

Cation Exchange Resin from Sulfonated Poly-*N*-Vinylcarbazole-Formaldehyde Copolymer

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Synopsis

A cross-linked copolymer of poly-*N*-vinylcarbazole and formaldehyde has been sulfonated to yield a cation exchange resin. The resin has been characterized by elemental analysis and by evaluation of total and salt-splitting capacities and pH-metric titration behavior. The resin has improved capacity (ion exchange) relative to other *N*-vinylcarbazole based resins and behaves as a polymeric dye.

INTRODUCTION

During recent years extensive studies on the synthesis of cation exchange resins from *N*-vinylcarbazole polymers (NVC)—unmodified as well as modified by chemical means—have been made by Biswas and co-workers.¹⁻⁸ More recently, formalin, which is much cheaper in comparison to other crosslinking agents like DVB, has been copolycondensed with NVC polymers.⁹ Detailed studies on the synthesis and evaluation of the ion-exchange properties of a sulfonic acid resin from the NVC formalin crosslinked product have since been undertaken. The salient features of these studies are highlighted in the present article.

EXPERIMENTAL

Materials. PNVC (BASF, West Germany) of DP = 5750 was used. Formalin, a 37% solution of formaldehyde vapor in aqueous solution, was a B.D.H. product. All other reagents were analytical grade certified chemicals.

Preparation of PNVC-FO.⁹ To a 25 mL solution (toluene) of PNVC (4% w/v) 10 mL formalin was added. HCl gas, generated by adding concd H₂SO₄ to solid NH₄Cl in a separate glass assembly, was passed through the solution which was maintained at the reflux temperature. The bubbling of HCl gas was stopped after 1 h, but the reaction was continued for 3-4 h. A solid material separated out which was treated with dilute ammonia solution, filtered, washed with deionized water, and air-dried. The homopolymer of PNVC was removed by refluxing the product several times with toluene. Finally, the copolymer was dried *in vacuo*.⁹

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TABLE I
Dependence of Ion-Exchange Capacity of PNVC-FOS on the Amount of the Sulfonating Agent (H₂SO₄)

H ₂ SO ₄ ^a (g/g resin)	Ion-exchange capacity (meq/g resin)		Sulfur (%)
	Total	Salt splitting	
10	5.15	4.50	13.5
15	5.20	4.60	13.7
20	5.20	4.60	13.7
25	5.10	4.40	13.6
50	4.60	3.50	13.7

^a 98% concd H₂SO₄ used for sulfonation of PNVC-FO for 5 h at 100°C.

Preparation of Cation Exchange Resin (PNVC-FOS) from PNVC-FO. Sulfonation of PNVC-FO was carried out by reacting a definite amount of the copolymer with varied quantities (10, 15, 20, 25, and 50 g/g dry resin) of concd H₂SO₄ with occasional shaking at different temperatures (35°C, 50°C, 60°C, and 100°C) and for different time (3, 4, 4.5, 5, and 5.5 h). However, the latter two variations in time and temperature were done using the sulfonated polymer of highest sulfur incorporation (Table I). The resin, thus treated, was finally filtered, washed free of SO₄⁼ by repeated washing with deionized water, and subsequently with dehydrated alcohol to remove the water, and finally dried *in vacuo* at 60°C.

Elemental Analysis. Detection of nitrogen and estimation of sulfur were done by standard methods.¹⁰⁻¹²

Evaluation of Ion-Exchange Capacity. The total ion exchange capacity and the salt-splitting capacity in equilibrium with an electrolyte like NaCl were determined by conventional procedures.¹³

pH Titration. Incremental quantities of NaOH solution (0.1N) were added to different mixtures containing a known weight of the resin and 10 mL NaCl solution (1.0M), keeping the total volume at 50 mL by adding deionized water. The equilibrium pH of the solution was measured in each case by a digilog pH meter. The capacities were evaluated after the attainment of a constant pH in each case.^{1,13-15}

Rate of Exchange. Accurately weighed quantities of the resin in the H⁺ form were taken in different flasks and 50 mL of 0.1N NaOH was added to each flask and shaken occasionally at 30°C. The capacity was determined after a prede-

TABLE II
Dependence of Ion-Exchange Capacity of PNVC-FOS on the Time of Sulfonation

Time of sulfonation ^a (h)	Ion-exchange capacity (meq/g resin)		Sulfur (%)
	Total	Salt splitting	
3	4.8	4.1	11.8
4	4.9	4.1	12.0
4.5	5.1	4.5	13.0
5	5.2	4.6	13.7
5.5	5.2	4.6	13.7

^a Sulfonation performed with 20 g of concd H₂SO₄/g resin at 100°C.

