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Synthesis of alkylated potato starch derivatives and their potential in the aqueous solubilization of benzo[a]pyrene

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ABSTRACT

For the development of renewable bioproducts able to solubilize organic persistent pollutant such as benzo[a]pyrene (BaP), modified potato starch was synthesized by alkylation. The addition of alkyl chains was performed with three different alkylation agents: epoxyalkane, alkenyl succinic anhydride and 1,4-butane sultone. Twelve alkylated starches were obtained with different molar substitutions (MS) and various alkyl chain lengths (to three carbons up to sixteen). The chemical structural characteristics were investigated by methods of ^{1}H NMR and FTIR. In comparison with the native starch, the ether modified starches showed in general an enhancement of their aqueous solubility whereas the ester modified starches stimulated the BaP aqueous solubilization. Indeed, the compounds P6 and P12, which increased 40-fold the BaP aqueous concentration, present high surfactant properties.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are very toxic chemical compounds in the environment which were identified as carcinogenic and mutagenic compounds (White, 1986). PAHs, especially high molecular weight ones such as benzo[a]pyrene (BaP), tend to persist in the environment because of their low water solubility and their tendency to be absorbed onto soil organic matter (Cerniglia, 1992; Wilson & Jones, 1993). Among the processes available for soil rehabilitation, the surfactant-enhanced remediation has been suggested as a promising remediation technology (Mulligan, Yong, & Gibbs, 2001; Zhu & Zhang, 2010). Desorption enhancement of hydrophobic organics from soil by surfactants is the key principle of the surfactant washing process. A surfactant containing both hydrophobic and hydrophilic portions can effectively enhance the aqueous solubility of hydrophobic organics by partitioning them into the hydrophobic core. Such surfactants could be used in pre-treatment washing of soil contaminated with PAHs in order to transfer them into the aqueous solution (Mulligan et al., 2001). This is a prerequisite to stimulate the first steps of PAHs oxidation (Flotron, Delteil, Padellec, & Camel, 2005) which is one of the most limiting factors for PAHs degradation by chemical or/and biological processes (Rafin, Veignie, Fayeulle, & Surpateanu, 2009; Rosu, Veignie, Surpateanu, Brabie, Miron, & Rafin, 2011).

For this purpose, polysaccharides in particular modified biopolymers derived from chitin and starch could be used (Crini, 2005; Dias, Hussain, Marcos, & Roque, 2011; Zhu & Zhang, 2010). These polysaccharides which are abundant, renewable and biodegradable resources, have been more and more investigated as potential adsorbents materials for removing pollutants from contaminated water (Crini, 2005; Kim & Lim, 1999). Nevertheless, the weak aqueous solubility of starch is also known to be a major constraint that seriously limits the development of starch-based materials. For non-food uses, starch is generally modified in order to obtain products with properties suitable for various and searched applications (Wesslén & Wesslén, 2002).

The aims of the present work were to synthesize potato starch derivatives either by esterification or by etherification in order to fulfill two main objectives: firstly to increase the aqueous solubility of modified starch and secondly to allow BaP solubilization permitting therefore its retention in polysaccharide-based materials.

2. Materials and methods

2.1. Chemicals

The materials used were as follows: benzo[a]pyrene (BaP) at 96% HPLC purity was purchased from Fluka (St. Quentin Fallaviers,

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France); propylene oxide (C3) at 99% purity; 1,4-butane sultone (C4) at 99% purity; 1,2-epoxyhexane (C6) at 97% purity, 1,2-epoxydecane (C10) at 96% purity, 1,2-epoxyhexadecane (C16) at 96% purity and sodium hydroxide (NaOH) micropearls for analysis were provided by Acros Organics (Noisy-Le-Grand, France); 2-octen-1-ylsuccinic anhydride (C12) at 97% purity and 2-dodecen-1-ylsuccinic anhydride (C16) at 95% purity were purchased from Sigma Aldrich (Steinheim, Germany). Dimethyl sulphoxide (DMSO) at 99.5% purity and potato starch (**P0**) were provided by Panreac Quimica SA (Barcelona, Espana). Methanol (MeOH), dichloromethane (DCM), pyridine and other chemicals, except when specified otherwise, were obtained in the highest purity available from Fisher Scientific (Illkirch, France). Deionized water was used throughout this work.

2.2. Synthesis of monoalkylated starch derivatives

2.2.1. Synthesis with epoxyalkane

The reaction was carried out in a round-bottomed flask in continued high agitation at 21 °C. The dried potato starch (**P0**) was dissolved in DMSO at concentration of 1 g to 10 ml (Kavitha & BeMiller, 1998; Rosu et al., 2011). After starch solubilization (at 21 °C for 48 h), the 1,2-epoxyalkane was added at molar ratios of epoxyalkane to the alcohol function present in the starch anhydroglucose unit (OH-AGU) of 3–1.0. The reaction mixture was vigorously stirred at 21 °C for 6 h. Finally, the reaction was catalyzed by NaOH addition (in a concentration of 10% based on starch). On completion of reaction, the modified starch was neutralized with hydrochloric acid and, after solvent evaporation, dialyzed during 4 days using a cellulose membrane (Medicell International, MWCO of 12–14,000 Da) and lyophilized. Three products were obtained following this procedure: hydroxypropylated starch (**P1**) alkylated with propylene oxide, epoxyhexanylated starch (**P3**) obtained with 1,2-epoxyhexane, epoxydecanylated starch (**P4**) prepared with 1,2-epoxydecane.

