

Studies on α -Pinene-Furfural-Based Cation Exchange Resins. I. Preparation of Polymeric Compositions and Resins

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Synopsis

A crosslinked polymer based on α -pinene and furfural suitable for processing into ion exchangers was prepared. The polymer has been processed chemically into different types of cation exchange resins. The role of various parameters such as catalyst concentration, proportion of crosslinking agent, etc., for preparing the polymer is systematically studied and presented. Similarly, the conditions for preparing the various cation exchange resins (sulfonic, phosphonic, and hydroxy phosphonic acid type from the polymer) are also described. A probable/possible composition for the repeating unit in the basic polymer is proposed and supported by experimental evidences.

INTRODUCTION

A perusal of the literature reveals that besides styrene divinylbenzene copolymers, a large number of materials can be converted into ion exchange resins by chemical treatments. Synthesis of polymer based on α -pinene and furfural and preparation of cation exchange resins therefrom were reported for the first time by the authors.¹ A detailed study of these is given in this article.

EXPERIMENTAL

Polymerization

Measured quantities of α -pinene and furfural were taken in a three-necked reaction kettle provided with a thermometer, stirrer, and condenser. A known quantity of a Friedel-Craft catalyst such as anhydrous zinc chloride or anhydrous aluminium chloride was added and the contents were stirred with heating at 120–25°C until a gel was formed (Fig. 1). The gel was removed, dried, and cured in an electrically heated oven at 90–95°C. The cured samples were allowed to cool to room temperature and then weighed. The proportion of reactants used and percentage yield of polymer are presented in Table I.

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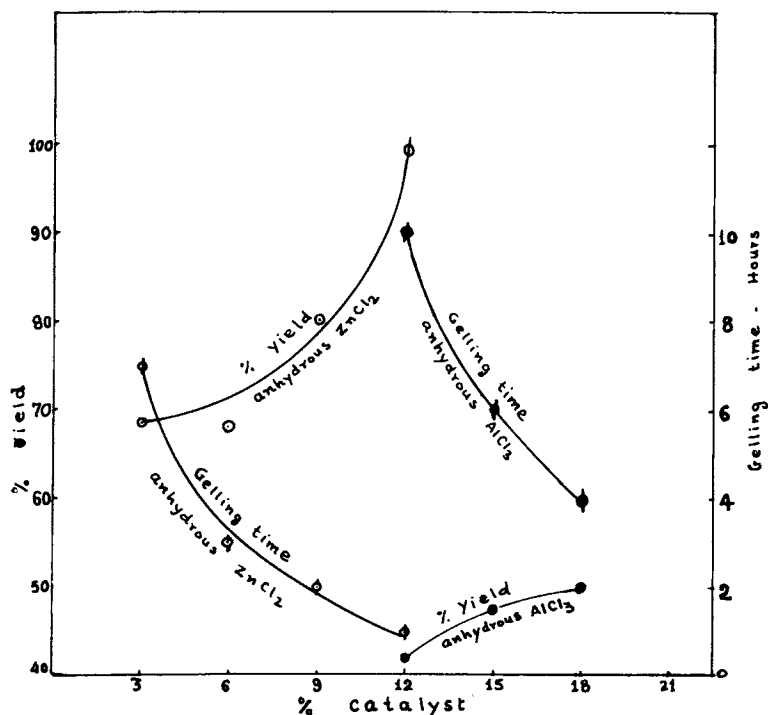


Fig. 1. Effect of varying catalyst concentration on time of gelling and yield of products.

Preparation of Cation Exchange Resins

The polymer obtained by reacting 1.0 mole α -pinene with 1.0 mole furfural was chemically processed into cation-exchange resins.

Sulfonic Acid-Type Cation Exchange Resin (PFS). Ten grams of α -pinene-furfural (1:1) polymer [–20 + 40 British Standard Sieve (B.S.S.)] was taken in a reaction flask and 100 g of sulfuric acid (98% w/w) was added and stirred. The contents were then poured into ice-cold water. The resin obtained was washed free of acid, conditioned, and evaluated for capacities by a standard method.² The time and temperature of sulfonation were varied, and the results are presented in Figures 2 and 3. The polymers obtained

TABLE I
Effect of Variation of Furfural Ratio on the Quality of Product^a

Quantity of furfural, moles	Time to gel formation	Time required for curing hrs.	Yield, %	Remarks
2.0	0'35''	5	71.02	black, shining material
1.0	1'10''	7	99.40	black, shining material
0.5	no gel formation	up to 8 hr		thermoplastic material

^a Quantity of α -pinene: 136 g (1.0 mole); quantity of catalyst (anhydrous zinc chloride): 16.32 g (12% based on the weight of α -pinene); temperature for reaction; 120–25°C; temperature for curing: 90–95°C.