TABLE III
Dependence of Ion-Exchange Capacity of PNVC-FOS on the Temperature of Sulfonation

Temperature of sulfonation (°C) ^a	Ion-exchange capacity (meq/g resin)		Sulfur (%)
	Total	Salt splitting	
35	4.0	3.0	10.00
50	4.4	3.7	10.50
60	4.5	3.9	11.00
100	5.2	4.6	13.73

^a Sulfonation of PNVC-FO performed with 20 g H₂SO₄ (98%)/g resin for 5 h.

terminated time interval following a standard procedure.^{1,16} The same procedure was repeated using 1.0M NaCl.

Thermal 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. The contents were then taken out, washed, dried, and capacities were evaluated.

RESULTS AND DISCUSSION

General Properties. The virgin copolymer is light brown in color, while PNVC-FOS is a deep-bluish-green-colored granular solid. The material is insoluble in hydrocarbons, chlorinated hydrocarbons, acetonitrile, nitrobenzene, and dimethyl sulfoxide. It is also insoluble in inorganic acids or alkalis.

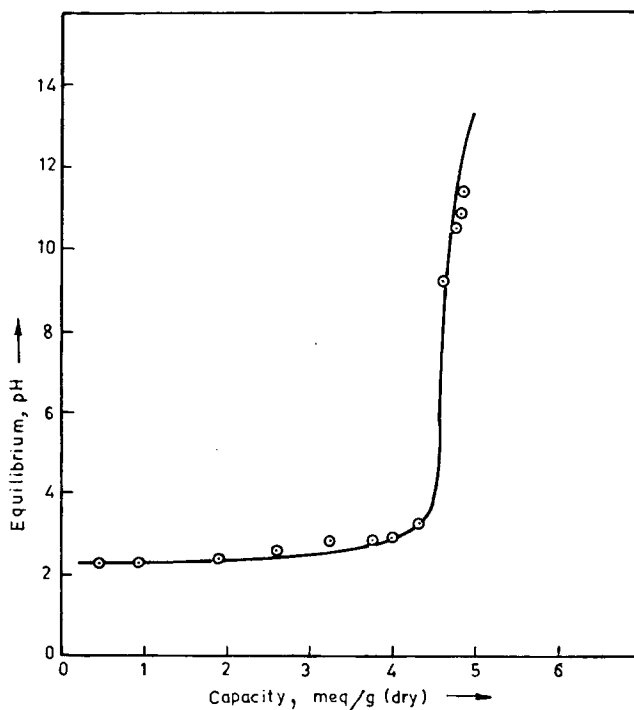


Fig. 1. Equilibrium pH vs. ion-exchange capacity plot for *N*-vinylcarbazole-formaldehyde copolymer sulfonated resin.