2.2.2. Synthesis with 1,4-butane sultone

The reaction was carried out in a round-bottomed flask in continued high agitation at 50 °C. After starch (**P0**) solubilization (at 50 °C for 48 h) in DMSO at concentration of 1 g to 10 ml, 4.6 mol of 1,4-butane sultone were added for each mole of OH-AGU. The reaction mixture was vigorously stirred at 50 °C for 14 h. The reaction was catalyzed by NaOH addition (in a concentration of 90% based on starch). On completion of the reaction, the final procedure was followed as described previously. One product was obtained: sulfobutylated starch (**P2**).

2.2.3. Synthesis with alkenylsuccinic anhydride

After starch (**P0**) solubilization (at 21 °C for 48 h) in DMSO at concentration of 2 g to 40 ml, 0.03 mol of alkenyl succinic anhydride solubilized in 3.4 ml pyridine were added at molar ratios of alkenyl succinic anhydride to the OH-AGU of 1–10. The reaction was carried under nitrogen atmosphere for 24 h. On completion of the reaction, the final procedure was followed as described previously. Two products were obtained: octenyl succinic anhydride starch (**P5**) and dodecenyl succinic anhydride starch (**P6**).

2.3. Synthesis of bialkylated starch derivatives

The same procedure was followed for the synthesis of bialkylated starch derivatives, using hydroxypropylated starch (**P1**) previously obtained as stock product. Six products were obtained: hydroxypropyl-epoxyhexanylated starch (**P7**), hydroxypropyl-sulfobutylated starch (**P8**), hydroxypropyl-epoxydecanylated starch (**P9**), hydroxypropyl-epoxyhexadecanylated starch (**P10**), hydroxypropyl octenyl succinic anhydride starch (**P11**) and hydroxypropyl dodecenyl succinic anhydride starch (**P12**). All the products synthesized are presented in Table 1 and Fig. 1.

Table 1
Characteristics of alkylated potato starches.

Code	Alkyl chain length	Chemical link	MS	Aqueous solubility (g/L)
Monoalkylated starch				
P0	–	–		0.35
P1	C3	Ether	1.70	14.41
P2	C4	Ether	1.00	20.63
P3	C6	Ether	0.06	15.64
P4	C10	Ether	0.03	3.98
P5	C12	Ester	0.32	2.79
P6	C16	Ester	0.63	0.82
Bialkylated starch				
P7	C3 + C6	Ether	0.04	16.72
P8	C3 + C4	Ether	2.80	18.63
P9	C3 + C10	Ether	0.01	15.64
P10	C3 + C16	Ether	0.02	2.68
P11	C3 + C12	Ester	1.63	4.41
P12	C3 + C16	Ester	2.38	2.26

2.4. Structural characteristics of starch

2.4.1. Infrared spectroscopy

The Fourier Transform Infrared (FTIR) spectroscopy analyses were done using a FTIR Bruker Tensor 27 apparatus. For all the products synthesized, FTIR spectra were recorded with a resolution of 4 cm^{-1}, with a total of 8 scans, over a region of 400–4000 cm^{-1}.

2.4.2. ^1H NMR spectroscopy

NMR spectra were measured with a 250 MHz Spectrospin NMR spectrometer (Bruker, France). Spectra were recorded either in deuterated water (D_2O) or in deuterated DMSO (DMSO-d_6), with the following spectra acquisition parameters: ambient temperature, relaxation delay 1 s, pulse angle 30 °C, acquisition time 6 s and with a total of 50 scans.

2.4.3. Determination of the aqueous solubility

In order to assess the aqueous solubility, a saturated solution of each modified starch (**P1**–**P12**) was done in deionized water at ambient temperature (21–22 °C). After 24 released hours, 10 mL of the solubilized starch were lyophilized and weighed. The same procedure was performed with native starch (**P0**) as control. The solubility was evaluated in three replicates for native and each modified starch and the solubility mean was expressed in Table 1.

2.4.4. Calculation of the molar substitution

MS represents the average number of substituents per mole of OH-AGU. The MS of each hydroxypropylated starch was determined from NMR spectra according to the method of De Graaf, Lammers, Janssen, and Beenackers (1995). The MS of other alkylated starches was calculated from the integral of the peak corresponding to CH_2 protons in the alkyl residues and the integral of the peak corresponding to the single proton in anomeric equatorial position of anhydroglucose unit (Bien, Wiege, & Warwel, 2001). The MS of each modified starch was expressed in Table 1.