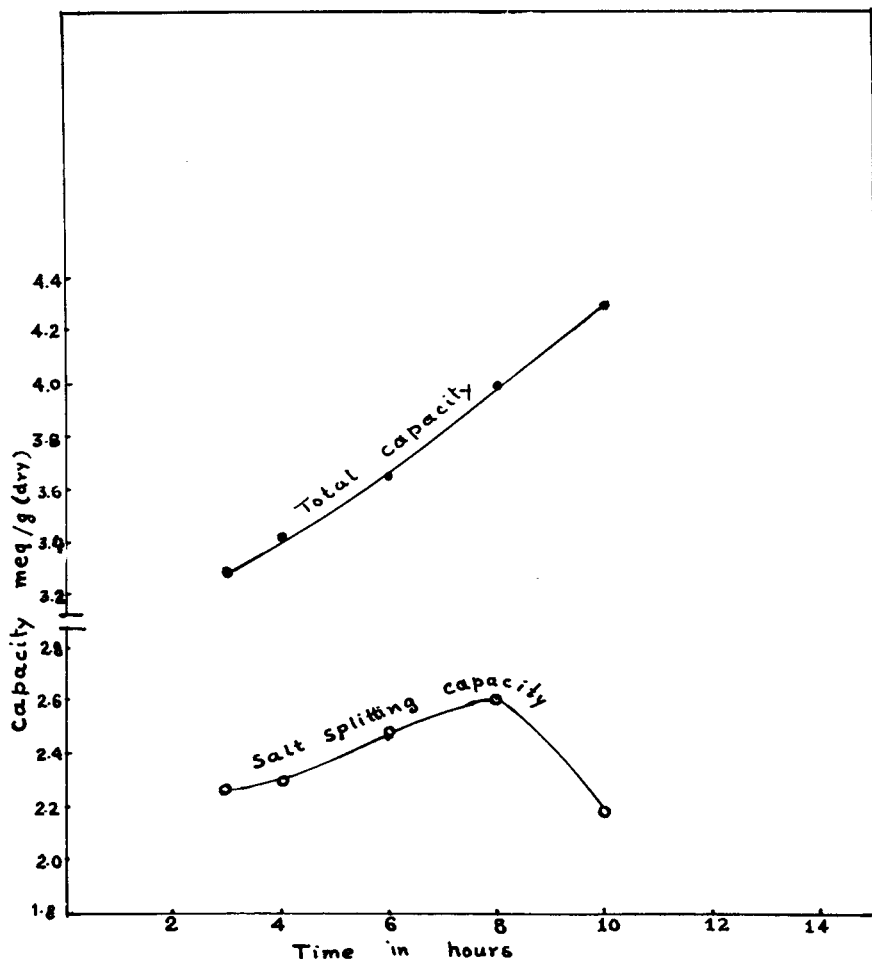


Fig. 2. Effect of varying time of sulfonation on capacity.

using anhydrous zinc chloride as well as anhydrous aluminum chloride (in different proportions) were also sulfonated, and the data are presented in Table II.

Phosphonic Acid-Type Cation-Exchange Resin (PFP). Ten grams of α -pinene furfural (1:1) polymer ($-20 + 40$ B.S.S.) was swollen in 20 ml ethylene dichloride for 10 min at $25^\circ \pm 1^\circ\text{C}$ in a three-necked flask carrying a condenser and a guard tube containing anhydrous calcium chloride. Phosphorus trichloride, 20 ml, containing the known amount of anhydrous aluminum chloride was added. The contents were vigorously stirred and refluxed at 80°C and then allowed to cool, poured into ice-cold water, and filtered. The product was washed free of reactants, air dried for about 12 hr, and hydrolyzed with 100 ml of 4% sodium hydroxide solutions for 2 hr at $60\text{--}70^\circ\text{C}$ in a 500-ml round-bottom flask. The resulting resin was filtered, washed free of reactants, conditioned, and capacity determined by the usual procedure.²

The time of phosphorylation and the catalyst concentration were varied, and the results are presented in Tables III and IV.

