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Chemical Modification of Poly-N-vinylcarbazole: Synthesis of Sulfonated Poly[N-vinylcarbazole-3,6-bis-(4-keto-1-naphthol)]—A Polyfunctional Cation Exchanger

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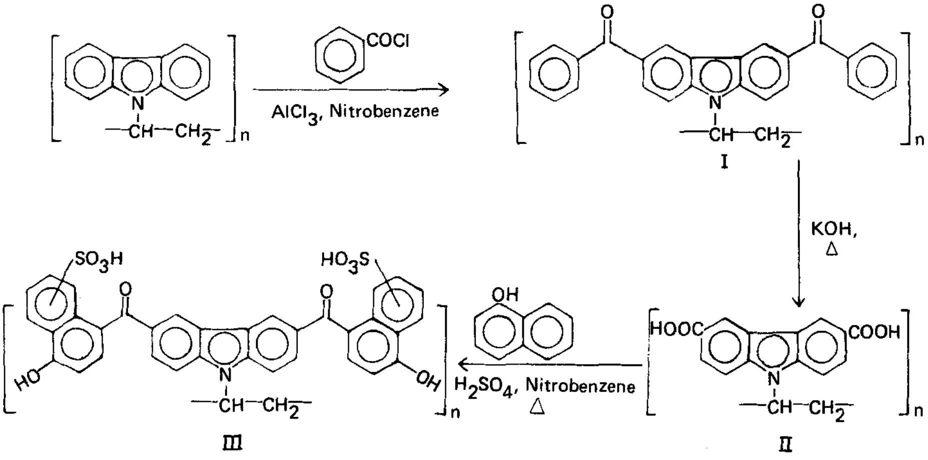
ABSTRACT

Poly-N-vinylcarbazole has been chemically modified through the reaction of poly(N-vinylcarbazole-3,6-dicarboxylic acid) and 1-naphthol in the presence of concentrated sulfuric acid to a polyfunctional cation exchanger of improved thermal properties. The compound has been characterized in respect of its structure, polyfunctionality, ion exchange capacity, and thermal stability.

INTRODUCTION

In the course of our studies [1-4] on the chemical modification of polymer systems, we now report the modification of poly-N-vinylcarbazole (PNVC) through the reaction of poly(N-vinylcarbazole-3,6-dicarboxylic acid) and 1-naphthol in the presence of concentrated H_2SO_4. This reaction affords a polyfunctional cation exchanger of improved thermal properties compared to those for PNVC [5, 6] or sulfonated PNVC [7].

PNVC undergoes Friedel-Crafts acylation with benzoyl chloride in the presence of anhydrous aluminum chloride, and on subsequent heating the product (I) with potassium hydroxide poly(N-vinylcarbazole-3,6-dicarboxylic acid) (II) is isolated. II undergoes condensation with 1-naphthol in the presence of sulfuric acid, and this reaction is accompanied by simultaneous sulfonation, yielding sulfonated poly[N-vinylcarbazole-3,6-bis-(4-keto-1-naphthol)] (III) as illustrated in Scheme 1.



SCHEME 1.

EXPERIMENTAL

Materials

Purification of NVC (BASF, Germany) and preparation of PNVC (DP 19) were accomplished by following the procedure of Biswas et al. [8, 9]. Benzoyl chloride and nitrobenzene (A.R. grade) were fractionally distilled. 1-Naphthol (E. Merck) was recrystallized from dilute alcohol. Aluminum chloride (Riedel) was purified by sublimation using the standard procedures [6].

Preparation of Poly(3,6-dibenzoyl N-Vinylcarbazole) (I)

PNVC and benzoyl chloride (1:4 ratio by weight) were mixed with anhydrous aluminum chloride (4 times the weight of PNVC) in nitrobenzene. The red viscous liquid thus obtained was kept at 0°C for 8 h and then poured in ice-cold HCl (10%) in order to decompose aluminum chloride. The nitrobenzene layer was thoroughly washed with water and poured in an excess of methanol. The green compound which separated out was collected and refluxed first in methanol and then in benzene for 30 min and subsequently filtered and dried in vacuum at 55° C (yield 50.0%).

Preparation of Poly(N-vinylcarbazole-3,6-dicarboxylic Acid) (II)

A known weight of I was added to potassium hydroxide (10 times the weight of I) which was melted with a little water and the temperature was raised slowly until reaction occurred. A dark yellow compound was obtained, the potassium salt of the dicarboxylic acid. When cold, the solid mixture was taken in water. The medium was made acidic by the addition of 10% HCl when a pale yellow compound separated out. The whole mass was diluted with water, filtered, and thoroughly washed with distilled water until free of chloride ions and finally dried in vacuum at 55° C (yield 80.6%).

