Synthesis and Study of Polyacids from Soluble Starch and Chloroacetic Acids

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The optimum conditions for the condensation of soluble starch with sodium salt of monochloroacetic acid in aqueous sodium hydroxide solution are determined. Condensation of soluble starch with sodium salt of di- and tri-chloroacetic acids was carried out under the same optimum conditions found for the former reaction. Higher values of yield, acid number, specific viscosity and consequently degree of substitution are attained upon repeating the process of carboxyalkylation for at least three times.

FROM the plots of pH+log $(1+x)/x$ vs x the apparent pK values, defined as pH at half-neutralisation point for the three polymeric acids, have been determined. The apparent strength which is lower than the corresponding chloroacetic acid, temperature, quantity of sodium salt of monochloroacetic acid, overall reaction time and dilution, are determining factors. Each factor was studied in detail, while the others being kept constant, and the optimum condition determined in a series of experiments was used in the following series. The validity of each factor was evaluated through the determination of the acid number[1], specific viscosity (0.05 g / 10 ml water at 25°[a]) and yield of the obtained product.

Polyelectrolytes do not follow the classical Henderson equation[a], according to which,

$$pH + \log(1-x)/x = \log K$$

should remain constant with the progress of neutralisation in contrast to the behaviour of monomeric acids. The departure in the three polyacids has been investigated by following the change in log K with the degree of neutralisation, x.

Experimental

All chemicals used were of analytical reagent grade ; monochloroacetic acid (m.p. 63°), dichloroacetic acid (b.p. 194°), trichloroacetic acid (m.p. 57.5°), pure soluble starch (mol. wt. $(162.14)_n$, Chemapol, Praha, Czechoslovakia), absolute methanol (b.p. 64°), hydrochloric acid (AnalaR, sp. gr. 1.18 at 35°), sodium chloride (mol. wt. 58.5, Medexport), potassium chloride (mol. wt. 79.56, B.D.H.), potassium hydroxide (mol. wt. 56.11, Merck) and sodium hydroxide pellets (B.D.H.) were used.

Preparation of sodium salt of chloroacetic acids : Sodium hydroxide (250 g) dissolved in absolute alcohol (2 dm³) was added to monochloroacetic

acid (500 g), with cooling, till the end-point of phenolphthalein. The precipitated sodium salt of monochloroacetic acid was filtered, pressed and dried in air ; yield ~85% of the theoretical.

The same process was used for the preparation of the sodium salts of both di- and tri-chloroacetic acids.

Condensation of starch with sodium salts of chloroacetic acids : General procedure : Starch (1.0 g) was dissolved in the requisite amount of sodium hydroxide solution, diluted to the desired concentration, followed by the addition of formaldehyde solution (40%, 1 ml), and the solution was heated at 40—50° for 30 min on a water-bath. The calculated amount of the acid salt was then added to the cooled mixture at room temperature, and the reaction mixture was stirred at 40—50° for 60 min. After repeating the process of carboxyalkylation for three times, the product was acidified with 0.1 N hydrochloric acid to pH 2, precipitated with methanol, filtered off, and dried on a sintered glass funnel. The product was further dissolved in water and precipitated and the process was repeated several times. Its solution was passed through strong cation- and then strong anion-exchanger, till it gave no precipitate with silver nitrate solution. The product was finally dried in a vacuum oven at 50—60° to constant weight.

Potentiometric titration : A weighed amount of the pure polymer (1 g/25 ml deionised water) in the H-form was titrated, using sodium hydroxide solution upon vigorous stirring. The pH-titration was carried out slowly (about 1 ml per 30 min) with sodium hydroxide solution (0.1 N) using glass-calomel assembly. The same series of experiments was carried out for the polymers dissolved in different concentrations (0.1, 0.5 and 1.0 N) of aqueous potassium chloride solutions.

Each sample was also back-titrated using hydrochloric acid (0 400 2 N).

Results and Discussion

Reaction with sodium salt of monochloroacetic acid : *Effect of sodium hydroxide* : A series of experiments was carried out using different quantities of aqueous sodium hydroxide (20% solution), in presence of formaldehyde (1 ml, 40% solution) / soluble starch (1.0 g). The mixture was heated at 40—45° for 30 min on a water-bath with stirring and then cooled to room temperature. Sodium salt of monochloroacetic acid (2.0 g) was then added and stirring continued at 30° for further 1 h.

