

# Phosphoric Acid Cation Exchange Resins from Chemically Modified Polyvinyl Chloride

MUKUL BISWAS and SUBRATA MOITRA, *Department of Chemistry, Indian Institute of Technology, Kharagpur 721 302, India*

## Synopsis

PVC modified by Cl displacement reaction with meta-aminophenol (MAP), bisphenol A (BIS A), and phenolphthalein (PHEN) has been converted into phosphoric acid cation exchange resins. These resins have been characterized in regard to their structure, ion exchange properties, and thermal stability. The ion exchange capacities fall into the range 5.5–8.0 (meq/g) for the resins. The overall thermal stability is considerably higher than that for the corresponding sulfonic acid resins, as well as for the PVC–MAP, PVC–BIS A, and PVC–PHEN condensates. The resins exhibit ca. 4–6% capacity losses under isothermal hydrolytic cleavage at 100°C for 24 h.

## INTRODUCTION

Recently Biswas and Moitra<sup>1–3</sup> described the preparation and characterization of sulfonic acid cation exchange resins from polyvinyl chloride (PVC) chemically modified through Cl displacement reaction with meta-aminophenol (MAP), bisphenol A (BIS A) and phenolphthalein (PHEN). Thermal stabilities of these sulfonated resins have been found to be significantly enhanced relative to PVC.<sup>4</sup>

It has now been possible to prepare phosphoric acid cation exchangers from PVC–MAP, PVC–BIS A, and PVC–PHEN, which exhibit significantly high ion exchange capacity values relative to commercial phosphoric acid ion exchanger, and possess appreciable thermal stability.

A review by Biswas and Packirisamy<sup>5</sup> disclosed the rather conflicting and meager literature on PVC-based ion exchangers. Therefore this report on PVC-based phosphoric acid resins may be of considerable significance. The publication will highlight the preparation, ion exchange, and thermal stability characteristics of these resins.

## EXPERIMENTAL

### Materials

Polyvinyl chloride (NOCIL;  $\bar{M}_v = 8.6 \times 10^4$ ) was reprecipitated from the THF solution by alcohol several times and finally dried in vacuum at room temperature. Phenolphthalein (Merck), bisphenol A (Merck), *m*-aminophenol (BDH),  $\text{PCl}_3$  (Merck), anhydrous  $\text{AlCl}_3$  (Riedel, West Germany), and THF (Merck) were used as supplied. All other materials were of analytical grade.

### Preparation of PVC-X Condensates

Into a 100-mL two-necked flask fitted with a stirrer, a condenser, and an insert tube for nitrogen, 1 g PVC, 1.5 g X (X = MAP, BIS.A, PHEN), 25 mL THF, and 10 mL ethylene diamine (catalyst) were added. The reaction was carried out for 8–10 h at 60°C. The resultant polymer was precipitated by adding methanol in excess and was filtered, washed several times with hot methanol, and dried at vacuum for 8 h at 50°C. The crude polymer-X condensate was purified by heating it with benzene (1 : 25 w/v) for 24 h at 55°C. The purified condensate was filtered, washed with hot benzene, and dried at vacuum at 50°C for 8 h.

### Preparation of PVC-X-PO<sub>3</sub>H<sub>2</sub> Resins

Two grams of the PVC-X was swollen in 30–40 mL of ethylene dichloride for 30 min at 25°C in a flask equipped with a reflux condenser and a CaCl<sub>2</sub> guard tube. To this, PCl<sub>3</sub> and AlCl<sub>3</sub> (catalyst) were added, the ratio of the polymer : PCl<sub>3</sub> : AlCl<sub>3</sub> being 1 : 5 : 2. After refluxing the mixture with stirring for 5 and a half h, the contents were poured into ice-water mixture slowly and then filtered. The product was heated with 4% NaOH solution (25 mg/g resin) at 65–75°C for 2 h. It was filtered and washed free of alkali with deionized water. The resin was then stirred with 2 N HCl (25 mL/g resin) for 24 h at 25°C, washed with deionized water until free of Cl<sup>-</sup>, air-dried, and finally cured for 6–8 h at 50°C.

## CHARACTERIZATION

### IR Spectra

IR spectra of PVC-X-PO<sub>3</sub>H<sub>2</sub> resins were taken on a Perkin-Elmer 237B Infrared Spectrophotometer.

