

Furfural-Based Phosphonic Acid Cation Exchange Resins from *N*-Vinylcarbazole and Its Polymer. II

MUKUL BISWAS and S. PACKIRISAMY, *Department of Chemistry, Indian Institute of Technology, Kharagpur, 721302, India*

Synopsis

Thermal stabilities of the crosslinked *N*-vinylcarbazole/poly(*N*-vinylcarbazole)-furfural polymers and of the phosphonic acid resins prepared therefrom were studied by thermogravimetric analysis. The overall thermal stability of the crosslinked polymers is greater than the same for poly(*N*-vinylcarbazole) and is further improved upon phosphorylation. The resins are stable in 5*N* acids and water at 100°C. Isothermal oxidative degradation studies of the resins indicate significant increase in the capacities. pH metric titration of the resins shows the presence of mono and dibasic phosphonic acid groups. The resins realize about 90% of their capacities within 2 min of equilibration.

INTRODUCTION

In earlier work¹ we described the synthesis of crosslinked polymers from the reaction of *N*-vinylcarbazole (NVC) and poly(*N*-vinylcarbazole) (PNVC) with furfural (F) and the subsequent chemical modification to phosphonic acid cation exchange resins.

In this part the thermal properties of the crosslinked polymers (NVCF and PNVCF) and the corresponding phosphonic acid resins (NVCFP and PNVCFP) are described, and some of the characteristic properties of the latter are reported.

EXPERIMENTAL

Materials

Furfural based phosphonic acid resins from NVC/PNVC, synthesized as described earlier,¹ were used for further study. The pertinent of the physico chemical characteristics of the resins used are shown in Table I. The parent crosslinked polymers, from which these resins were derived, were used for thermogravimetric analysis.

pH Metric 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 50 mL. The equilibrium pH and the capacity were measured after 48 h of equilibration.

TABLE I
Pertinent Physico Chemical Characteristics of NVCFP and PNVCFP Resins Used for Further Study

Physico chemical characteristics	NVCFP ^a	PNVCFP ^a
Total capacity	4.64 meq/g (dry)	4.84 meq/g (dry)
Salt splitting capacity	0.74 meq/g (dry)	0.75 meq/g (dry)
Furfural content	0.25 g/g NVC	0.09 g/g PNVC
Nitrogen content	3.39%	3.89%
Phosphorus content	8.56%	10.52%

^a Time of phosphorylation, 7 h; PCl₃, 3 mL/g (dry) resin; solvent dichloroethane 5 mL/g (dry) resin; AlCl₃ 1 g/g (dry) resin; temperature, 80°C.

Rate of Exchange

Accurately weighed quantities of the resins in the H⁺ form were taken in different 100-mL glass stoppered flasks, 50 mL of 0.1N NaOH was added to each flask and shaken occasionally at 25 ± 1°C. The capacity was determined after a predetermined time interval following a standard procedure.² The same procedure was repeated using 1.0N NaCl as the contact solution. The acidity liberated and the capacity realized were determined at various time intervals.

Thermal Stability

The thermal characteristics of the crosslinked polymers and the ion exchange resins were studied with a MOM derivatograph over temperatures up to 1000°C in air. The heating rate was maintained at 10°C/min.

Thermal Stability in Water and Acids

Known weights of the resins were treated with 25 mL of deionized water in different glass ampoules. The ampoules were sealed and heated at desired temperatures for a period of 24 h. The contents were removed, washed, and dried, and the capacities were evaluated.

Similar procedure was adopted for evaluating the thermal stability of the resins in mineral acids at 100°C for a period of 24 h.

Isothermal Oxidative Degradation Studies

Known weights of the resins in the H⁺ form were heated in Muffle furnace at 200°C. At regular time intervals of 5 h the weight losses and the capacities of the resins were determined.

