

# Phthalic Anhydride-Based Cation Exchange Resin from *N*-Vinylcarbazole

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## Synopsis

A condensation product based on phthalic anhydride and *N*-vinylcarbazole has been prepared and processed into a sulfonic acid cation exchange resin. The resin produced has been characterized by measuring its total and salt splitting capacities and by studying its thermal characteristics, rate of exchange, and behavior to pH metric titration.

## INTRODUCTION

Recent publications by Biswas et al.<sup>1-3</sup> described the preparation of condensation products of *N*-vinylcarbazole (NVC), isobutylvinyl ether (IBVE), and their polymers with furfural and their subsequent chemical modification to cation exchange resins. It has now been possible to condense phthalic anhydride with NVC to a polymeric end product which on appropriate chemical modification yields a cation exchange resin of comparatively higher thermal stability. The present paper describes the synthesis and characterization of the cation exchange resin obtained from NVC-phthalic anhydride system.

## EXPERIMENTAL

### Materials

NVC (BASF, Germany) was purified following the procedure of Biswas et al.<sup>4,5</sup> Phthalic anhydride (BDH) was purified by sublimation. Sulfuric acid (BDH 98.8%) was used. Aluminum chloride (BDH) was purified by sublimation following the procedure of Howie et al.<sup>7</sup>

### Preparation of NVC-Phthalic Anhydride Condensate (NVCPA)

NVC and phthalic anhydride (1:1 by weight) were dissolved in benzene and mixed with anhydrous AlCl<sub>3</sub> (reactants:catalyst ratio 2:1 by weight) in a two-necked reaction flask fitted with a condenser and a stirrer. The condensation was carried out at 55°C for 2 hr. The condensed product which separated out in benzene medium was collected and refluxed with benzene, and unreacted NVC, PNVC, and phthalic anhydride were filtered off. The condensate was washed several times with hot water and cured at 100-110°C for 5 hr.

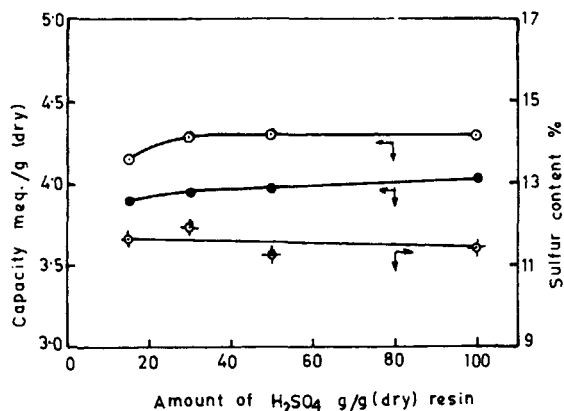


Fig. 1. Effect of variation of sulfuric acid amount on capacity: (○) total capacity; (●) salt splitting capacity; (◇) sulfur content.

### Preparation of Cation Exchange Resin (NVCPAS)

Sulfonation of the condensate was carried out by reacting the condensate with H<sub>2</sub>SO<sub>4</sub> (98.8%) with stirring in a Pyrex flask under varied conditions (Figs. 1–3). The contents were poured into excess ice-cold water with stirring. The resin was filtered, washed several times with deionized water till free from sulfate ion, and finally dried at 100–110°C for 5 hr.

### Characterization of NVCPA and NVCPAS

Determination of exchange capacity, rate of exchange, effect of heating on ion exchange capacity, and pH titration of the resin were carried out following standard procedures.<sup>1,2,9</sup>

The nitrogen content of NVCPA and NVCPAS was determined by the micro Dumas method. The sulfur content of various resins was determined using a standard procedure.<sup>8</sup>

Thermal characteristics of NVCPA and NVCPAS were studied with a MOM derivatograph over temperatures up to 1000°C in air. The heating rate was maintained at 10°C/min.

