

Preparation of Cation-Exchange Starches Containing Phosphoric Acid Groups *

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SYNOPSIS

Poly (glycidyl methacrylate)-starch graft copolymer was prepared using hydrogen peroxide/ferrous sulphate/thiourea dioxide redox system as initiator. The copolymer was treated with orthophosphoric acid (H_3PO_4) under a variety of conditions to discover appropriate conditions for synthesizing the copolymer that can serve as cation exchanger. Results obtained indicated that the cation-exchange capacity is enhanced by: (a) increasing the H_3PO_4 /epoxy molar ratio up to 4; (b) using material-to-liquor ratio 1 : 2; (c) increasing duration (15–300 min) and temperature (60–90°C); (d) increasing the amount of epoxy groups of the copolymer; and (e) increasing the percent neutralization of H_3PO_4 up to 33.3%. Based upon the results obtained with these parameters, it was postulated that three reactions are involved during treatment of the copolymer with H_3PO_4 . These reactions are phosphorylation, crosslinking, and hydrolysis. Conditions were established under which the phosphorylation reaction occurs exclusively. Studied also were the ion-exchange properties of the phosphorylated copolymer, namely, pK_a values, capacity for heavy metal ions removal, moisture content, durability, swellability, and solubility.

INTRODUCTION

Cation-exchange resins containing phosphoric acid groups or phosphono groups have been studied.^{1–4} These resins acquire high adsorption capacities towards heavy metals. During the last few decades, much attention was given to cation-exchange starches. Starch has been phosphorylated by its reaction with orthophosphate^{5–14} or with tetrasodium pyrophosphates¹⁵ or phosphoric acid^{16,17} or sodium tripolyphosphates.^{5,11,15,18,19} Also, a combination of urea and phosphate salts has been used for phosphorylation of starch.^{20,21}

This work aims at preparing cation-exchange starches containing phosphate groups via reaction of orthophosphoric acid with poly (glycidyl methacrylate (GMA))-starch graft copolymer. Major factors affecting this reaction, such as phosphoric acid/epoxy molar ratio, material-to-liquor ratio, re-

action medium, temperature and duration, as well as neutralization percent, of phosphoric acid are examined. The work is further extended to include characterization of the prepared cation exchangers.

EXPERIMENTAL

Materials

Rice starch was supplied by Misr Co. for Starch and Yeast, Alexandria, Egypt. Chemical analysis showed that this starch had a moisture content of 11.35%, ash content of 0.53%, and protein content of 0.01%. Orthophosphoric acid, benzene, ethyl methyl ketone, dioxane, ferric nitrate, lead nitrate, and cobalt nitrate were of analytical grade chemicals.

Poly (GMA)-starch graft copolymer was prepared by polymerization of GMA with starch using a hydrogen peroxide/ferrous sulphate/thiourea dioxide system as initiator according to a reported method.²²

Phosphorylation Reaction

Ground copolymer (2 g) was allowed to react with an aqueous solution of phosphoric acid in a 50-mL

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stoppered glass bottle. The reaction was carried out in a thermostatic water bath at a specified temperature and period of time. The sample was then thoroughly washed with ice-cold water, followed by acetone, and then was dried at 50°C, and finally was dried over P₂O₅ for 24 h before analysis.

The extent of phosphorylation was monitored by determining the acidity value, expressed as m eq/100 g sample, as well as by determining the phosphorus content using a reported method.²³ The remaining epoxide was determined using the pyridine hydrochloride method.²⁴

The exchange capacity and the moisture content of the cation-exchangers were determined by a method reported by Kunin.²⁵ A pH-metric titration study, swellability, and solubility were carried out according to Kunin.²⁶ The *pK_a* values were determined by a method reported by Helffrich.²⁷

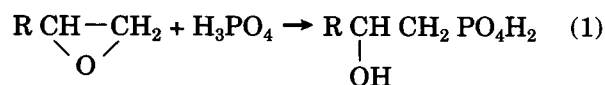
Removal of Heavy Metal Ions

Solutions (50 mL) containing different metal ions were treated with the cation-exchange starches (0.25 g), added as solid. After 24 h contact time, the solutions were filtered and the residual metal ions concentrations in the filtrate were measured, using atomic absorption spectrophotometry. (Instrumentation Lab. an/ae spectrophotometer 175, USA).

