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Preparation of ion-exchangers by cross-linking of starch or polygalacturonic acid with 1,3-bis(3-chloro-2-hydroxypropyl)imidazolium hydrogen sulphate

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Abstract

The reaction conditions for cross-linking of starch (S) or polygalacturonic acid (PGA) with 1,3-bis(3-chloro-2-hydroxypropyl)imidazolium hydrogen sulphate (BCHIHS) in the presence of NaOH and water were studied in terms of the molar ratio of the reaction components, the yields of water-insoluble product, the nitrogen content and the BCHIHS conversion. The optimum for S-derivatives was at the molar ratio of $S/BCHIHS/NaOH/H_2O = 0.01{:}0.02{:}0.04{:}0.333$ with 348% yield on the amount of used S, 7.71% nitrogen content and 78% conversion of BCHIHS. Analogically on PGA the optimum was at $PGA/BCHIHS/NaOH/H_2O = 0.005{:}0.005{:}0.1{:}0.2$ with 125% yield, 7.99% nitrogen content and 63% conversion. The linkage of dihydroxypropylimidazolum (DHPI) groups was confirmed by NMR in solution on water-soluble products as well as by ^{13}C solid-state NMR and FTIR on insoluble products. Under the used conditions much more NaOH is consumed on PGA while the yields of water-insoluble materials are lower than on S. The calculated $T_{1\rho}(H)$ relaxation times gave similar values obtained previously on different polysaccharides cross-linked with different cross-linkers. The elemental composition of samples in different cycles confirmed the ionic interaction between the quaternary ammonium group and the PGA carboxyls.

Keywords: Cross-linking; Ion-exchangers; Starch; Polygalacturonic acid; Solid-state NMR; FTIR

1. Introduction

Cross-linked polysaccharides with ion-exchanging properties might find applications related to their ability to remove dyes and ions from wastewaters (Rutenberg & Solarek, 1984) or as heparin adsorbers (Antal & Micko, 1993). Cellulose or lignocellulosics could be cross-linked and quaternized in one step with 1,3-bis(3-chloro-2-hydroxypropyl)imidazolium hydrogen sulphate (BCHIHS) (Antal & Micko, 1992, 1993; Šimkovic, 1999). The reaction could be schematically written as:

$$
\begin{aligned}
&a\text{P–OH} + b\text{Cl–CH}_2\text{–CH(OH)–CH}_2\text{–I}^+(\text{HSO}_4^-)\text{–CH}_2\\
&\quad\text{–CH(OH)–CH}_2\text{–Cl} + c\text{NaOH} + d\text{H}_2\text{O} \rightarrow m\text{P–O–CH}_2\\
&\quad\text{–CH(OH)–CH}_2\text{–I}^+(\text{HO}^-)\text{–CH}_2\text{–CH(OH)–CH}_2\text{–O–P}\\
&\quad+ n\text{Na}_2\text{SO}_4 + o\text{NaCl} + p\text{NaOH} + r\text{H}_2\text{O},
\end{aligned}
$$

where P represents the polysaccharide, I^+ represents an imidazolium ring bounded on nitrogens and *a*–*r* are quantities of reagents used or formed products. In the present, study one neutral (S) and one acidic (PGA) polysaccharide was used. The analysis was focused on the reaction in relation to the quantity and the ratio of the used polysaccharide, NaOH, BCHIHS and water. The goal was to prepare ion-exchangers under optimal conditions in terms of yield of water-insoluble product, nitrogen content and conversion of BCHIHS and to characterize the products with NMR and FTIR spectroscopy as well as to test their ion-exchanging properties.