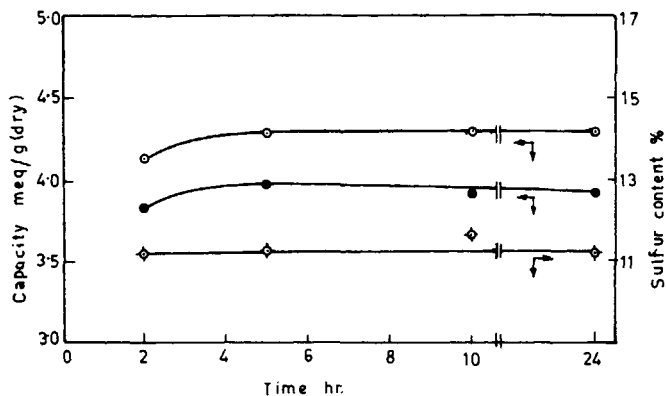


Fig. 2. Effect of variation of time of sulfonation on capacity: (○) total capacity; (●) salt splitting capacity; (◇) sulfur content.

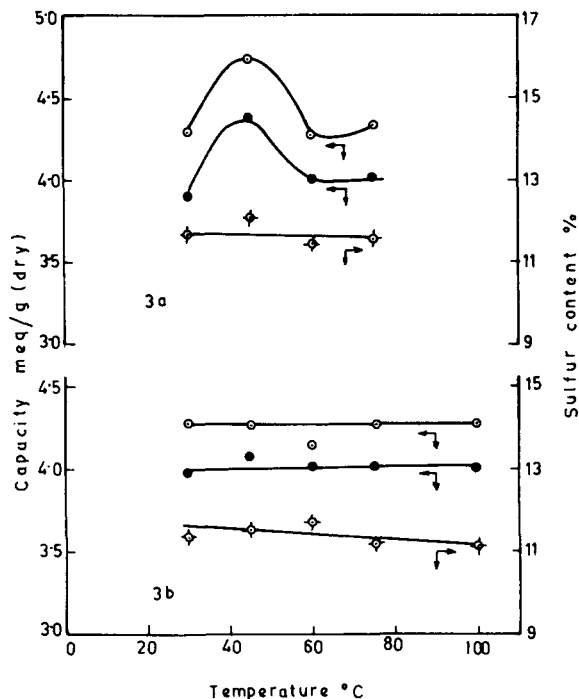


Fig. 3. Effect of variation of temperature of sulfonation on capacity: (a) sulfonation time 10 hr; (b) sulfonation time 5 hr; (○) total capacity; (●) salt splitting capacity; (◇) sulfur content.

## RESULTS AND DISCUSSION

### Physical Properties

The resin is black in color and insoluble in organic solvents, including aliphatic and aromatic hydrocarbons, alcohols, acetone, acetonitrile, nitrobenzene, halogenated hydrocarbons, and also in inorganic acids and alkalis. In the wet form NVCPAS is a gel-like greenish-brown mass. On heating to 100°C the gel nature disappears and the mass changes to brittle black in color. Elemental analysis reveals the presence of both nitrogen and sulfur in NVCPAS. The percentage of nitrogen in NVCPA and NVCPAS is approximately 4.85 and 2.35, respectively.

Table I presents a comparative evaluation of some NVC/PNVC-based cation exchange resins with NVCPAS. Evidently, the NVCPAS resin compares favorably with the other NVC/PNVC-based resins as also with the conventional styrene-based resins.

### Effect of Variation of Sulfuric Acid Amount on Capacity

Figure 1 shows that a total capacity of 4.29 meq/g and a salt splitting capacity of 3.96 meq/g are realized when the resin is sulfonated using  $\text{H}_2\text{SO}_4$ , 25 g/g (dry) resin, at 30°C for 5 hr. Further increase in the quantity of  $\text{H}_2\text{SO}_4$  does not affect these values.

TABLE I  
Comparison of Capacities of Various *N*-Vinylcarbazole-Based Cation Exchangers

Resin	Ionogenic groups	Capacity, meq/g	Reference
NVCPAS	SO <sub>3</sub> <sup>-</sup> H <sup>+</sup>	4.73	this work
PNVCS	SO <sub>3</sub> <sup>-</sup> H <sup>+</sup>	4.50	1
PNVCP	PO <sub>3</sub> <sup>2-</sup> (H <sup>+</sup> ) <sub>2</sub>	3.20	6
NVCFS (NVC-furfural)	SO <sub>3</sub> <sup>-</sup> H <sup>+</sup>	4.62	2
	COO <sup>-</sup> H <sup>+</sup>		
PNVCFS (PNVC-furfural)	SO <sub>3</sub> <sup>-</sup> H <sup>+</sup>	4.01	2
	COO <sup>-</sup> H <sup>+</sup>		
Amberlite IR-120 (styrene-divinylbenzene)	SO <sub>3</sub> <sup>-</sup> H <sup>+</sup>	4.20	10

### Effect of Sulfonation Time

Figure 2 shows the effect of variation of time of sulfonation. When the resin is sulfonated for 5 hr at 30°C, 4.29 and 3.98 meq/g are realized for total and salt splitting capacities, respectively. With further increase in time of sulfonation, the total capacity remains the same and a little variation is found in the salt splitting capacity.