2.5. BaP solubilization in the presence of modified starch

BaP was initially dissolved in DCM (40 mg/L), then deposited into a hemolysis tube by the addition of 375 μL of BaP solution and allowing DCM solvent to evaporate. 3 mL of water (as reference) or tested potato starch (native or modified one) was added into the hemolysis tube. All concentrations of carbohydrate polymers were tested at 5 mM equivalent AGU of starch. The tubes

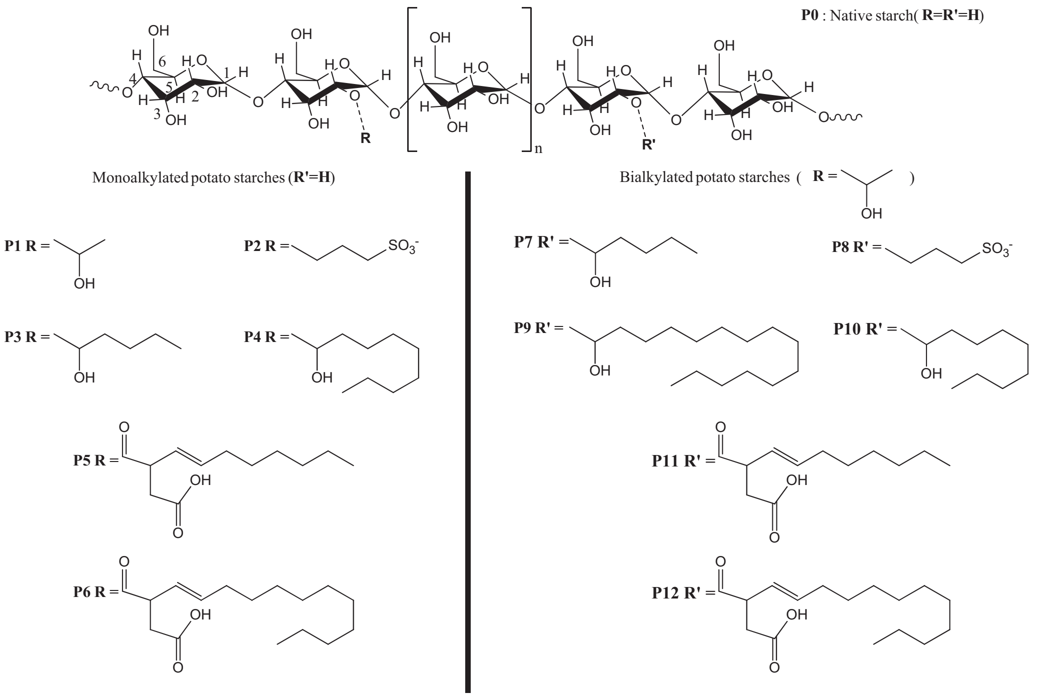


Fig. 1. Chemical structure of starch and the most probable structures of the alkylated starches (for the starch codes, refer to the text).

were incubated in the dark for 4 days. BaP fluorescence in carbohydrate polymer solutions was analyzed on a Perkin Elmer LS B50 spectrofluorimeter (excitation 295 nm, emission 406 nm, time integration 10 s according to Veignie, Rafin, Landy, Fourmentin, & Surpateanu, 2009). Three separate experiments were conducted under the same conditions for calculating the BaP solubilization mean. Results are expressed as BaP concentration in aqueous phase versus modified starch solubility (Fig. 8).

3. Results and discussion

3.1. Characterization of the initial stock starch

The first goal of the present work was to use either native starch (**P0**) or hydroxypropylated starch (**P1**), as starting materials, for further modifications with epoxides or anhydrides with various alkyl chain lengths, in order to obtain monoalkylated and bialkylated starches (Table 1). As alkylation by nucleophilic substitution could occur at 2,3,6 positions of OH-AGU given therefore many starch derivatives, we chose to represent the chemical structure of **P0** and the most probable structures obtained for the alkylated starches (Fig. 1), according to Steeneken and Woortman (1994).

