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Quaternization/cross linking of starch with choline chloride/epichlorohydrin

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Starch (S) was quaternized/cross linked with choline chloride (CC)/epichlorohydrine (E) in one step with the goal of preparing ion exchangers under optimal conditions. At the molar ratio of S:E:CC:NaOH:H_2O = 0.005:0.025:0.005:0.1:0.2 the yield of water-insoluble product was 237% at 2.37% nitrogen content and 64% of CC was incorporated. With futher increase of E (up to 0.06) at 0.01 mol of S and CC the yield could be further improved (up to 313%), although the nitrogen content and the amount of CC reacted did not improve. At the highest nitrogen content the E:CC = 5 molar ratio was used. This indicates that under optimal conditions on five hydroxyprophyl groups there might be four cross links of starch and one quaternary ammonium group linkage. The use of 0.01 mol of S is more beneficial because a larger ion exchanger quantity could be produced in this way. The expected structures in water-insoluble products were confirmed by solid-state ^{13}C NMR and elemental analysis.

INTRODUCTION

For the quaternization of polysaccharides and lignocellulosics chlorine-containing compounds are used. However, environmental concerns call for the substitution of these chemicals with halogen-free compounds (Hileman *et al.*, 1994). Apart from quaternizing agents, epichlorohydrin, used as a cross linker, also causes environmental concern. It is difficult to find an environmentally safe cross linking agent so we decided to use only one compound to covalently bind chlorine instead of two, as we did previously (Šimkovic, 1996). In this paper we use choline chloride (CC) as the quaternary compound and crosslink it with starch using epichlorohydrin. The expected chemistry can be summarized as:

$$a\mathrm{S-OH} + b\mathrm{E} + c\mathrm{HO-CH_2CH_2N^+(CH_3)_3Cl^-} + d\mathrm{NaOH} + e\mathrm{H_2O} \rightarrow$$

$$m\mathrm{S-O-CH_2-CH(OH)CH_2-O-S-O-CH_2-CH(OH)-CH_2-O-R} + n\mathrm{NaCl} + o\mathrm{H_2O} + p\mathrm{NaOH}$$

where R represents hydrogen or the $(CH_2)_2N^+(CH_3)_3^-OH$ group and *a* to *p* are the amounts of chemicals used and the amounts of products formed. Our goal was to prepare a water-insoluble ion exchanger at the highest possible yield and nitrogen content with minimal consumption of chemicals. The products were analysed by solid-state ^{13}C NMR spectroscopy and elemental analysis.

EXPERIMENTAL

Experiments were run in closed glass vials (200 ml) under vigorous stirring at room temperature (22°C) for 24 h in the molar ratios of chemicals listed in Table 1. Subsequently the mixtures were washed with water until a neutral reaction of eluent on pH paper was obtained. The residue was washed with 96% ethanol and dried in vacuo. All the chemicals were commercial grade and all the methods were as described previously (Šimkovic *et al.*, 1996).

RESULTS AND DISCUSSION

The properties of the products obtained in all experiments are listed in Table 1. With the minimal molar amounts of components used (S:E:CC:NaOH:H_2O = 0.01:0.01:0.005:0.1:0.2) only

Table 1. Results of quaternization/cross linking of starch[a] with CC/E

Sample	Moles of reactants				Yield[b](%)	N[c](%)	BondedCC[d]
	E	CC	NaOH	H_2O			
1	0.01	0.005	0.1	0.2	88[e]	1.13	23
2	0.015	0.005	0.1	0.2	114[e]	0.94	25
3	0.02	0.005	0.1	0.2	127[e]	0.74	22
4	0.025	0.005	0.1	0.2	122[e]	1.25	35
5	0.025	0.005	0.1	0.2	237[e,f]	2.37	64
6	0.015	0.01	0.1	0.2	94[e]	0.65	7
7	0.02	0.01	0.1	0.2	85[e]	1.34	13
8	0.04	0.01	0.1	0.2	199[e]	1.66	38
9	0.05	0.01	0.1	0.2	188[e]	2.43	53
10	0.06	0.01	0.1	0.2	313[e]	1.64	59
11	0.10	0.01	0.2	0.4	214[e]	1.29	32
12	0.01	0.01	0.025	0.4	99[e]	0.78	9
13	0.01	0.01	0.025	0.1	92[e]	0.39	4

[a]Same quantity of starch (1.62 g, 10 mmol, M_n = 19 060 Da) used in all experiments except for sample 5.
[b]Calculated on dry basis of starch used.
[c]Nitrogen content.
[d]Amount of CC bonded (%).
[e]Water-insoluble residue.
[f]Only 0.005 mol (0.81 g) of starch was used in this experiment.

