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PII: S0144-8617(97)00011-8

Carbohydrate Polymers 32 (1997) 209–212
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0144-8617/97/$17.00 + .00

Thallium(I) starchate

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(Received 12 June 1996; revised version received 30 October 1996; accepted 10 December 1996)

Thallium(I) starchates of various degrees of substitution were prepared from potato, corn and hydrogen starch by reaction with either thallium(I) hydroxide or with thallium ethanolate. After thallation, hydrogen and potato starch exhibited typical characteristics of gelation whereas that of corn starch did not. The chemical structure of the products was investigated using X-ray photoelectron spectroscopy. Potato starch was thallated and contained chemically bound thallium whereas corn starch formed complexes with thallium(I) hydroxide and ethoxide. © 1997 Published by Elsevier Science Ltd

INTRODUCTION

Organic thallium(I) compounds are widely used in organic synthesis. Because of the properties of Tl—C and Tl—O bonds, corresponding thallium(I) derivatives are utilized in the generation of nucleophiles (Menzies and Kieser, 1927; Menzies, 1947; McKillop *et al.*, 1970; Taylor and McKillop, 1970). On the other hand, thallium(I) compounds are strongly toxic, they are absorbed either via the respiratory tract, alimentary canal or via the skin. Thallium is accumulated in the liver, brain and muscles. The peripheral nerves are damaged by deterioration of the nerve insulating coat. Skin tissues and glands, as well as hair bulbs, suffer extended damage, but respiratory paralysis, and heart and vessel collapse bring about death. Toxicity symptoms appear after an induction period lasting from hours to 4 days (Doull *et al.*, 1980; Bogdanik, 1988). Because thallium compounds are odorless and tasteless, they are utilized as rat poison. The properties of thallium(I) compounds prompted us towards the synthesis of thallium(I) derivatives of starch as a novel synthon in starch chemistry as well as a rat poison. Derivatives bearing the Tl—O bonds were prepared from potato, hydrogen and corn starch using either thallium(I) hydroxide or ethoxide.

MATERIALS AND METHODS

Materials

Potato starch was manufactured by Potato Industry Enterprise in Niechlów (Poland) in 1991. Corn starch 'Bermagold' was kindly provided by Instytut Hodowli i Aklimatyzacji Roslin in Radzików at Warsaw (Poland).

Thallium metal (99.9%) as well as thallium(I) ethoxide were products of Merck.

Hydrogen starch was prepared according to Gibinski (1987) by rinsing native potato starch with 0.1 M hydrochloric acid followed by redistilled water.

Thallium(I) hydroxide was prepared from thallium metal via thallium(I) sulfate according to Galecki (1964).

Methods

(i) Five grams of air-dried maize or potato, or wet hydrogen starch was suspended in distilled water (20 ml). The suspension was stirred at room temperature with either 0.05, 0.2 M or saturated aqueous thallium(I) hydroxide (50 ml). Stirring was continued for 24 h, the supernatant was then decanted and the residue was rinsed with absolute ethanol until the filtrate was neutral to litmus. The colorless product was filtered and dried in a vacuum desiccator over KOH and finally in an oven at 40°C to a constant weight.

(ii) Five grams of oven-dried starch (120°C, 3 h) was suspended in 20 ml absolute ethanol and treated on stirring either at room temperature or under reflux with thallium(I) ethoxide (either 2.5 or 5 g). The reactions lasted 24 h. The supernatant was then decanted and the residue processed as under method (i).

The thallium content of the products was determined using an atomic absorption spectrometer ASA Phillips Pll-9100X with the Tl lamp of Phatron. The samples

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(0.2 g) were mineralized in aqua regia (5 cm^3) by heating the suspensions in a MLS-1200-MEGA microwave oven according to the standard program recommended by the manufacturer (1 min at 250 W, 2 min at 0 W, 5 min at 250 W, 5 min at 400 W and 5 min at 600 W). The mineralized samples were then diluted to 25 cm^3 with distilled water.

The characteristics of the gelation were recorded using a Rheotest-2 rotary viscometer according to the basic program.