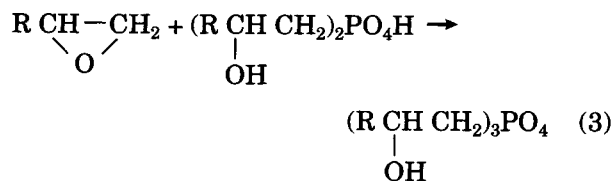
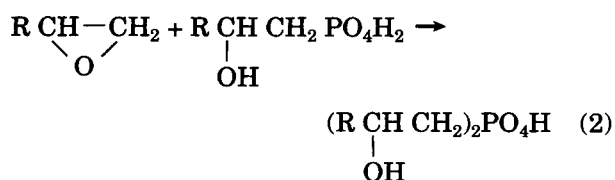
RESULTS AND DISCUSSION

During treatment of poly(GMA)-starch copolymer with aqueous orthophosphoric acid, various reactions take place. Among these reactions are the following:

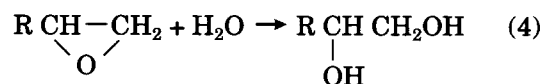
Phosphorylation Reaction



Crosslinking Reactions



Hydrolysis Reaction



With the above reactions in mind, treatment of poly(GMA)-starch graft copolymer with orthophosphoric acid was carried out in such a way that the formation of the side reactions (i.e., reactions 2–4) were eliminated or at least minimized. This necessitates studying major factors affecting the treatment, as given below.

Phosphoric Acid to Epoxy Molar Ratio

Poly(GMA)-starch graft copolymer containing 258 m eq epoxy/100 g sample was treated at 80°C for 3 h with orthophosphoric acid, using H₃PO₄/epoxy molar ratios varying from 1 : 1–6 : 1. A material-to-liquor ratio of 1 : 4 was used. Reactions involved in the treatment were assessed by determination of the cation-exchange capacity for the reaction product. The results obtained are shown in Figure 1.

It is seen (Fig. 1) that the cation-exchange capacity of the produced exchanger increases by increasing the H₃PO₄ to epoxy molar ratio up to 4; after this the capacity levels off.

Beyond this value, the crosslinking reactions seem to be outweighed by reaction 4 (i.e., hydrolysis owing to the higher acidity value).

Liquor Ratio

Poly(GMA)-starch graft copolymer containing 258 m eq epoxy/100 g sample was treated with phosphoric acid solution at a concentration of H₃PO₄/epoxy ratio of 4, at 80°C for 3 h using different material-to-liquor ratios (1 : 1–1 : 20). Figure 2 shows variation of the total ion-exchange capacity of the phosphorylated copolymer with the liquor ratio. As is evident, the ion-exchange capacity exhibits maximum value at a material-to-liquor ratio of 1 : 2. Ratios below or above this value create ion-exchangers with lower capacity. Hence, a material-to-liquor ratio of 1 : 2 is optimal as far as this parameter is concerned.

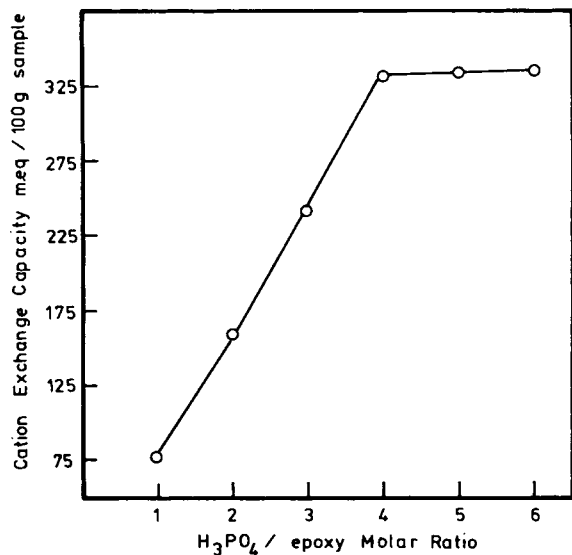


Figure 1 Effect of H₃PO₄/epoxy molar ratio on the phosphorylation of poly (GMA)-starch graft copolymer. Material-to-liquor ratio, 1 : 4; Reaction time, 3 h; Temperature, 80°C; Initial epoxy content, 258 m eq/100 g sample.

