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### Ion-Exchange and Chelation Resins Derived from Poly(t-butyl N-Vinyl Carbamate)

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## Ion-Exchange and Chelation Resins Derived from Poly(*t*-butyl *N*-Vinyl Carbamate)

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### ABSTRACT

Cross-linked resins containing vinyl amine units spaced by cyclic urea units are obtained by pyrolysis of poly(*t*-butyl *N*-vinyl carbamate) at 200° C, followed by treatment of the pyrolysate with HBr/HOAc solution and subsequent neutralization. The resins are very stable and are suitable for chromatographic separation of acidic amino acids, peptides, and heavy metal ions. The selectivity of the resins for metal ions is in the order  $\text{Cu}^{+2} \gg \text{Zn}^{+2} > \text{Ni}^{+2} \sim \text{Co}^{+2} \gg \text{Na}^+ \sim \text{Mg}^+$ .

### INTRODUCTION

Resins containing ethyleneimine [1-3], vinyl amine [4-13], diaminostyrene [14], etc. [15, 16] units are good complexing agents for heavy metal ions and are of potential value for metal ion separations.

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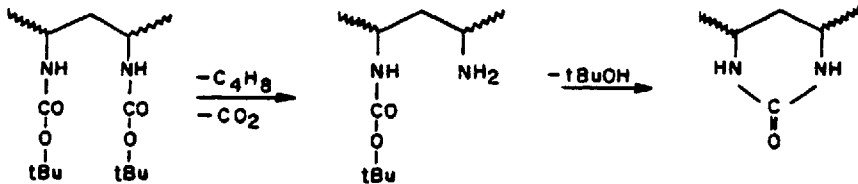
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Resins containing amino groups are also of potential value as weak base ion-exchange resins and as matrices for binding enzymes, substrates for affinity chromatography, or peptide chains in automated synthesis or stepwise degradation applications.

Earlier studies on cross-linked varieties of poly(vinyl amine) have been concerned with the factors determining the binding characteristics of the resins, but chromatographic separations do not seem to have been attempted. We wish to report a new route to cross-linked resins containing vinyl amine units and to describe several chromatographic applications of the resins.

In an earlier study [17], we noted that pyrolysis of poly(*t*-butyl *N*-vinyl carbamate) yields a polymer containing the statistically expected amount of cyclic urea units, assuming that the cyclization process involved adjacent pairs of carbamate units. Thus amine units generated by the pyrolysis reaction react rapidly with adjacent carbamate units to form cyclic urea units. Isolated carbamate units decompose to form primary amine units which impart weak base ion-exchange properties to the pyrolyzed polymers.



In the present paper we describe the preparation and characterization of ion-exchange and chelation resins from poly(*t*-butyl *N*-vinyl carbamate) by a pyrolysis-hydrolysis technique.

## RESULTS AND DISCUSSION

### Resin Preparation

Pyrolysis of poly(*t*-butyl *N*-vinyl carbamate) in bulk at 200°C affords carbon dioxide, isobutylene, *t*-butanol, and a rigid cross-linked foam of medium density [17]. Depending on the degree of pyrolysis obtained, which can be characterized by fractional weight loss *W*, the product contains various amounts of untreated carbamate (I), cyclic urea (III) and vinyl amine (II) units, as well as small amounts of linear urea cross-links (IV).

Figure 1 shows a plot of polymer weight loss at 200° as a function

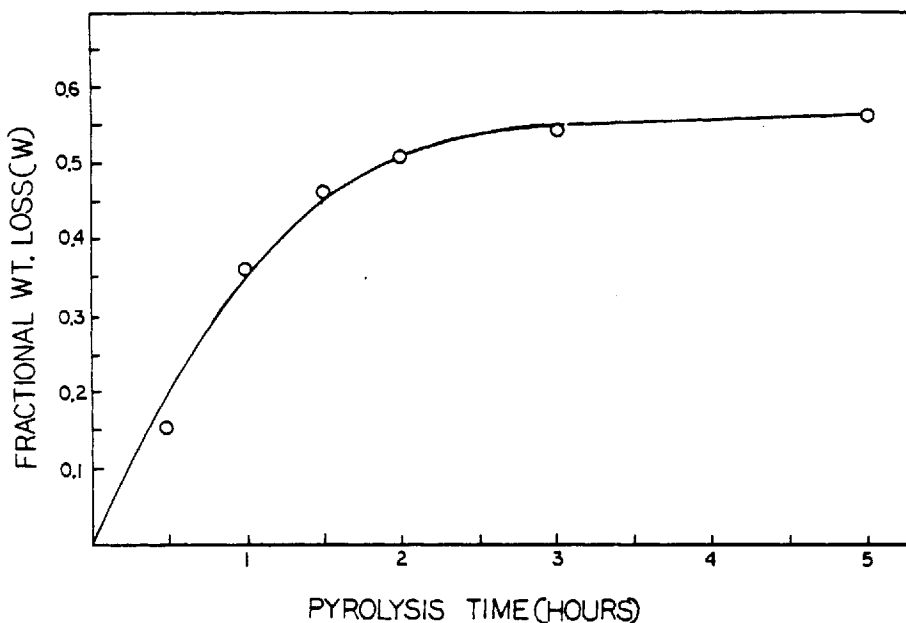
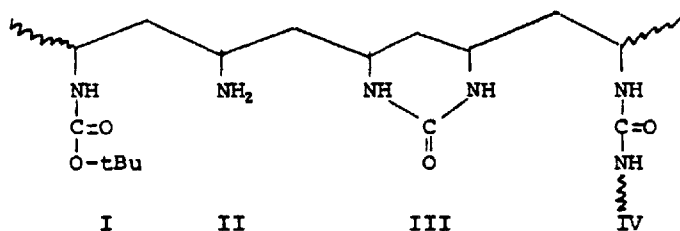


