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One-step quaternization/crosslinking of starch with 3-chloro-2-hydroxypropylammonium chloride/epichlorohydrin in the presence of NH_4OH

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Quaternization/crosslinking of starch with 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHMAC)/epichlorohydrin (E) in the presence of NH_4OH, NaOH and water was studied. The reaction was optimized and the products analyzed using solid-state NMR, acid–base titration methods and dye-binding tests. The solid-state NMR data in the presence of water confirmed the hydroxypropyl and trimethylammoniumhydroxypropyl groups in the obtained ion-exchanger. Although the linkage to starch could not be proved, the CH_2 groups linked to nitrogen and to oxygen could be tentatively assigned. Optimal molar quantities and ratios are at starch:-E:NH_4OH:NaOH:H_2O:CHMAC = 0.01:0.03:0.05:0.1:0.01. The exchange capacities (Q's) determined by potentiometric titration are smaller than values calculated from elemental analysis. This might be due to longer equilibrium times required for the exchange of ions, than those, which we could use on the automatic titrator. The dye binding properties are pH-dependent for the ion-exchangers containing tertiary amine groups next to quaternary ammonium groups and close to pH-independent when containing only quaternary ammonium groups (prepared in absence of NH_4OH). Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

Quaternized starches when applyed as ion-exchangers need to be crosslinked to remain water-insoluble. Several types of anion-exchanging starches have been asscribed (Chan, 1993; Antal & Toman, 1983; Rayford & Wing, 1979). Starch anion exchangers might be used for decolorization of textile wastewaters, which has not yet been studied (Laszlo, 1994). We have previously prepared weakly basic starches (Šimkovic *et al.*, 1996) by crosslinking with E, NH_4OH and NaOH. The goal of this present study is to demonstrate the preparation of quaternized/crosslinked starch containing strong and weak basic grouops in one step by using E, NaOH, CHMAC, water and NH_4OH. The products were analyzed and characterized with solid state NMR, acid–base titrations and dye-binding tests.

EXPERIMENTAL

Materials

Water-soluble starch {WSS, 19,060 Da; steam osmometry; $[\alpha]^{20} = +154.0°$ (c,1; H_2O), ZŠ, Dolná Krupá, Slovakia} was used as starting material. All the chemicals were commercial grade. CHMAC (50% solution, Spolek pro Chemickou a Hutní Výrobu, Ústí nad Labem, Czech Republic or 60% solution, Serva or 65% solution, Quat 188, Dow Chem. Co.) was used without further purification.

Methods

The elemental analysis were run on a Fisons EA-1108 instrument. All the other methods were described previously (Šimkovic *et al.*, 1996).

Preparation of samples

WSS (1.62 g, 10 mmol) was mixed with E, CHMAC, NH_4OH (25% solution) and NaOH in ratios listed in Table 1 and stirred for 24 h at room temperature in a closed vial. For sample 8 the experiment was run without using starch. The mixture was washed on sinterered glass (10–15 μm) with water until it was neutral (determined by pH paper). It was then washed with ethanol, then acetone and then dried *in vacuo* at room temperature until constant weight. In some cases (see Table 1) the reaction mixture was dialysed (8–15 kDa MWCO, Serva) and separated into a water-soluble part and insoluble residue. The yields were calculated on the weight of starch used on on the dry basis.