### Elemental Analysis

The amount of phosphorous in the PVC-X-PO<sub>3</sub>H<sub>2</sub> resins was quantitatively estimated by the following procedure. An accurately weighed amount (ca. 50 mg) of the dry resin was mixed with a mixture of Na<sub>2</sub>O<sub>2</sub> and Na<sub>2</sub>CO<sub>3</sub> (3 : 1) in a nickel crucible, and the contents were fused for 30 min. The phosphorous present in the resin was thus converted into sodium phosphate, which was estimated gravimetrically using ammonium phosphomolybdate by the standard procedure.

### Thermogravimetric (TG) Analysis

TG analyses of the resins were carried out on a Stanton-Redcroft thermal analyzer in air with a heating rate of 10°C/min.

### Evaluation of Ion Exchange Capacity

The total ion exchange capacity was evaluated by the usual procedure.<sup>6</sup>

TABLE I  
Preparation, Characterization, and Ion Exchange Properties of PVC-X-PO<sub>3</sub>H<sub>2</sub> Resins

Synthesis		Ion-exchange properties							
Condensate	Temp. of phosphorylation (°C)	Characterization		Ion exchange capacity (meq/g)	pK values		Capacity <sup>a</sup> after heating	Reference	
		Yield (%)	Color		pK <sub>1</sub>	pK <sub>2</sub>			
1 PVC-MAP-PO <sub>3</sub> H <sub>2</sub>	60	75	Black	5.5	3.5	7.4	6.2	5.3	This work
	75	72	Brownish-black	4.8	—	—	—	—	—
2 PVC-BIS A-PO <sub>3</sub> H <sub>2</sub>	60	76	Brownish-black	7.8	3.3	7.8	8.5	7.4	This work
	75	70	Brownish-black	5.4	—	—	—	—	—
3 PVC-PHEN-PO <sub>3</sub> H <sub>2</sub>	60	70	Deep brown	8.0	3.2	8.1	8.9	7.6	This work
	75	71	Deep brown	3.4	—	—	—	—	—
4 Duolite ES-63 (S/DVB/P)	—	—	—	6.1	—	—	—	—	6
5 NVC-DVB-P	—	—	—	5.4	—	—	—	—	9
6 NVC-F-P	—	—	—	5.2	—	—	—	—	5
	—	—	—	5.1	—	—	—	—	—
7 NVC-FO-P	—	—	—	3.7	—	—	—	—	10
8 SFP	—	—	—	4.9	—	—	—	—	11
9 PFP	—	—	—	4.0	—	—	—	—	8
	—	—	—	2.6	—	—	—	—	—

<sup>a</sup> Heating the resin in sealed tube in water at 100°C for 24 h. S = styrene; DVB = divinylbenzene; NVC = N-vinylcarbazole and its polymer = PNVC; F = furfural; FO = formaldehyde; P = alpha-pinene.