2. Materials and methods

Partially hydrolyzed, water-soluble potato starch (S) (ZŠ, Dolná Krupá, Slovakia; $M_w = 19{,}060$ Da; determined osmometrically; $[\alpha]^{20} = +154.0°$ (c 1; H_2O)) was solubilized in a water solution of NaOH and subsequently BCHIHS was added in the quantities listed in Table 1. After 24 h stirring at room temperature the reaction mixture was acidified with hydrochloric acid to pH 2, stirred overnight, dialyzed (12–14 kDa MWCO; Serva) and the water-insoluble part separated on fritted glass funnel (G4)

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Table 1
Molar quantities of reactants and results of cross-linking of starch

Sample no.	Moles of reactants			NaOH/BCHIHS	Yield[a] (%)	N[b] (%)	BCHIHS reacted[c]
	BCHIHS	NaOH	H_2O				
1	0.005	0.010	1	2	95	3.42	38
2	0.005	0.020	1	4	118	3.48	48
3	0.005	0.030	1	6	103	3.22	38
4	0.005	0.040	1	8	91	2.40	25
5	0.005	0.050	1	10	90	1.96	20
6	0.005	0.100	1	20	71	1.33	11
7	0.010	0.040	1	4	133	4.62	36
8	0.010	0.040	0.5	4	145	5.03	42
9	0.005	0.020	0.5	4	119	4.07	56
10	0.007	0.033	0.3	5	125	3.92	43
11	0.007	0.017	0.3	2.4	163	5.64	76
12	0.007	0.023	0.3	3.4	159	5.18	68
13	0.020	0.040	0.3	2	348	7.71	78
14	0.025	0.100	0.2	4	336	8.39	65

[a] Insoluble residue calculated on the quantity of used starch (1.62 g; 0.01 mol).
[b] Nitrogen content.
[c] Conversion of BCHIHS (%).

and freeze dried. PGA (Fluka, reg. #81325; 25–50 kDa) was treated in the same way as S, at the ratios and amounts listed in Table 2. The reaction mixtures of PGA were worked out as above. The results were controlled by running two parallel experiments from which the average was listed (the balance was 1–2%). Four ionic forms were prepared by recycling the samples with 5% solutions of H_3PO_4, H_2SO_4, HCl or NaOH for 48 h, washed with an excess of deionized water and freeze dried. The amounts of individual elements in the sample were determined by microanalysis (Šimkovic, Laszlo & Thompson, 1996). The NMR methods were described previously (Šimkovic, Hricovíni, Šoltés, Mendichi & Cosentino, 2000). Infrared spectra were measured on a NICOLET Magna IR 750 spectrometer with a DTGS detector and OMNIC 3.2 software. The samples were pressed into KBr pellets with sample/KBr ratio 2/200 mg (128 scans at a resolution of 4 cm^{-1} were averaged). The nitrogen content was determined using a Perkin–Elmer elementary analyzer, Model 240.

3. Results and discussion

All the results obtained on S are listed in Table 1. The maximal yield, nitrogen content of water-insoluble product as well as the conversion of the quaternizing agent at

Table 2
Conditions and results on cross-linking of PGA (for all experiments the same quantity of PGA — 0.88 g, 0.005 mol — was used)

Sample no.	Moles of reactants			NaOH/BCHIHS	Yield[a] (%)	N[b] (%)	BCHIHS reacted[c]
	BCHIHS	NaOH	H_2O				
1	0.0025	0.075	0.2	30	51	8.30	53
2	0.0025	0.100	0.2	40	81	7.41	75
3	0.0025	0.150	0.2	60	35	6.65	29
4	0.0025	0.200	0.2	80	17	6.20	13
5	0.0025	0.100	0.1	40	33	6.18	26
6	0.0050	0.050	0.2	10	4	6.56	2
7	0.0050	0.075	0.2	15	105	8.02	53
8	0.0050	0.100	0.2	20	125	7.99	63
9	0.0050	0.125	0.2	25	101	8.04	51
10	0.0050	0.150	0.2	30	51	8.44	27
11	0.0050	0.100	0.1	20	18	7.87	9
12	0.0050	0.100	0.3	20	78	7.92	39
13	0.0100	0.100	0.2	10	101	9.29	29

[a] Insoluble residue.
[b] Nitrogen content.
[c] Conversion of BCHIHS (%).

