Palladium-Catalyzed Telomerization of Butadiene with Starch

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Dedicated to Roger Sheldon on the occasion of his 60th birthday.

Abstract: In order to modify the hydrophilic properties of native starch for its incorporation in polymers, the telomerization of butadiene with native starch was investigated. Low to moderate degrees of substitution (DS = 0.04 – 0.52) were obtained depending upon experimental conditions, particularly, reaction time, temperature and solvent. With 0.3‰ water-soluble palladium catalyst (Pd/TPPTS), the reaction occurred in *i*-PrOH/NaOH 0.1 N solvent mixture even at 50 °C and after 3 h reaction the DS reached 0.08, a value suitable for the application.

Keywords: butadiene; hydrophobic starch; palladium-catalyzed telomerization; TPPTS

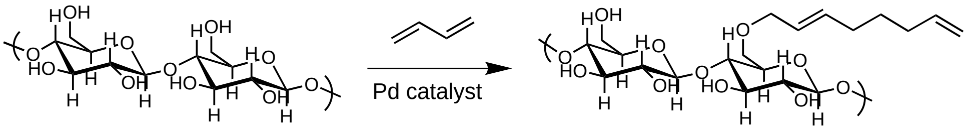
Introduction

Starch is an abundant, inexpensive and renewable natural raw material that has been widely applied in the food, paper, textile, adhesive, plastic, and pharmaceutical industries. Partial substitution of petroleum-based resources with materials from agroresources is attractive not only due to their low price but also because of their biodegradability properties and their potential contribution to reducing CO_2 emission.[1]

For these applications, starch is modified to improve its physico-chemical properties. Starch modification can prevent retrodegradation, improve gel texture, clarity and sheen, improve film formation or stabilize emulsion.[2] Partial substitution of starch with acetate, hydroxypropyl, alkylsiliconate or fatty-acid ester groups modifies its properties. All those reactions that have been largely described in the literature affect the hydrophobic/hydrophilic balance of starch which is required for the incorporation of modified starches in polymers.[3]

An alternative route for the synthesis of more hydrophobic starch is based on the telomerization reaction of butadiene with natural starch. The telomerization reaction has been known for a long time and a wide variety of nucleophiles has been used such as amines, carboxylic acids, alcohols, and even water under particular conditions.[4] This palladium-catalyzed reaction produces no salt, and provides a 100% atom-efficiency. Due to its availability and low price, 1,3-butadiene is an especially attractive starting material for this transformation. The starch octadienyl ethers so obtained are expected to be much less sensitive towards hydrolysis compared to the esterified starches. It was shown previously that the use of a hydrosoluble palladium-catalytic system, prepared from palladium diacetate and trisodium tris(*m*-sulfonatophenyl)phosphine (TPPTS), catalyzed the telomerization of sucrose in water medium. The modification of reaction conditions affected deeply the degree of substitution ranging from 1 to 4.[5]

The transposition of this reaction to starch was challenging as this substrate is insoluble in water at room temperature and gelatinizes at temperatures higher than *ca.* 70 °C. Within The European Commission Fifth Framework Programme within "Competitive and Sustainable Growth" Project No: GRD1-1999-10200 – High Performance Industrial Polymers based on Modified Starch, our objective was to prepare modified starches for introduction into industrial polymer preparations so that portions of the polymer substrates derived from fossil fuel can be replaced by



Scheme 1. Telomerization of butadiene with starch.

modified starches derived from renewable resources. The degree of substitution (DS) should be kept low enough because the modified starch should not be too hydrophobic. In this paper, the influence of several factors on the DS of native, insoluble starch is described.

Results and Discussion

The degree of substitution (DS) of starch is defined as moles of substituted hydroxy groups per glucoside unit of starch; so the theoretical maximum DS is 3. The DS determined by ^{1}H NMR analysis, was never higher than 1. The fine structure of the modified starch was not elucidated but the substitution should occur on the primary alcohol of the glucopyranoside unit preferentially to the secondary alcohol as it was shown that the reactivity of *i*-PrOH is much lower than that of linear alcohols.[6] The NMR analysis of modified starch did not allow us to differentiate between the linear or branched isomer but the main product is probably 1-substituted 2,7-octadiene as observed for sucrose telomerization.[5] Moreover, considering the mechanism recently described by Beller et al.,[7] due to the steric hindrance of the starch, the nucleophilic attack at the terminal carbon of the cationic palladium complex is largely preferred (Scheme 2). 1,3,7-Octatriene (dimerization of butadiene) and 2,7-octadien-1-ol (reaction with water) were the two major by-products that can be formed during the reaction. Extensive washings of the modified starch with acetone and dichloromethane removed them. In fact, their amount was not significant as the washings did not affect the weight of the solid and the ^{1}H NMR spectra were similar.