RESULTS AND DISCUSSION

Thermal Stability

Thermal stability of NVCF and PNVCF: Figure 1 compares the thermograms of NVCF, PNVCF, and PNVC. PNVC as well as PNVCF are initially stable up to 400°C, where NVCF suffers 22.5% weight loss. It is observed further

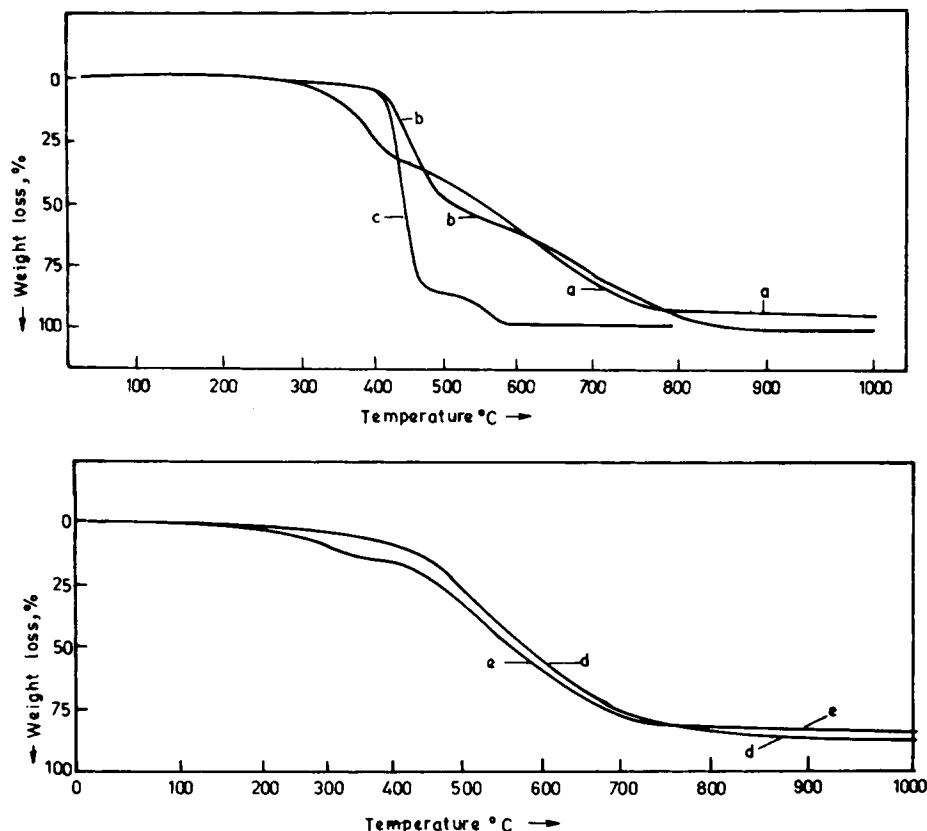


Fig. 1. TG curves of: (a) NVCF; (b) PNVCf; (c) PNVC; (d) NVCFP; (e) PNVCfP.

that PNVC undergoes complete weight loss at 600°C, at which temperature NVCF and PNVCf lose 58% and 61% weight, respectively. These data therefore suggest that in general the condensation of furfural with NVC/PNVC results in improved thermal stability.

Between NVCF and PNVCf, the former undergoes more weight loss in the temperature region 300–400°C. It is possible that, due to the simultaneous polymerization of NVC along with the process of condensation with furfural, some low molecular weight less crosslinked products are also formed along with the highly crosslinked matrix. The former should undergo degradation within the lower temperature region. However, NVCF undergoes 35% weight loss in the wide temperature range of 300–470°C, whereas PNVCf experiences the same weight loss in a comparatively narrower temperature range 400–470°C. Further, the degradation process is apparently faster in the temperature range 400–500°C for PNVCf than for NVCF. These observations are consistent with the earlier conclusion¹ that NVCF offers a more crosslinked matrix than PNVCf.

TGA and DTA Studies of NVCFP and PNVCfP: Figure 1 shows that NVCFP and PNVCfP undergo 25% and 31% weight losses at 500°C, respectively, as against 39% and 48% for the corresponding crosslinked polymers. Up to 500°C NVCFP is more stable than PNVCfP, and thereafter the stability becomes more or less comparable. It is remarkable also that even at 1000°C the resins are degraded to about 85% in either case. In any case after phosphorylation the