### Effect of Temperature of Sulfonation

Figure 3(a) represents the effect of variation of temperature when the sulfonation is carried out for a period of 10 hr. It follows that maximum values of 4.73 and 4.38 meq/g are realized for the total and salt splitting capacities, respectively. With increase in temperature the capacities decrease. But when the sulfonation period is reduced to 5 hr, only a slight variation in the capacities is found even up to 100°C. At higher temperatures (above 150°C) the product dissolves.

### pH Metric Titration Curve

Figure 4 represents a typical pH metric titration curve of NVCPAS resin. The capacity sharply increases from 0.26 to 3.55 meq/g corresponding to a pH change from 2.08 to 4.35 and thereafter increases very slowly over the pH range of 4.35 to 9.0. Above pH 9 the capacity continues to increase. The pH titration curve

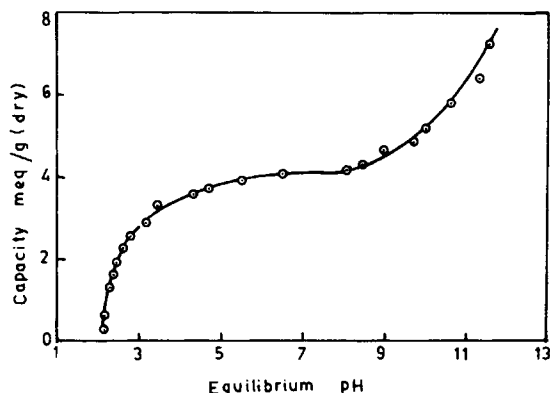


Fig. 4. Capacity vs. equilibrium pH curve.

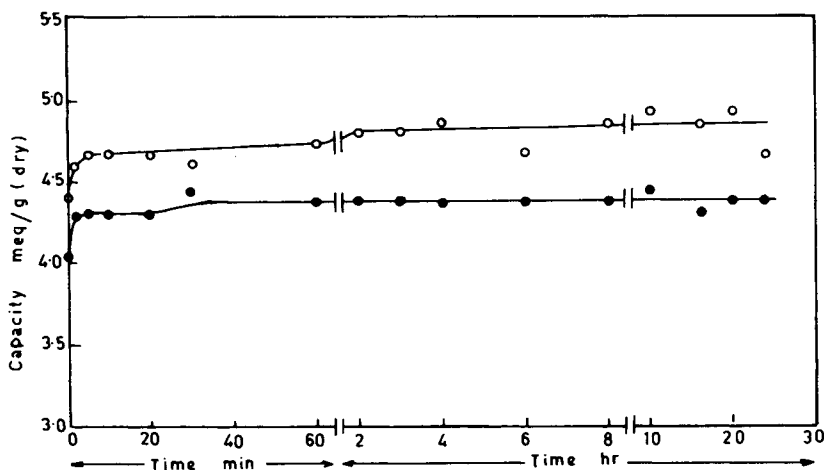


Fig. 5. Capacity vs. time curve: (O) total capacity in sodium hydroxide solution; (●) salt splitting capacity in sodium chloride solution.

shows only one inflection. The apparent pK value of the resin calculated by applying the procedure of Helfferich<sup>9</sup> to the data of Figure 4 turns out to be about 1.50. This pK value corresponds to that due to a sulfonic acid group.<sup>9</sup> The absence of the second inflection rules out the possibility of a weakly dissociable group such as  $-\text{COOH}$ . The reason for the increase in capacity above pH 9 is obscure. The increase in capacity at pH > 11 is observed in the case of PNVC sulfonated resin which is a monofunctional strong acid resin.<sup>1</sup> Amberlite IR-120, which is a strong nuclear sulfonic acid resin,<sup>10</sup> also shows an increase in capacity at pH > 10.