RESULTS AND DISCUSSION

The quantities of reactants used in individual experiments and properties of obtained resins are listed in Table 1. At the ratio E:NH_4OH = 3:1 a resin in good yield and nitrogen content is obtained (sample 1). When equimolar quantities of E and NH_4OH are used, even at lower concentrations of NaOH and higher quantity of CHMAC the yield (sample 2) is close to the value obtained from sample 1. However, because higher amounts of NH_4OH and CHMAC were used, the nitrogen content of sample 2 is higher. At lower quantities of E, NH_4OH, NaOH and water the yield is decreased (sample 3), even at the same amount of CHMAC as used in comparison to sample 1. On the other hand the nitrogen content increased. The yield and nitrogen content could be further increased by maintaining the quantity of E, NH_4OH and NaOH and increasing the amount of water and CHMAC (sample 4). The presence of larger amounts of NH_4OH and CHMAC used, resulted in increasing the density of the crosslinking of the product, which is showed by a smaller packing value (PV) of sample 2 in comparison to samples 3 and 4 (Table 1). It seams that increasing the amount of NH_4OH increases the density of crosslinking (smaller PV's), while increasing the amount of CHMAC decreases this value as seen from higher PV's for samples 1, 3 and 4 than determined from sample 2. By decreasing the amount of E (compare samples 5 and 3) the yield and nitrogen content of insoluble residue decreased and a water-soluble part with a high nitrogen content was obtained. The ^{13}C-NMR spectrum of the water-soluble fraction of this sample showed signals relating to hydroxypropyl (67.6, 62.4 ppm) and methyl (55.1 ppm) groups predominating over the anomeric signal of starch (101.0 ppm). This indicates that the water-soluble fraction contained minor quantities of starch. The increase of quantity of NH_4OH in the mixture decreased the yield and nitrogen content of both the water-soluble product and residue (compare samples 6 and 5). The slight decrease of water (sample 7) in the mixture further decreased the yield and nitrogen content. But when the reactants were treated in absence of starch (compare samples 5 and 8) the nitrogen content of the insoluble product was higher than in all the other experiments while the yield was low. At the 1 mmol quantity of CHMAC (sample 9 compared to sample 5) the yield and nitrogen content were half of the product obtained when 10 mmol of quaternizing agent was used. The increase in PV's might be due to predominant condensation of E, CHMAC and NH_4OH without crosslinking the polysaccharide. Omitting the NH_4OH results under similar conditions (compare samples 10 and 5) to a higher yield of ion-exchanger and PV of 13.1 ml/g. The nitrogen content of 2.39% indicates good quaternization under these conditions. On the other hand the lower yield indicates better incorporation of E and CHMAC into the water-insoluble product in the presence

Table 1. Quantities of reactants and the properties of obtained products of crosslinking of starch[a]

Sample no.	Moles of reactants					Yield (%)	PV (ml/g)	*N* (%)
	E	NH_4OH	NaOH	H_2O	CHMAC			
1	0.060	0.030	0.250	0.279	0.010	166[b]	10.7	2.19
2	0.060	0.060	0.060	0.684	0.071	176[b]	4.9	6.61
3	0.030	0.010	0.050	0.163	0.010	133[b]	7.8	3.00
4	0.030	0.010	0.050	0.372	0.030	328[b]	17.4	6.37
5	0.010	0.010	0.050	0.163	0.010	95[b]	16.0	2.04
						74[c]	—	8.18
6	0.010	0.030	0.050	0.279	0.010	82[b]	15.6	0.79
						39[c]	–	7.69
7	0.010	0.030	0.050	0.245	0.010	60[b]	21.4	0.68
						10[c]	—	4.07
8[d]	0.010	0.010	0.050	0.163	0.010	17[b,e]	—	7.73
9	0.010	0.010	0.050	0.060	0.001	48[b]	26.9	1.05
10	0.010	0	0.025	0.100	0.010	104[b]	13.1	2.39

Key: [a]For reaction conditions see Experimental; [b]insoluble residue; [c]water-soluble part; [d]experiment without starch; [e]yield calculated on quantity of CHMAC used.

of NH_4OH. The optimum seams to be at molar quantities and ratio of starch:E:NH_4OH:NaOH:H_2O:CHMAC = 0.01:0.03:0.01:0.05:0.1:0.01 ratio, which is close to conditions run on sample 3.