Results given in Fig. 1 show that relatively small quantities of sodium hydroxide are not
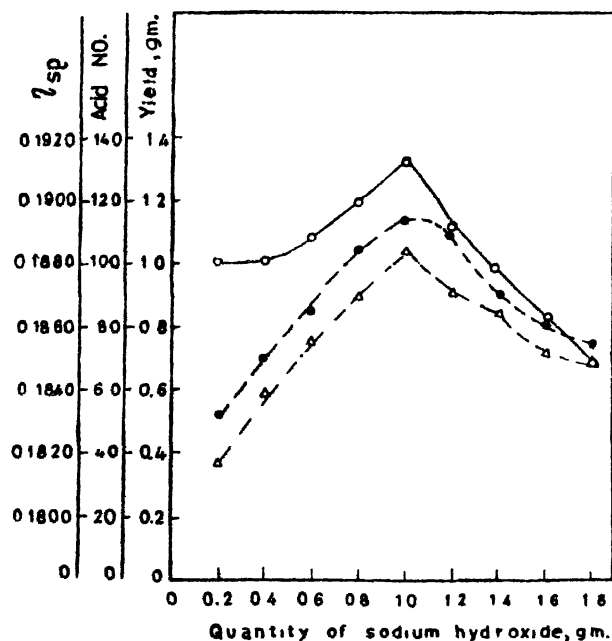

Fig. 1. Effect of sodium hydroxide : (O) yield, (●) η_{sp}, and (△) acid number.

quite sufficient for the reaction to proceed, so that the acid number, specific viscosity, and consequently, the numbers of introduced carboxylic groups in starch are relatively small. Quantities of sodium hydroxide higher than 1.0 g (the optimum quantity), at such reaction temperature, lead to a relatively low degree of substitution. It is probable that the hydrolysis of chlorine atom in the sodium salt of monochloroacetic acid proceeds in presence of excess of sodium hydroxide, and consequently the yield, acid number, and specific viscosity gradually decrease.

Effect of temperature : The above series of experiments was carried out at different tempera-

tures after the addition of sodium salt of monochloroacetic acid, in presence of NaOH (1.0 g ; 20% aqueous solution, 5 ml)/soluble starch (1.0 g).

Results given in Fig. 2 show that the highest values of yield and acid number are obtained at reaction temperature 40—50°. It is probable that monochloroacetic acid (or its sodium salt) may be hydrolysed to glycolic acid ($CH_2OHCOOH$) in hot water or in alkali, and consequently, the reaction temperature seems to have a significantly effect on the yield, acid number and the degree of substitution.
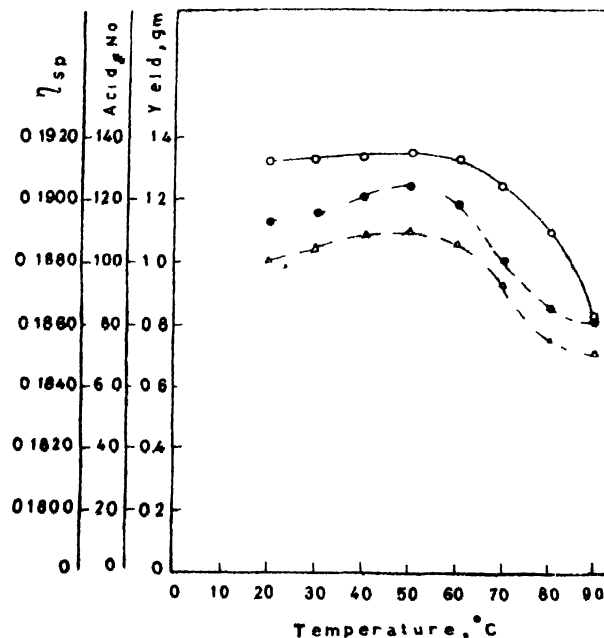

Fig. 2. Effect of temperature : (O) yield, (●) η_{sp}, and (△) acid number.

Effect of quantity of sodium salt of monochloroacetic acid : Experiments in the previous step were repeated using different quantities of sodium salt of monochloroacetic acid. Results given in Fig. 3 show that at small quantities of sodium salt of monochloroacetic acid, the acid number is relatively low, and the specific viscosity of the obtained product is nearly the same as that for soluble starch. The acid number, specific viscosity and yield reach their highest values with about 2.0 g (0.017 mol) sodium salt of monochloroacetic acid per g of soluble starch.