The above findings can be explained in terms of homogeneity and dilution. Lack of homogeneity in the reaction environment would be expected at lower liquor ratios. As a result, all reactants would not have equal opportunity to come into intimate association. On the other hand, higher liquor ratio

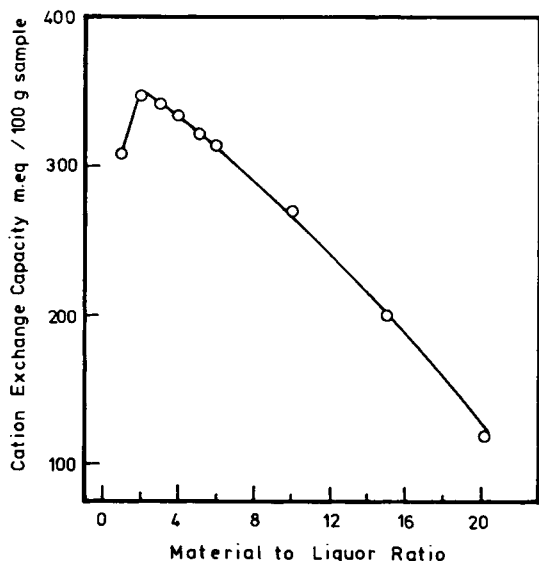


Figure 2 Effect of material-to-liquor ratio on the phosphorylation of poly (GMA)-starch graft copolymer. Reaction time, 3 h; Temperature, 80°C; Phosphoric acid/epoxy molar ratio, 4 : 1; Initial epoxy content, 258 m eq/100 g sample.

causes a decreased concentration of reactants, thereby giving rise to lower extent of reactions. In addition, the hydrolysis (reaction 4) is more pronounced at higher liquor ratios since dilution is effected with water.

Reaction Duration and Temperature

In order to study the effect of reaction time and temperature on the ion-exchange capacity of the poly (GMA)-starch graft copolymer in question, this copolymer was treated with orthophosphoric acid at different temperatures (60–90°C) for different durations (¼–5 h) using H₃PO₄/epoxy molar ratio of 4 and material to liquor ratio 1 : 2. The results obtained are set out in Figure 3. The results signify that the ion-exchange capacity of the cation exchanger obtained increases with increasing reaction duration and temperature, though there is a tendency for the reaction to level off after 3 h at 80°C and 90°C. The results signify also that maximum ion-exchange capacity is estimated to be 383 m eq/100 g sample, which means a reaction efficiency of 74.2% of the initial epoxide used.

Based on the foregoing, it is probably correct to conclude that phosphorylation of poly(GMA)-

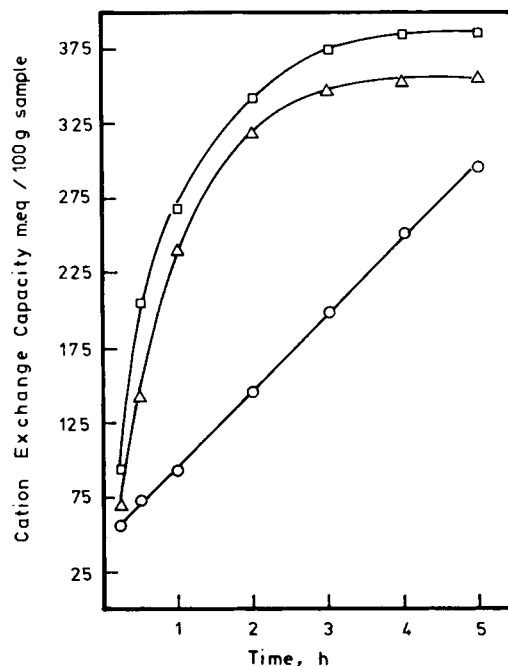


Figure 3 Effect of reaction time and temperature on the phosphorylation of poly (GMA)-starch graft copolymer. Phosphoric acid/epoxy molar ratio, 4 : 1; Material-to-liquor ratio 1 : 2; Initial epoxy content 258 m eq/100 g sample. (O) 60°C, (Δ) 80°C, (□) 90°C.