### Rate of Exchange

The rate of exchange of ionogenic groups with time is shown in Figure 5. The values of 4.60 and 4.31 meq/g are realized within 2 min of equilibration, and negligible variations are observed thereafter. This characteristic of the resin reveals that the sulfonated NVCPAS may be used as a moderately fast cation exchanger.

### Effect of Heating on Capacity

Table II represents the effect of heating on capacity. No loss in capacity is realized when the resin is heated in water up to 80°C. A loss of about 1.27%

TABLE II  
Effect of Heating<sup>a</sup> on Capacity

Temperature, °C	Total capacity, meq/g		Loss in capacity, %
	Before heating	After heating	
60	4.73	4.73	No loss
80	4.73	4.73	No loss
100	4.73	4.67	1.27

<sup>a</sup> All samples were heated with deionized water for 24 hr.

occurs at 100°C, which is remarkable for this resin, since PNVCS, NVCFS, and PNVCFCS under this condition undergo 25.5, 7.72, and 5.23% loss in capacity, respectively.<sup>1,2</sup> These data imply that NVCPAS may be used for ion exchange even up to 100°C.

### Thermal Properties

Figure 6 represents the TG, DTG, and DTA curves for NVCPAS resin. Thermal analysis of NVCPAS (sulfur content 12.06%) reveals that the resin is stable up to 200°C. A marked endothermic effect is observed on the DTA curve in the range 50–190°C, with the minimum point at 110°C. The TG curve shows

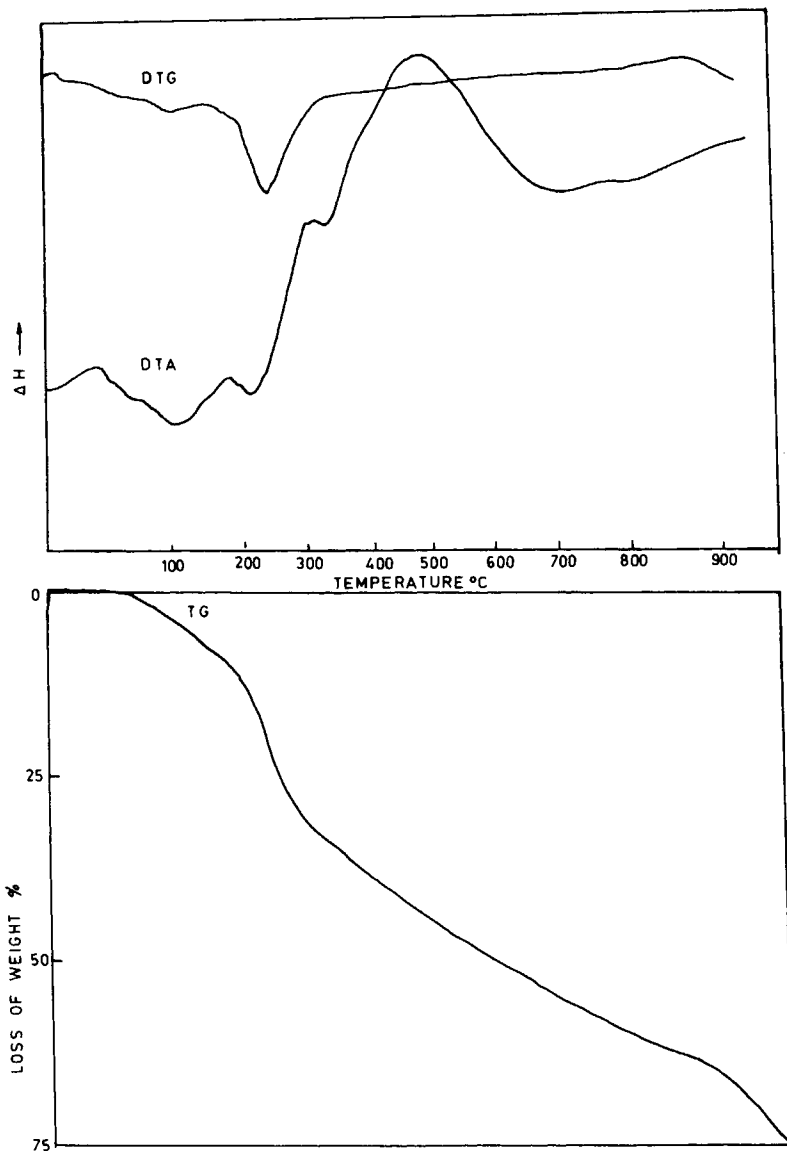
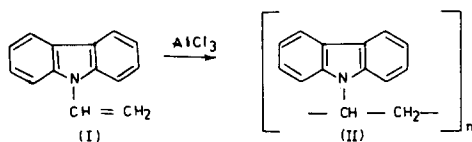


Fig. 6. TG, DTG, and DTA curves.