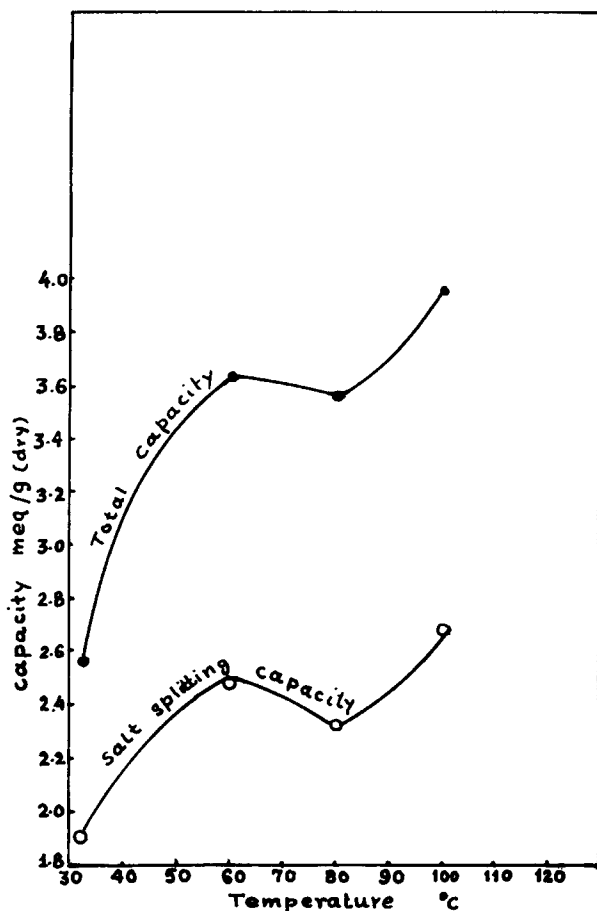


Fig. 3. Effect of varying temperature of sulfonation on capacity.

In order to increase capacity of PFP, resin prepared using 17% catalyst (based on the weight of polymer) was rephosphorylated following the same procedure. The results are presented in Figure 4.

Hydroxyphosphonic Acid-Type Cation-Exchange Resin (PFAP).

Acetylation: Ten grams of α -pinene-furfural (1:1) polymer (-20 $+40$ B.S.S.) was swollen in 60 ml carbon disulfide for 10 min at $30^\circ \pm 1^\circ\text{C}$, and 15 ml acetyl chloride containing a known quantity of anhydrous aluminum chloride was added slowly with stirring. The stirring was continued for 8 hr at $30^\circ \pm 1^\circ\text{C}$. The reaction mixture was then poured into ice-cold water, filtered, washed free of reactants, and air dried.

Phosphorylation of the Acetylated Polymer: The acetylated air-dried product obtained as above was swollen in 25 ml ethylene dichloride for 10 min in a tightly stoppered bottle and 25 ml phosphorus trichloride was added. The mixture was then kept at $30^\circ \pm 1^\circ\text{C}$ for 24 hr with occasional shaking, then poured into ice-cold water and filtered. The residue was washed free of reactants and the resin obtained was conditioned and capacity determined.

Following the same procedure, the polymer was acetylated using different concentrations of anhydrous aluminum chloride in separate experiments and processed further. The results are presented in Figure 5.

In order to increase the capacity of the PFAP, repeated acetylation followed by phosphorylation was carried out. The results are given in Table V.

TABLE II
Effect of Variation of Catalyst Concentration on Capacity of Sulfonated Copolymer^a

Catalyst	Catalyst, %	Salt-splitting capacity, meq/g(dry)	Total capacity, meq/g(dry)
Anhydrous zinc chloride	3	2.48	3.65
-do-	6	2.01	2.64
-do-	9	2.10	2.80
-do-	12	2.50	3.19
Anhydrous aluminum chloride	12	2.04	3.42
-do-	15	2.08	3.43
-do-	18	1.63	3.46

^a α -Pinene: furfural (1:1) polymer: sulfuric acid 1:10 (weight by weight); reaction temperature 60°C; time: 6 hr.