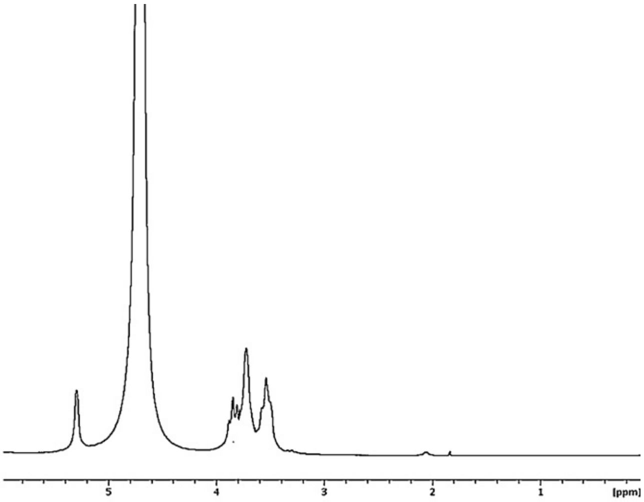
Fig. 2 presents the ^{1}H NMR spectrum in D_2O and the FTIR spectrogram of the native potato starch (**P0)** as reference. The NMR spectrum of **P0** was characterized by a very broad and complex multiple proton resonance signals between 3.35 and 4.20 ppm due to protons of the starch AGU. The proton signal around 5.20–5.45 ppm was attributed to the anomeric equatorial proton of the starch AGU (De Graaf et al., 1995). The detailed ^{1}H NMR data for **P0** in D_2O are δ (ppm): 3.80–4.10 (m, $H_{2,3,4,5,6}$); 5.20–5.45 (s, H_1); and in DMSO-d_6, δ (ppm): 3.45–3.80 (m, $H_{2,3,4,5,6}$); 4.60 (s, OH-6); 5.20 (m, H_1); 5.65 (m, OH-3,2), as indicated in Fig. 2.

In the **P0** FTIR spectrum, the bands around 1021, 1080 and 1156 cm^{-1} in the fingerprint region corresponded to the C—O ether stretching vibration in glucose bonds (Fang, Fowler, Sayers, & Williams, 2004), while the bands at 1470 and 1650 cm^{-1} were ascribed to absorbed water (Dragunski & Pawlicka, 2001). The band at 2900 cm^{-1} was attributed to the asymmetrical stretching of the C—H bond. The wide band observed around 3400 cm^{-1} can be attributed to the O—H stretching and ascribed to the formation of inter and intramolecular hydrogen bonds (Mathew & Abraham, 2007).

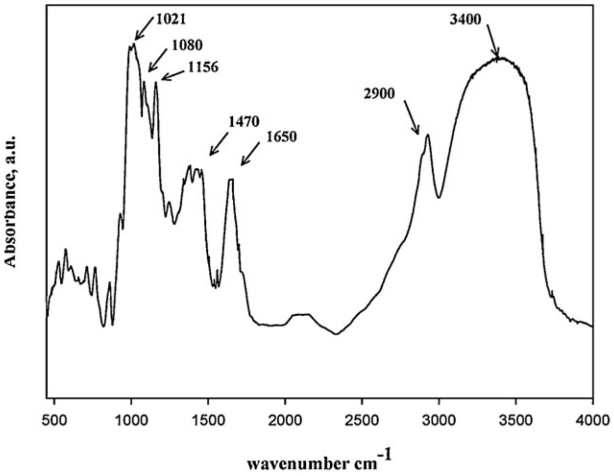
The ^{1}H NMR spectrum of the hydroxypropylated starch **P1** (Fig. 3) showed not only the characteristic proton peak of starch but also clearly the apparition of the singular proton resonance signal at 1.15–1.25 ppm indicating the grafting of the alkyl chain C3 on starch structure (Rosu et al., 2011; Teramoto, Motoyama, Yosomiya, & Shibata, 2002). Moreover, the alteration of the chemical shifts of anomeric protons (5.5–5.7 ppm) observed in the spectrum could be an indication of the substitution at position C-2. The detailed ^{1}H NMR data for **P1** in D_2O are δ (ppm): 1.25 (s, CH_3); 2.25 (s, CH_2); 3.80–4.10 (m, $H_{2,3,4,5,6}$); 5.45 (s, H_1). The **P1** medium MS product was 1.7. (De Graaf et al., 1995). Infrared spectroscopy was used to confirm the graft modification of starch with the propylene oxide (Fig. 3). In the **P1** FTIR spectrum, the band around 2970 cm^{-1} corresponded to the stretching of the C—H (CH_3) group (Dragunski & Pawlicka, 2001).

3.2. Characterization of the modified starch

Fig. 4 represents ^{1}H NMR spectra of the monoalkylated ethers starch derivatives in D_2O. The NMR spectra confirmed the success of alkylation via the apparition of the proton resonance signals around 1.15–1.25 ppm. Nevertheless, the low MS values obtained, respectively 0.06 and 0.03 for **P3** and **P4** (i.e. 30-fold and 60-fold inferior in comparison with the MS of **P1**) indicated unsuccessful alkylated graft, due probably to a lower electrophilic reactivity of alkyl chains with a higher number of carbon atoms in comparison with a C3 alkyl chain. The FTIR spectra of **P3** and **P4** confirmed the presence of the band around 2970 cm^{-1} corresponded to the stretching of the C—H (CH_3) group (spectra not shown). The sulfobutylated starch (**P2**) showed a MS value of 1 indicating an acceptable graft modification of starch. In the **P2** NMR spectrum in D_2O, the peak at 3.01 ppm results from the 2 Hs of the —CH_2-group which bonds to the SO^{3-} group (Fig. 4). The peak at 1.82 ppm includes 4 Hs which belong to the 2 central-CH_2-groups of the sulfobutyl group. Similar results

