%.

Characterization of the catalytic systems and their efficacy in the telomerization reactions will be presented.

¹ C. Donzé, C. Pinel, P. Gallezot, P.L. Taylor, *Adv. Synth. Catal.*, 2002, 344(8), 906-910 ; A. B. Sorokin, S. L. Kachkarova-Sorokina, C. Donzé, C. Pinel, P. Gallezot, *Top. Catal.*, 2004, 27, 67-76

² E. Kuntz, A. Amgoune, C. Lucas, G. Godard, *J. Mol. Catal. A*, 2006, 244, 124; E. Kuntz is acknowledged for a gift of TPPTS