

Cation Exchange Resin from Phosphorylated *N*-Vinylcarbazole Formaldehyde Copolymer

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Synopsis

Crosslinked copolymers of *N*-vinylcarbazole and poly(*N*-vinylcarbazole) and formaldehyde have been phosphorylated using PCl_3 and anhydrous AlCl_3 under different conditions. The cation exchange resins, thus obtained, have been characterized by elemental analyses, evaluation of total ion-exchange capacities and salt-splitting capacities, pH metric titration behavior, and IR analysis. The phosphorylated resin exhibits significantly better thermal stability than the corresponding sulfonated *N*-vinylcarbazole-formaldehyde cation exchange resin or the unmodified *N*-vinylcarbazole-formaldehyde copolymer, as well as the phosphorylated poly(*N*-vinylcarbazole). The phosphorylated resins also behave as polymeric dyes with pH dependent color change. Possible explanations for color change and ion-exchange capacity differences have been attempted on the basis of the structural characteristics of the resins.

INTRODUCTION

In an earlier publication¹ we observed that the novel copolymerization of *N*-vinylcarbazole (NVC) with formalin (FO) yields a crosslinked product of better thermal property than the unmodified poly(*N*-vinylcarbazole) (PNVC). Subsequently, we reported² the synthesis and characterization of a sulfonic acid cation exchange resin from the NVC-FO copolymer. We now describe in this paper the synthesis, characterization, and some pertinent physicochemical property evaluation of the phosphorylated cation exchange resin based on the NVC-FO copolymer, which appears to possess greater thermal stability than the other polymers or resins reported in the series.

EXPERIMENTAL

N-vinylcarbazole (NVC), poly(*N*-vinylcarbazole) (PNVC), DP = 5750 were both supplied by BASF, West Germany, and NVC was purified by the standard procedure.³

Formalin, a 37% aqueous solution of formaldehyde gas, was supplied by B.D.H., India.

PCl_3 (E. Merck, West Germany) and anhydrous AlCl_3 (Riedel, West Germany) were used without further purification. All other materials were of analytical grade certified reagents.

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Preparation of *N*-Vinylcarbazole-Formaldehyde Copolymers

This was prepared in two ways.¹ In the first method, NVC and FO were reacted in toluene solvent in the presence of HCl vapor at 110°C. The resulting copolymer, P[NVC-FO], was processed as before¹ and used for phosphorylation. In the second method, PNVC and formalin were reacted together in toluene at 110°C in the presence of HCl vapor. The details of these preparations have been described earlier.¹ Both the copolymers, P[NCV-FO] and PNVC-FO were freed from homopolymers and unreacted monomers¹ and used for phosphorylation.

Preparation of the Cation-Exchange Resin

Two grams of any of the above copolymers were swollen in 30–40 mL of ethylene chloride for 15 min at room temperature in a flask fitted with a reflux condenser and a CaCl₂ guard tube. A known volume of PCl₃ and a weighed amount of AlCl₃ were then added to the solution, the weight ratio of the polymer:catalyst:phosphorylating agent being generally 1:2:5. After refluxing with stirring for a predetermined time interval, the contents were poured into ice cold water and were subsequently filtered. The product was washed free of the reactants and treated with 4% solution of NaOH (25 mg/g resin) for 2 h at 60–75°C. The resulting resin was filtered, washed free of alkali, treated with 2*N* HCl for 24 h (25 mL/g resin) at the room temperature (20°C), and finally washed with deionized water till free of Cl⁻ (sorbed HCl). The resin was then air-dried and then cured⁴ for 6–8 h at 100–110°C.

Characterization

Elemental Analysis. Phosphorus in the resins was estimated by the following procedure. An accurately weighed quantity (ca. 50 mg) of the resin in the H-form was mixed intimately with a mixture of Na₂O₂ and Na₂CO₃ (3:1) in a nickel crucible and the contents were fused for 30 min. The phosphorus present in the resin was thus converted into sodium phosphate, which in turn, was estimated quantitatively with ammonium phosphomolybdate gravimetrically with a standard procedure.⁵

