Cation Exchange Resin from Sulfonated
N-Vinylcarbazole and Divinylbenzene Copolymer

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Synopsis

A copolymer of N-vinylcarbazole and divinylbenzene has been sulfonated to yield a cation exchange resin of improved thermal properties compared to other vinylcarbazole-based resins. The resin has been characterized by measuring its total and salt-spliting capacities, pH metric titration, and thermal stability characteristics.

INTRODUCTION

In earlier publications Biswas et al.[1-4] reported the novel condensation of N-vinylcarbazole (NVC) isobutylvinyl ether (IBVE) and their polymers with furfural and phthalic anhydride (PA) and their subsequent modification to cation exchange resins. Biswas and Das have lately reported[5,6] that the thermal stability of NVC polymer systems can be appreciably increased through appropriate chemical modification of the polymer.

It has now been observed[7] that in the presence of anhydrous $AlCl_3$ NVC yields a polymer with divinylbenzene (DVB) insoluble in almost all solvents, which is characterized by a higher thermal stability compared to NVC and DVB homopolymers. The copolymer (NVC–DVB) can be sulfonated to give a strong cation exchange resin with improved properties compared to other vinylcarbazole-based resins. The present article describes the preparation and characterization of the resin prepared from NVC and DVB copolymer.

EXPERIMENTAL

Materials

NVC (BASF, Germany) and DVB (Fluka AG.) were purified by following standard procedures.[8-10] Nitrobenzene and anhydrous $AlCl_3$ (Riedel, Germany) were purified by conventional methods.[11,12]

Preparation of NVC–DVB copolymer. The NVC–DVB copolymer was prepared[7] by the reaction of NVC and DVB in nitrobenzene solvent in the presence of anhydrous $AlCl_3$ at 0°C.

Preparation of cation exchange resin. Sulfonation of NVC–DVB copolymer was carried out by reacting 0.5 g copolymer with the requisite quantity of conc. H_2SO_4 (98.8%) with constant stirring in a 100-ml Pyrex flask under varied conditions. The contents were subsequently poured into an excess of ice-cold deionized water with stirring. The resin was filtered, washed free of SO_4^{2-} with deionized water, and finally cured at 100–110°C for 6 hr.

Elemental analysis. Detection of nitrogen and estimation of sulfur were done by standard methods.[13,14]

Evaluation of capacity. The total ion exchange capacity and the salt-splitting capacity in equilibrium with an electrolyte such as NaCl were determined by recommended procedures.[2,4,15]

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 ($1.0N$) keeping the total volume at 100 ml by addition of deionized water. The equilibrium pH of the solutions was measured[1,16,17] in each case. The capacities were evaluated after the attainment of constant pH (after about 24 hr).

Thermal characteristics. The thermal characteristics of the resin were studied with a MOM derivatograph over temperatures up to 1000°C in air. The heating rate was maintained at 10°C/min. The loss in capacity of the resin on heating at different temperatures for 24 hr with deionized water was also estimated as described elsewhere.[1,16]

RESULTS AND DISCUSSION

Physical Properties

The resin is black in color and insoluble in organic solvents, including hydrocarbon, acetone, acetonitrile, nitrobenzene, halogenated hydrocarbons, dimethyl sulfoxide, and in inorganic acids and alkalies. It is only slightly soluble in conc. H_2SO_4 when heated above ~100°C. On heating to ~100°C, the gel nature of the resin dissappears and the mass changes to a brittle shiny black material. Elemental analysis reveals the presence of both nitrogen and sulfur in the resin.

Table I compares some NVC-based cation exchangers with the NVC–DVB copolymeric resin. Apparently, the latter exhibits higher capacities than the other NVC-based resins and the conventional styrene–DVB copolymeric sulfonated resins. The thermal stability, as will be seen later, is also better.