Effect of overall reaction time : It appears that the reaction is more or less rapid, so that longer reaction time than 60 min does not affect much the values of the yield, specific viscosity and acid number of the reaction product.

Effect of dilution : A series of experiments was carried out under the above determined optimum conditions in presence of different quantities of

water. Results given in Fig. 4 show that the values of acid number and specific viscosity and relatively low, and reach their maximum values when the quantity of water is 15 ml/1.0 g soluble starch.

monochloroacetic acid (2.0 g)/carboxyalkylated starch (1.0 g). The results of each repeated step are given in Table 1.
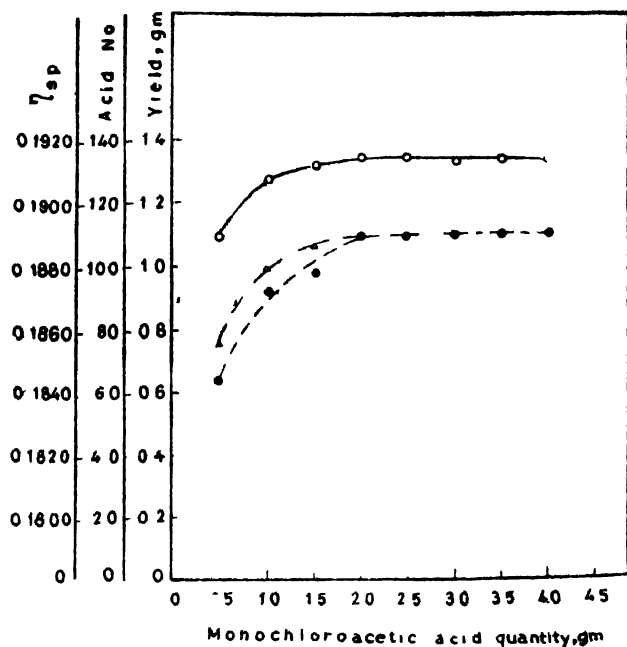

Fig. 3. Effect of quantity of sodium salt of monochloroacetic acid : (O) yield, (●) η_{sp}, and (△) acid number.
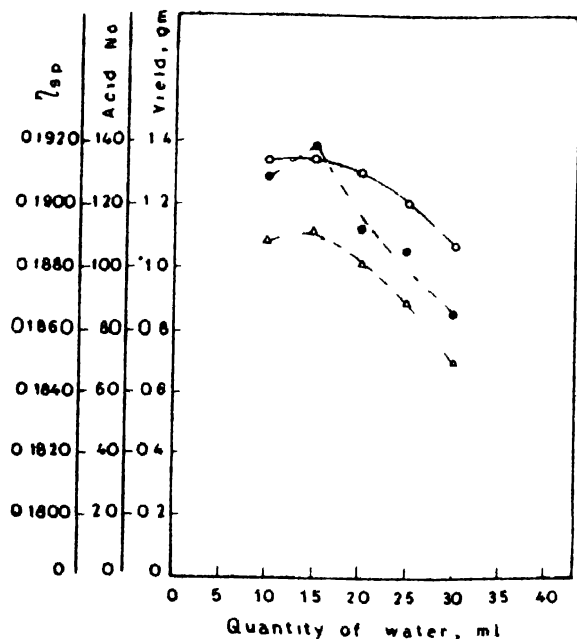

Fig. 4. Effect of dilution : (O) yield, (●) η_{sp}. and (△) acid number.

Effect of repeated carboxyalkylation on properties of the product : Carboxyalkylation was carried out at the optimum conditions, using

TABLE 1—EFFECT OF REPEATED CARBOXYALKYLATION OF STARCH ON PROPERTIES OF THE PRODUCT

No. repetition	Yield g	Acid number mg	η_{sp} at 25°
1	1.351 4	112.13	0 191 8
2	1.491 2	126 23	0 192 1
3	1.551 3	156 00	0.193 1
4	1.552 1	158 41	0.193 2
5	1 553 1	158 63	0 193 4

It is observed that with repeated carboxyalkylation the values of yield, acid number and specific viscosity increase, tending towards certain limits in the third or fourth repetition.