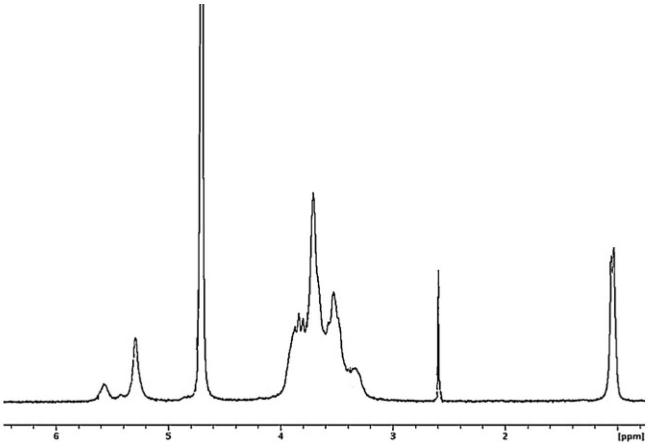


(a) ^{1}H NMR spectrum of gelatinized potato starch (**P0**)

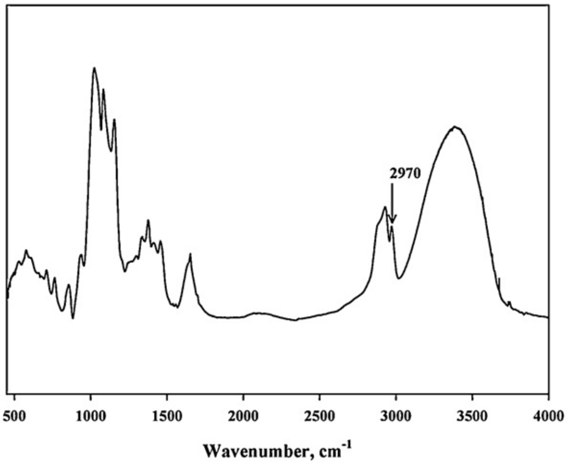


(b) FTIR spectrum of native potato starch (**P0**)

Fig. 2. (a) ^{1}H NMR spectrum of gelatinized potato starch in D_2O (**P0**) and (b) FTIR spectrum of native potato starch (**P0**).



(a) ^{1}H NMR spectrum of hydroxypropylated potato starch in D_2O (**P1**)



(b) FTIR spectrum of hydroxypropylated potato starch (**P1**)

Fig. 3. (a) ^{1}H NMR spectrum of hydroxypropylated potato starch in D_2O (**P1**) and (b) FTIR spectrum of hydroxypropylated potato starch (**P1**).

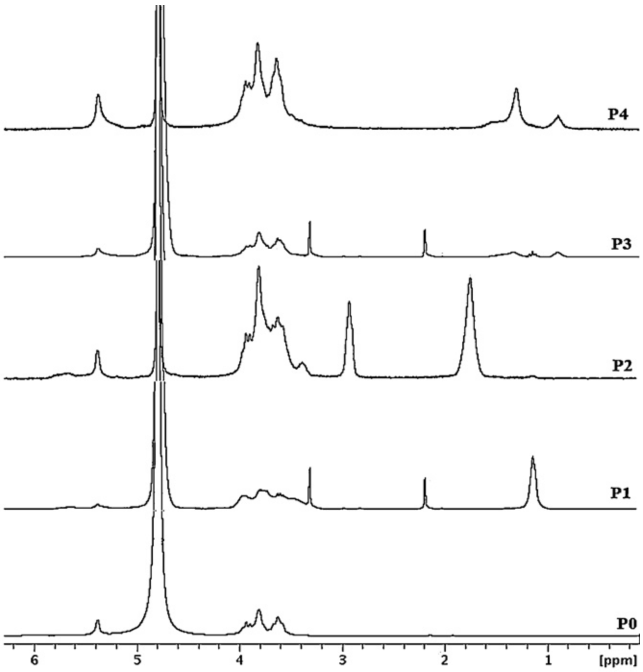
were also observed in the NMR spectra of sulfobutyl ether cyclodextrin derivatives (Qu, Tucker, & Christian, 2002; Rogmann, Seidel, & Mischnick, 2000). The **P2** FTIR spectrum was not very informative concerning specific absorption bands of sulfobutyl group. Nevertheless, we observed a reduction of absorbance around 3400 cm^{-1} due to the disappearance of OH stretching vibration of OH-AGU. This result was explained by the high MS of **P2**.