Evaluation of Ion-Exchange Capacity. The total ion-exchange capacity and the salt-splitting capacity, i.e., the capacity of the resin in equilibrium with an electrolyte such as NaCl,⁶ were determined after 24 h of equilibration of the resin in the electrolyte solution by following the procedure described by Helfferich.^{6,7}

pH-Metric Titration. Incremental quantities of NaOH solution (0.1*M*) were added to different mixtures containing a known weight of the resin and 10 mL NaCl solution (1.0*M*), keeping the total volume at 50 mL by adding deionized water. The equilibrium pH of the solution was measured with a Digilog pH Meter. The ion-exchange capacities were evaluated after the attainment of a constant pH in each case.^{4,6,7}

Rate of Exchange. Accurately weighed quantities of the resins in the H-forms were taken in different glass stoppered flask (100 mL) and 50 mL of 0.1*M* NaOH solution was added to each flask, which was then shaken

occasionally at room temperature. The ion-exchange capacity was then determined after a predetermined time interval. The same procedure was repeated using 1.0M NaCl as the contact solution.

Thermal Hydrolytic Stability in Water. A known weight of the resin was treated with 25 mL of deionized water in different glass ampoules, which were then sealed off and maintained at desired temperatures for a period of 24 h.^{4,5,8} The contents were then taken out, washed, and dried, and their ion-exchange capacities were evaluated.

IR Spectra. The IR spectra of the resins were recorded on a Perkin-Elmer 237B Spectrophotometer in KBr pellets.

Thermogravimetric Analysis (TGA). TGA of the resin samples were performed with a Shimadzu DT 30 Thermal Analyser.

RESULTS AND DISCUSSION

Physical Properties of the Resins

The P[NVC-FO] copolymer is colorless and the PNVC-FO copolymer is light brown in color, while the phosphorylated P[NVC-FO], hereinafter designated as P[NVC-FO]-P, and the phosphorylated PNVC-FO, PNVC-FO-P, are colored clear green and dirty green, respectively. The resins are insoluble in common organic solvents. In presence of concd H₂SO₄, P[NVC-FO]-P resin becomes brilliant blue and the PNVC-FO-P resin becomes intense green in color.

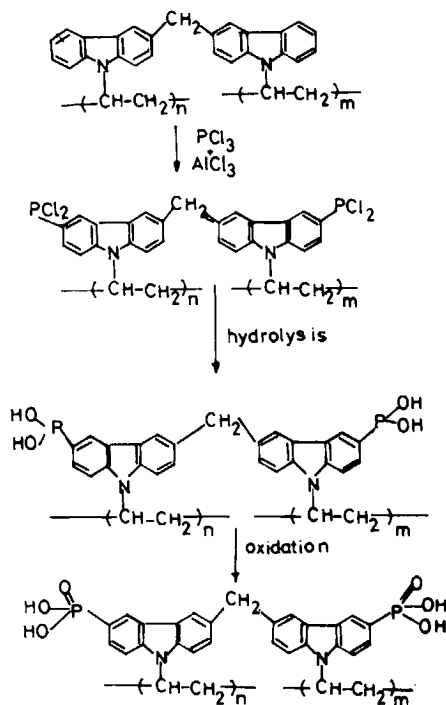
Factors Affecting the Phosphorylation Reaction

With an optimum polymer:catalyst:phosphorylating agent ratio of 1:2:5, the phosphorus content, total ion-exchange capacity, and the salt-splitting capacities of the resins are influenced by the time of phosphorylation, as suggested by the data of Table I. Highest phosphorus incorporation and total ion exchange capacity values are realized for either resins when the phosphorylation is conducted for 5.5 h. Pertinently, with both P[NVC-FO]-P and PNVC-FO-P, the total ion-exchange capacity values of 3.7 meq/g and 4.9 meq/g are significantly higher than the same for phosphorylated PNVC,⁹ 2.9 meq/g. It is also remarkable that the phosphorus contents of P[NVC-FO]-P, PNVC-FO-P, and PNVC-P are almost the same (11.8%, 10.9%,

TABLE I
Results of Phosphorylation of P[NVC-FO] and PNVC-FO Copolymers^a

| Copolymer | Time of phosphorylation (h) | Phosphorus (%) | Ion-exchange capacity, total salt-splitting (meq/g resin) | |
|-----------|-----------------------------|----------------|---|------|
| P[NVC-FO] | 3 | 8.0 | 3.0 | 0.49 |
| P[NVC-FO] | 5 $\frac{1}{2}$ | 11.8 | 3.7 | 0.59 |
| PNVC-FO | 3 | 6.3 | 3.2 | 0.48 |
| PNVC-FO | 5 $\frac{1}{2}$ | 10.9 | 4.9 | 0.61 |

^a Amounts of PCl₃, catalyst (AlCl₃), and copolymers described in text; temperature of phosphorylation = 76°C.