Solid-state ^{13}C-NMR CP spectrum of the quaternized/crosslinked starch (Table 1, sample 2) in dry state and H^+-form gave signals at 103.0 (C-1), 82.4 (C-4), 72.9 (C-2,3,5), and 63.0 (C-6) with the shoulder band between 53 and 56 ppm. The band at 53–56 ppm was absent in the spectrum of unmodified starch and probably belongs to methyls of trimethylammonium-2-hydroxypropyl (TMAHP) groups (Killinger *et al.*, 1995). This seems to be close to chemical shifts of this group obtained from water-soluble derivatives (Šimkovic *et al.*, 1990). The same sample in the OH^--form in a dry state gave less sharp signals (CP spectrum) than the H^+-form (there were signals at 102.9, 82.0, 72.9, 63.0 and 56.0 ppm). In the presence of 50% of water in the H^+-form, the high power decoupled spectrum showed a different pattern in comparison to the OH^--form. The signals of the H^+-form were at: 100.5 (C-1), 78.1, 74.2, 72.3, 64.6, 63.7, 62.7 (C-6), 61.5, 59.8, 53.9, 51.3, 43.5, 31.6 and 31.2 ppm, while those of the OH^--form were at: 100.5, 77.8, 74.1, 72.2, 70.2, 68.6, 62.2, 61.3, 60.5, 53.5 and 45.5 ppm. The new signals, which were not present in the absence of water might be related to poly(hydroxypropylamine) bridges. These noncarbohydrate substituents are mobile in water in contrary to polysaccharide parts which are similarly nonmobile in a dry state as well as in the presence of water (Morgan *et al.*, 1994). The change in the spectrum of the H^+-form in comparison to the OH^--form might be due to the conformational change of the ion-exchanging groups. On sample 4 (in OH^--form) which had the highest yield and PV and about the same nitrogen content as sample 2, both the CP and high power decoupled experiments gave identical spectra in the dry state with predominant signals at 72.3 (CH_2), 62.2 (CH) and 55.2 ppm (CH_3) and smaller signals at 168.3 (carbonate) and 102.6 ppm [some carbohydrate fragment linked to poly(hydroxypropylamine) chain]. In the presence of 50% of water the high power decoupled spectrum yields three signals (67.9, 62.5 and 54.2 ppm; Fig. 1A). On non-decoupled spectrum these signals split to triplet, doublet and multiplet indicating CH_2, CH and a mixture of CH_2, CH and CH_3 groups. The CP spectrum of this sample at 30% of water looked like unmodified starch (with an additional signal at 54.4 ppm, which is in the region of N^+-CH_3 groups). No change was observed on the starch backbone by the modification. Sample 10, which was quaternized/crosslinked with CHMAC and E in absence of NH_4OH gave as expected a simpler spectra in comparison to the previous one. The CP experiment on a dry sample had a sharp signal at 55.0 ppm, predominant broad signal with peak at 72.3 ppm and a small and broad signal around 100 ppm. With the high power experiment the dry sample just had a sharp signal at 55.1 ppm and a less intensive broad peak with a maximum at 71.3 ppm. It seems that the polysaccharide chain could not be observed under these conditions and only hydroxypropyl bridges and TMAHP-ion-exchanging groups were present in the spectrum. The CP experiment with the presence of 50% water gave the same results (no new signals), but broader signals than the experiment without water. The decoupled high power experiment with the presence of 50% water (Fig. 1B) gave a very intense signal at 55.0 ppm, which split into a quartet on the undecoupled spectrum (spectrum not shown), indicating the TMAHP-methyl group. The other, less intense signals were at 63.6, 65.7, 69.0, 69.8, 71.3, 73.0 and 73.6 ppm. They belong to the carbons of CH(OH) and CH_2 groups of hydroxypropyl and TMAHP groups. There were no signals at 51 to 43 ppm, which were present in samples 2 and 4, and might belong to CH_2 groups linked to tertiary nitrogen, because these samples were crosslinked in the presence of NH_4OH. These signals were also observed previously on weakly basic polyhydroxypropylamine-starch (Šimkovic *et al.*, 1996). So by solid-state NMR the presence of hydroxypropyl and TMAHP groups was proved, but the linkage to the polysaccharide could not be supported. This is probably because of lower concentration of CH_2-groups etherically linked to the polysaccharide and higher rigidity of the polysaccharide chains in water in comparison to poly(hydroxypropylamine) side-chains. Although the linkage of hydroxypropyl and TMAHP groups to starch was not proved by solid-state NMR,

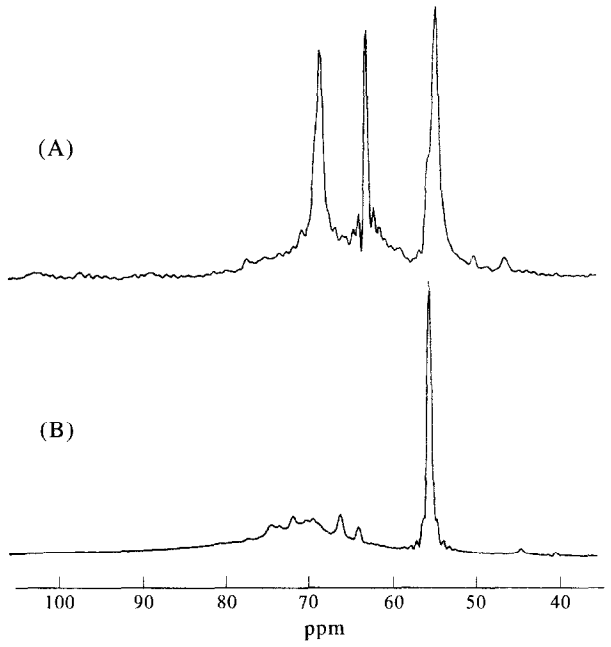

Fig. 1. Solid-state NMR spectra (high power decoupled experiments): (A) starch quaternized/crosslinked with CHMAC/E in presence of NH_4OH; (B) starch quaternized/crosslinked with CHMAC/E without using NH_4OH.

the obtained product contained starch and was water-insoluble, we believe that the poly(hydroxypropylamine) blocks were linked to starch, because water-soluble starch was used for the modification.