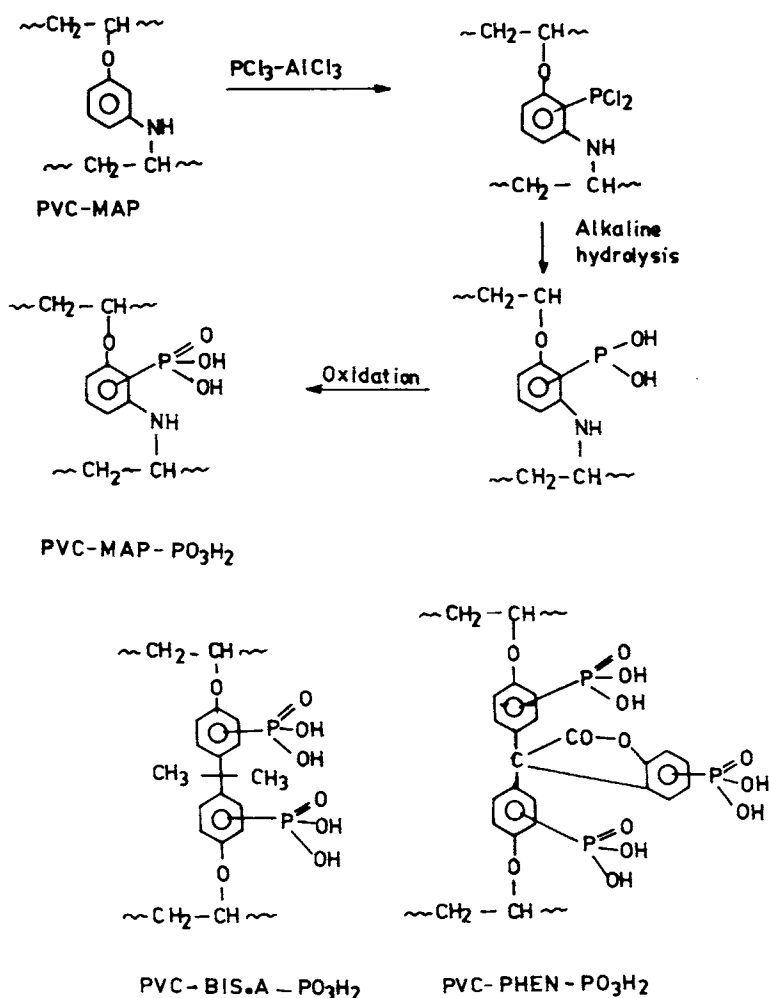


Fig. 1. Suggested scheme for the formation of PVC-MAP- $\text{PO}_3\text{H}_2$ , PVC-BIS A- $\text{PO}_3\text{H}_2$ , and PVC-PHEN- $\text{PO}_3\text{H}_2$ .

### pH-Metric Titration

The pH-metric titration behavior of the PVC-X- $\text{PO}_3\text{H}_2$  resins was examined following a procedure detailed elsewhere.<sup>6</sup>

## RESULTS AND DISCUSSION

Table I presents the relevant data on the synthesis and some properties of all the PVC-X- $\text{PO}_3\text{H}_2$  resins. Limiting yields (ca. 70–75%) could be realized for all the resins at 60°C used for the phosphorylation reaction with a fixed ratio of PVC-X :  $\text{PCl}_3$  :  $\text{AlCl}_3$  (1 : 5 : 2). The choice of  $\text{PCl}_3\text{-AlCl}_3$  as the phosphorylating agent is in accordance with the literature.<sup>6–9</sup> The phosphorylation mechanism proposed in Figure 1 is similar to that established for the

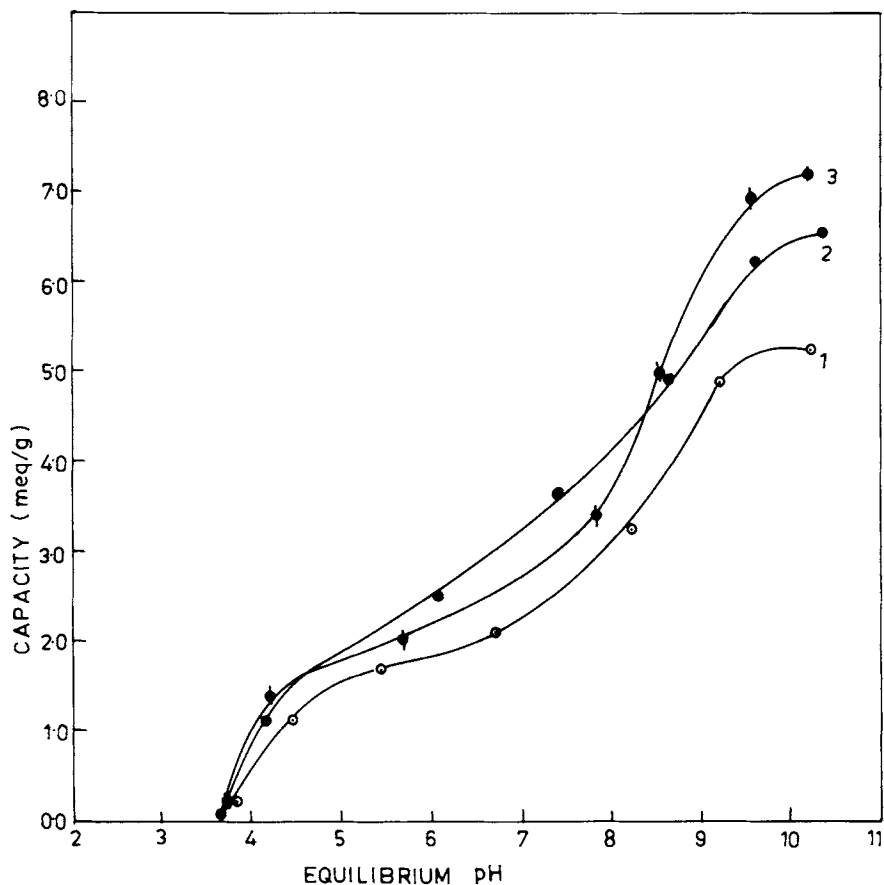


Fig. 2. Ion exchange capacity -pH plots for (1) PVC-MAP- $\text{PO}_3\text{H}_2$ , (2) PVC-BIS A- $\text{PO}_3\text{H}_2$ , and (3) PVC-PHEN- $\text{PO}_3\text{H}_2$  resins.

phosphorylation of poly-*N*-vinylcarbazole by Pielichowski<sup>7</sup> and of PNVC-furfural/formaldehyde copolycondensates by Biswas et al.,<sup>6,9</sup> which use the same procedure for the phosphorylation reaction.