Scheme 1. Schematic representation of the phosphorylation action.

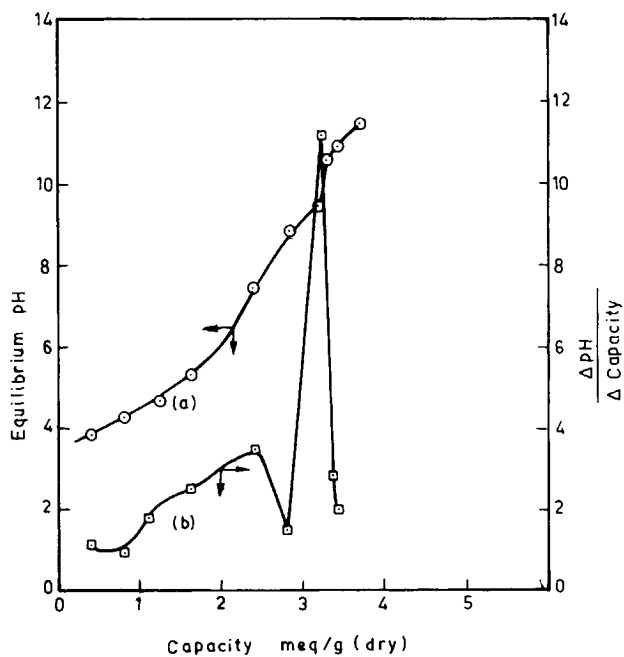


Fig. 1. pH metric titration of P[NVC-FO]-P: (a) pH-ion exchange capacity plot; (b) differential plot.

10.84%, respectively), although the ion-exchange capacity values of the former two are greater than that for the latter. This may be explained in terms of the structures of the polymers obtained in the present context. Thus, both P[NVC-FO]-P and PNVC-FO-P are apparently more crosslinked through $-\text{CH}_2-$ moiety (Fig. 3) than PNVC-P, so that chain flexibility is expected to be more in the latter case than in the former. Now, the fact that PNVC-P has comparable P content, but lower ion-exchange capacity than the others two, implies that somehow the activity of the ionogenic group is shielded. It is possible that greater chain flexibility in PNVC-P allows the interaction between $-\text{P}(\text{OH})_2$ or $-\text{P}(\text{OH})_2$ ionogenic groups,⁹



leading to the formation of inactive phosphone groups, as also pointed out by Pielichowski and Morawiec.⁹ Apparently, the more rigid network in P[NVC-F]-P or PNVC-FO-P disfavors such interaction between the ionogenic groups, so that higher ion-exchange capacity is exhibited.

pH-Metric Titration of P[NVC-FO]-P and PNVC-FO-P

Figures 1 and 2 represent the pH-metric titration behavior of P[NVC-FO]-P and PNVC-FO-P resins, respectively. The differential plots indicate that there are two degrees of dissociation for either resins, the first degree of dissociation occurring in the pH range 3.86–9.48 and the second one in the range 9.48–11.45 for P[NVC-FO]-P, and in the pH range 3.12–6.75 and 6.75–11.80 for PNVC-FO-P resin. The maximum capacities realized for the