starch graft copolymer could best be achieved when H_3PO_4 /epoxy molar ratio of 4 and material to liquor ratio of 1 : 2 are used, and the reaction is carried out at 90°C for 3–4 h.

Reaction Medium

Phosphorylation of poly(GMA)-starch graft copolymer with phosphoric acid in various solvents, viz. water, benzene, ethyl methyl ketone, and dioxane, was effected using phosphoric acid/epoxy molar ratio 4, and material-to-liquor ratio 1 : 2 at 80°C for 3 h. The results obtained are shown in Table I. Obviously, the magnitude of total ion-exchange capacity depends upon the solvent and it follows the order: benzene > water > ethyl methyl ketone > dioxane. This order may be associated with differences among the solvent used, particularly with regard to its ability to swell the copolymer as well as to cause homogeneity and compatibility of all reaction ingredients.

Percent Neutralization of the Acid

Poly(GMA)-starch graft copolymer was phosphorylated using phosphoric acid neutralized to different extents. The phosphorylation reaction was carried out using H_3PO_4 /epoxy molar ratio of 4 and material-to-liquor ratio of 1 : 2 at 80°C for 3 h. This was done with a view to investigate the effect of percent neutralization of the acid on the capacity of the ion-exchangers formed. The results obtained are summarized in Table II.

It is seen (Table II) that the cation-exchange capacity of the phosphorylated samples first increases by increasing the percent neutralization of phosphoric acid up to 33.3%, which is equivalent to its monosodium salt. Further increment in the percent

Table I Effect of Reaction Medium on the Ion-Exchange Capacity of the Phosphorylated Poly(GMA)-starch Graft Copolymer

Type of Solvent	Benzene	Water	Ethyl Methyl Ketone	Dioxane
Ion exchange capacity (m eq/100 g sample)	379	357	341	320

Reaction Conditions: Epoxy content of the copolymer, 258 m eq/100 g sample; Phosphoric acid/epoxy molar ratio, 4 : 1; Material-to-liquor ratio, 1 : 2; Reaction time 3 h; Temperature, 80°C.

Table II Dependence of Ion-Exchange Capacity and Phosphorus Content of Phosphorylated Poly(GMA)-starch Graft Copolymer on Percent Neutralization of Phosphoric Acid

Phosphoric Acid Neutralization %	Total Ion-Exchange Capacity (m eq/100 g sample)	Calculated Phosphorus Content (%)	Measured P Content (%)
0	340	5.27	5.20
20	372	5.70	5.66
33.3	406	6.30	6.30
50	362	5.60	5.60
66.6	323	5.00	5.01
80	290	4.15	4.13
100	206	3.20	3.22

Reaction Conditions: Epoxy content of the copolymer, 258 m eq/100 g sample; Phosphoric acid/epoxy molar ratio, 4 : 1; Material-to-liquor ratio, 1 : 2; Reaction time, 3 h; temperature, 80°C.

neutralization of H_3PO_4 is accompanied by a decrement in the ion-exchange capacity of the phosphorylation. Similar observation was reported when oxalic acid or citric acid were independently reacted with poly(GMA)-cellulose graft copolymer.²⁸

The enhancement in ion-exchange capacity of the poly(GMA)-starch graft copolymer, by increasing the percent neutralization of H_3PO_4 up to the monosodium salt, can be interpreted in terms of the increased extent of phosphorylation. On the other hand, the decrement in ion-exchange capacity of copolymer brought about by using H_3PO_4 of higher percent neutralization can be associated with conversion of the reaction medium to the alkaline range where the self-polymerization reaction of the epoxide is more favored. The effect of reaction is to decrease the amount of epoxide available for the reaction and, hence, it decreases the extent of phosphorylation.