Initially, the reactions were performed in *i*-PrOH/H_2O at 90 °C in the presence of sodium hydroxide due to the fact that for the telomerization of butadiene with sucrose, it was shown that the presence of base avoided the formation of C_4 ethers.[5]

Effect of the Reaction Time

The influence of the reaction time on the DS is given in Figure 1. It is shown that after only 1 h reaction, the DS reached 0.35 but then did not increase significantly with

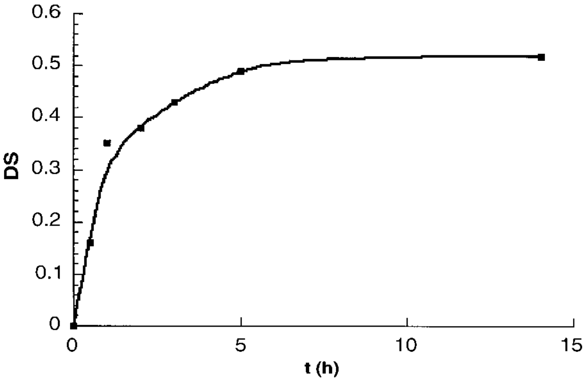
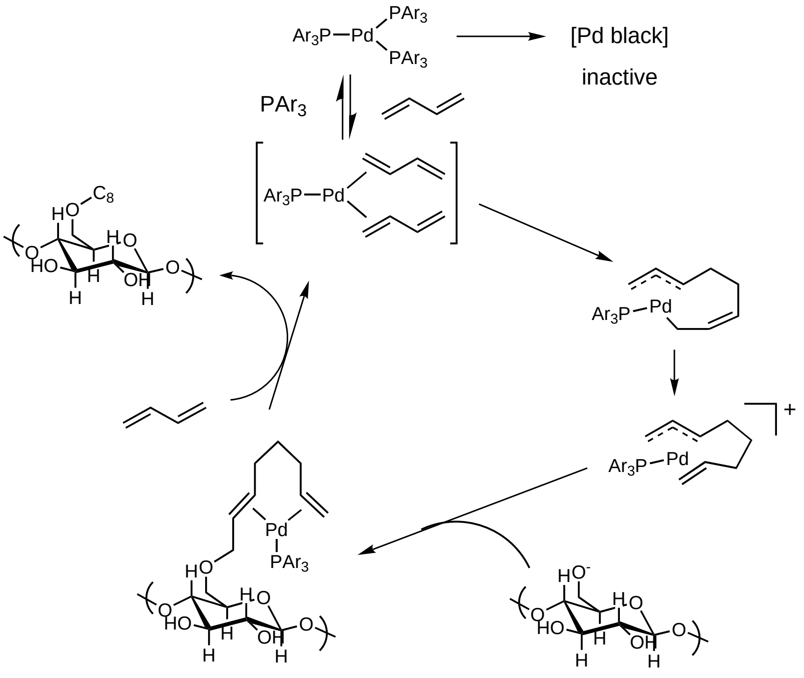


Figure 1. Evolution of the degree of substitution with reaction time. Reaction conditions: butadiene/starch = 3/1; catalyst content = 0.25% [Pd(OAc)$_2$/3 TPPTS], *i*-PrOH/NaOH 0.1 N = 1/5, 90 °C.



Scheme 2. Proposed mechanism.