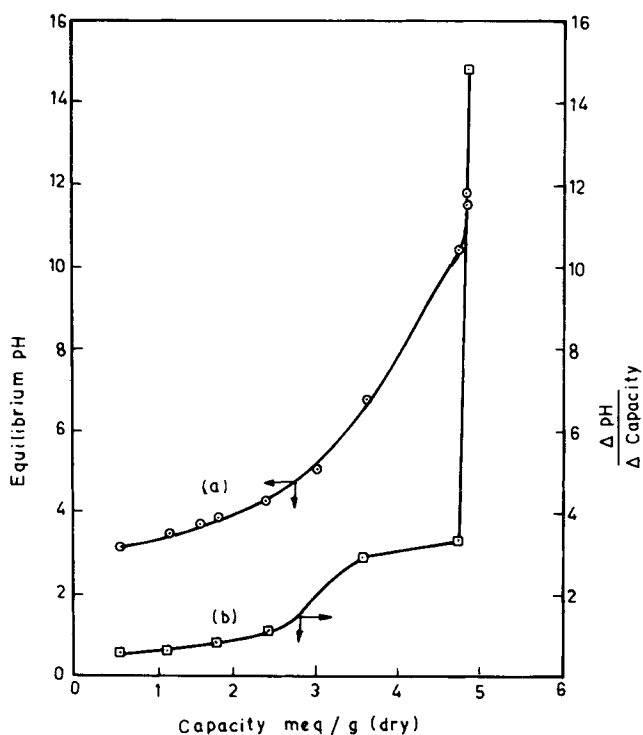


Fig. 2. pH metric titration of PNVC-FO-P: (a) pH-ion exchange capacity plot; (b) differential plot.

first and the second degrees of dissociation are 3.2, 0.5 and 3.6, 1.2 meq/g for P[NVC-FO]-P and PNVC-FO-P resins, respectively. The apparent pK values, as calculated from these data by the procedure of Helfferich,⁶ are presented in Table II along with the corresponding data for some other NVC-based and styrene-based phosphorylated resins.

Comparison of Ion-Exchange Capacity of P[NVC-FO]-P and PNVC-FO-P

Between the above two resins PNVC-FO-P possesses a higher ion exchange capacity than P[NVC-FO]-P. In the synthesis of P[NVC-FO] matrix, the condensation of the formaldehyde with the aromatic ring to form the —CH₂— bridge occurs competitively with chain growth for the PNVC. The molecular weight of the polymer cannot be very high under these conditions, more so in the presence of the basic formaldehyde during the cationic polymerization of NVC. In contrast, in the PNVC matrix (high DP = ca. 5750) condensation with formaldehyde produces a comparatively less compact structure than in the case with P[NVC-FO]. Consequently, in P[NVC-FO]-P the more compact structure opposes the accessibility of the ions showing a lower ion-exchange capacity.

Thermal Stability of P[NVC-FO]-P and PNVC-FO-P

Hydrolytic Stability. Both the resins undergo negligible loss in ion-exchange capacity when heated in a sealed tube in presence of water at 100°C for 24 h. Similar features were also observed for the furfural modified PNVC resins also.^{4,10}

Thermogravimetric Analysis of the Resins. Table III clearly indicates that PNVC-FO-P possesses a significantly higher thermal stability than unmodified PNVC and also the corresponding formaldehyde-modified sulfonated PNVC as well as the unsulfonated formaldehyde-modified PNVC. In fact, at ca. 493°C only 43% decomposition is realized for PNVC-FO-P while the corresponding sulfonated PNVC-FO-P is virtually completely

TABLE II
Comparison of Certain Properties of Phosphonic Acid Cation Exchange Resins

| Resin | Total ion-exchange capacity (meq/g) | pK ₁ | pK ₂ | Color | Reference |
|--------------------------|-------------------------------------|-----------------|-----------------|-------------|-----------|
| P[NVC-FO]-P ^a | 3.7 | 4.50 | 10.90 | Green | This work |
| PNVC-FO-P | 4.9 | 2.90 | 10.65 | Light green | This work |
| PNVC-P | 2.99 | — | — | — | 9 |
| P[NVC-F]-P ^b | 5.18 | 3.88 | 11.30 | Black | 4,10,13 |
| PNVC-F-P | 5.12 | 3.08 | 8.85 | Brown | 4,10,13 |
| P[SF]-P | 4.33 | 2.74 | 7.23 | — | 14 |
| P[αpynene-F]-P | 3.01 | 2.62 | 8.70 | — | 15 |
| Duolite ES-63b (S-DVB) | 6.05 | 2.78 | 6.09 | — | 14 |
| P[NVC-DVB]-P | 5.4 | 4.0 | 10.0 | Brown | 3 |

^a P indicates the phosphorylated resin.

^b F = furfural; S = styrene; DVB = divinylbenzene.