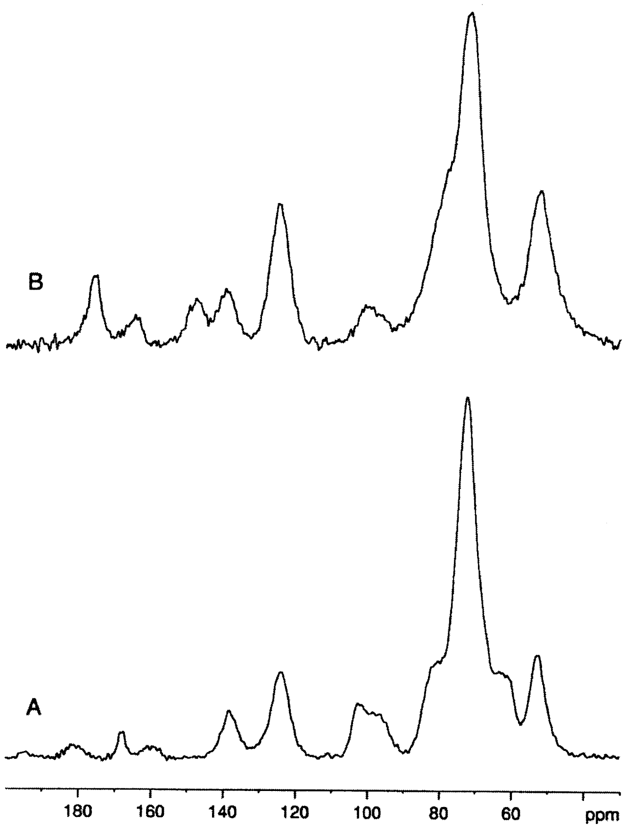

Fig. 1. ^{13}C CP/MAS NMR spectrum of: (A) DHPI-S (Table 1, sample 14) and (B) DHPI-PGA (Table 2, sample 8).

5 mmol BCHIHS quantity (samples 1–6) was at the molar ratio of S/BCHIHS/NaOH/H_2O = 2:1:4:200 (sample 2). On doubling the amount of BCHIHS and NaOH, the yield and nitrogen content increased further, but the conversion of BCHIHS decreased (sample 7). The concentration of BCHIHS could be further increased by decreasing the quantity of water used to half (samples 8 and 9). This resulted in an optimum at S/BCHIHS/NaOH/H_2O = 1:2:4:33 (sample 13), when the maximal conversion of BCHIHS also was achieved. It seems that the optimal ratio of NaOH/BCHIHS = 4 (samples 2, 7–9 and 14) when optimal yields and conversions were obtained. At the yield of 336% on the amount of used S (sample 14) the material contains less than one-third of polysaccharides and the ratio of NaOH/BCHIHS used does not affect the yield so dramatically when such big amounts are used (compare samples 13 and 14).

The results obtained on PGA are listed in Table 2. To save the material only half of the amount used for S (5 mmol) was taken into the reaction. At 2.5 mmol of BCHIHS (samples 1–4), the optimum was at the ratio of PGA/BCHIHS/NaOH/H_2O = 1:0.5:20:40 (sample 2; NaOH/BCHIHS = 40). The further decrease of water amount resulted in lower yield and conversion (compare samples 2 and 5). The yields of water-insoluble PGA-derivative in