TABLE III
Effect of Variation of Duration of Phosphorylation on Capacity (PFP Resin) of the Product^a

Reaction time, hr	Salt-splitting capacity, meq/g(dry)	Total capacity, meq/g(dry)
3	0.20	1.88
6	0.19	1.47

^a α -Pinene: furfural 1:1 polymer: 10 g; quantity of catalyst (anhydrous aluminum chloride): 17%; temperature for reaction: 80°C; temperature for hydrolysis: 60–70°C; hydrolysis time: 2 hr.

TABLE IV
Effect of Variation of the Catalyst Concentration During Phosphorylation on Capacity (PFP Resin)^a

Amount of catalyst, %	Salt-splitting capacity, meq/g(dry)	Total capacity, meq/g(dry)
10	—	0.98
17	0.2	1.88
50	0.34	1.99
100	0.34	2.17
135	0.45	2.62

^a α -Pinene: furfural (1:1) polymer: 10 g; temperature for phosphorylation: 80°C; temperature for hydrolysis: 60–70°C; time for phosphorylation: 3 hr; time for hydrolysis: 2 hr; catalyst: anhydrous aluminum chloride.

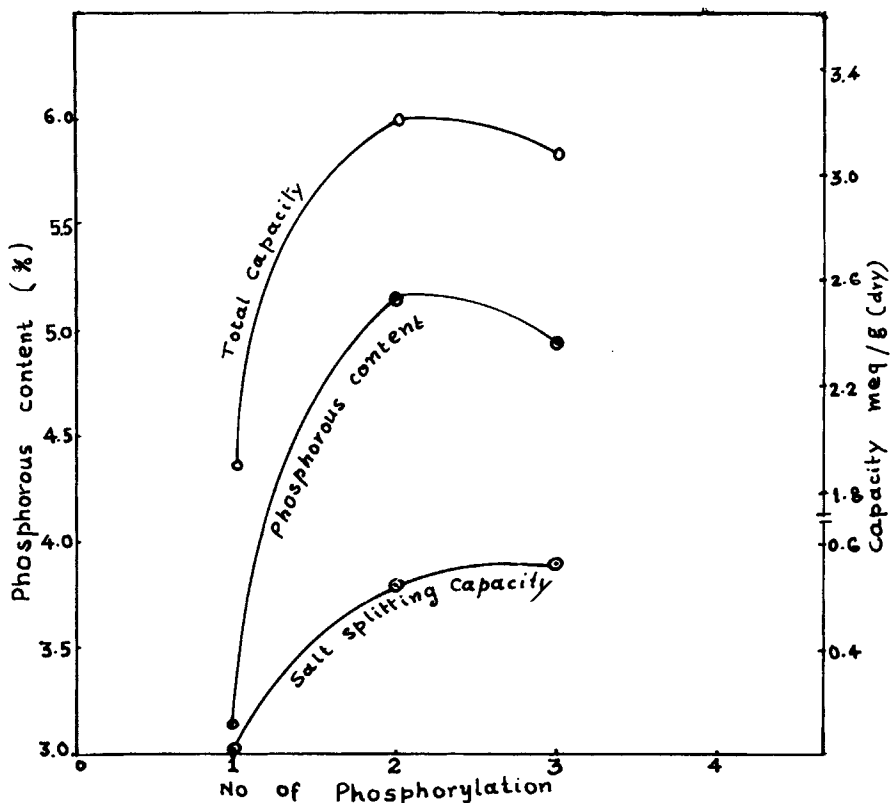


Fig. 4. Effect of rephosphorylation on capacity.

Elemental Analysis of Sulfonic and Phosphonic Acid-Type Resins

Determination of Sulfur Content in PFS. The S content of the PFS resin was determined by adopting a standard procedure.³ The results are given in Table VI.

Determination of P Content in PFP and PFAP. Accurately weighed quantities of absolute dry resin in the H^+ form were digested in a mixture of concentrated sulfuric acid and concentrated nitric acid (2:1) in a Kjeldahl flask. The phosphorus content in the digested sample was estimated by a standard procedure.⁴ The results are presented in Table VI.