TABLE I
Comparison of Capacities and Thermal Stability of NVC-Based Cation Exchangers

Resin	Ionogenic groups	Capacity mequiv/g	Thermal stability Maximum degrada-tion, %	Temp., (°C)	Refer-ence
NVC–DVBS (N-vinylcarbazole–divinylbenzene sulfonated)	$SO_3^- H^+$	4.9	95	900	this work
NVC–PAS (N-vinylcarbazole–phthalic anhydride sulfonated)	$SO_3^- H^+$	4.73	75	900	4
NVC–FS (N-vinylcarbazole–furfural sulfonated)	$SO_3^- H^+$, COO^-H^+	4.62	100	950	2
Sulfonated poly[NVC–3,6-bis(4-keto-1-napthol)]	$SO_3^- H^+$	5.1	90	820	5
PNVC S (poly-N–vinyl-carbazole sulfonated)	$SO_3^- H^+$	4.5	100	750	1
Amberlite IR-120 (styrene–divinylbenzene sulfonated)	$SO_3^- H^+$	4.2	—	—	18

Effect of Variation of Sulfuric Acid Amount on Capacity

Table II shows that both total and salt-spliting capacities tend to attain a limiting value with varying amount of H_2SO_4 used for sulfonation of the resin. The decrease in capacities of the resin is attributable to the possibility of chain degradation with increasing amount of H_2SO_4. Significantly, the sulfur content of the resin remains practically constant throughout the range. This constancy in sulfur precentage, despite the fall in capacity, possibly implies the formation of nonionizable entities such as sulfones,[15] which would not add to the capacity of the resin.

Effect of Sulfonation Time

Table III shows the effect of sulfonation time on total and salt-spliting capacities and sulfur content. Corresponding to a sulfonation time of 3 hr at 75°, 4.1 and 3.9 mequiv/g are realized for total and salt-spliting capacities, respectively, the values increasing to 4.9 and 4.4 mequiv/g corresponding to a sulfonation time of 5 hr. Subsequently, the capacities virtually remain unchanged up to ~24 hr of sulfonation. The parallel trend in the sulfur content of the resin is also significant. The results suggest that maximum sulfonation must have taken place after 5 hr of sulfonation.

TABLE II
Variation of Capacity with the Amount of Sulfuric Acid

H_2SO_4, g/g (dry resin)[a]	Capacity[b]		Sulfur %
	Total	Salt splitting	
23	4.9	4.4	10.9
46	4.1	3.9	11.2
92	4.1	3.8	10.7
138	3.5	3.5	10.9
184	3.7	3.5	10.7

[a] 98.8% H_2SO_4 used for sulfonation of NVC–DVB copolymer for 5 hr at 75°C.
[b] Total and salt-splitting capacities were determined by equilibrating the resin with NaOH and NaCl, respectively.

TABLE III
Variation of Capacity with Time of Sulfonation[a]

Time of sulfonation, hr	Capacity		Sulfur, %
	Total	Salt-splitting	
3	4.1	3.9	10.96
5	4.9	4.4	11.24
12	4.7	4.3	12.59
18	4.8	4.3	12.59
24	4.8	4.2	12.88

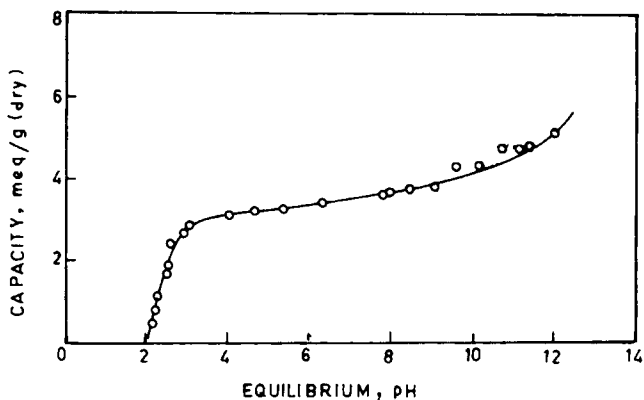[a] Sulfonation was carried out with 23 g H_2SO_4 (98.8%) at 75°C.