Preparation of Sulfonated Poly[N-vinylcarbazole-3,6-bis-(4-keto-1-naphthol)] (III)

In a Pyrex reaction vessel, Compound II and 1-naphthol (1:3)ratio by weight), dissolved in nitrobenzene, were mixed with a known catalytic amount of concentrated sulfuric acid (98.8%). The red colored mixture was then heated at 175° C with continuous stirring for 15 min, when a dark colored compound settled down in the medium. The reaction mixture was cooled to room temperature, the nitrobenzene layer was decanted off, and the black compound was thoroughly washed with distilled water to remove traces of sulfuric acid and undesirable side products. The compound was then refluxed in excess methanol for 1 h, filtered, and thoroughly washed with methanol. It was finally refluxed with chloroform and dried in vacuum at 100° C for 4 h. A shiny black thin film compound was obtained (yield 37.6%).

CHARACTERIZATION

IR Spectra

IR spectra of Compounds I-III were recorded on a Perkin-Elmer 237B spectrophotometer.

Elemental Analysis

Nitrogen was quantitatively estimated by the micro-Dumas method and sulfur of Compound III by the standard procedure [10].

Viscosity

Viscosity of Compound III was determined with an Ostwald viscometer in concentrated H_2SO_4 (0.1% solution).

Thermal Stability

The thermal characteristics of Compound III were studied with a MOM derivatograph over the temperature range up to 900°C in air. The heating rate was maintained at 10°C/min.

Evaluation of Capacity

The total ion exchange and the salt-splitting capacities for Compound III were determined by recommended procedures [11].

pH Titration

pH values were measured by a Digilog pH Meter. Incremental quantities of NaOH (0.095 N) were added to different mixtures containing a known weight of Compound III and 10 mL NaCl solution (1 N), keeping the total volume at 50 mL by the addition of deionized water. The equilibrium pH of the solutions was measured [7, 12, 13] in each case. The capacities were evaluated after the attainment of a constant pH (after about 48 h). Figure 1 represents the equilibrium pH versus capacity plot for Compound III.

RESULTS AND DISCUSSION

Table 1 summarizes the relevant information about Compounds I, II, and III. The results of elemental analysis and IR absorptions are consistent with the suggested Structures I-III.

Thermal Characteristics

Figure 2 represents the DTG, DTA, and TG curves for Compound III. There is an exothermic effect starting from 160°C and reaching a maximum at ~480°C. A loss of weight of 16.6% occurs at 160°C and

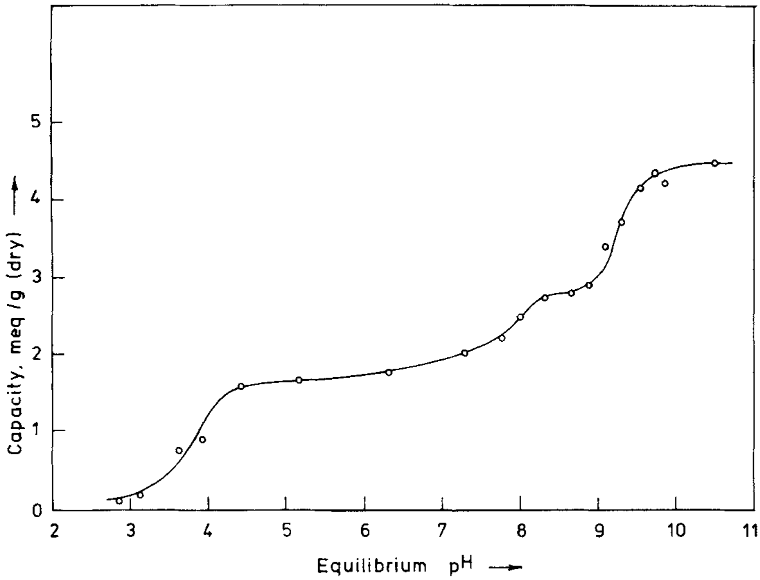


FIG. 1. Equilibrium pH versus capacity for Compound III.

remains constant up to 240°C. The loss of weight at 340°C is ~33%. The maximum degradation of the polymer (90%) occurs at 820°C. It is significant to point out in this context that unmodified poly-N-vinylcarbazole degrades almost completely [5, 6] at ~520°C. This suggests that thermal stability of PNVC is appreciably enhanced through chemical modification.