Carboxyalkylation of starch with sodium salts of di- and tri-chloroacetic acids : The carboxyalkylation of starch with the sodium salt of dichloro-(2.59 g), and trichloro-acetic acid (3.185 g)/starch (1.0 g) was carried out at the same optimum conditions as for the sodium salts of monochloroacetic acid. It will be noted from the data given in Table 2 that for five successive carboxyalkylations, the yield, acid number and specific viscosity increase, and tend to limiting values similar to that observed in the case of the sodium salt of monochloroacetic acid.

Characterisation of reaction products :

The reaction products have been characterised by means of their infrared spectra and potentiometric titrations

Infrared spectra . The ir spectra of starch were studied and compared with those of its condensation products with mono-, di-, and tri-chloroacetic acids. The latter have characterised peaks at 1 725—1 700 cm^{-1} for C=O group in aliphatic acids. The reaction product with dichloroacetic acid is further characterised by valency deformation for C—Cl (720—700 cm^{-1}) and that with trichloroacetic acid by valency deformation for C—Cl$_3$ polysubstitution (740—720 cm^{-1})[4,5].

Potentiometric titration of the reaction products : Potentiometric titrations of the reaction products have been done in deionised water and also in presence of different concentrations of potassium chloride. The apparent pK values are obtained from the plots of pH + log (1 + x)/x vs x[5,6] at $x = 0.5$, where x represents the fraction neutralised. Graphs in Fig. 5 show these plots for the condensation products of starch with monochloroacetic acid. Similar graphs have been obtained

TABLE 2 —EFFECT OF REPEATED CARBOXYALKYLATION OF STARCH WITH SODIUM SALTS OF DI- AND TRI-CHLOROACETIC ACIDS ON PROPERTIES THE END-PRODUCTS

No. of repetition	Carboxyalkylation with sodium salt of dichloroacetic acid			Carboxyalkylation with sodium salt of trichloroacetic acid		
	Yield g	Acid number mg	η_{sp} at 25°	Yield g	Acid number mg	η_{sp} at 25°
1	1.541 2	120 24	0.194 0	1.742 5	132.71	0.195 3
2	1.601 2	152 25	0 194 2	1.796 5	165.63	0.195 9
3	1.645 1	175.90	0.194 4	1.817 5	210.26	0.196 5
4	1.646 1	176 21	0.194 5	1.819 2	212.41	0.196 7
5	1.646 5	178.16	0.194 7	1.819 5	213.21	0.196 7

TABLE 3 —APPARENT pK-VALUES, AND EXCHANGE CAPACITIES (m.e./g) FOR POLYMERIC ACIDS IN DIFFERENT MEDIA

Medium	pK* values of polyelectrolyte from starch and					
	Monochloroacetic acid		Dichloroacetic acid		Trichloroacetic acid	
	pK	Capacity m.e./g	pK	Capacity m.e./g	pK	Capacity m e./g
Deionised water	4.00	2.769	3.90	2.915	3.20	3.510
0.10 N KCl	3.90	2.964	3.80	3.145	3.00	3.706
0.50 N KCl	3.60	3.198	3.60	3.277	2.95	3.979
1.00 N KCl	3.50	3.549	3 50	3.884	2.85	4.09

*For comparison, pK values of mono-, di-, and tri-chloroacetic acids are 2 83, 1.29, and 0 83, respectively (Ref. 7).
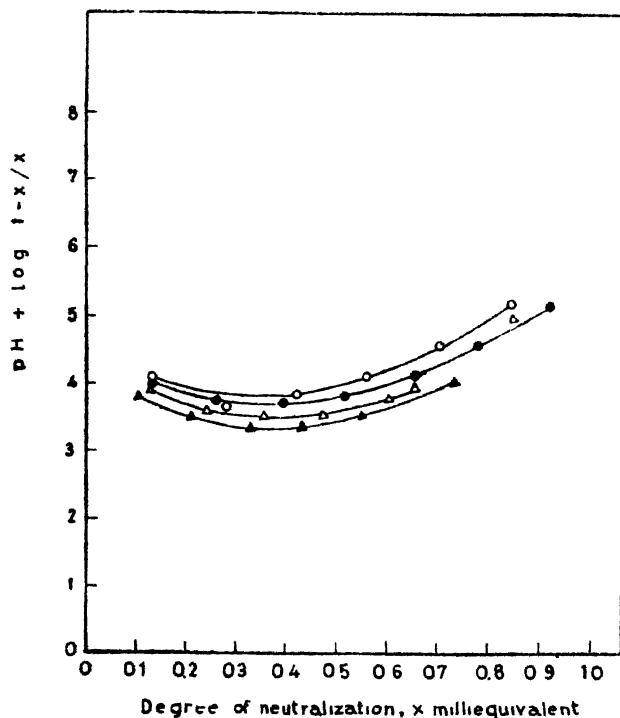
there is little difference in acid strength among the polymeric acids themselves. The order is for the condensation products of starch with dichloro- and trichloro-acetic acids. The apparent pK-values obtained from these plots are given in Table 3. Although the parent chloroacetic acids differ in strength by a few orders of magnitude,

