

Furfural-Based Cation-Exchange Resins from *N*-Vinylcarbazole and Its Polymer

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Synopsis

Cation-exchange resins have been synthesized through the condensation of *N*-vinylcarbazole and poly(*N*-vinylcarbazole) with furfural in presence of anhydrous AlCl_3 and subsequent sulfonation of the condensates. The resins have been characterized in respect to their polyfunctionality, exchange capacity, and thermal stability.

INTRODUCTION

In course of our work¹ on the chemical modification of poly(*N*-vinyl carbazole) (PNVC), it was observed that sulfonated PNVC can be successfully processed into a cation-exchange resin with reasonable ion-exchange capacity and thermal stability. Aldehydes are known^{2,3} to undergo condensation reaction with basic substances in the presence of protonic or aprotic acids. This prompted us to isolate the condensation products of NVC and PNVC with furfural, a cyclic aldehyde. Condensation polymers of furfural with styrene,^{4,5} α -pinene,⁶ and cyclohexanone⁷ after suitable chemical modifications like sulfonation and phosphorylation have been reported to yield cation-exchange resins. In this paper we report the synthesis and characterization of cation-exchange resins based on the condensation of furfural with NVC and PNVC in presence of anhydrous aluminium chloride.

EXPERIMENTAL

Materials

Purification of NVC (BASF, Germany) and preparation of PNVC (*DP* 15) were accomplished by following the procedure of Biswas et al.^{8,9} Furfural (BDH) was distilled under reduced pressure and the fraction between 54 and 55°C at 17 mm Hg was collected and stored from light and heat. Sulfuric acid (BDH 98.8%) was used. Aluminium chloride (BDH) was purified by sublimation using the standard procedure.¹⁰

Preparation of NVCF and PNVCF

The condensation, first carried out in presence of HCl , at 40–45°C was slow, the product separating out only after 24 hr. So anhydrous AlCl_3 was preferred as the catalyst. Known weights of NVC or PNVC and furfural, dissolved in benzene, were mixed with anhydrous AlCl_3 (6% by weight based on NVC or

PNVC) in a double-necked reaction flask with a condenser and a stirrer. The mixture was heated at 40–45°C for 1 hr with stirring. The black mass which separated out was collected and refluxed with benzene for 30 min and filtered from any unreacted monomer or polymer and furfural. It was further refluxed with methanol to dissolve any polyfurfural formed under these conditions. The product was separated and washed with hot methanol until the extract became colorless. Finally, the condensate was washed with acetone, followed by hot water, and cured at 100–110°C for 10 hr.

Preparation of Cation-Exchange Resin

Sulfonation of the condensates was carried out by reacting 1.0 g NVCF or PNVCF with 70 g H₂SO₄ (98.8%) with stirring in a Pyrex flask under varied conditions (Tables II and III). The contents were subsequently poured into an excess of ice-cold water with stirring. The resin was filtered, washed several times with deionized water until free from sulfate ions, and finally dried at 100–110°C for 10 hr.

Elemental Analysis

Detection of nitrogen and estimation of sulfur were done by standard methods.^{11,12}

Characterization

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

pH Titration. Incremental quantities of NaOH solution (0.1*N*) were added to different mixtures containing a known weight of the resin and 10 ml NaCl solution (1.0*N*), keeping the total volume at 100 ml by the addition of deionized water. The equilibrium pH of the solutions was measured^{1,6,14} in each case. The capacities were evaluated after the attainment of a constant pH (after about 10 hr). Figure 1 represents the equilibrium pH versus capacity plots for NVCF and PNVCF resins.

Thermal Stability. The thermal stability of the resins (1:10) was studied with a MOM derivatograph. Figures 2 and 3 present the TG, DTG, and DTA data for NVCF and PNVCF, respectively.

The loss in capacity of the resins (1:10) on heating to 100°C for 24 hr with water was also estimated as described elsewhere.^{1,6} Table IV compares the thermal stability of NVCF and PNVCF.