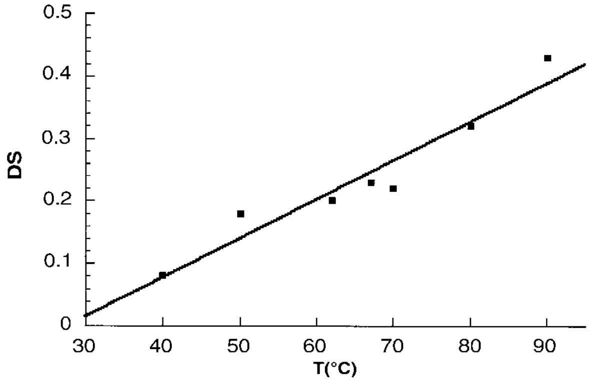


Figure 2. Evolution of the degree of substitution with the reaction temperature. Reaction conditions: butadiene/starch = 3/1; catalyst content = 0.25% [$Pd(OAc)_2$/3 TPPTS], *i*-PrOH/NaOH 0.1 N = 1/5, 3 h.

the reaction time. The plateau could be due to diffusion limitation of the catalyst in the gelatinized starch, or to a progressive decomposition of the Pd/TPPTS complex (*vide infra*).

Effect of the Temperature

The influence of the reaction temperature on the DS in the presence of the water-soluble catalyst $Pd(OAc)_2$/3 TPPTS is given in Figure 2.

With 0.25% of $Pd(OAc)_2$, from 40 up to 90 °C, a linear improvement of the degree of substitution was observed from 0.08 up to 0.43. The higher DS could be due either to an increase of the reaction rate or to a higher diffusion in the catalyst in the starch polymer with temperature. The temperature had also an impact on the texture of the product after reaction: at 50 °C, solids were easier to work-up than at 90 °C due to the gelatinization of the starch at high temperature. Moreover, at temperatures lower than 60 °C white solids were obtained, while at higher temperature black particles were found in the solid that were attributed to partial decomposition of catalyst and formation of black palladium particles.

Effect of Catalyst Amount

The effect of starch/catalyst ratio was evaluated at 50 and 90 °C; the evolution of the degree of substitution with the catalyst content is given in Figure 3.

At 90 °C, the degree of substitution was dramatically affected by the palladium content. With 4 ‰ (w/w) of $Pd(OAc)_2$, the DS reached almost 0.6 while less than 0.3 was achieved with 1.2‰ Pd content. At 50 °C, the DS was lower but much less affected by the starch/catalyst ratio and varied from 0.08 to 0.15 whatever the amount of the catalyst. This can be attributed to the stability of the catalyst with temperature. At 90 °C, the Pd/TPPTS was unstable and decomposed progressively into palladium metal as proposed in Scheme 2. At 50 °C, the catalyst was stable enough and substitution occurred with a catalytic level as low as 0.3‰.

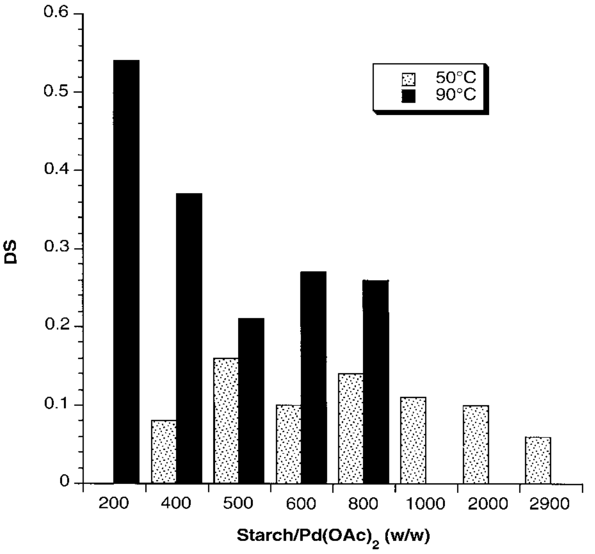


Figure 3. Influence of the palladium content on the degree of substitution. Reaction conditions: butadiene/starch = 3/1; *i*-PrOH/NaOH 0.1 N = 1/5, 3 h.

It is of particular interest to decrease the catalyst concentration, not only due to the cost of the metal and the ligand but also to avoid the presence of residual catalyst in the final product. When the reaction was performed in the presence of 0.25% palladium acetate, 0.14% and 0.08% palladium was detected by chemical analysis of modified starch after reaction at 90 °C and 50 °C, respectively. On the other hand, no palladium was detected in the solid when the reaction was conducted at 50 °C in the presence of 0.5‰ palladium.

Effect of Solvent and Reagent Concentration

The influence of the nature of the solvent, the starch/butadiene ratio as well as the starch concentration on the DS was studied.