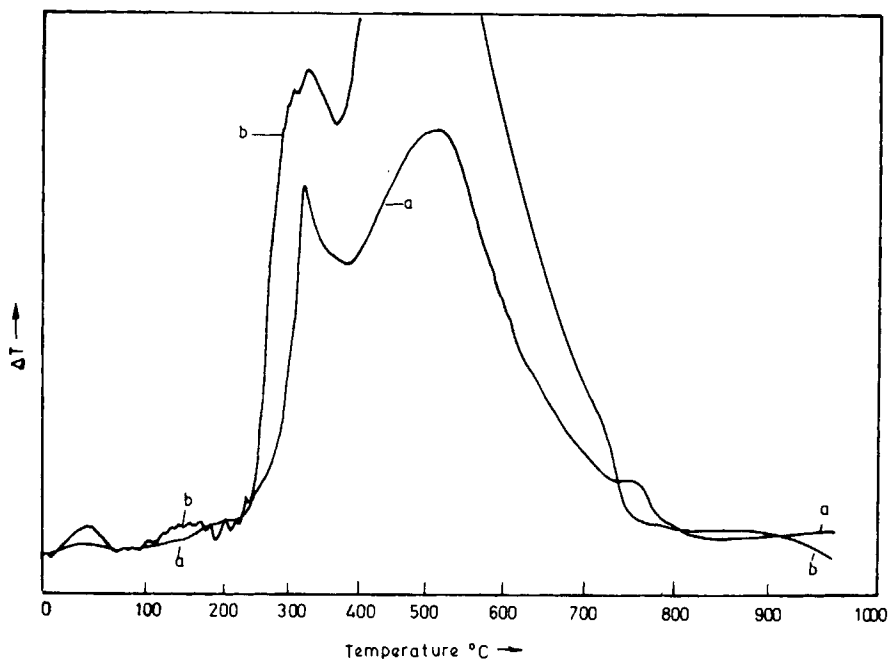


Fig. 2. DTA curves of: (a) NVCFP; (b) PNVCFP.

overall stability of the resins is improved compared to the crosslinked polymers. It is relevant to note that sulfonated NVC³ and PNVC³, as also phosphorylated PNVC,⁴ are thermally less stable than NVCFP and PNVCFP.

DTA curves (Fig. 2) for NVCFP and PNVCFP reveal that exothermic effects resulting from the oxidative degradation effects start at about 240°C for both and end at 780°C and 740°C, respectively. In general, the overall exothermic effects are more pronounced in the case of PNVCFP than in the case of NVCFP resin.

Effect of heating of NVCFP and PNVCFP with water: Table II represents the stability of NVCFP and PNVCFP in presence of water at different temperatures, 60°C, 80°C, and 100°C. It is seen that practically no loss in capacity is observed for these resins when they are heated with water for 24 h at these temperatures. However, it has been reported that sulfonated NVC/PNVC based resins^{3,5,6} undergo loss in capacity up to 25%. These data imply that NVCFP and PNVCFP resins may be used for ion exchange even up to 100°C.

TABLE II
Effect of Heating^a of NVCFP and PNVCFP with Water

Temperature (°C)	NVCFP resin		PNVCFP resin	
	Total capacity [meq/g (dry)]		Total capacity [meq/g (dry)]	
	Before heating	After heating	Before heating	After heating
60	4.64	4.64	4.84	4.83
80	4.64	4.62	4.84	4.84
100	4.64	4.63	4.84	4.82

^a All samples were heated with deionized water for 24 h.

Effect of heating of NVCFP and PNVCFP with acids: Table III compares the stability of NVCFP and PNVCFP in the presence of mineral acids at 100°C for 24 h. NVCFP resin does not undergo any loss in capacity with HCl and H₂SO₄, whereas PNVCFP resin does so under these conditions. However, with 5N HNO₃, which is an oxidizing agent, NVCFP undergoes more loss than PNVCFP. It has been experimentally observed that the color of the resins changes to yellow, when they are heated with 5N HNO₃. IR spectra of the resins heated with HNO₃ show peaks at 1525 and 1710 cm⁻¹ corresponding to the nitro and carboxylic acid groups. These peaks are absent in the IR spectra of the parent resins. The treatment with HNO₃ under these conditions leads to the introduction of the nitro group into the polymeric matrices and the formation of carboxylic acid groups, probably by the oxidation of furfurylic bridges and/or any other aliphatic bridges. In addition, hydrolysis of phosphonic acid groups may also occur under these conditions. The net decrease in the capacity of the resins may be the combined effect of all these modifications in the resin matrices introduced during treatment with HNO₃.