RESULTS AND DISCUSSION

Physical Properties

The resins are black in color and insoluble in organic solvents, including hydrocarbons, alcohols, acetone, acetonitrile, nitrobenzene, and halogenated hydrocarbons, and also in inorganic acids and alkalis. On heating to ca. 100–

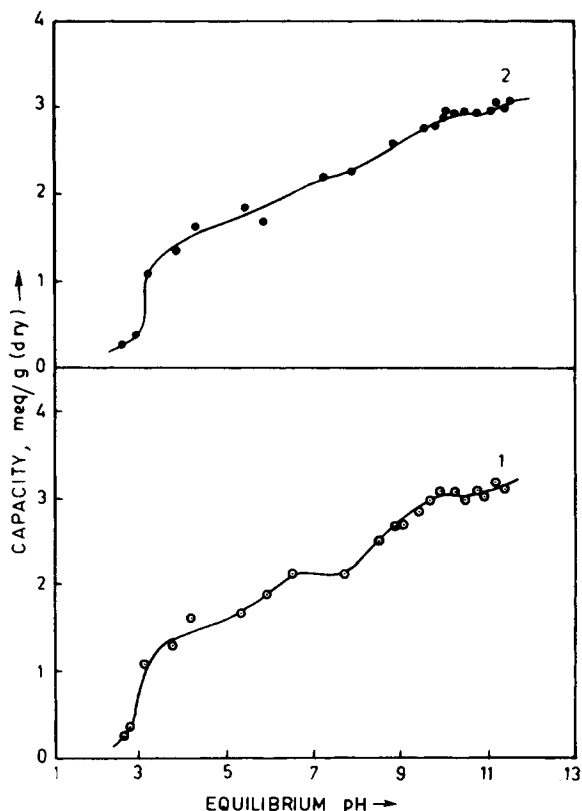


Fig. 1. Equilibrium pH versus capacity: (1) NVCFS; (2) PNVCFS.

110°C, they become shiny black materials. Elemental analysis reveals the presence of both nitrogen and sulfur in the resins.

Table I presents a comparative evaluation of some furfural-based cation-exchange resins with NVCFS and PNVCFS resins.

Effect of Furfural Concentration on Capacity

Table II shows that both the total and salt-splitting capacities of NVCFS increase with furfural concentration. On the contrary, the capacities of PNVCFS decrease consistently with increasing furfural concentration.

It is known that diethylaniline, a tertiary amine, undergoes condensation with furfural in presence of $ZnCl_2$ with the elimination of water molecules.³ A similar condensation reaction between NVC or PNVC and furfural is therefore likely.

The degree of crosslinking in an ion exchanger is an important factor which affects the ion-exchange capacity and stability of the resin.¹³ During the present condensation it is possible that furfural not only acts as a condensing agent, but also as a crosslinking agent like formaldehyde in phenol-formaldehyde resin.¹³ The changes in such crosslinking are likely to be greater in PNVCFS than NVCFS resin because of the longer chain length in the former. This implies that the probability of occupying more positions in the carbazole molecule by the

