



# Synthesis of modified potato starches for aqueous solubilization of benzo[*a*]pyrene



Isabelle Delsarte, Pierre-Edouard Danjou, Etienne Veignie, Catherine Rafin\*

ULCO, Université du Littoral Côte d'Opale, Unité de Chimie Environnementale et Interactions sur le Vivant, Dunkerque 59140, France

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2-Octen-1-ylsuccinic anhydride (PubChem CID: 5362689)

1,4-Butane sultone (PubChem CID: 15411)

Deuterium oxide (PubChem CID: 24602)

Dichloromethane (PubChem CID: 6344)

## ABSTRACT

For soil rehabilitation, the surfactant-enhanced remediation has emerged as a promising technology. For this purpose, starch derivatives were difunctionalized by 1,4-butane sultone (BS) and 2-octen-1-ylsuccinic anhydride (OSA). Eight distinct products were obtained under different synthesis conditions. The chemical structural characteristics were investigated by <sup>1</sup>H NMR spectroscopy. The compounds were evaluated for their apparent aqueous solubility and their ability to increase the solubility of a hydrophobic pollutant such as benzo[*a*]pyrene (BaP), used as a polycyclic aromatic hydrocarbon model. In comparison with native starch, the best obtained compound increased starch apparent aqueous solubility by a factor of 10 (up to 3.50 g/L) and also stimulated 77-fold BaP aqueous solubilization (up to 232.97 μg/L) underlining its very high surfactant property. In this study, the right balance between hydrophobic character (octenyl succinate group (OS) grafted) of starch derivatives and starch apparent aqueous solubility (BS grafted) was highlighted.

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## 1. Introduction

Polycyclic Aromatic Hydrocarbons (PAHs) pose a real threat to environment and human health due to their high toxicity. These pollutants are mainly released into the atmosphere from anthropogenic sources before being deposited into the soil. They tend to persist in the environment because of their high chemical stability, low water solubility and tendency to be adsorbed onto soil organic matter (Cerniglia, 1993; Juhasz & Naidu, 2000). For soil rehabilitation, the surfactant-enhanced remediation has emerged as a promising technology, especially for biodegradation involving saprotrophic soil fungi (Goltapeh, Danesh, & Varma, 2013). Indeed, in contaminated soils, PAHs need to be transferred from the solid soil phase to the aqueous one in order to be bioavailable to fungi and consequently be biodegraded (Flotron, Delteil, Padellec, & Camel, 2005; Rafin, De Foucault, & Veignie, 2013).

For this purpose, surfactant like nonionic ones or cyclodextrins could be used to increase the PAHs biodegradation rates in soils (Bardi, Mattei, Steffan, & Marzona, 2000; Ortega-Calvo et al., 2013). Previous studies (Molnár et al., 2005; Veignie, Rafin, Landy, Fourmentin, & Surpateau, 2009) have demonstrated the interest of using cyclodextrins which are cyclic oligomers composed of α-1,4-linked glucose units (Szejtli, 1988). For most non-polar contaminants, formation of inclusion complex between the hydrophobic cavity of cyclodextrin and the contaminant increases the apparent solubility of pollutant (Frömming & Szejtli, 1994; Fava, Di Gioia, & Marchetti, 1998).

The existence of similar hydrophobic cavities was also highlighted in starches in our previous study (Rosu et al., 2011). These natural polysaccharides represent a material of choice for surfactant-enhanced remediation approaches owing to several advantages: they are non-toxic, abundant, cheap, renewable, biodegradable and easily modifiable (Liu & Budtova, 2013; Richardson & Gorton, 2003; Rodrigues & Emeje, 2012). Nevertheless, the weak aqueous solubility of native granular starches is also known to be a major constraint that could limit the development

\* Corresponding author. Tel.: +33 (0)328658278; fax: +33 (0)328658231.  
E-mail address: [rafin@univ-littoral.fr](mailto:rafin@univ-littoral.fr) (C. Rafin).

of such starch-based materials and derived applications (Bai, Shi, Herrera, & Prakash, 2011; Waterschoot, Gomand, Fierens, & Delcour, 2014). In our previous research, modified starches with 2-octen-1-ylsuccinic anhydride (OSA) presented the highest capacity to desorb BaP despite a quite low water solubility (Rosu et al., 2013). This result indicated that amphiphilic properties of OSA were not sufficient for native starch solubilization. Therefore, in the same study, we decided to conduct disubstitutions. So, native starches were modified with 1,4-butane sultone (BS) which stimulated starch solubility in water thanks to charged sulfonate groups solubility (Rosu et al., 2013). Moreover, for bioremediation processes, the high molecular size of starch must be preserved in order to avoid a side effect of the surfactant-enhanced remediation i.e. the pollutant discharge in the environment. That is why the acid hydrolysis of starch was not the synthesis strategy chosen in order to preserve the highest starch molecular size possible. These previous syntheses allowing a right balance between hydrophobic and hydrophilic characters of starch derivatives were promising. This strategy was used as our guideline for the present research.

The originality of the present research was to use 1,4-butane sultone (BS) and 2-octen-1-ylsuccinic anhydride (OSA) as starting materials for synthesizing difunctionalized starches. These new modified starches were then evaluated for their apparent aqueous solubility and their ability to increase the solubility of hydrophobic pollutants such as benzo[*a*]pyrene (BaP), used as a PAH model.