Fig. 1. Capacity vs. equilibrium pH curve.

Effect of Temperature of Sulfonation

Table IV indicates the effect of temperature variation on the sulfonation (5 hr) of the resin. The maximum values of 5.2 and 4.6 mequiv/g for total and salt-spliting capacities, respectively, are realized at 90°C. With further decrease in temperature, the capacities decrease steadily. Almost a similar trend in sulfur content has been observed in the same temperature range, 90–120°C. The fall in capacities indicates partial degradation of the resin. At 150°C, however, the resin becomes soluble in conc. H_2SO_4, yielding a black solution.

pH Metric Titration Curve

Figure 1 presents a typical pH metric titration curve of NVC–DVB copolymeric sulfonated resin. The capacity increases sharply from 0.4 to 2.83 mequiv/g corresponding to a pH change from 2.07 to 3.15, which is atypical of monofunctional strong cation exchange resins.[15] The capacity thereafter tends to remain constant corresponding to a pH zone of 4.0 to 6.35. Above pH 7.5, the capacity continues to increase slowly.[4] The pH titration curve shows only a single inflection. The apparent pK value of the resin calculated following the procedure of Helfferich[15] turns out to be 1.47, corresponding to that of a sulfonic acid group.[15]

TABLE IV
Variation of Capacities with Temperature of Sulfonation[a]

Temperature of sulfonation, °C	Capacity		Sulfur, %
	Total	Salt-splitting	
30	4.0	3.2	10.96
45	4.5	3.7	11.24
60	4.6	4.0	11.76
75	4.9	4.4	11.24
90	5.2	4.6	12.34
120	4.8	4.1	12.06

[a] The sulfonation of the copolymer was carried out with 23 g H_2SO_4 (98.8%) for 5 hr.
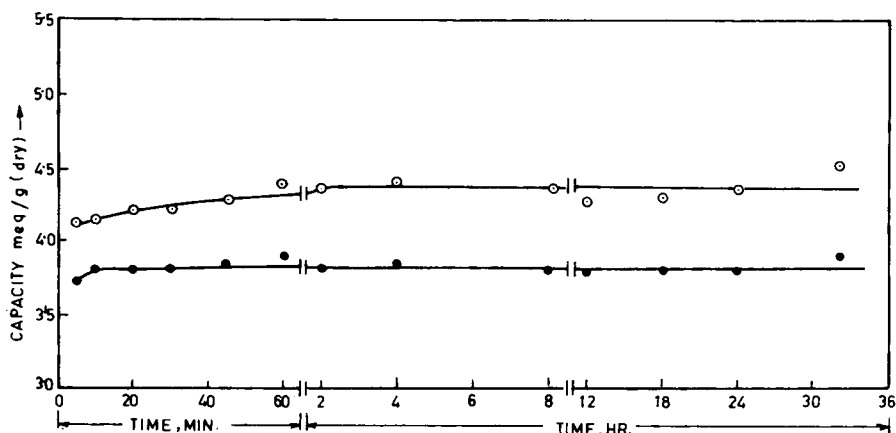
Fig. 2. Capacity vs. time curve: (○) total capacity in sodium hydroxide solution; (●) salt-spliting capacity in sodium chloride solution.

Rate of Exchange

The rate of exchange of ionogenic groups with time is shown in Figure 2. The values of 4.13 and 3.74 mequiv/g are realized for total and salt-splitting capacities, respectively, within 5 min of equilibration, and negligible variation occurs up to 45 min of equilibration. After 1 hr of equilibration, the values of total and salt-splitting capacities increase to 4.41 and 3.93 mequiv/g, respectively, and thereafter remain more or less constant. This character of the resin reveals that the sulfonated NVC–DVB copolymer can be used as a moderately fast cation exchanger. This character appears to be rather similar for all NVC-based resins so far reported.