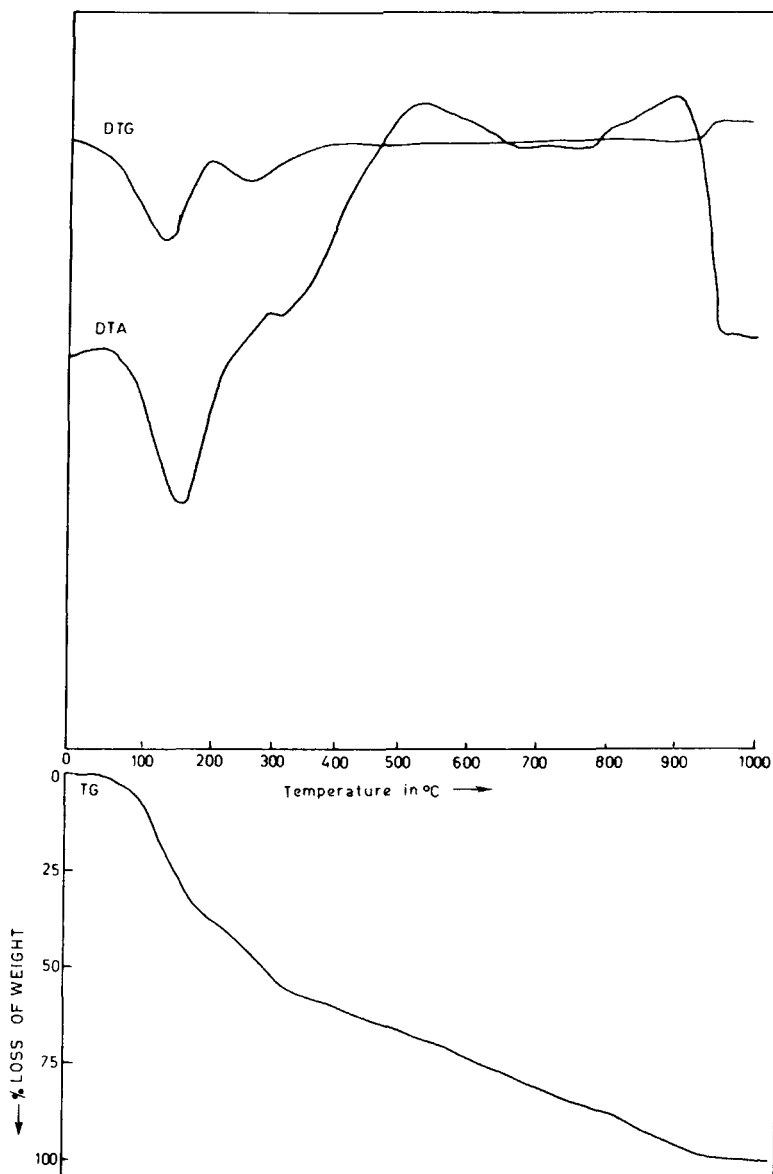


Fig. 2. TG, DTG, and DTA curves for NVCFS.

ionizable $-\text{SO}_3\text{H}$ group is comparatively less in PNVCFS. In polymers with highly crosslinked structure, the mobility of the counterion is very slow and the capacity is affected accordingly.¹³ In light of this it may be argued that with an increase in the quantity of furfural (ca. 1:5–1:15) in PNVCFS, the degree of crosslinking may be enhanced and hence the capacities lowered. A similar feature has also been observed in the case of styrene–furfural resins.⁴

In the case of NVCFS resin, the increase in furfural concentration may progressively reduce the chance of simultaneous polymerization of NVC, so that there is less chance for the formation of a highly crosslinked matrix as in the case of PNVCFS. The observed increase in capacity with increasing furfural concentration appears to be consistent with such a situation.