The X-ray photoelectron spectra were recorded with a Physical Electronics Model 5500 Multitechnique Surface Analysis System. The pass energy was 29.350 eV using a Mg source at 300 W, and the samples were

Table 1. Thallium(I) content in thallium(I) starchate prepared from thallium(I) hydroxide and thallium(I) ethoxide

	Thallium content, %, concentration of TlOH (TlOEt)[a] and notation used in Table 2			
Starch	0.05 M	0.125M	0.2 M	Saturated
Potato	0.55 P1		1.35 P2	37.2 P3
	(0.49) P4	(27.41)* P7	(0.70) P5	(0.86) P6
Maize	0.25 M1		1.25 M2	35.6 M3
	(3.19) M4	(26.72)* M7	(2.35) M5	(4.00) M6
Hydrogen	0.4 H1		1.35 H2	33.7 H3

[a]If not denoted by asterisks the samples were prepared by a treatment of starch with TlOH at room temperature for 24 h. Otherwise the sample was refluxed in 0.125 M ethanolic TlOEt for 24 h.

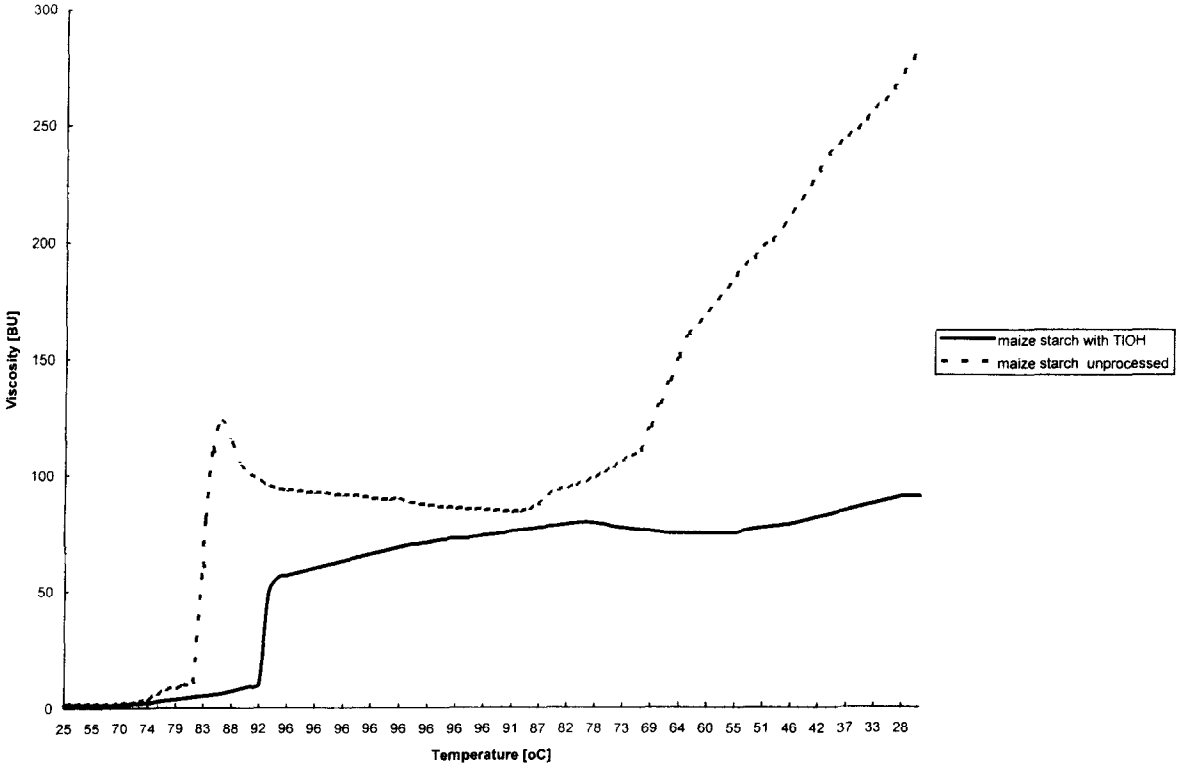

Fig. 1. Characteristic of gelation of maize starch unprocessed (broken line) and maize starch treated with 0.05 M aq. TlOH on cold (solid line).