## 2. Material and methods

### 2.1. Chemicals

Soluble potato starch (P0 121096, 0000108507), sodium hydroxide (NaOH) and dimethyl sulfoxide (DMSO) at 99.5% purity were provided by Panreac Quimica SA (Barcelona, Spain). Benzo[*a*]pyrene (BaP) at 96% HPLC purity and 2-octen-1-ylsuccinic anhydride (OSA) at 97% purity were purchased from Sigma Aldrich (Steinheim, Germany). The reagent 1,4-butane sultone (BS) at 99% purity was supplied by Acros Organics (Noisy-Le-Grand, France), dichloromethane (DCM) by Fisher Scientific (Illkirch, France), deuterium oxide (D<sub>2</sub>O) at 99.8% purity by Carlo Erba Reagents (Val-de-Reuil, France). Cellulose membrane (MWCO of 12–14 kDa) was supplied by Medicell International (London, United Kingdom). Deionized water was used throughout this work.

### 2.2. Synthesis of difunctionalized starch derivatives

Reactions were performed sequentially (P1, P2, P3, P4, P5, P6) or in one pot (P7, P8). All the reaction parameters are given in Table 1. Representative procedures were described for P1 and P8.

**Table 1**  
Parameters of difunctionalized starches synthesis (OSA/AGU ratio = 1/2).

Product	Starch	T (°C)	Duration (h)	DMSO/H <sub>2</sub> O	NaOH/AGU	BS/AGU
P1	Native	20	48	4/1	1/2	1/2
P2	Dispersed <sup>a</sup>	20	48	4/1	1/2	1/2
P3	Native	20	48	4/1	1/2	1/1
P4	Native	70	48	1/1	4/3	1/1
P5	Native	70	48	1/1	4/3	1/2
P6	Native	70	48	1/1	1/2	1/6
P7 <sup>b</sup>	Native	20	24	4/1	1/2	1/1
P8 <sup>b</sup>	Native	70	24	4/1	1/2	1/1

<sup>a</sup> Native starch was dispersed into water and heated at 70 °C during 30 min prior to synthesis.

<sup>b</sup> One pot reaction.

**P1:** Potato starch (1.00 g, 6 mmol per anhydroglucose unit (AGU)), 5 mL H<sub>2</sub>O, 20 mL DMSO and NaOH (0.10 g, 2.5 mmol) were placed in a 100 mL round bottomed flask and were stirred at 20 °C for 24 h. To this mixture, BS (0.92 mL, 9 mmol) was added and the reaction was carried out for 24 h. Finally, OSA (1.90 mL, 9 mmol) was added and the resulting mixture was stirred for 24 h. A total of NaOH pellets (0.40 g, 10 mmol) was added to maintain the pH between 8 and 9.

**P8:** Potato starch (1.00 g, 6 mmol AGU), 5 mL H<sub>2</sub>O, 20 mL DMSO and NaOH were placed in a 100 mL round bottomed flask and were stirred at 70 °C. To this mixture, BS (1.85 mL, 18 mmol) and OSA (1.90 mL, 9 mmol) were simultaneously added and the reaction was carried out for 24 h. A total of NaOH (0.40 g, 10 mmol) was added to maintain the pH between 8 and 9.

On completion of the reactions, the modified starches were dialyzed in water during 3 days using a cellulose membrane. The water was changed twice a day and the products were lyophilized (Rosu et al., 2013). Eight products were obtained.

### 2.3. Structural <sup>1</sup>H NMR characterization of starch

<sup>1</sup>H NMR spectra were measured with a 400 MHz Spectrospin NMR spectrometer. The NMR spectrometer is an Avance III 400 spectrometer and the supplier is Bruker, France. Spectra were recorded in D<sub>2</sub>O with the following spectra acquisition parameters: 25 °C or 70 °C, relaxation delay 1 s, pulse angle 30°, acquisition time 6 s with a total of 16 scans. The routine NMR conditions chosen did not yield quantitative NMR spectra and the ratio values (*R*) determined in this work were thus apparent *R* values. This still enabled a qualitative comparison between samples, provided the NMR spectra were recorded in the exact same conditions for the samples being compared.

The apparent ratio (*R*) between octenyl succinate groups (OS) and BS, which represents the apparent ratio of substituents grafted, was determined from <sup>1</sup>H NMR spectra. *R* is calculated by the equation:

$$R = \frac{I_{OS/3}}{I_{BS/4}} \quad (1)$$

The integration of the peak (*I*<sub>OS</sub>) was determined at 0.89 ppm matching to (CH<sub>3</sub>)<sub>a</sub> protons in the alkyl residues as referred to Fig. 1. The integration of BS at 1.70–1.95 ppm corresponding to (CH<sub>2</sub>)<sub>B-C</sub> protons in the alkyl residue of BS (Fig. 1) was used to determine *I*<sub>BS</sub>.

### 2.4. Determination of the apparent aqueous solubility of modified starch

A saturated solution of each modified starch was prepared in deionized water at room temperature and pH 6 (21–22 °C). This solution was stirring during 1 h. After 24 h of decantation, the saturation was confirmed by the presence of undissolved material. A precise volume (10 mL) of supernatant was lyophilized and weighed. Apparent solubility experiments were done at three replicates for each modified starch to evaluate repeatability (Rosu et al., 2013).

### 2.5. BaP solubilization in the presence of modified starch

A BaP solution was initially prepared in DCM at a concentration of 40 mg/L. Then, 375 μL (15 μg) of this solution was deposited into a hemolysis tube allowing DCM solvent to completely evaporate at 60 °C. An aliquot of 3 mL of water (as reference) or of aqueous starch solution (at a concentration of 0.45 g/L) was added into the BaP coated hemolysis tube (Rosu et al., 2013). Tubes were incubated in the dark for 24 h. BaP molecular fluorescence in carbohydrate

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