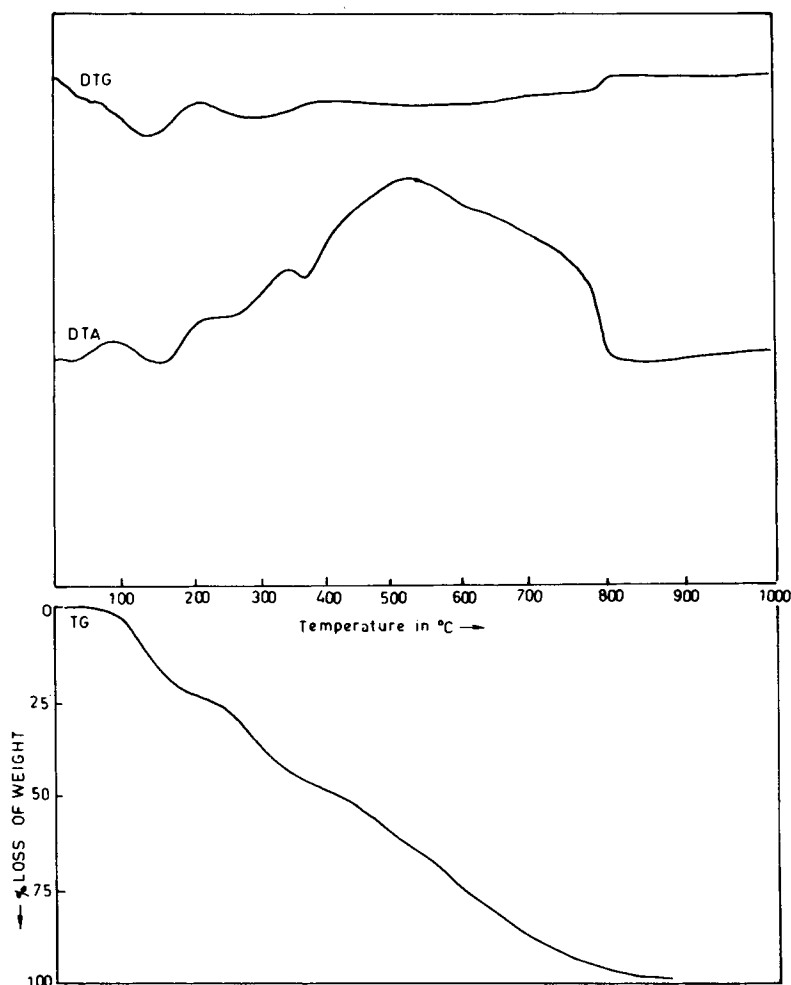


Fig. 3. TG, DTG, and DTA curves for PNVCFS.

TABLE I
Comparison of Capacities of Various Furfural-Based Cation Exchangers

Resin	Ionogenic Groups	Capacity (meq/g, dry)	Ref.
NVCFS	SO ₃ ⁻ H ⁺	4.62	This work
	COO ⁻ H ⁺		
PNVCFS	SO ₃ ⁻ H ⁺	4.01	This work
	COO ⁻ H ⁺		
SFS ^a (styrene)	SO ₃ ⁻ H ⁺	4.0-4.2	4
	COO ⁻ H ⁺		
α-PFS (α-pinene)	SO ₃ ⁻ H ⁺	3.36	6
	COO ⁻ H ⁺		

^a Sulfonation temp., 100°C.

Table II further shows that the sulfur content remains almost the same in both the resins obtained at various NVC or PNVC/furfural ratios. All the sulfur present should not necessarily exist as the ionizable -SO₃H group during sul-

TABLE II
Effect of Furfural Concentration on Capacity

Resin ^a	NVC (or PNVC):F ^b (w/w)	Total Capacity (meq/g, dry)	Salt-Splitting Capacity (meq/g, dry)	S (%)
NVCFS	1:5	4.50	3.40	9.90
NVCFS	1:10	4.62	4.02	10.78
PNVCFS	1:1	black solution		
PNVCFS	1:5	4.34	3.55	9.98
PNVCFS	1:10	4.01	3.01	10.20
PNVCFS	1:15	3.25	2.70	10.00

^a Sulfonation time, 5 hr; temp.; 60°C; sulfuric acid, 70 g/g resin.

^b F, furfural.

fonation. The possibility of the formation of nonionizable sulfone groups,¹³ $R-SO_2-R$, may not be ruled out. Pieliowski and Morawiec¹⁴ have shown that some phosphone groups, $R-PO_2-R$, are formed during the phosphorylation of PNVC. The formation of sulfone groups was reported by Biswas and John¹ during the sulfonation of PNVC.

Effect of Time and Temperature of Sulfonation on Capacity

Table III compares the effect of time and temperature of sulfonation on the capacities of NVCFS and PNVCFS resins. The low capacity at 30° for both resins may be due to incomplete sulfonation. A maximum capacity of 4.62 meq/g (dry) at 60°C for 5 hr is observed for NVCFS, which subsequently decreases with time and temperature. However, the sulfur content does not decrease accordingly. This may be due to the formation of nonionizable $R-SO_2-R$ groups^{1,13} during sulfonation, the extent of which may depend on the time and temperature of sulfonation.

It is interesting to note that the total capacity of PNVCFS resin increases with the increases in time and temperature as reported for styrene-furfural resin.⁴ A maximum capacity of 4.40 meq/g (dry) is observed with the resin sulfonated at 100°C (5 hr) and 60°C (24 hr). The sulfur content in PNVCFS resin also increases with time and temperature of sulfonation.