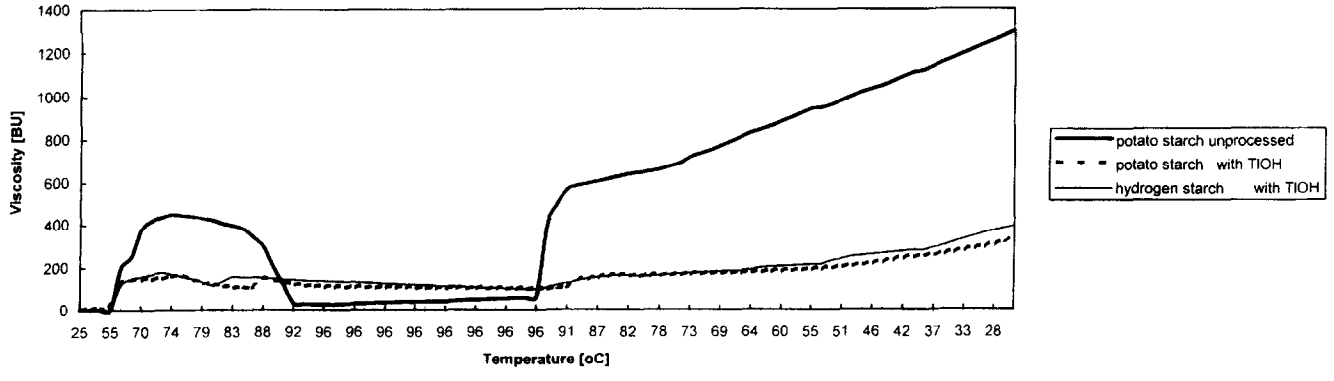

Fig. 2. Characteristic of gelation of potato starch unprocessed (solid line), treated with 0.05 M aq. TlOH (dotted line) and hydrogen starch treated with 0.05 M aq. TlOH (thin solid line).

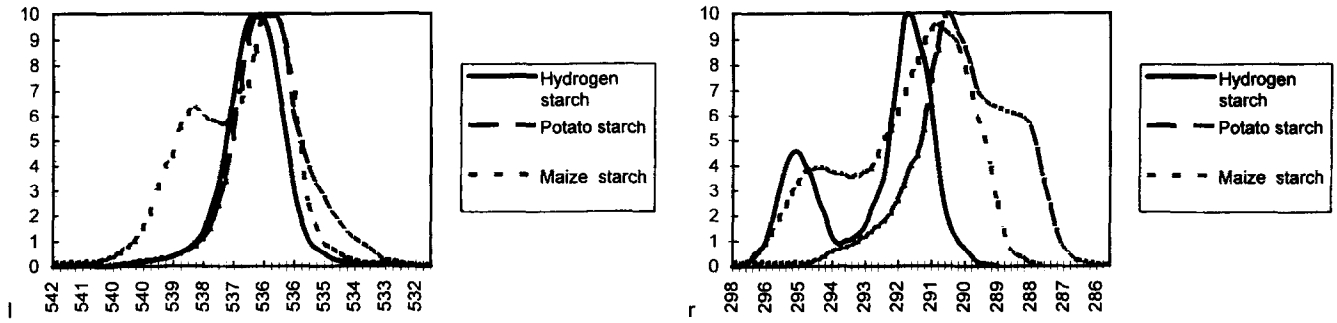

Fig. 3. The fragments of the XPES spectra after the gaussian analysis for samples H4 (solid line), P4 (broken line) and M4 (pointed line). The binding energy for the oxygen atoms (left portion of the spectra) and carbon atoms (to the right) is given in eV.

Table 2. Parameters of XPES spectra of thallated starch after the gaussian analysis of the spectral curves