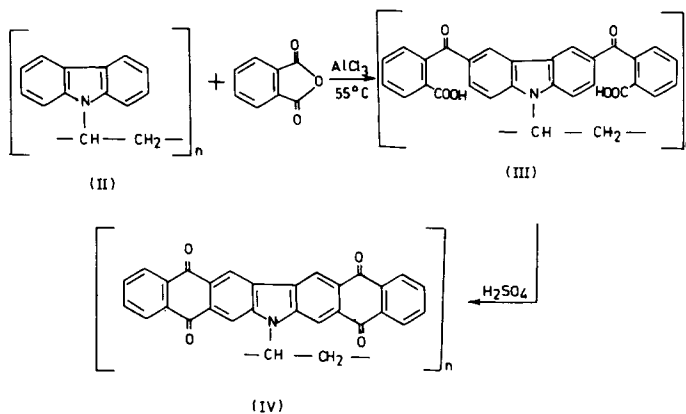
a loss of 10% in the same temperature range. An endothermic hump is observed in the temperature range 190–230°C. The exothermic effect starts below 230°C and ends at 680°C, the maximum point being at 475°C. The DTG curve shows a rise in the weight loss in the temperature range 190–300°C. A marked loss of weight of 10.5–31.5% is shown in the TG curve in the same temperature range. The weight loss occurring in this temperature range is due to destructive oxidation. The TG curve reveals a weight loss of 65% at 900°C, whereas the other NVC-based resins degrade almost completely.<sup>1,2</sup>

### Tentative Structure of Resin

The condensation of phthalic anhydride with NVC and its polymer in the presence of anhydrous  $\text{AlCl}_3$  is thought to proceed in two steps. Since the polymerization of NVC by  $\text{AlCl}_3$  in hydrocarbon solvents<sup>5</sup> is appreciably fast, step I of this process possibly involves the formation of PNVC:



This is followed by the condensation of II with the phthalic anhydride unit, resulting in the formation of the polyketo acid III:



The formation of a similar keto acid from the condensation of carbazole and phthalic anhydride in the presence of  $\text{AlCl}_3$  has been confirmed,<sup>11</sup> and as such the formation of III may as well be feasible. The pH metric titration curve (Fig. 4) of the sulfonated resin does not show any inflection due to a  $-\text{COOH}$  group. This is understandable if III is assumed to undergo cyclization in the presence of  $\text{H}_2\text{SO}_4$  to the polyketone IV. A similar cyclization of keto acid from carbazole-phthalic anhydride condensate (carbazole-3,6-diphthaloylic acid) to the corresponding cyclic ketone (2,3,6,7-diphthaloylcarbazole) has been reported.<sup>11</sup>

The observed nitrogen percentage of the condensate and that of the sulfonated resin reveal that probably not all the aromatic rings in the PNVC entity are condensed with phthalic anhydride units. An approximate calculation on the basis of observed nitrogen and sulfur percentages in the resin and nitrogen percentage in the condensate suggests the mole ratio of NVC to phthalic anhy-

dride in the product to be about 4:2.2–2.6, with 5.5–6 sulfonic acid groups. This will approximate to a scientific weight capacity of about 3.8 meq/g, which compares favorably with the observed capacity.

### CONCLUSIONS

A monofunctional sulfonic acid resin can be obtained by sulfonation of the polymeric condensation product of NVC and phthalic anhydride in the presence of anhydrous  $\text{AlCl}_3$ . The resin compares favorably with the other NVC-based resins in respect of capacity and rate of exchange with  $\text{NaOH}$  and  $\text{NaCl}$ . However, the resin undergoes practically no loss in capacity on heating with water at  $100^\circ\text{C}$  for 24 hr, a feature distinguishing it from the other NVC-based resins which undergo about 7–25% loss in capacity under this condition.

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