It is significant that the salt-splitting capacities of the resins in all these cases (Tables II and III) are lower than the corresponding total capacities. This is

TABLE III
Effect of Time and Temperature of Sulfonation on Capacity

Temp. (°C)	Time (hr)	NVCFS ^a			PNVCFS ^a		
		Total Capacity (meq/g, dry)	Salt-Splitting Capacity (meq/g, dry)	S (%)	Total Capacity (meq/g, dry)	Salt-Splitting Capacity (meq/g, dry)	S (%)
30	5	4.38	3.80	9.80	3.80	2.90	9.10
60	5	4.62	4.02	10.78	4.01	3.01	10.20
60	10	4.35	3.75	10.20	4.20	2.98	12.75
60	24	3.88	2.91	11.00	4.40	2.90	14.00
100	5	3.80	3.53	11.10	4.40	3.00	15.10
150	5	Product dissolved			Partially dissolved		

^a NVC or PNVC:F, 1:10; sulfuric acid, 70 g/g resin.

probably reasonable, since ion exchangers can sorb solutes from solutions with which they are in contact^{1,13} and, consequently, salting out in presence of an electrolyte decreases the ion-exchange capacity.

pH Titration Curves

Figure 1 represents the typical pH titration curves of NVCFS and PNVCFS resins and indicates their polyfunctional nature. The behavior in the pH range 2–5 is characteristic of that of a monofunctional strong cation-exchange resin of sulfonic acid type. The pK_1 values 2.40 and 2.7 calculated¹³ from Figure 1 agree with that of a typical sulfonic acid resin.^{1,15} The second inflection over the pH range 5–9 is sharper in NVCFS than in PNVCFS and indicates the presence of a weak acid group, which is probably the —COOH group ($pK_2 = 4.83$ for curve 1), resulting from the oxidation of furfural during the sulfonation process. This is consistent with the reported observation of the presence of carboxyl group activity in furfural-based sulfonated resins.¹⁶

Thermal Stability

Table IV compares the stability of NVCFS and PNVCFS in the presence of water at 100°C for 24 hr. The liberation of acid indicates that the resins undergo thermal hydrolysis on heating. The results clearly show that PNVCFS possesses somewhat more chemical and thermal stability than NVCFS resin, even though the capacity of the former is lower than the latter. These observations are reasonable, since the resins obtained from polymers are usually found to be more stable due to the effect of crosslinking.^{5,17}

Figures 2 and 3 represent the TG, DTG, and DTA curves for NVCFS and PNVCFS resins (1:10), respectively. A marked endothermic effect is seen on the DTA curves in the range of 120–180°C (minimum point, 150°C; loss of weight, 25%) for NVCFS and 120–180°C (minimum point, 140°C; loss of weight, 15%) for PNVCFS. The transformation occurring in this range is due to the loss of water. The exothermic effects start below 250 and 230°C and end at 520 and 530°C for NVCFS and PNVCFS, respectively. The DTG curves also reveal the same feature for both. A marked loss of weights of 52 and 37% occurs at 300°C, as indicated on the TG curves for NVCFS and PNVCFS resins, respectively. Above this temperature the rate of degradation is fast due to the destructive oxidation processes.

TABLE IV
Thermal Stability with Water^a

Resin	NVC (or PNVC):F (w/w)	Total Capacity (meq/g, dry)		Loss in Capacity (%)	Acid Liberated During Heating (meq)
		Before Heating	After Heating		
NVCFS	1:5	4.50	4.00	11.10	0.1606
PNVCFS	1:5	4.34	4.00	7.72	0.1339
NVCFS	1:10	4.62	3.90	15.00	0.2141
PNVCFS	1:10	4.01	3.80	5.23	0.1071

^a Period of heating, 24 hr; temp., 100°C.

CONCLUSIONS

It is possible to prepare cation-exchange resins of polyfunctional nature by sulfonation of the condensation products of *N*-vinylcarbazole and poly(*N*-vinylcarbazole) with furfural in presence of anhydrous aluminum chloride. The capacities and other properties of these resins compare well with those reported for other furfural-based cation exchangers.

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