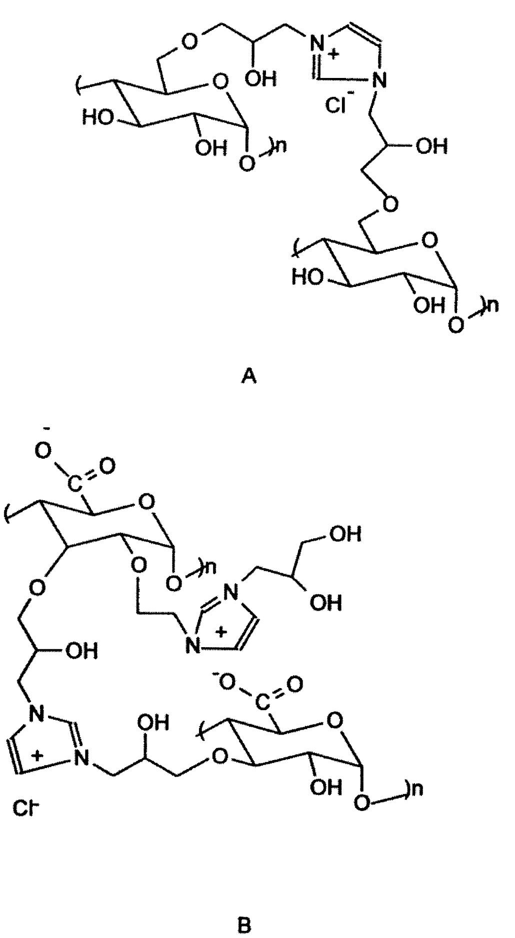

Fig. 2. Proposed structures of: (A) DHPI-S and (B) DHPI-PGA.

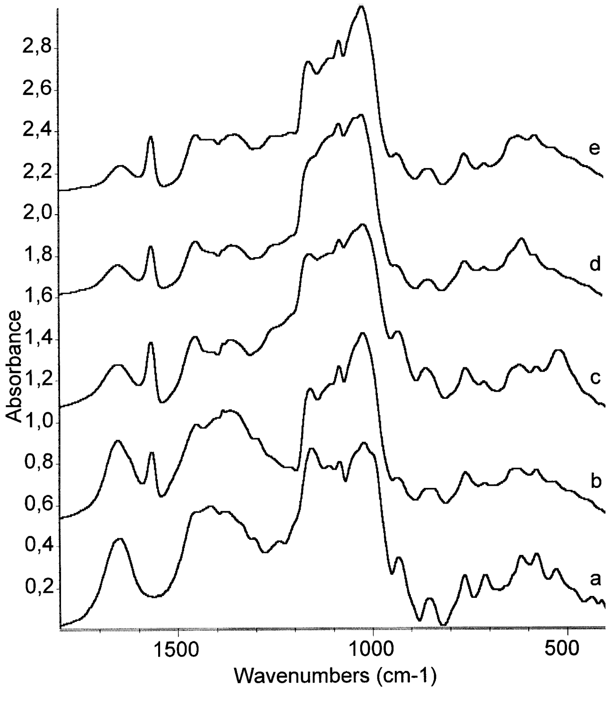

Fig. 3. FTIR spectra of S (a), DHPI-S (Table 1, sample 14) in HO^- (b), $H_2PO_4^-$ (c), HSO_4^- (d) and Cl^- cycle.

Table 3
FTIR bands of BCHIHS, S, DHPI-S, PGA and DHPI-PGA

Frequency (cm^{-1})					Band assignment
BCHIHS	S	DHPI-S	PGA	DHPI-PGA	
3155, 3116		3155, 3112		3145, 3109	C–H stretching, imidazole
1630		1650–1644		1654	C=N and C=C stretching, imidazole
			1607	1611	$(COO)^-$ asymmetric stretching
1566		1567		1568–1666	N–C=N stretching, imidazole
1446–1308	1456–1305	1450–1348		1452–1349	C–H bending
			1331		Ring vibration
			1409	1405	$(COO)^-$ symmetric stretching
1257, 1227		1255, 1212		1257, 1226	O–H bending, alcohol
	1240		1238		C–O, C–C, ring
1166, 1100					C–O stretching, alcohol
	1155		1146		C–O–C stretching, glycosidic bond
	1109, 1084, 1022		1099, 1075, 1045, 1016		C–O, C–C, ring

comparison to results obtained on S are lower. This could be related to the much higher optimal NaOH/BCHIHS ratio needed for PGA cross-linking than was observed for S. It is probably due to the fact that in this case additional NaOH is consumed for uronic acid ionization. With further increase of the amount of the cross-linking agent (samples 6–12) the conversion reached a maximum at NaOH/BCHIHS = 20 (sample 8) but was lower than before (sample 2) although the yield further increased. With the slight change in water amount the yields and conversions decreased (compare samples 8, 11 and 12).