The concentration of NaOH had a strong influence on the degree of substitution (Table 1). It increased dramatically from 0.07 when 0.01 N NaOH (entry 2) was used up to 0.43 with 0.1 N NaOH (entry 1). In the absence of base, the degree of substitution was low (entries 3 and 4). It was shown previously that, higher reaction rate were obtained by addition of sodium hydroxide for the butadiene telomerization of sucrose.[5] Recently, Beller et al. observed higher initial reaction rates by addition of triethylamine.[8]

To study the effect of the starch/butadiene ratio, we kept the amount of starch constant (12 g = 75 mmol of glucose unit), while the quantity of butadiene was

Table 1. Telomerization of 1,3-butadiene with starch.

Entry	Solvent (60 mL)	m_{starch} (g)	$m_{butadiene}$ (g) (butadiene/starch) w/w)	$m_{Pd(OAc)2}$ (mg) (Pd/starch, w/w) ‰)	T [°C]/t [h]	DS
1	**NaOH 0.1 N/*i*-PrOH (5/1)**	12	38 (3.2)	33 (2.8)	90/3	0.43
2	**NaOH 0.01 N/*i*-PrOH (5/1)**	12	48 (4)	30 (2.5)	90/3	0.07
3	**H_2O/*i*-PrOH (5/1)**	5	32 (6.4)	24 (4.8)	90/14	0.12
4	**H_2O**	6	49 (8.3)	30 (5)	90/14	0.09
5	NaOH 0.1 N/*i*-PrOH (5/1)	12	**40 (3.3)**	12 (1)	50/3	0.12
6	NaOH 0.1 N/*i*-PrOH (5/1)	12	**17 (1.4)**	12 (1)	50/3	0.15
7	NaOH 0.1 N/*i*-PrOH (5/1)	12	**9 (0.7)**	12 (1)	50/3	0.15
8	NaOH 0.1 N/*i*-PrOH (5/1)	**12**	40 (3.3)	6 (0.5)	50/3	0.10
9	NaOH 0.1 N/*i*-PrOH (5/1)	**24**	39 (1.6)	12 (0.5)	50/3	0.06
10	NaOH 0.1 N/*i*-PrOH (5/1)	**30**	33 (1.1)	15 (0.5)	50/3	0.04
11	NaOH 0.1 N/*i*-PrOH (5/1)	**36**	24 (0.7)	18 (0.5)	50/3	0

decreased from 40 to 9 g that corresponded to molar ratio glucose unit/butadiene from 2.2 equivalents up to 10 equivalents, respectively (entries 5 to 7). At 50 °C, and for 3 h reaction time, this parameter had no significant effect on the DS. This was probably due to the limited solubility of butadiene in the solvent.

To improve the productivity of the reaction, the concentration of starch was increased from 200 g/L up to 600 g/L (entries 8 to 11). The DS decreased while the starch amount increased, no substitution was detected by ^{1}H NMR analysis at 600 g/L. This could be due to the increase of the viscosity of the reaction mixtures at high starch concentration, which induces mass transfer limitation. However, it is remarkable that some transformation was achieved at a very high concentration such as 500 g/L.

Influence of the Nature of the Catalyst

Other catalyst precursors coordinated by three equivalents of TPPTS were tested (Table 2). All palladium complexes were efficient in telomerization reaction, the best results being achieved with $Pd(dba)_2$ precursor. Inorganic precursors such as palladium nitrate or palladium chloride gave lower activities as previously observed for the reaction of butadiene with water.[9] Under the same conditions, the nickel catalyst was not active for this transformation.

Table 2. The influence of butadiene with starch: effect of palladium precursors.[a]

Catalyst precursor	DS
$PdCl_2$	0.09
$Pd(NO_3)_2$	0.11
$Pd(dba)_2$[b]	0.22
$Ni(OAc)_2$	0

[a] General conditions: butadiene/starch = 3/1; catalyst content = 0.20%, *i*-PrOH/NaOH 0.01 N = 1/5, 90° C, 3 h.

[b] dba = dibenzylideneacetone.