DISCUSSION

Harvey⁵ has reported condensation of α -pinene and formaldehyde in the ratio of 1:1-7 in the presence of water and an acid catalyst. The product obtained was a liquid. Isagulants and Khomko⁶ have also reported condensation of α -pinene and formaldehyde in the presence of a strongly acidic cation-exchange resin. Since the product obtained was a liquid, an attempt was made to crosslink the same (in this investigation) by treating separately with phenol and furfural. It was observed that crosslinked products could be obtained. This observation prompted the use of furfural in place of formaldehyde to obtain crosslinked products.

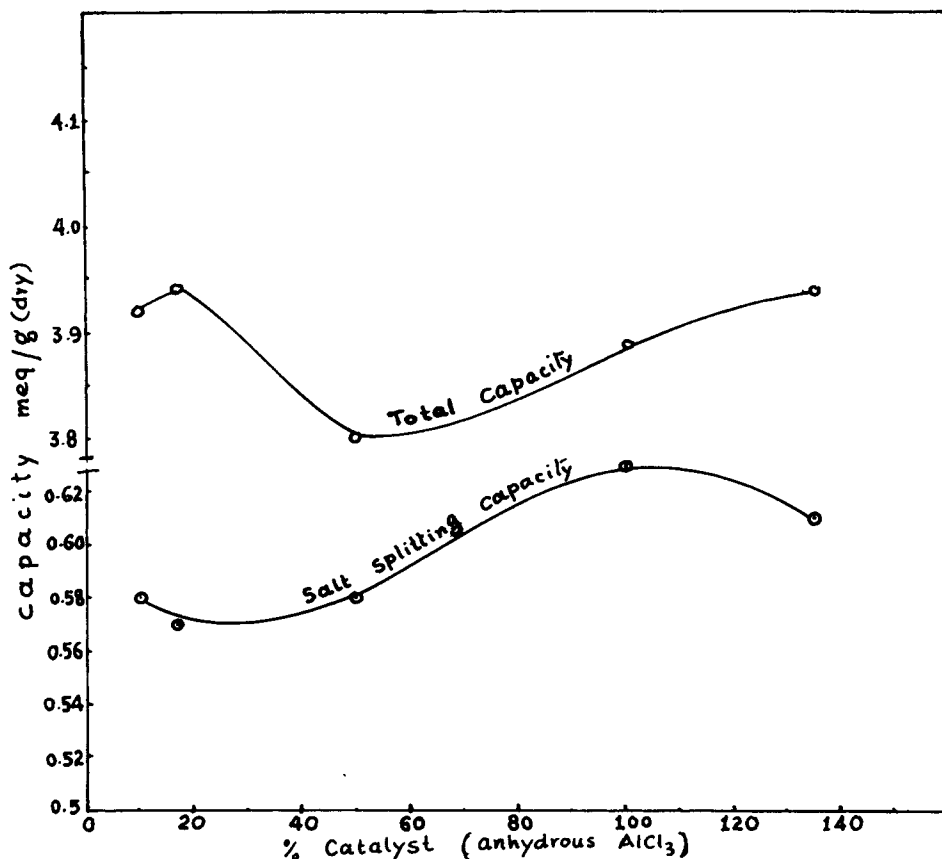


Fig. 5. Effect of varying catalyst concentration on capacity of product (PFAP resin).

Data in Table I reveal that the product obtained by reacting α -pinene and furfural in the ratio 1:0.5 was thermoplastic. The polymers obtained with 1:1 and 1:2 molar ratios were thermosetting hard, shining materials suitable for further processing. The 1:1 mole has given a maximum yield. As a catalyst for the above reaction, it was observed that anhydrous aluminum chloride was not very suitable as evidenced by the poor yield of a polymer. Anhydrous zinc chloride, however, was suitable and a concentration range of 3–12% (based on the weight of α -pinene) yielded a satisfactory product (Table II, Fig. 1).