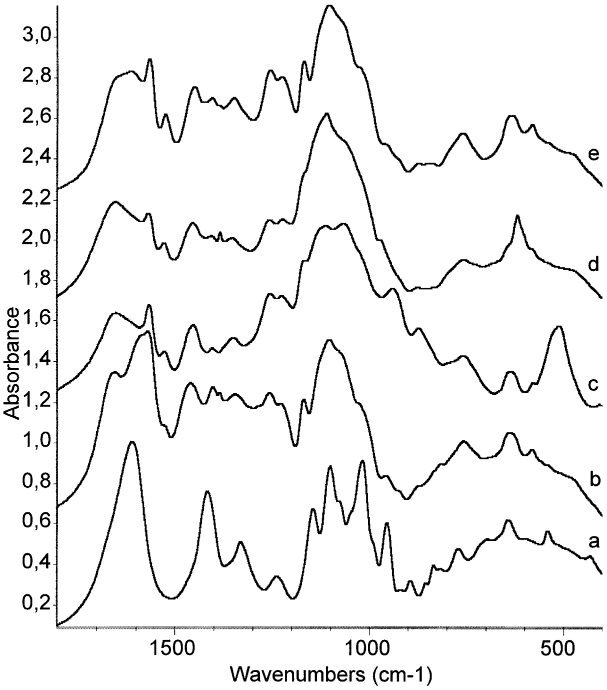

Fig. 4. FTIR spectra of PGA (a), DHPI-PGA (E, Table 2, sample 8) in HO^- (b), $H_2PO_4^-$ (c), HSO_4^- (d) and Cl^- cycle.

Further increase of BCHIHS did not improve the results (sample 13).

The water-soluble products which represented up to 10% yield (data not shown) on the amount of S were analyzed by ^{13}C NMR in D_2O to confirm the linkage of the cross-linker to S. New signals at 137.9, 124.1, 70.7, 70.3 and 52.9 ppm, which were not present in the original S were observed. According to the spectrum of BCHIHS (137.9, 124.2, 70.0, 53.3 and 46.7 ppm) as well as the water solubility, we assume the presence of monofunctionally substituted quaternizing agent on S. Analogically, the soluble part of the PGA-derivative showed new signals at 137.9, 124.1, 70.3, 69.5 and 52.9 ppm. Additionally, there were three small signals at 182.2, 175.8 and 170.0 ppm, which might originate from esterified carboxyls. The unmodified PGA had carboxyl sodium salt signal at 176.4 ppm.

^{13}C CP/MAS NMR spectrum of the water-insoluble modified S (Table 1, sample 14) is in Fig. 1A. The signals were observed at 52, 62, 72, 82, 102, 123, 138 and 167 ppm. The signals at 52, 72, 123 and 138 ppm originate from DHPI-groups as found from comparison with BCHIHS spectrum in solution. The dipolar dephasing spectra showed that quaternary carbons are at 160–180 ppm (data not shown). Some of the signals might also originate from carbonate ions ionically linked to imidazolium cations of DHPI-groups. A very similar spectrum was obtained on PGA (Table 2, sample 8), where the signals were at 52, 69, 72, 80, 100, 123, 138, 160–170 and 175 ppm (Fig. 1B). Comparison of both spectra reveals that the ratio between the DHPI-group and polysaccharide signals is bigger in the PGA sample although the nitrogen content in both samples is similar. This might be due to the interaction of HPI-groups with PGA carboxyls as proposed in Fig. 2. Only ether linkages are possible on S.