23% of CC remained in the insoluble residue (sample 1). By gradually increasing the amount of E while keeping CC constant at 5 mmol, a yield of 122% insoluble product, with 1.25% nitrogen content, was obtained, indicating that 35% of CC had reacted (sample 4). When only 5 mmol of S was used the results were further improved. Under these conditions 64% of CC remained in the insoluble residue and less of the ion exchanger (by weight) was produced (sample 5). With 0.01 mol of CC and S and a gradual increase in E, again increases in yield, nitrogen content and amount of CC incorporated were obtained (samples 6 to 11), but the value obtained at 5 mmol of CC (sample 5) could not be reached. The identical nitrogen content of sample 5 and 9 indicates that at the optimal molar ratio of E:CC = 5 the formation of four crosslinking hydroxypropyl groups on one linkage of choline to S through the hydroxypropyl group might be obtained. The presence of a surplus of NaOH and water guarantees the activation of the hydroxyl groups of S and the transport of chemicals. The conditions of sample 9 seem to be optimal because larger quantities (by weight) of ion exchanger were produced when 0.01 mol of S was reacted. A decrease in yields and nitrogen contents was observed (samples 12 and 13) when a smaller amount of NaOH, in comparison with sample 11, was used. This could not be improved by increasing the concentration of NaOH and using less water (sample 13).

The ion exchanger with the highest nitrogen content (sample 9) was analysed by solid-state ^{13}C NMR using the high-power decoupled experiment in the presence of 50% of water. The spectrum obtained showed sharp signals at 54.6, 63.5, 65.4, 65.9, 67.3, 69.6, 70.6, 71.1, 72.8, 76.3 and 80.1 ppm (Fig. 1). There was also a small signal at 162.8 ppm, which might belong to some carbonate ions bound to quaternary groups (this is not shown on the figure). In the non-decoupled spectrum the signal at 54.6 ppm was split to a quartet (Fig. 2), proving the presence of the methyl choline group. This is close to the signal of the methyl-trimethylammoniumhydroxypropyl group (TMAHP) observed before (Šimkovic, 1996). The signals at 65.5 and 65.9 ppm were assigned to the two CH_2 groups of the choline substituent because they are close to each other and they split to form triplets. The peaks at 63.5 and 78.3 ppm were assigned to CH groups because they split to form doublets on the non-decoupled spectrum. The signals between 69.6 and 72.8 ppm seem to be related to the CH_2 and CH groups of the

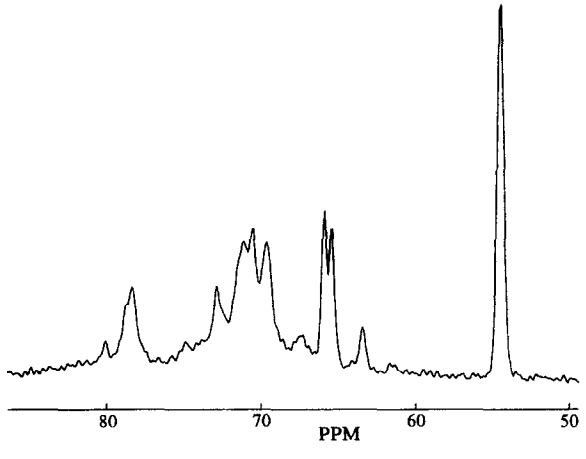

Fig. 1. The decoupled solid-state ^{13}C NMR spectrum of sample 9.

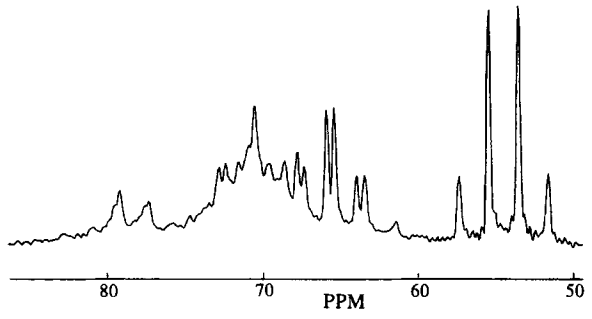

Fig. 2. The non-decoupled solid-state ^{13}C NMR spectrum of sample 9.

hydroxypropyl bridges. Because there were no signals that could be assigned to the starch macromolecule, we assume that the polysaccharide chain was rigid because of the hydroxypropyl groups crosslinking S or linking to the choline group. These groups gave sharp signals, as did previous starch ion exchangers (Šimkovic *et al.*, 1996; Šimkovic, 1996).

When compared with previous methods of preparation of ion exchangers (Šimkovic *et al.*, 1996; Šimkovic, 1996), the yields and nitrogen contents with this method are comparable. The advantage of this method in comparison to the previous quaternizing method (Šimkovic, 1996) is the use of a quaternizing agent that has no covalently bonded chlorine.

CONCLUSIONS

Starch was cross linked and quaternized in one step with E and CC in water and in the presence of NaOH. At the optimal molar ratio (S:E:CC:NaOH:H_2O = 0.01:0.05:0.01:0.1:0.2), 53% of CC was incorporated in the insoluble product. The yields and nitrogen contents proved the efficiency of this method in comparison to the previous one in which chlorine-containing quaternizing agents were used. The chemistry was confirmed by the solid-state ^{13}C NMR results.

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