Fig. 5 represents the ^{1}H NMR spectra of the monoalkylated ester starch derivatives (**P5** and **P6**) obtained with alkenyl succinic anhydride. The presence of the succinic anhydride is confirmed by the apparition of peaks around 0.92 ppm and 1.38 ppm assigned to the methyl, methylene and methenyl group of succinic anhydride starch (Chi, Xu, Xue, Song, Zhang, & Wang, 2007). The anhydride acids are more effective to graft alkyl chains than the epoxides resulting in higher MS. For example, **P5** presents a 10-fold superior MS (0.32) in comparison with **P4** (0.03), although the concentration of anhydride was lower during the reaction (respectively 0.1 mol of anhydride and 3 mol of epoxide). In the FTIR spectrograms of **P5** and **P6** (data not shown), some characteristics peaks were found at 1734 cm^{-1}, corresponding to the stretch ester carbonyl group, and at 1571 cm^{-1} relating to the asymmetrical stretching vibration of carboxylate RCOO$^-$ (Chi et al., 2007).

The same procedure was followed for the synthesis of the bialkylated starch, using hydroxypropylated starch (**P1**) previously obtained as stock product. ^{1}H NMR spectra of bialkylated ether-ether starch derivatives in D_2O confirmed the modification of hydroxypropylated starch (**P1)** by the appearance of the supplementary peaks around 0.85–1.25 ppm assigned to the CH_3 and CH_2 groups of anhydride (Fig. 6). The three following products **P7**, **P9** and **P10** obtained by alkylation using a ether bond etherification showed low MS (respectively 0.04, 0.01 and 0.02) indicating again an unsuccessful grafting in our chemical synthesis, whatever the length of the alkyl chain (superior to 6 atoms of carbon). The FTIR spectra of **P7**, **P9** and **P10** confirmed the presence of the band around 2970 cm^{-1} corresponded to the stretching of the C—H (CH_3) group (spectra not shown).

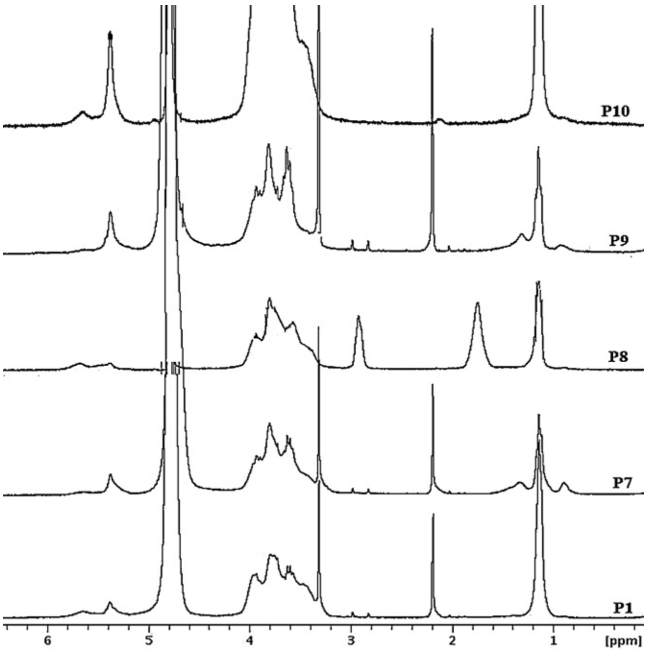
Concerning **P8** prepared by addition of 1,4-butane sultone to **P1**, this product had a MS value of 2.8. Its NMR spectrum allowed to identify clearly the proton resonance signal around 1.18–1.29 ppm indicating the presence of the propyl group on starch structure (Fig. 6) and also the presence of the sulfobutyl groups (peaks at 1.63 ppm and at 3.02 ppm) as for the monoalkylated **P2** (Fig. 4). On **P8** FTIR spectrum, a reduction of the absorbance around 3400 cm^{-1} was again observed due to the disappearance of OH stretching vibration of OH-AGU as observed in the monoalkylated **P2**. *This result was corroborated the high MS of* **P8**.

At least, dealing with both bialkylated products obtained by esterification (**P11** and **P12**), their NMR spectra in DMSO-d$_6$ indicated the success of the bialkylation synthesis (Fig. 7). Indeed, the 2-octen-1-ylsuccinic anhydride ($C_{12}H_{16}O_3$) was proofed by the apparition of peaks around values 0.90 ppm and 1.40 ppm (Chi et al.,



P0: Potato starch
P1: Hydroxypropylated starch
P2: Sulfobutylated starch
P3: Epoxyhexanylated starch
P4: Epoxydecanylated starch

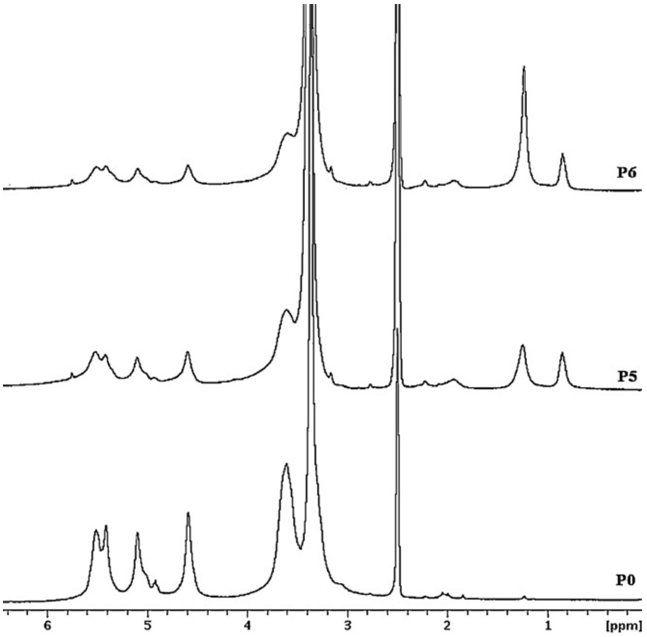
Fig. 4. ^{1}H NMR spectra of monoalkylated ethers starch derivatives in D_2O.