TABLE II  
Comparison and Thermal Stability Characteristics of Some PVC-based Resins

Resin	Ion exchange capacity (meq/g)	Temperature ( $^{\circ}\text{C}$ ) for percent weight losses				References
		10	50	75	80	
PVC-MAP- $\text{PO}_3\text{H}_2$	5.5	110	605	725	820	This work
PVC-MAP-S	3.4	150	470	555	570	4
PVC-PHEN- $\text{PO}_3\text{H}_2$	8.0	125	350	575	605	This work
PVC-PHEN-S	3.1	95	370	510	555	4
PVC-BIS A- $\text{PO}_3\text{H}_2$	7.8	150	380	700	760	This work
PVC-BIS A-S	3.2	105	505	650	675	4

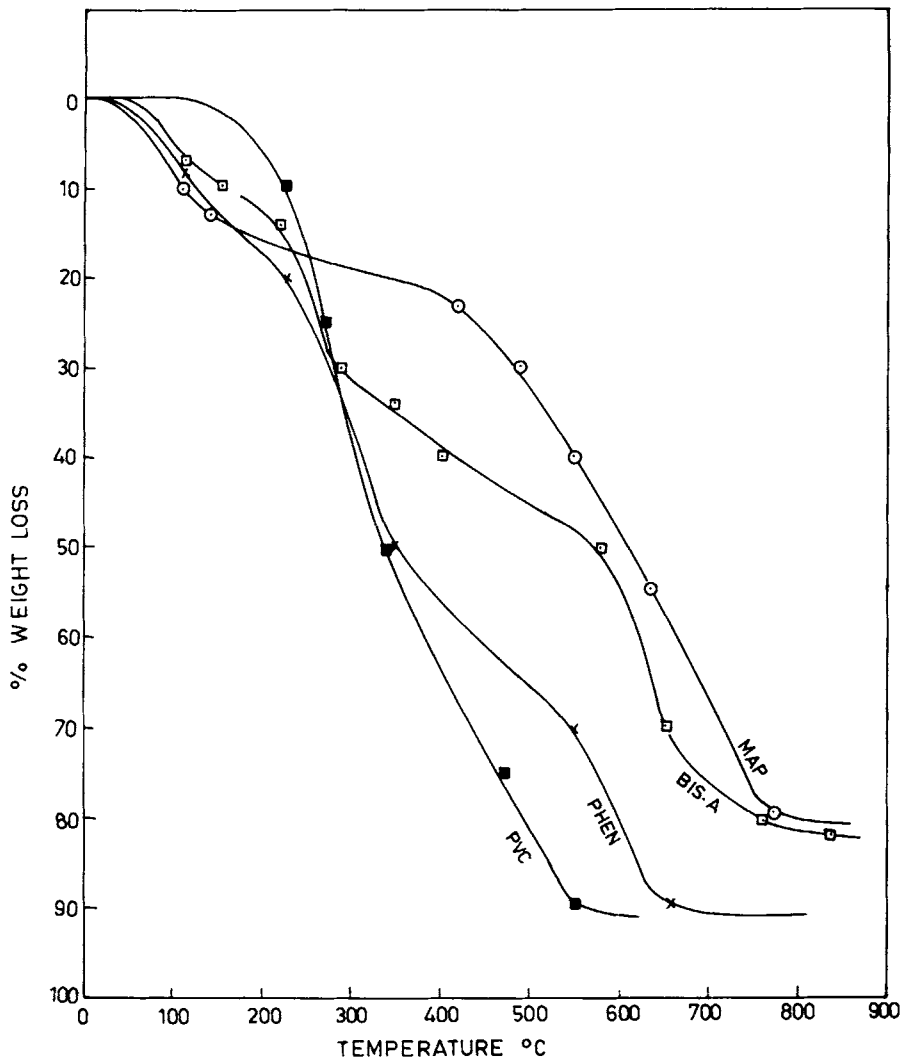


Fig. 3. Percent weight loss versus temperature graph for the phosphorylated PVC resins.