The potentiometric titration using the residual base method (Šimkovic *et al.*, 1996) gave for the sample with the highest nitrogen content (Table 1, sample 2) Q = 3.2 mmol/g, which is less than the value calculated from the nitrogen content (4.7 mmol/g). By direct titration of sample in the OH^--form with HCl solution (60 s equilibrium times) a Q of 5 mmol/g was determined with the endpoint at pH 6.2. There was also a second endpoint at pH 4.9 which corresponded to a Q of 1.9 mmol/g. We assume that the first endpoint was related to quaternary groups, while the weekly basic amines were titrated at the second endpoint. By the direct titration of the H^+-form with NaOH solution using long equilibrium times (9999s) again two endpoints could be determined. The first at pH 4.7 related to tertiary amine groups (Q = 0.7 mmol/g) and the second at pH 9.0 (Q = 2.9 mmol/g) relating to the quaternary ammonium groups. By the use of long equlibrium intervals a slightly higher Q could be determined than with the residual base titration method. These values were still smaller than those calculated from the nitrogen content. This indicates that the penetration and exchanging of ions requires longer times than could be run on automatic titrator, to reach the equilibrium.

The dye binding of prepared ion exchangers with monovalent (Alizarin Red S, ARS) and trivalent (hydrolyzed Remazol Brilliant Red F3B, 'F3B') dye showed pH dependent curves which were similar for weakly basic modified starch described previously (Šimkovic *et al.*, 1996). On sample 2 (Fig. 2) the pH dependence could be observed for both dyes indicating the presence of weakly basic amine groups. At low pH the ARS-binding capacity is close to the Q of total exchange capacity determined potentiometrically. The stechiometrical relation between dye-binding quantities for mono- and trivalent dye is evident. Sample 10, which does not contain weakly basic amine groups gave slightly different pH-dependent ARS- and F3B-binding curves. Quaternary ammonium groups should exchange the ions through the whole pH range. The lower binding of dyes at higher pH might be explained by the repulsation between dye anions, OH^- ions and deprotonated of hydroxyls of starch. This might also affect the results of potentiometric titrations.

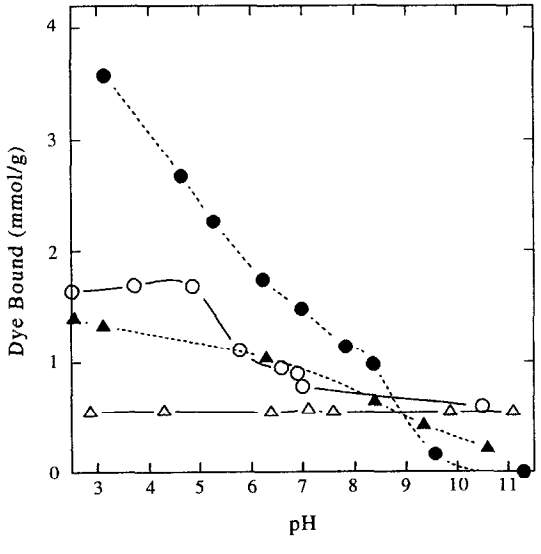

Fig. 2. The relation between quantity of dye binded and pH for quaternized/crosslinked starch in the presence [Table 1, sample 2 (filled symbols)] and the absence of NH_4OH [Table 1, sample 10 (empty symbols); Alizarin Red S (circle) and hydrolyzed Remazol Brillant Red F3B (triangle)].

CONCLUSIONS

By one-step quaternization/crosslinking of water-soluble starch with CHMAC/E in NH_4OH presence, ion exchangers in high yields and nitrogen contents could be prepared. At the absence of NH_4OH the yields and nitrogen contents were much lower. The optimum seems to be at molar quantities and ratio of starch: E:NH_4OH:NaOH:H_2O:CHMAC = 0.01:0.03:0.01:0.05:0.1:0.01. The penetration of ions requires several hours to reach equilibrium at every change of concentration of titrant, as determined by potentiometric titration. The dye-binding tests showed pH dependence for combined ion exchangers and stoichiometric relation between mono- and trivalent dye. The quaternized/crosslinked starch without weakly basic groups showed a less pH-dependent dye-binding relation. The lower binding of dyes at high pH might be due to repulsation of deprotonated hydroxyls of polysaccharides and dye anions and the OH^- ions.

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