P1: Hydroxypropylated starch
P7: Hydroxypropyl-epoxyhexanylated starch
P8: Hydroxypropyl-sulfobutylated starch
P9: Hydroxypropyl-epoxydecanylated starch
P10: Hydroxypropyl-epoxyhexadecanylated starch

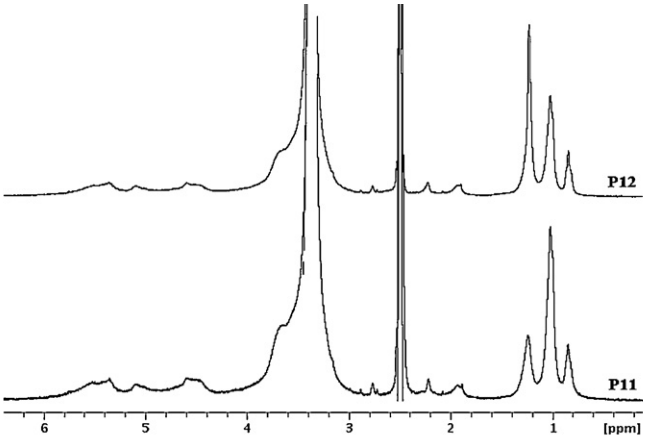
Fig. 6. ^{1}H NMR spectra of bialkylated ether–ether starch derivatives in D_2O.

2007; Marcazzana, Vianelloa, Scarpab, & Rigoa, 1999). Moreover, the permanence of the proton resonance signal at 1.25 ppm confirms the presence of propoxylation (C_3) of the stock product. In the **P11** FTIR spectrogram (data not shown), the characteristics peaks were similar to those obtained with **P5** and **P6**. The high values of MS obtained (1.63 and 2.38 respectively for **P11** and **P12**) indicated that the esterification was more effective on hydroxypropylated starch (**P1**) than on the native potato starch (**P0**).



P0: Potato starch
P5: Octenyl succinic anhydride starch
P6: Dodecenyl succinic anhydride starch

Fig. 5. ^{1}H NMR spectra of monoalkylated esters starch derivatives in DMSO-d_6.



P11: Hydroxypropyl-octenyl succinic anhydride starch
P12: Hydroxypropyl-dodecenyl succinic anhydride starch

Fig. 7. ^{1}H NMR spectra of bialkylated ether-ester starch derivatives in DMSO-d_6.

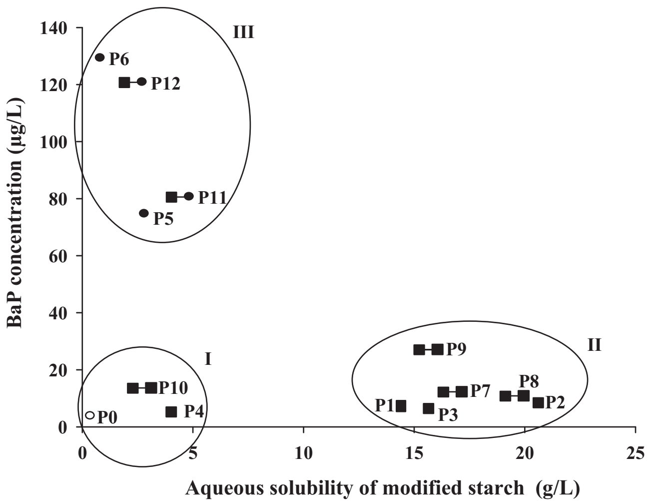


Fig. 8. Relationship between the aqueous solubility (g/L) and the BaP solubilization (µg/L) for all the starch products studied. ○, native starch; ●, monoalkylated ester starch; ■, monoalkylated ether starch; ■-■, bialkylated ether-ether starch; ■-●, bialkylated ether–ester starch. For the explanation of the three groups (I, II and III), refer to the discussion.