It is further noted that little or no crosslinking (reactions 2 and 3) occurs since the determined phosphorus content of the phosphorylated sample is equal to the phosphorus content calculated from the acidity.

Initial Epoxy Content

Poly(GMA)-starch graft copolymer having different epoxy contents was reacted with aqueous orthophosphoric acid solution using H_3PO_4 /epoxy molar ratio of 4, and material-to-liquor ratio 1 : 2 at 90°C

Table III Effect of the Initial Epoxy Content of the Copolymer on Ion-Exchange Capacity of the Phosphorylated Poly(GMA)-starch Graft Copolymer and Reaction Efficiency

Initial Epoxy Content (m eq/100 g sample)	Ion-Exchange Capacity (m eq/100 g sample)	Reaction Efficiency (%)
258	383	74.2
358	484	62.9
414	500	60.4

Reaction Conditions: Phosphoric acid/epoxy ratio, 4 : 1; Material-to-liquor ratio, 1 : 2; Reaction time 5 h; Temperature, 90°C.

for 5 h. The total ion-exchange capacity of the phosphorylated samples, as well as the reaction efficiency, are given in Table III. It is clear that increasing the initial epoxy content of poly(GMA)-starch graft copolymer causes enhancement in the ion-exchange capacity of the formed exchanger, while it decreases the reaction efficiency. This could be ascribed to lower penetration power of phosphoric acid into the poly(GMA)-starch graft copolymer having different epoxy content. It is believed that increasing the polymeric part (graft) decreases the hydrophilicity of the total (copolymer) and therefore decreases the swellability. In any event, however, the highest efficiency of the phosphorylation reaction obtained is 74.2%.

Reaction Mechanism

It has been shown above that during the course of treatment of poly(GMA)-starch graft copolymer

with phosphoric acid, three main reactions are likely to occur, namely phosphorylation, crosslinking, and hydrolysis. It has also been stated that research in this investigation was directed to discover the most appropriate conditions under which the phosphorylation reactions take place exclusively, or at least those reactions in which phosphorylation prevails over the other two reactions, namely, crosslinking and hydrolysis. When this was done, it was thought to be of interest to investigate the extent to which the phosphorylation reaction take place.

Table IV shows the consumption of both phosphoric acid and epoxy groups of the poly(GMA)-starch graft copolymer during phosphorylation of the latter and it also shows the onset of these consumptions on the ion-exchange capacity and the phosphorus content of the phosphorylated copolymer. Treatment of the copolymer (having 258 m eq/100 g sample) with phosphoric acid was carried out using phosphoric acid/epoxy molar ratio of 4 and a material-to-liquor ratio of 1 : 2 at 80°C for the reaction periods of time indicated in the Table.

The results (Table IV) signify (a) that the total ion-exchange capacity (formed acidity) is equal to $\frac{2}{3}$ of the consumed phosphoric acid throughout the entire duration of the treatment, (b) that the consumed epoxy groups of the copolymer throughout the entire course of the phosphorylation reaction amount to $\frac{1}{2}$ of the formed acidity, and (c) that the measured phosphorus content of the phosphorylated poly(GMA)-starch graft copolymer is equal to the calculated phosphorus content derived from the formed acidity.

The above results show that treatment of poly(GMA)-starch graft copolymer with phos-

Table IV Consumption of Phosphoric Acid and the Epoxy Groups of the Copolymer During Phosphorylation of Poly(GMA)-starch Graft Copolymer and the Onset of these Consumptions on the Ion-Exchange Capacity (Formed Acidity) and the Phosphorus Content of the Phosphorylated Copolymer

Time (min)	Acid Formed (m eq/100 g sample)	Acid Consumption (m eq/100 g sample)	Epoxy Consumption (m eq/100 g sample)	Calculated P% from Acidity	Determined P %
15	88	132.0	44.0	1.36	1.36
30	110	165.0	55.2	1.70	1.67
45	180	270.0	91.0	2.79	2.82
60	240	361.0	120.0	3.72	3.74
90	284	426.5	142.5	4.40	4.40
120	320	481.0	160.2	4.96	4.98

Reaction Conditions: Epoxy content, 258 m eq/100 g sample; Phosphoric acid/epoxy molar ratio, 4 : 1; Material-to-liquor ratio, 1 : 2; Temperature, 80°C.