The resins are deeply colored and insoluble in all solvents for PVC. The general insolubility is apparently due to incorporation of bulky groups in the PVC chain at the cost of chain flexibility. Further, bifunctional moiety like MAP, BIS A or PHEN would introduce intermolecular crosslinking<sup>1</sup> that would also enhance the general insolubility.

#### Ion Exchange Properties

Table I summarizes the ion exchange capacities of the phosphorylated PVC resins. The ion exchange capacities show high values at 60°C as the phosphorylation temperature; and as this temperature increases, the former tends to fall. The ion exchange capacities vary with the various moieties in the following order: PHEN > BIS A > MAP. This may be due to the possibility that

TABLE III  
Isothermal Hydrolytic Stability of Some PVC-based Phosphorylated Resins

Resin	Percent loss in capacity	References
NVC-DVB-P	7.40	9
NVC-F-P	—	5
PNVC-F-P	—	5
S-F-P	4.10	11
P-F-P	28.39	8
PVC-MAP-PO <sub>3</sub> H <sub>2</sub>	3.78	
PVC-BIS A-PO <sub>3</sub> H <sub>2</sub>	5.12	
PVC-PHEN-PO <sub>3</sub> H <sub>2</sub>	5.00	This work

the larger the number of aromatic groups introduced the higher will be the extent of phosphorylation and hence the ion exchange capacity. The presence of phosphorous and the PO<sub>3</sub>H<sub>2</sub> ionogenic groups in the resin is endorsed by the results of elemental analysis and pH titration behavior (Fig. 2); the latter confirms the occurrence of two dissociation equilibria (Table I) expected for the PO<sub>3</sub>H<sub>2</sub> ionogenic groups in the resins.<sup>6</sup>

### Thermal Stability

Phosphorylated PVC-X resins show higher overall thermal stability than the sulfonated PVC-X,<sup>4</sup> (Table II) unmodified PVC-X,<sup>4</sup> and PVC<sup>4</sup> itself. The order in stability for the three resins is PVC-PHEN-P < PVC-BIS-P < PVC-MAP-P (Fig. 3), which is parallel to what has been observed for the sulfonated PVC-X resins.<sup>4</sup> It appears that during phosphorylation with PCl<sub>3</sub> : AlCl<sub>3</sub>, a milder reagent than fuming sulfuric acid, the weakening of the PVC-X matrix due to oxidative rupture will be to a lesser extent, implying an enhanced stability for the PVC-X-P resins compared to PVC-X-SO<sub>3</sub>H resins, as actually observed.

The PVC-X-P resins also show only 3.6–6.4% capacity losses after isothermal heating at 100°C for 24 h (Table I). This is appreciably low as compared (Table III) to the capacity losses under similar conditions for some phosphorylated copolymer resins reported in the literature.

### CONCLUSIONS

Phosphoric acid resins with ion exchange capacities comparable to commercial S-DVB resins can be prepared by phosphorylation of PVC modified by Cl displacement reaction with *m*-aminophenol, bisphenol A, and phenolphthalein. These resins possess higher overall thermal stability than the corresponding sulfonic acid resin and undergo 3–6% capacity losses under isothermal heating at 100°C for 24 h.

### References

1. M. Biswas and S. Moitra, *Polymer Preprints*, Am. Chem. Soc., Division of Polymer Chem., **27**(2), 76 (1986).

2. M. Biswas and S. Moitra, unpublished results.
3. M. Biswas and S. Moitra, *Polym. Bull.*, **17**, 361 (1987).
4. M. Biswas and S. Moitra, *J. Appl. Polym. Sci.*, **37**, 1855 (1989).
5. M. Biswas and S. Packirisamy, *Adv. Polym. Sci.*, **70**, 71, (1985).
6. F. Helfferich, *Ion Exchange*, McGraw-Hill, New York, 1962; M. Biswas and S. Packirisamy, *J. Appl. Polym. Sci.*, **27**, 149 (1982) and related papers.
7. J. Pielichowski and E. Morawiec, *J. Appl. Polym. Sci.*, **20**, 1803 (1976).
8. B. J. Mehta and N. Krishnaswamy, *J. Appl. Polym. Sci.*, **20**, 2239 (1976).
9. M. Biswas and S. Bagchi, *J. Polym. Mat.*, **2**, 123 (1985).
10. M. Biswas and S. Bagchi, *J. Appl. Polym. Sci.*, **29**, 3753 (1984).
11. R. Ramaswamy and N. Krishnaswamy, *Ind. J. Tech.*, **10**, 185 (1972).

Received January 27, 1989

Accepted June 21, 1989