Ion-Exchange Characteristics

Compound III was also characterized as a cation exchange resin by capacity measurements and pH titration characteristics.

Effect of 1-Naphthol Concentration on Capacity

Table 2 shows that both the total and salt-splitting capacities of III decrease with increasing amounts of 1-naphthol used in the condensation reaction, while the yields and the relative viscosities of the products increase consistently. Interestingly, the sulfur content of the resins remains almost the same in all these cases. Apparently, formation of III is favored by an increase of 1-naphthol amounts in the reaction. Further, the sulfur content should not be expected to

TABLE 1. Characterization of Polymers

Compound	Solubility	Elemental N analysis (%)		Characteristic IR absorptions (cm^{-1})
		Found	Calc	
I	Nitrobenzene, chloroform, DMSO, DMF	5.16	4.99	1660 (C=O, aromatic diaryl ketone)
				1580 (–C=C–, aromatic)
II	Nitrobenzene, chloroform, DMSO, DMF	-	-	1675 (C=O, aromatic carboxylic acid)
				1610, 1350 (–COO–)
				1600 (–C=C–, aromatic)
III	98.8% H_2SO_4 on keeping for 7 d with warming	4.39	3.18	1650-1670 (C=O, aromatic diaryl ketone)
				1590 (–C=C–, aromatic)
				1170, 1035 and 650 (–SO_3H)
				3200-3550 (phenolic –OH stretching)
				1325 (phenolic –OH bending)

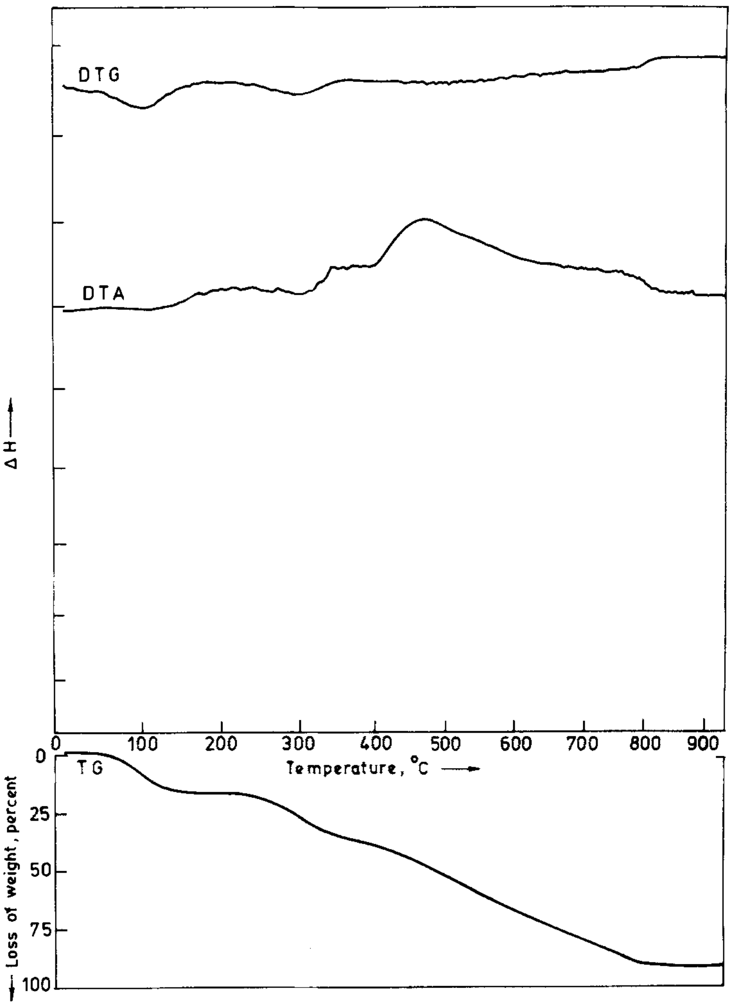


FIG. 2. DTG, DTA, and TG curves for Compound III.

TABLE 2. Effect of 1-Naphthol Concentration on Capacity[a]

Compound II:1-napththol (w/w)	Total capacity (mEq/g, dry)	Salt-splitting capacity (mEq/g, dry)	S found (%)	Yield (%)	Relative viscosity
1:1	5.12	2.03	10.96	27.3	1.05
1:2	4.61	1.72	10.50	32.9	1.09
1:3	4.48	1.64	9.86	37.6	1.14

[a] Time of reaction, 15 min; temperature, 175°C; sulfuric acid (98.8%), 9.2 g/g Compound II.