Sample[a]	Band positions (eV) [fitted peak areas (%)]
Potato starch	C: 285(28); 286.5(51); 287.7(14); 288.4(7)
	O: 531.6(10); 532.9(83); 534.2(7)
Corn starch	C: 285(33); 287.7(11); 288.5(5)
	O: 531.8(16); 533.1(71); 534.0(12)
Potato starch + TiOH	Tl: 117.8(21)
	C: 285(55); 285.7(6); 286.8(5); 288.6(34)
	O: 529.2(17); 530.7(70)
Thallated hydrogen starch	
H1	Tl: 119.5
	C: 285(43); 286.5(39); 287.8(12); 289.6(6)
	O: 531.7(32); 533(68)
H2	Tl: 119.7
	C: 285(26); 286.5(45); 288.1(16); 290.0(13)
	O: 531.7(50); 533(50)
H3	Tl: 118.6
	C: 285(58); 285.6(6); 286.5(6); 288.5(30)
	O: 530.6 (100)
Thallated maize starch	
M1	Tl: 119.5
	C: 285(35); 286.6(46); 288.0(18); 289.5(1)
	O: 531.6(12); 533.0(88)
M2	Tl: 119.1
	C: 285(44); 286.5(30); 287.6(21); 289.3(5)
	O: 531.2(17); 532.7(15)
M3	Tl: 118.7
	C: 285(65); 286.3(8); 286.8(5); 288.6(23)
	O: 530.6(85); 532.7(15)
M4	Tl: 118.8
	C: 285(54); 286.4(24); 288.4(21)
	O: 530.6(61); 532.6(39)
Thallated potato starch	
P4	Tl: 119.4
	C: 285(37); 286.6(48); 288.1(12); 289.6(4)
	O: 531.8(28); 533.0(72)
P5	Tl: 119.4
	C: 285(21); 286.6(57); 288.1(18); 289.7(4)
	O: 531.4(26); 532.9(74)
P6	Tl: 118.7
	C: 285(68); 285.9(4); 286.8(4); 288.6(24)
	O: 530.7(93); 532.5(7)
P7	Tl: 119.4
	C: 285(50); 286.5(47); 287.8(14); 288.6(3)
	O: 531.2(13); 532.8(87)

[a]See Table 1 for sample notation.

mounted on two-side Scotch tape. The positions of the peaks were normalized to the position of the main component of the C1s band at 285 eV. This value was reported by Gelius *et al.* (1970) for the carbon atom in inositol.

RESULTS

Thallated starch was characterized by the thallium content given in Table 1 as well as by the characteristics of gelation presented in Figs 1 and 2.

The analysis of the XPES spectra (some of which are presented in Fig. 3) is given in Table 2.

DISCUSSION

Based on the results of the reaction of thallium(I) hydroxide with sucrose and cellulose, one may suppose that starch could also be thallated by this reagent. The products of thallation of sucrose (Purves and Hudson, 1937) and cellulose (Assaf *et al.*, 1944) with thallium(I) hydroxide were identified as sucrose tetrathallate and cellulose di- and trithallate, respectively. On the other hand the products of the reaction of starch with sodium hydroxide (Champetier and Yovanovitch, 1951; Yovanovitch, 1951) and other hydroxides of group I and II nontransition metals (Lloyd, 1911; Rakovskii, 1912; Rakowski, 1912, 1913; Leach *et al.*, 1961; Deulin, 1970; de Willigen and de Groot, 1971), as well as with ammonia and copper(II) hydroxide (Kuchikata *et al.*, 1979) and aluminum hydroxide (Ivekovic *et al.*, 1956; Sato, 1958) have been characterized as starch metal hydroxide either sorption or inclusion complexes. Therefore, the results of the starch thallation needed a thorough insight.

The amount of thallium bounded to the starch depended on the concentration of the hydroxide in the reaction mixture. When the starch was treated with thallium(I) hydroxide, cold potato starch showed better thallium uptake than maize starch, indicating that granules of potato starch are more accessible to the reagent than maize starch granules. This is not surprising because lipids are usually present in maize starch, making the interior of its granules more hydrophobic. The preparation of hydrogen starch always destroys the starch granules which opens the granules interior to the reagents. Thus, if the thallation of starch is the result of the formation of starch thallate the yield of the thallium uptake should be higher for hydrogen starch than for native potato starch. The yields of thallation shown in Table 1 suggest that the thallium(I) hydroxide formed complexes with starch and not the corresponding starch thallate. The characteristics of gelation of unprocessed free starches and those treated with thallium hydroxide show a remarkable destruction of native potato and hydrogen potato starch on gelatinization. The destruction could be a result of gelatinization in the presence of basic hydroxide.

ACKNOWLEDGEMENTS

The authors are very much indebted to the Polish Research Council (KBN) for Grant No. 5 0738 91 01.

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