It is clear from Figures 2 and 3 that the α -pinene furfural polymer can be sulfonated successfully into a cation exchange resin. An increase in temperature has resulted in an increase in capacity. However, sulfonation at 60°C for 6 hr was found ideal. It is interesting to observe that with increase in time and temperature of reaction, the difference between salt-splitting capacity and the total capacity increased. This polyfunctionality of the resin is explained elsewhere.⁷

The effect of variation of the duration of the phosphorylation and amount of catalyst on the capacity of the resulting product as observed from Tables III and IV has not been significant. The results of rephosphorylation attempted with a view to increase the capacity presented in Figure 4 are self-

TABLE V
Effect of Duration of Acetylation and Phosphorylation on Capacity (PFAP Resin)^a

No. of acetylations	No. of phosphorylations	Salt-splitting capacity, meq/g(dry)	Total capacity, meq/g(dry)	Phosphorus content observed, %
1	1	0.58	3.92	4.80
1	2	0.54	4.32	6.50
1	3	0.65	4.02	6.56
2	1	0.54	3.53	5.90
2	2	0.69	4.82	6.70
2	3	0.72	4.62	7.50
3	3	0.69	4.91	7.50

^a α -Pinene: furfural (1:1) polymer: 10 g; quantity of catalyst (anhydrous aluminum chloride): 10% (based on the weight of polymer).

explanatory. The capacity has not improved in proportion with the increase in phosphorus content.

Compounds containing an aldehyde or ketone group react with phosphorus trichloride in the presence of glacial acetic acid to yield products containing hydroxyphosphonic acid groups after hydrolysis.⁸ In this investigation, the possibility of introducing a ketone group in the polymer matrix was investigated by acetylating the α -pinene furfural polymer. Data in Figure 5 reveal that the acetylated polymer after phosphorylation and hydrolysis has yielded a resin of higher capacity. This is in conformity with the reported data in the literature.⁸ Attempts were also made to increase the capacity of this resin by repeating acetylation and phosphorylation. Data in Table V reveal that re-acetylation and rephosphorylation of PFAP have not proved advantageous as the capacity of the product was not increased remarkably.

With a view to identify the repeating unit in the basic polymer, the phosphorus contents of PFP and PFAP were determined.⁴ The possible phosphorylation scheme is shown below:

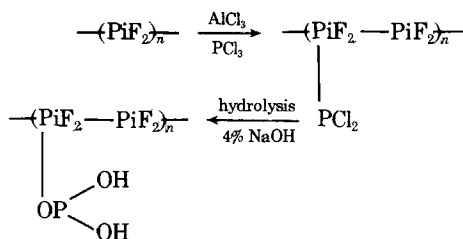
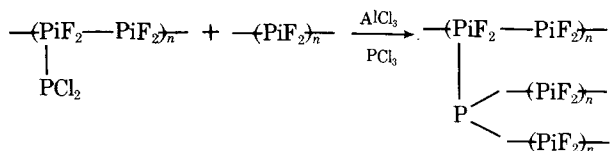


TABLE VI
Properties of Cation Exchange Resins

Name	Capacity theoretical based on S or P content, meq/g(dry)	Capacity observed, meq/g(dry)		Wet absolute density	S or P content, theoretical, %	S or P content, observed, %
		Salt-splitting	Total			
PFS	2.69	2.48	3.65	1.09	1.72	1.0
PFP	3.01	0.56	3.06	1.16	4.67	4.91
PFAP	4.23	0.69	4.91	1.11	4.37	7.45

where PiF_2^- shown as the repeating unit consists of one α -pinene and two furfural groups, and Pi is α -pinene. It is observed that after rephosphorylation, the phosphorus content and the capacity were 4.8% and 3.92 meq/g dry resin, respectively. The phosphorus content was higher after the third phosphorylation than what it should be for the capacity realized (Fig. 4), thus indicating that a significant portion of phosphorus was rendered inactive. A net increase in phosphorus content without proportionate increase in capacity can be explained by the following:



CONCLUSIONS

α -Pinene was polymerized with furfural in different proportions in the presence of anhydrous zinc chloride or aluminum chloride. It was established that α -pinene:furfural (1:1) polymer prepared using 3% anhydrous zinc chloride was found to be suitable and hence used for introducing ionogenic groups.

Three types of cation exchange resins were prepared from α -pinene-furfural (1:1) polymer. A strongly acidic cation exchange resin was prepared by sulfonation of the polymer at 60°C with 98% sulfuric acid for 6 hr (PFS).

A phosphonic acid-type resin (PFP) was prepared by phosphorylation of the polymer with phosphorous trichloride in the presence of anhydrous aluminum chloride (catalyst 17%) followed by hydrolysis.

A hydroxyphosphonic acid-type resin (PFAP) was prepared by phosphorylation of the acetylated polymer followed by hydrolysis with glacial acetic acid.

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