Isothermal oxidative degradation studies: For practical applications it is often useful to examine the decomposition behavior in isothermal measurements for sustained periods.⁷ Figure 3 shows the effect of heating in air at 200°C on the capacity and the loss in weight of NVCFP and PNVCFP. Usually, heating the ion exchange resins in air causes a decrease in capacity. Surprisingly, NVCFP and PNVCFP resins shows very high increase in capacity on heating in air at 200°C. Within 5 h NVCFP resin shows a 54.3% increase in capacity, whereas PNVCFP shows a 71.7% increase. Overall increase in capacity is 108.6% and 141.3% for NVCFP and PNVCFP, after heating the resins for a period of 40 h, when the weight losses reach to limiting values of 26.1% and 23.6%, respectively. The loss in weight on heating the resins in air shows that the resins undergo thermal degradation.

Armitage and Lyle⁸ reported that the thermal decomposition of ion exchange resins yields carboxyl groups on the aromatic nucleus, formed by oxidative cleavage of the aliphatic backbone of the polymer, especially at points where crosslinking occurs. Poly(NVC) after crosslinking with furfural will have furfurylic crosslinks and also ethylenic backbones. Moreover, during phosphorylation the solvent, CH₂ClCH₂Cl, used may also introduce additional aliphatic ethylenic bridges.⁹ These aliphatic backbone/crosslinks and furfurylic bridges probably undergo oxidative thermal degradation forming carboxylic acid groups, as suggested by Armitage and Lyle.⁸ It is also seen that the increase in

TABLE III
Effect of Heating^a of NVCFP and PNVCFP with Acids

Acid	NVCFP Resin			PNVCFP Resin		
	Total capacity [meq/g (dry)]		Loss in capacity (%)	Total capacity [meq/g (dry)]		Loss in capacity (%)
	Before heating	After heating		Before heating	After heating	
5N HCl	4.64	4.64	No loss	4.84	4.55	5.99
5N H ₂ SO ₄	4.64	4.64	No loss	4.84	4.69	3.10
5N HNO ₃	4.64	3.98	14.22	4.84	4.40	9.09

^a All samples were heated with acids for 24 h at 100°C.

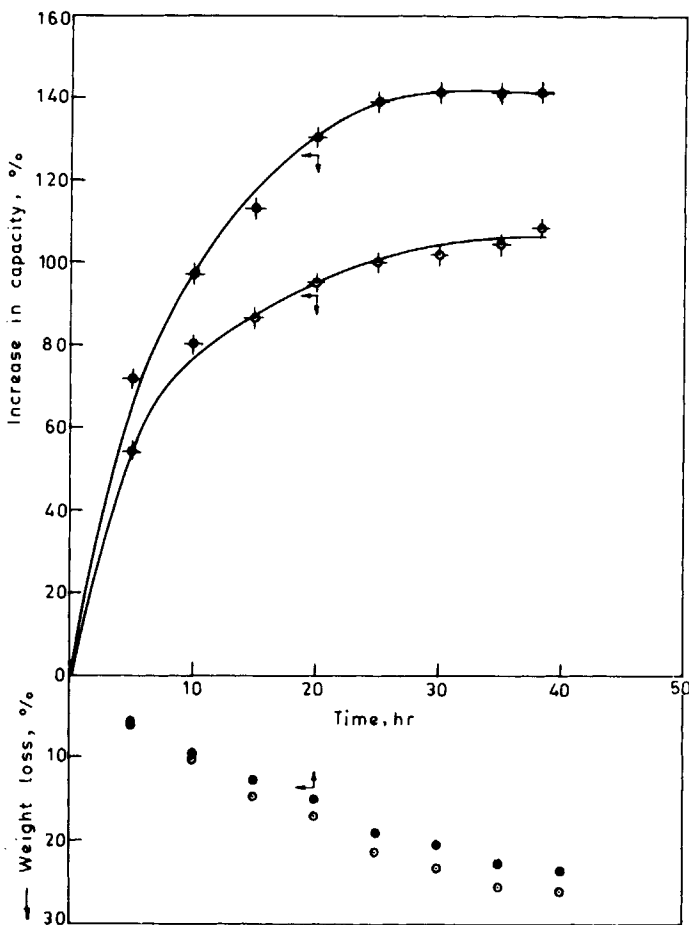


Fig. 3. Isothermal oxidative degradation studies of NVCFP and PNVCFP: (\diamond) increase in capacity of NVCFP; (\blacklozenge) increase in capacity of PNVCFP; (\circ) weight loss of NVCFP; (\bullet) weight loss of PNVCFP.