Further analyses were performed using $T_{1\rho}(H)$ relaxation

Table 4
Ion exchanging values of S- and PGA-derivatives

Sample	N (%)	Cl (%)	P (%)	S (%)	Cycle	Yield (%)	C (%)	H (%)
1[a]	7.71	3.89	1.89	0	Cl^-	88	41.77	6.32
	7.53	0	4.69	0	HO^-	69	42.48	6.34
	6.36	0	2.33	0	$H_2PO_4^-$	56	37.88	6.05
	7.63	0	3.71	5.58	HSO_4^-	83	39.33	6.18
2[b]	8.05	1.55	3.10	0	Cl^-	84	43.45	6.73
	7.95	0	2.87	0	HO^-	98	42.80	6.63
	6.73	0	3.84	3.11	HSO_4^-	88	41.17	5.90
	7.33	0	4.38	0	$H_2PO_4^-$	84	41.86	6.36

[a] S-derivative (Table 1, sample 13).
[b] PGA-derivative (Table 2, sample 8).

times. These values were found uniform in the modified S (2.9–3.1 ms) and PGA (5.5–7.4 ms). Such uniform values indicate that spin diffusion is complete and homogeneous due to spatial proximity of spins within the domains of small dimensions. The quantitative analysis gave the values of the distances of the domains at 5 and 7 nm for S and PGA, respectively. The size of the crystalline dimensions could be considered therefore as comparable. Similar values were observed on hyaluronic acid and cellulose derivatives (Šimkovic, Hricovíni, Šoltés, Mendichi & Cosentino, 2000; Torri, Cosentino, Delben, Simonutti & Sozzani, 1999).

The FTIR spectra of the insoluble DHPI-S samples in HO^-, $H_2PO_4^-$, HSO_4^- or Cl^- cycles gave a new band at 1564–1568 cm^{-1} (N=C–N stretching) in comparison to unmodified material (Fig. 3a), which was present also in the quaternizing agent (Table 3). The imidazole ring is characterized by two bands at 1566 and 1630 cm^{-1} (Bassignana, Cogrossi, Gandino & Merli, 1965). The latter interacts with the water band (H–O–H banding) at 1640 cm^{-1}. The specific polysaccharide bands of S in the 1200–1000 cm^{-1} region overlapped with the bands of the DHPI-group, which resulted in band broadening and loss of the typical shape of the starting material. The resulting overall shape we suppose is due to a new supramolecular interaction of modified polysaccharides and could not be ascribed to certain groups. This is more evident on PGA (Fig. 4) than on S derivatives. The cycling of the samples did not affect the position of the band at 1564–1568 cm^{-1} for both derivatives. In the case of the hydroxyl anion the characteristic region is at 3700–3500 cm^{-1}, which overlaps with the O–H stretching of polysaccharides. That is why HO^- could not be assigned with FTIR. The $H_2PO_4^-$ anion is indicated with bands overlapping at 1060 cm^{-1} (P–O stretching) and 515 cm^{-1} (O–P–O bending). The presence of the HSO_4^- anion results in shoulders at 1130 cm^{-1} (S–O stretching) and a strong band at 615 cm^{-1} (O–S–O bending). The Cl^- ion is not visible in the region between 4000 and 400 cm^{-1} (Nakamoto, 1963). The results support the chemical bonding of the DHPI-group and the presence of HSO_4^- and $H_2PO_4^-$ ions in the prepared material.

The recycling of S- and PGA-derivatives (Table 4) resulted in losses of the material up to 34%, but for PGA-derivatives the maximal loss of the ion-exchanger was 16%. It seems that the simultaneous presence of quaternary nitrogen cations and carboxyl anions on PGA hinders ion-exchange owing to ionic bonding of these groups (Fig. 2), which is evident from the lower amounts of chlorine, sulphur and phosphorus as it should be according to nitrogen content. This means that S-derivatives are better materials for the preparation of ion-exchangers with quaternary ammonium groups.

4. Conclusions

The one-step cross-linking/quaternization of S and PGA with BCHIHS could be achieved at the molar ratio of $S/BCHIHS/NaOH/H_2O = 0.01:0.02:0.04:0.3$ or $PGA/BCHIHS/NaOH/H_2O = 0.005:0.005:0.1:0.2$ with optimal results as far as regards of the yields of water-insoluble derivatives. The prepared S-derivatives are more suitable than PGA-modified materials owing to the interaction of quaternary nitrogen cations and PGA-carboxyl anions.

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