3.3. *Solubility of starch derivatives versus BaP desorption and solubilization in aqueous phase*

In order to characterize the properties of modified starch obtained, two parameters were then used: firstly the aqueous solubility of modified starches, expressed on X-axis in g/L and secondly BaP solubilization expressed on Y-axis in µg/L. Fig. 8 led the classification of the modified starch products in 3 groups, labeled I to III, according to both these parameters. Group I contained the native potato starch **P0** characterized by low water solubility and also low ability to desorb BaP. Products **P4** and **P10** also characterized by a weak solubility (< to 5 g/L) and a weak efficiency to desorb BaP (< to 20 µg/L) belong to the same group. As explained before, these compounds, obtained both by etherification, either monoalkylated or bialkylated, had a low MS (0.02–0.03) indicating a weak chemical modification. So, their chemical properties were similar to those of **P0**.

The group II included six products: **P1**, **P2**, **P3** (all obtained by monoalkylation with ether) and **P7**, **P8**, **P9** (obtained by bialkylation with ether). These modified starches displayed a higher affinity for polar solvent such as water as their own water solubility was superior to 14 g/L. The length of the alkyl chains grafted was quite short (≤10 atoms of carbon). This result indicated that the addition of short alkyl chains did not stimulate the hydrophobic character of the modified products but rather their hydrophilic properties. This enhancement of the hydrophilic properties was probably due to the hydroxyl groups performed during the conversion of the epoxide reactions. Nevertheless, except for **P1**, these compounds had a low MS (≤0.06). So, their BaP desorption properties were not enhanced in comparison with the native starch. In order to enhance hydrophobic properties of starch derivatives for various applications, starch is commonly modified through reactions with long alkyl epoxides in DMSO solution. In order to reach MS values above 1.0, other synthesis parameters could be investigated such as the reaction duration (Wesslén & Wesslén, 2002), the reactants concentrations, the starch source and also the pressure in order to optimize the reaction parameters and consequently yield and MS (Bien et al., 2001).

Concerning products **P2** and **P8**, which are the most soluble compounds, their high polar characters were linked to the presence of the sulfonate groups. Rogmann et al. (2000) reported also that the sulfonylbutylation with 1,4-butane sulfone gave appropriate water soluble cyclodextrins due to the ionic character of the sulfonic acid residues. In our study, the hydrophilic property of the starch products obtained decreased dramatically their ability to desorb BaP.

The modified starch products within group III, viz. **P5**, **P6**, **P11** and **P12**, obtained by esterification, presented the highest capacity to desorb BaP (> to 60 µg/L) despite a quite low water solubility. These 4 products were obtained by esterification of starch with alkenyl succinic anhydrides, either C12 or C16. The length of the alkyl chains (>10 atoms of carbon) and the degree of substitution stimulated the hydrophobic character of the starch esters and consequently, their efficiency to desorb and solubilize BaP. Modifications of starch with alkenyl succinic anhydrides results in starch products with amphiphilic side-chains. Jeon, Viswanathan, and Gross (1999) reported that the alkenyl succinates are a family of highly versatile derivatives, as they obtained either modified starches with high hydrophilicity or high hydrophobicity, depending on the length of the alkenyl group and the degree of substitution. Tesch, Gerhards, and Schubert (2002) and Hui, Qi-he, Ming-liang, Qiong, and Guo-qing (2009) obtained also starch effective as an emulsifier, due to the addition of hydrophobic side chains to the originally merely hydrophilic starch molecule, after alkyl succinic anhydride modifications.

Twelve different products were synthesized by using two common chemical modifications of starch, either etherification or esterification. Compared to the native starch, the alkyl succinic anhydrides present high capacity to desorb BaP. This enhancement of BaP desorption is a prerequisite permitting initial oxidation of this pollutant in soil matrices. Moreover, the ester linkage, which is a common biomolecule linkage, is probably more biodegradable than the ether linkage (Song, He, Ruan, & Chen, 2006). These modified properties widen their applications in order to develop an environmentally friendly treatment of PAHs for soil remediation approaches. In wastewater treatment, increasing attention has been recently given to starch used as sorbent for removing pollutant, in particular heavy metals, aromatic molecules, dyes (Crini, 2005; Zhang & Chen, 2002). This requires chemical derivatization to improve starch sorption capacities (Cova, Sandoval, Balsamo, & Müller, 2010) in order to be used either as soil washing process or as a first step before oxidation processes (Rosu et al., 2011).

4. Conclusions

Three methods of preparing alkylation of starch (from either native potato starch or hydroxypropylated starch) were developed: by etherification with 1,2-epoxyalkanes, by etherification with 1,4-butane sultone and by esterification with succinic anhydride. Thus, starch derivatives with various MS were obtained and characterized by NMR and FTIR. In the experimental conditions chosen, the esterification was more performant than the etherification with 1,2-epoxyalkanes and especially on hydroxypropylated starch (**P1**) than on the native potato starch (**P0**). Furthermore, the aqueous solubility of the starch derivatives and their ability to solubilize the BaP depends also on the starch modifications. In view of BaP solubilization, a prerequisite in polluted soil treatment, the alkyl succinic anhydrides present the highest capacity to desorb BaP. Further research will be conducted for obtaining a right balance between hydrophobic character of starch derivatives and starch aqueous solubility.

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