capacity is much pronounced in the case of PNVCFP than in NVCFP. This suggests that PNVCFP undergoes more oxidative destruction than NVCFP. This is also supported by the fact that PNVCFP shows more pronounced exothermic effects than NVCFP as seen in DTA curves of NVCFP and PNVCFP (Fig. 2). Figure 3 reveals also that the differences between the weight losses for the two resins are not appreciable compared to the same for the capacities. This trend need not necessarily correlate with the TG data (Fig. 1), since the matrices are considerably modified under the conditions of isothermal degradation.

pH Metric Titration Characteristics of NVCFP and PNVCFP

The differential curves in Figures 4 and 5 clearly reveal two degrees of dissociation, the first degree of dissociation occurs in the pH range 2.81–10.40 in the case of NVCFP and 2.70–6.77 in the case of PNVCFP. The second degree of

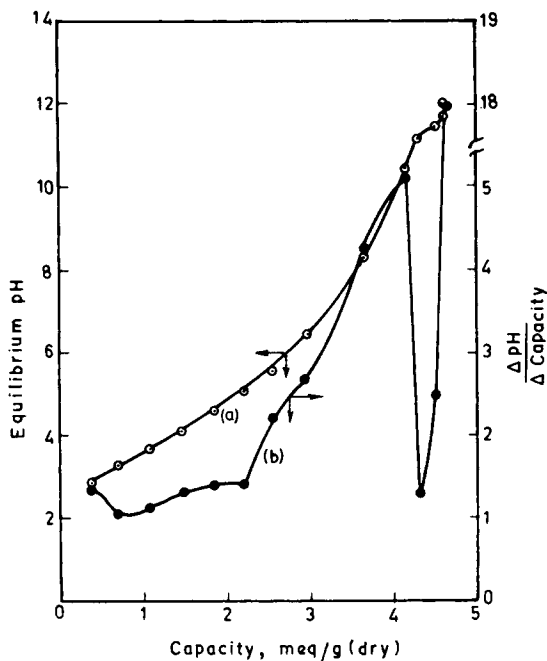


Fig. 4. pH metric titration of NVCFP: (a) pH vs. capacity curve; (b) differential curve.

dissociation starts after pH 10.40 and 6.77 and ends at pH 11.70 for NVCFP and PNVCFP resins, respectively. The maximum capacities corresponding to the first and the second degrees of dissociation are, respectively, 4.15 and 0.49 meq/g

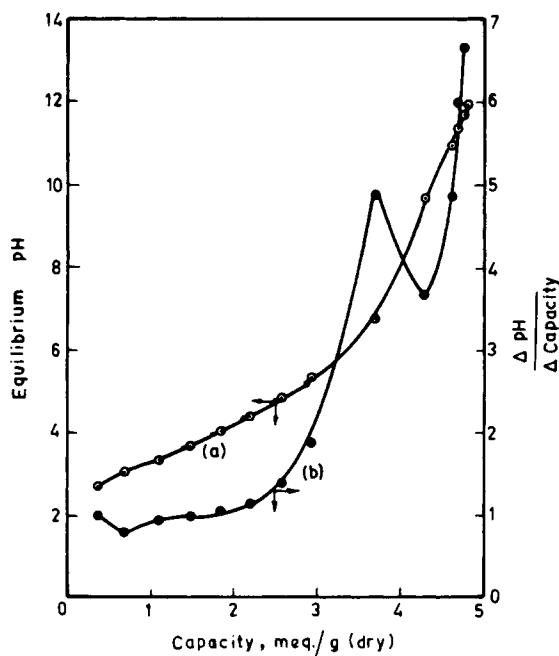
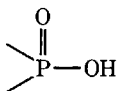


Fig. 5. pH metric titration of PNVCFP: (a) pH vs. capacity curve; (b) differential curve.