Fig. 5. Reaction product of starch with monochloroacetic acid. Plots of $pH + \log (1-x)/x$ vs x in (O) deionised water, (●) 0.1 N KCl, (△) 0.5 N HCl, and (▲) 1.0 N KCl.
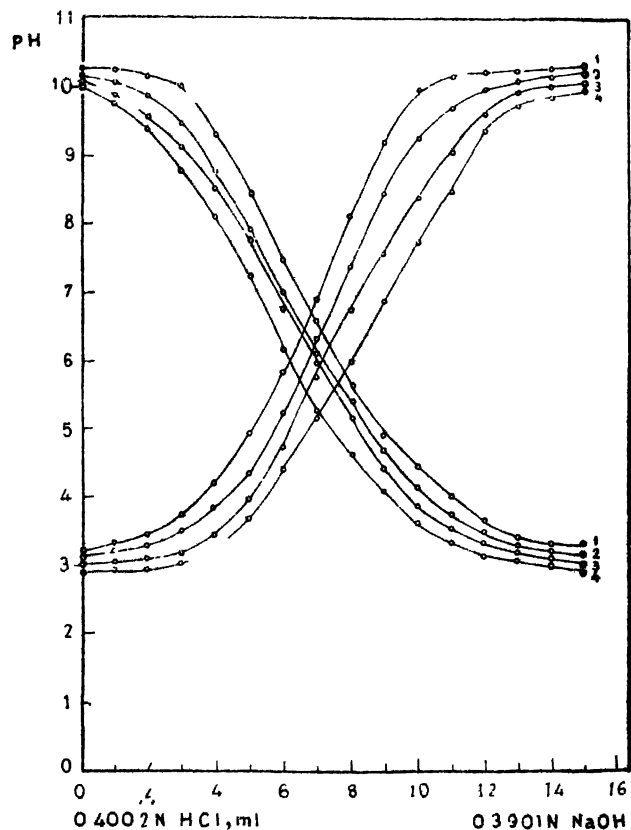

Fig 6. Polyelectrolyte from starch and monochloroacetic acid. Potentiometric titration curves and back-titration in (1) deionised water, (2) 0.1 NKCl, (3) 0.5 N KCl, and (4) 1.0 N KCl.

trichloro > dichloro > monochloro, and each polymeric acid is by a few orders of magnitude weaker than the corresponding chloro acid. The change in the apparent pK-value with the addition of KCl towards stronger acid character, is in agreement with the general behaviour of almost all polyacids[3,8].

The potentiometric titration curves (pH vs titrant added) and back-titration curves for the synthesised polyelectrolytes, are fairly sharp, and each curve either in deionised water or in aqueous KCl solution acquired only one break (Fig. 6). If alkali-binding capacity is defined as the weight of the alkali necessary to bring the pH to 7, the order (Table 3) will be evidently more or less same as mentioned above.

The values of exchange capacity in deionised water (Table 3) are comparable with those calculated (2.785, 3.14 and 3.755 m e./g) from the acid numbers for the three polyelectrolytes, respectively. It could also be deduced from the acid number values that, for the first polyelectrolyte, two units of starch probably react on the average with one molecule of monochloroacetic acid ; three units

react with two molecules of dichloroacetic acid in the second polyelectrolyte ; and in third polyelectrolyte, one unit reacts with one molecule of trichloroacetic acid. The calculated values of exchange capacity are therefore 2.5, 3 07 and 3.45 m.e./g, respectively, which satisfactorily agree with those experimentally determined from potentiometric titrations and those calculated from the acid numbers.

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