Some catalysts insoluble in water were tested such as palladacycle complexes {*trans*-di(μ-acetato)bis[*o*-(di-*o*-tolylphosphino)benzyl]dipalladium(II)} that are well known to perform C-C coupling with very high activity,[10] but they were not efficient for butadiene telomerization with starch. More surprisingly, the catalyst prepared from $Pd(OAc)_2$ and PPh_3 was efficient at 90 °C (Table 3). This is of particular interest as PPh_3 is much less expensive than TPPTS. In order to avoid modification of the structure of starch, we studied the telomerization reaction catalyzed with Pd/PPh_3 under milder temperature conditions. Unfortunately, at 60 °C no transformation was observed even at longer reaction time. Increasing the catalyst level, the NaOH concentration or the quantity of *i*-PrOH was not efficient.

Table 3. The reaction of butadiene with starch catalyzed by $Pd(OAc)_2/PPh_3$.[a]

Temperature, reaction time	Solvent	Starch/catalyst (w/w)	DS
90 °C, 14 h	*i*-PrOH/NaOH (0.1 N) = 1/5	400/1	0.16
90 °C, 3 h	*i*-PrOH/NaOH (0.1 N) = 1/5	400/1	0.09
60 °C, 14 h	*i*-PrOH/NaOH (0.1 N) = 1/5	400/1	0
60 °C, 3 h	*i*-PrOH/NaOH (0.1 N) = 1/5	400/1	0
60 °C, 3 h	*i*-PrOH/NaOH (0.1 N) = 1/5	200/1	0
60 °C, 3 h,	*i*-PrOH/NaOH (1 N) = 1/5	200/1	0

[a] General conditions: butadiene/starch = 3/1.

Conclusion

We have shown that palladium-catalyzed telomerization of butadiene with starch can be successfully achieved in spite of the fact that native starch is an insoluble polymer. Although some transformations occurred with organosoluble catalyst, the best results were obtained with Pd/TPPTS catalyst. The reaction temperature affected significantly the degree of substitution ranging from 0.08 up to 0.43 between 40 and 90 °C but at the latter temperature, starch gelatinization or catalyst decomposition occurred. Better results were obtained at 50 °C, at this temperature, the butadiene telomerization with starch can be catalyzed with only 0.3‰ palladium and modified starch with DS = 0.06 was obtained.

Some of these modified starches were evaluated by the industrial partners within The European Commission funded project in polymer preparations. Most of the modified starch samples obtained were much too hydrophobic and not suitable for aqueous polymer preparations. Some polymers were successfully prepared with octadienyl starches having DS smaller than 0.1, but the final industrial products did not fulfill all the required commercial specifications. Additional work is under progress to prepare different hydrophobic starches, which could have required properties.

Experimental Section

Materials

The potato starch was a gift from Raisio Chemicals (Finland). It contained 80% amylose and 20% amylopectine on a dry basis and had a moisture content of 16% by weight. TPPTS was a gift from Rhodia (France). The $Pd(OAc)_2$ (98%) was purchased from Aldrich and butadiene (99.5%) from Airliquide. NMR analysis was done on a Bruker 250 MHz machine with DMSO-d_6 as solvent. Pd analysis was performed at the "Service d'Analyse" of the IRC (AAS method).

Catalytic Experiment

In a typical experiment, the reaction was performed in a 150-mL stainless steel autoclave, equipped with a mechanically stirring and heating mantle. Starch (12 g), $Pd(OAc)_2$ (60 mg, 0.5% weight) and TPPTS (480 mg, Pd/TPPTS = 3/1) were introduced in the autoclave with solvent (60 mL *i*-PrOH/NaOH 0.1 M: 1/5). The mixture was stirred for a few minutes. The autoclave was purged with argon then frozen (−10 °C) and liquid butadiene (35 – 40 g) was transferred. The mixture was warmed to 5 °C and the solution was stirred for 1 h. Then, the mixture was heated to the desired temperature for 3 h. After reaction, the autoclave was cooled, degassed and purged with argon. The mixture was poured in 200 mL acetone and stirred for 15 min. The precipitate was filtered, washed with 200 mL acetone, 200 mL dichloromethane and dried under vacuum.

Determination of the Degree of Substitution (DS)

The degree of substitution was determined by ^1H NMR in DMSO-d_6 on a dried sample (1 night at 100 °C). One drop of trifluoroacetic acid was added to shift the mobile protons of the unsubstituted hydroxy groups downfield. The DS was estimated from the ratio of the area of the proton peak at 2.2 ppm (4H corresponding to the lateral chain) to that of the proton peaks between 3.5 and 5.5 ppm (7H of the glycoside structure, the 2H of the octadienyl chain were neglected as the DS were low).

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