(dry) for NVCFP and 3.69 and 1.15 meq/g (dry) for PNVCFP. The total capacity values of 4.64 and 4.80 meq/g (dry) for NVCFP and PNVCFP, respectively, obtained from pH metric titration correlate well with the total capacity values determined by a static method² (Table I). The capacities realized corresponding to the second degree of dissociation are much less in comparison with the capacities realized for the first degree of dissociation. This is probably due to the fact that some of the phosphorus is present as singly ionizable



groups, which would cause a decrease in capacity realized due to the second degree of dissociation. Starobinets and Kul'kina¹⁰ similarly concluded that styrene-divinylbenzene phosphonic acid resin synthesized by them contained mono and dibasic phosphonic acid groups.

Rate of Exchange of NVCFP and PNVCFP

Figure 6 shows the rate of exchange of ionogenic groups of NVCFP and PNVCFP. It is observed that 89.4% and 92% total capacity values are realized for NVCFP and PNVCFP, respectively, within 2 min of equilibration and the corresponding salt splitting capacity values are 85% and 90.6%, respectively. This feature sharply distinguishes these resins from the furfural based phosphonic acid resins from styrene¹¹ and α -pinene,¹² which are reported to realize about

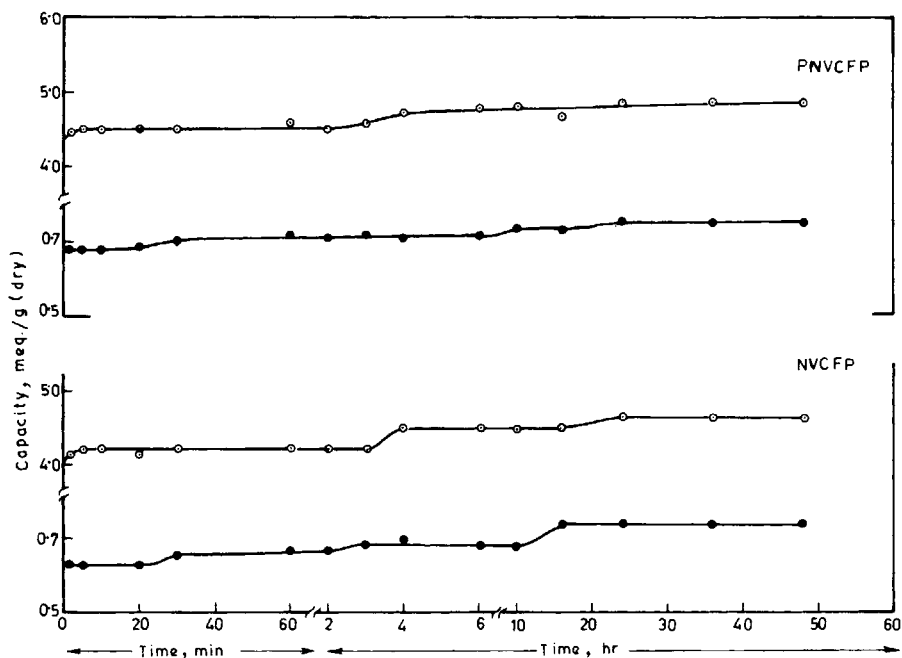
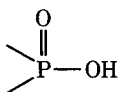


Fig. 6. Rate of exchange of NVCFP and PNVCFP: (⊙) total capacity in sodium hydroxide solution; (●) salt splitting capacity in sodium chloride solution.

37% and 50% of their total capacity values even in 15 min. This interesting feature is probably due to the fact that most of the ionogenic groups, as evidenced by pH metric titrations, are present as singly ionizable



which are expected to show a fast ion exchange process. NVCFP and PNVCFP resins take 24 h to attain 100% total and salt splitting capacity values. The rate of exchange characteristics show that these resins are moderately fast ion exchangers.

CONCLUSIONS

Phosphonic acid resins derived from NVC—furfural and PNVC—furfural crosslinked polymers are thermally more stable than PNVC. The resins are sufficiently stable at 100°C in water and acids, except in HNO₃, where some side reactions occur.

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