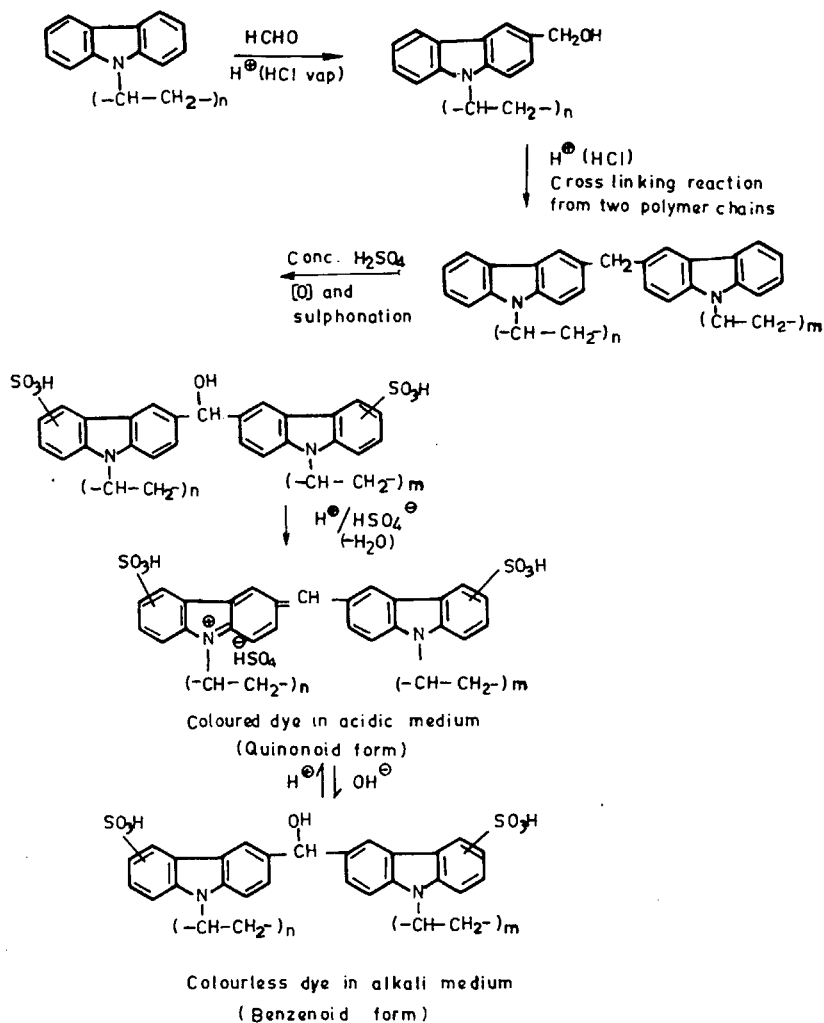


Fig. 2. Scheme showing formation of *N*-vinylcarbazole-formaldehyde copolymer sulfonated resin and mechanism of color change process.

Effect of the Amount of the Sulfonating Agent (H_2SO_4) on the Ion-Exchange Capacity of PNVC-FOS. Table I shows the variation of the ion-exchange capacity of PNVC-FOS with the amount of the sulfuric acid used for the sulfonation of PNVC-FO. The values of the total ion-exchange as also the salt-splitting capacities are steady up to ca., 20 g of $\text{H}_2\text{SO}_4/\text{g}$ resin, after which the capacities tend to fall. Thus, with 50 g of H_2SO_4 the ion-exchange capacity of the resin is 4.60, and the salt-splitting capacity 3.50 compared to the corresponding values of 5.20 and 4.60 at 15 g of H_2SO_4 , the values being in conventional units of meq/g resin. Notably, the sulfur percent of PNVC-FOS does not change. It is likely that, at higher amounts of the sulfonating agent, the ionogenic groups are converted to some extent to nonionogenic sulfone groups,¹⁶ thus resulting in a decrease in the ion-exchange capacity values.

Effect of the Time of Sulfonation on the Ion-Exchange Capacity of

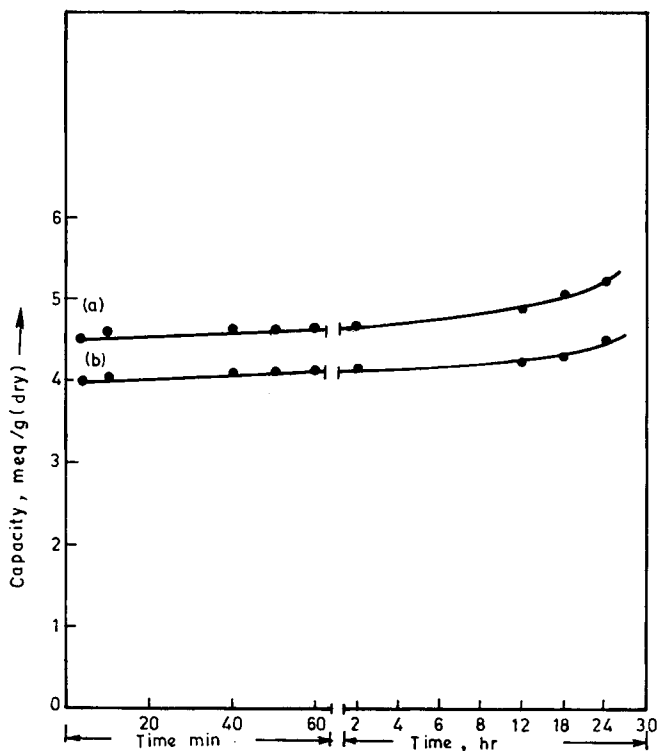


Fig. 3. Variation of ion-exchange capacity (a) and salt-splitting capacity (b) of *N*-vinylcarbazole-formaldehyde copolymer sulfonated resin with time.