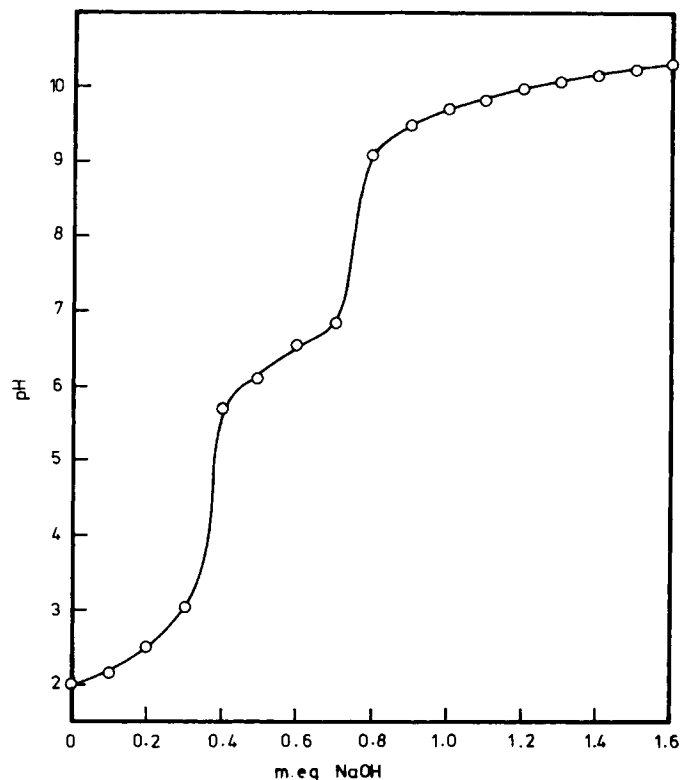


Figure 4 The pH-metric titration curve of phosphorylated poly (GMA)-starch graft copolymer (0.8 m eq).

phoric acid under the condition established in this investigation involves the phosphorylation reaction (reaction 1). The latter takes place exclusively and neither of the other two possible reactions, cross-linking and hydrolysis, occur under the conditions used.

Characterization of Cation-Exchangers

pH-Metric Titration Curve

In order to study the dissociation behavior of the phosphoric acid group of the phosphorylated poly(GMA)-starch graft copolymer, pH-metric

measurements were made. The results obtained are shown in Figure 4. It is clear that pH titration curve shows that the copolymer behaves like a dibasic acid. Furthermore, the characteristics of its ion-exchange capacity as a function of pH are similar to those of the neutralization curve for the first two hydrogen of phosphoric acid; the pK_a values amount to 2.4 and 6.6, respectively.

Removal of Metal Ions

In order to determine the actual capacity of the phosphorylated poly-(GMA)-starch graft copolymer, the latter was treated with different solutions

Table V Properties of Phosphorylated Poly(GMA)-starch Graft Copolymer Ion-Exchangers

Zero Cycle	Capacity (m eq/100 g sample) After			Solubility (%)		Moisture Content (%)	Swellability at 25°C
	5 Cycles	10 Cycles	20 Cycles	H Form	Na Form		
357	356	356	356	0.41	0.81	13.8	0
483.2	480	480	480	0.45	0.89	14.1	0
500	497	497	497	0.48	0.73	14.4	0

containing a Pb^{+2} , or Fe^{+3} , or Co^{+2} , and the percent retention of these cations was measured and found to be 85%, 81.2%, and 77.3%, respectively.

Other Properties

Table V shows the moisture content, solubility, durability, and swellability of ion-exchangers derived from phosphorylation of poly(GMA)-starch graft copolymers. The values of these properties make it evident that these ion exchangers acquire good stability which render them suitable for use.

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