TABLE 3. Effect of Sulfuric Acid on Capacity[a]

Sulfuric acid (g)	Total capacity (mEq/g, dry)	Salt-splitting capacity (mEq/g, dry)	S found (%)	Yield (%)	Relative viscosity
4.6	4.48	1.64	9.86	37.6	1.14
9.2	3.97	1.01	7.14	54.2	1.33
13.8	4.10	0.76	7.94	40.8	1.05

[a] Compound II:1-naphthol (w/w), 1:3; time of reaction, 15 min; temperature, 175°C.

change if the sulfonation occurs regularly at each moiety of 1-naphthol (as shown in the structure) condensing with II in which case maximum theoretical sulfur will be approximately 10%. The fall in the capacities may be due to the formation of nonionizable inactive sulfone groups [2, 11] in the polymer during the process of sulfonation. It is further suggested that the $-SO_3H$ entities may be hydrogen bonded with the carbonyl groups present in the polymer which may also lower the capacities.

Effect of Sulfuric Acid on Capacity

Table 3 shows that both the total and salt-splitting capacities of the resin tend to decrease as the amount of sulfuric acid used in the condensation reaction is increased. However, the total yield and the

TABLE 4. Effect of Time of Reaction on Capacity[a]

Time (min)	Total capacity (mEq/g, dry)	Salt-splitting capacity (mEq/g, dry)	S found (%)	Yield (%)	Relative viscosity
15	4.48	1.64	9.86	37.6	1.14
30	4.86	1.90	9.04	48.4	1.22
45	4.35	1.40	7.94	46.3	1.01

[a] Compound II:1-naphthol (w/w), 1:3; reaction temperature, 175°C; sulfuric acid, 9.2 g/g Compound II.

relative viscosity of the resin tends to first increase as the quantity of acid is doubled and subsequently falls. This implies that excess sulfuric acid degrades the polymer. It is also likely that increasing amounts of sulfuric acid progressively increase sulfone formation, resulting in consistent lowering of the capacity.

Effect of Time of Reaction on Capacity

Table 4 shows that the yield as well as the viscosity of the resins attain to highest values at 30 min of reaction and falls subsequently with a further increase of reaction time. The total and salt-splitting capacities reveal an exactly parallel trend. Evidently, longer reaction time results in degradation of the molecule.

Effect of Reaction Temperature on Capacity

Table 5 indicates that the yield and the capacities of the resin consistently increase in the temperature range 150-200°C. Apparently condensation and sulfonation are less favored at lower temperature regions.

Salt-Splitting Capacity

It is significant that the salt-splitting capacities of the resins in all these cases (Tables 2-5) are much lower than the corresponding total capacities. This is probably reasonable, since ion exchangers can sorb solutes from solutions with which they are in contact [7, 11] and consequently, salting out in the presence of an electrolyte decreases the ion exchange capacity.

TABLE 5. Effect of Reaction Temperature on Capacity[a]

Temperature (°C)	Total capacity (mEq/g, dry)	Salt-splitting capacity (mEq/g, dry)	S found (%)	Yield (%)	Relative viscosity
150	4.22	1.46	7.66	14.2	1.11
175	4.48	1.64	9.86	37.6	1.14
200	4.59	1.77	9.32	45.7	1.19

[a] Compound II:1-naphthol (w/w), 1:3; time of reaction, 15 min; sulfuric acid, 9.2 g/g Compound II.

pH Titration Curve

The polyfunctional nature of the resin is well endorsed by the results of pH titration (Fig. 1). The behavior in the pH range 2.8-5 is typical of that of a strong acid exchanger [2] of the sulfonic acid type. The second inflection appears in the pH range 5-9, which may be due to any unreacted –COOH group [2] present in the resin. The third inflection, observed in the pH range 9-11, is characteristic of a phenolic-OH group. The apparent pK values of the resin calculated by applying the procedure of Helfferich [11] to the data of Fig. 1 are, respectively, $pK_1 = 3.0$, $pK_2 = 5.8$, and $pK_3 = 9.4$. While the latter two values agree perfectly with the reported ones [14]. pK_1 seems to be somewhat higher than what is usually observed with sulfonic acid resins [14]. As pointed out earlier, this discrepancy is understandable on the basis of formation of H-bonds and nonionizable sulfone groups in the product which would evidently tend to suppress the apparent ionization of the strong acid group.

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