TABLE III
Thermal Stability of Some NVC-Based Resins

| Polymer | % Decomposition at different temperatures (°C) | | | | | maximum decomposition |
|------------------------|--|------|------|------|------|-----------------------|
| | 100 | 200 | 300 | 400 | 500 | |
| PNVC-FO-P | 2.6 | 6.0 | 9.9 | 38.1 | — | 42.8 (493°C) |
| PNVC-FOS ^a | 11.3 | 22.8 | 43.9 | 54.3 | 68.5 | 96 (586°C) |
| P[NVC-FO] ^b | 4.6 | 12.3 | 17.9 | 32.2 | 52.3 | complete (515°C) |
| PNVC ^b | 7.3 | 14.6 | 20.6 | 66.0 | 89.0 | 89.0 (550°C) |

^a Sulfonated PNVC-FO copolymer.²

^b Data reproduced from Ref. 1.

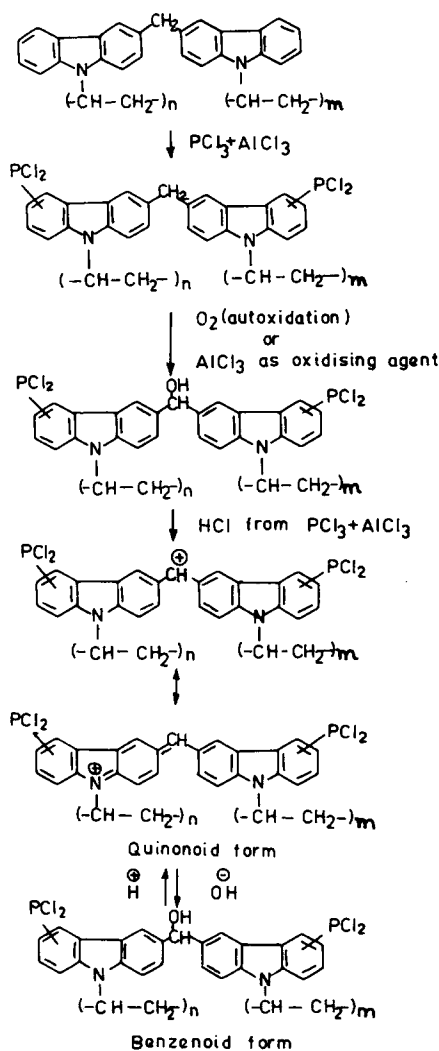


Fig. 3. Schematic representation of the color change behavior in P[NVC-FO]-P and PNVC-FO-P.

decomposed (96%) at 586°C. P[NVC-FO] shows remarkable initial stability (up to 500°C loss = 52%), but thereafter undergoes rapid decomposition essentially complete at 515°C. Notably, according to Peliechowski and Morawiec,⁹ phosphorylated PNVC undergoes ca. 37.5% loss at 550°C. Thus, formaldehyde-modified PNVC in the present work exhibits superior thermal stability than other related polymers in the series.

Color Change Behavior of P[NVC-FO] and PNVC-FO-P

As indicated earlier, both these resins undergo distinct color change depending on the pH of the medium. Both the resins assume green color during phosphorylation reaction, which is retained even after the resins are thoroughly washed with water after the phosphorylation reaction. A tentative mechanism for the change in color is suggested in Figure 3, which assumes the oxidation of the $-\text{CH}_2-$ bridge by autooxidation of O_2 or by AlCl_3 and the consequent formation of the quinoid form.^{11,12}

IR Spectra

The IR spectra of P[NVC-FO]-P and PNVC-FO-P exhibit a band around 1000 cm^{-1} , which is absent in unphosphorylated P[NVC-FO] and PNVC-FO. This indicates⁹ the presence of $-\text{P}-\text{OH}$ group in the polymer resulting from the hydrolysis⁹ of the $-\text{PCl}_2$ groups in the polymer (Fig. 3) and by oxidation⁹ during the processing of the resins (see the scheme).

CONCLUSION

Phosphoric acid cation exchange resins prepared from formaldehyde-modified NVC or PNVC exhibits significantly higher thermal and hydrolytic stability than the corresponding sulfonic acid cation exchange resin or phosphorylated PNVC.

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