Effect of Heating on Capacity

Table V presents some data on change of capacity on heating the resin with deionized water in a sealed tube for 24 hr at different temperatures (45–100°C). At 100°C, loss in capacity corresponds to ~14.3%, which indicates that the resin is reasonably stable at this temperature. Pertinently, the NVC–PAS resin[4] exhibits no loss in capacity even when heated to 100°C.

TABLE V
Effect of Heating on Capacity[a]

Temperature, °C	Total capacity, mequiv/g		Loss in capacity, %
	Before heating	After heating	
45	4.9	4.58	6.53
60	4.9	4.58	6.53
75	4.9	4.36	11.20
100	4.9	4.20	14.30

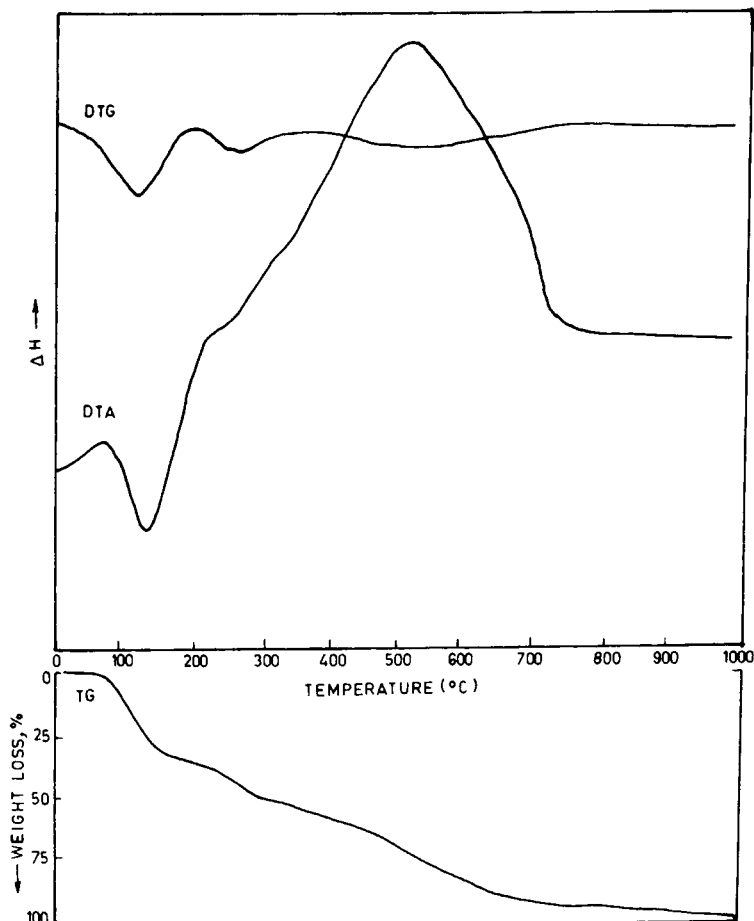[a] All samples were heated with deionized water in sealed tubes for 24 hr.

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

Thermal Characteristics

Figure 3 represents TG, DTA, and DTG for the NVC–DVB copolymeric resin. The TG curve shows a loss in weight of ~10–35% in the temperature range 100–220°C. A marked endothermic peak is also observed in the DTA curve in the range 75–180°C, with a maximum at 130°C. The exothermic effect starts below ~240°C and ends at 730°C. A marked loss of weight of 35–96% owing to destructive oxidation is revealed in the TG curve. The copolymeric resin is completely degraded at 900°C. Table I compares the thermal stabilities of several NVC-based cation exchangers reported by Biswas et al.[1,2,4,5] DVB-modified resin is comparable to PA-based resin from NVC and is appreciably stabler than other NVC-based resins.

CONCLUSIONS

Sulfonated N-vinylcarbazole–divinylbenzene monofunctional resin compares favorably with other NVC-based cation exchangers in respect of capacity and thermal stability.

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