PNVC-FOS. Table II shows the effect of sulfonation time on the total ion-exchange and the salt-splitting capacities of PNVC-FOS and the sulfur content. Clearly, the capacity values increase steadily to an optimum value and remain steady thereafter. The trend in the variation of the sulfur content values also follows a parallel trend.

Variation of Ion-Exchange and Salt-Splitting Capacities of PNVC-FOS with Sulfonation Temperature. Table III shows that both the total ion-exchange as well as the salt-splitting capacity values of PNVC-FOS increase with an increase in the temperature of sulfonation, the highest values being realized at ca. 100°C. This is somewhat remarkable in the sense that unmodified PNVC is considerably decomposed under these conditions.¹ Even at 200°C the

TABLE IV
Thermal Hydrolytic Stability of the Ion-Exchange Capacity of PNVC-FOS

Temperature of heating ^a (°C)	Total ion-exchange capacity (meq/g resin)		Loss in ion-exchange capacity (%)
	Before heating	After heating	
50	5.20	5.20	—
65	5.20	5.20	—
80	5.20	5.15	1
100	5.20	5.10	1.8

^a PNVC-FOS heated for 24 h in sealed ampoules at the respective temperature.

TABLE V
A Comparison of the Ion-Exchange Capacity of PNVC-FOS and Other PNVC-Based Cation Exchange Resins

Resin	Total ion-exchange capacity (meq/g)	Reference
PNVC-FOS	5.2	This work
NVC-DVB sulfonated	4.9	6
NVC-phthalic anhydride sulfonated	4.7	3
NVC-Furfural sulfonated	4.6	2
Sulfonated poly[<i>N</i> -vinylcarbazole-3,6-bis(4-keto-1-naphthol)]	5.1	7
PNVC sulfonated	4.5	1
PNVC-furfural phosphorylated	5.1	4

PNVC-FO does not appear to be severely affected on treatment with concd H_2SO_4 , whereas unmodified PNVC is charred and completely dissolved at this temperature on treatment with concd H_2SO_4 .

pH-Metric Titration Characteristics. Figure 1 presents a typical pH-metric behavior of PNVC-FOS. The capacity of the resin increases sharply from 0.5 to 3.5 meq/g, corresponding to a pH change from 2.3 to 2.85. Only one sharp inflexion in the pH-metric titration graph suggests PNVC-FOS to be a strong monofunctional resin. The apparent pK value, as calculated from these data by applying the procedure of Helfferich,¹³ is 1.35 (cf. pK for the $-SO_3H$ group¹³).

Color Change Behavior of PNVC-FOS. Interestingly, the resin exhibits a distinct color change in acid or alkali medium. The resin, which has originally a deep bluish color, assumes a green color in distilled water, which changes again to a light brown color in excess NaOH solution. When the excess alkali is titrated with HCl solution so as to obtain an acidic medium, the color of the resin sharply changes to blue. Figure 2 explains schematically the reactions involved in the formation of PNVC-FOS and also in the color change process occurring in the present context. H_2SO_4 is supposed to act as an oxidizing agent also. In acidic solution, sulfonation, dehydration, and protonation occur, when the resin becomes a colored dye in the quinoid form. In alkaline medium, it turns to the benzenoid form and becomes colorless.^{16,17}

Rate of Exchange. The rate of exchange of ionogenic groups with time is shown in Figure 3. It is observed that more than 80% of the total capacity and the salt-splitting capacity are realized within 2 min of equilibrium, which suggests the resin to be a fast cation exchanger.

Effect of Heating on Ion-Exchange Capacity. Table IV presents relevant data illustrating the effect of heating the resin with deionized water at various temperatures. Notably, PNVC-FOS suffers negligible ion-exchange capacity loss (1.8%) after being heated at 100°C for 24 h, which suggests that it may be used as an ion exchanger at higher temperatures.

Comparison of PNVC-FOS with Other NVC-Based Ion Exchangers. Table V compares the ion exchange capacity of this resin with other NVC-based cation exchangers. Evidently, PNVC-FOS exhibits better total ion exchange capacity value relative to others. This fact taken in conjunction with the relatively low cost of formalin makes this resin more attractive among the NVC-based cation exchangers.

CONCLUSION

Sulfonation of a crosslinked polymer of *N*-vinylcarbazole and formaldehyde (formalin) affords a strong sulfonic acid resin, which compares favorably in ion-exchange capacity and related properties with other *N*-vinylcarbazole-based cation exchange resins.

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