FIG. 1. Fractional weight loss of poly(t-butyl n-vinyl carbamate) when heated under nitrogen at 200°.

of time. The pyrolysis reaction is very reproducible and is easily controlled. The fractional weight loss,  $W$ , provides a measure of the fraction of carbamate units decomposed,  $P$ , and the fraction of carbamate units converted to vinyl amine units,  $Z$ . These quantities are related through Eqs. (1) and (2), which are derived [17] on the assumption that pairs of adjacent carbamate units react randomly to form cyclic urea units and that carbamate units which become isolated during the process are converted to vinyl amine units.

$$W = (87P + 13Z)/143 \quad (1)$$

$$Z = 0.1353 - (1 - P) \exp[(2P - 2)/(1 - P/2 + Z/2)] \quad (2)$$

These equations accurately predict the combined (vinyl amine) - (unreacted carbamate) contents of partial pyrolysates [17], as well as the composition of the polymer obtained when all carbamate units have decomposed. Thus the maximum weight loss occurring during pyrolysis should be 60.5%, and 13.5% of the carbamate units should be converted to vinyl amine units at the end of the reaction. It can be seen from Fig. 1 that the final weight loss is close to that expected. Our other studies [17] have shown that the final polymer contains approximately 13% vinyl amine units. Equations (1) and (2) were used to calculate the mole fractions of carbamate units unreacted, converted to urea units ( $P - Z$ ), and converted to vinyl amine units ( $Z$ ) as a function of  $P$ . The results of this calculation are presented in Fig. 2. Thus, by controlling the degree of pyrolysis, it is possible to prepare resins having a variety of compositions.

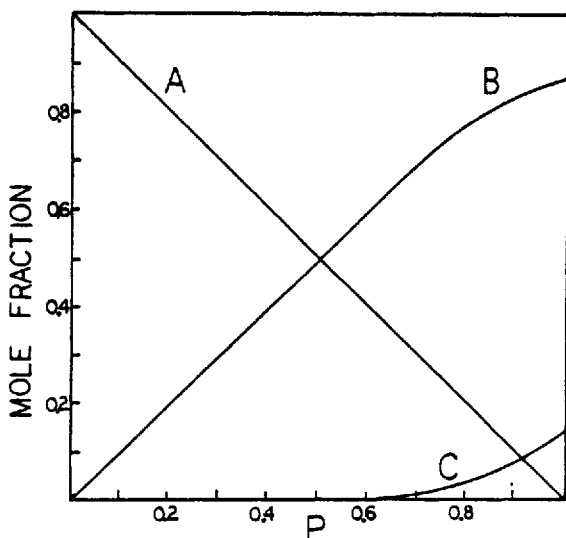


FIG. 2. Calculated proportions of unreacted carbamate units (A), of carbamate units incorporated into cyclic urea units (B), and into primary amine units (C) in pyrolyzed polymer as a function of conversion ( $P$ ).

In general, unreacted carbamate units in the polymer pyrolysates were converted to vinyl amine units by treatment with a solution of HBr in acetic acid, followed by washing with water and then with dilute alkali. Thus the capacities of the resins were a function of  $1 - P + Z$ . Figure 3 shows a plot of treated resin capacity vs conversion, the capacities being based on the weights of untreated pyrolysates (A) as well as on the weights of hydrolyzed pyrolysates (B).

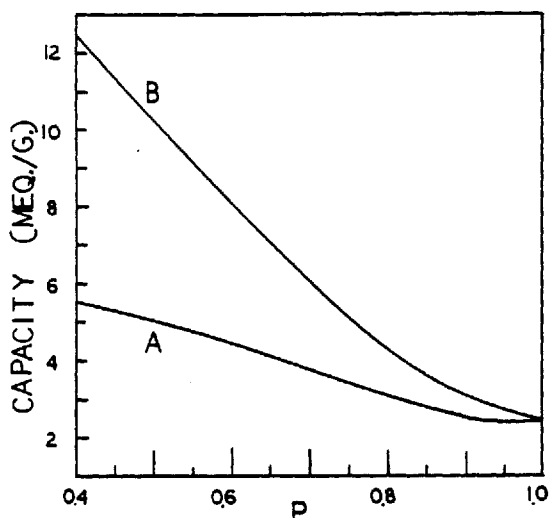
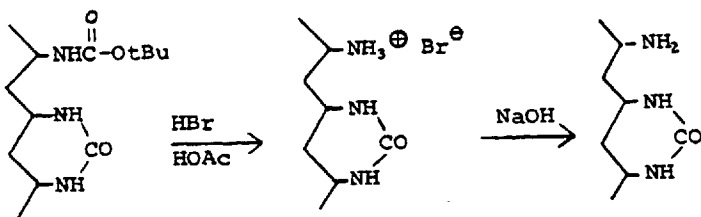


FIG. 3. Ion-exchange capacities calculated for pyrolyzed-hydrolyzed polymer as a function of conversion,  $P$ . Curve A represents capacities based on weights of pyrolyzed, unhydrolyzed polymers. Curve B represents capacities based on weights of pyrolyzed, hydrolyzed polymers.



The extent of cross-linking present in the resins varies with  $P$ , the maximum cross-linking occurring when  $P = 0.85$ . This was determined by measuring the swelling of the pyrolysates in glacial acetic acid (Fig. 4). The cross-links are believed to involve urea linkages formed

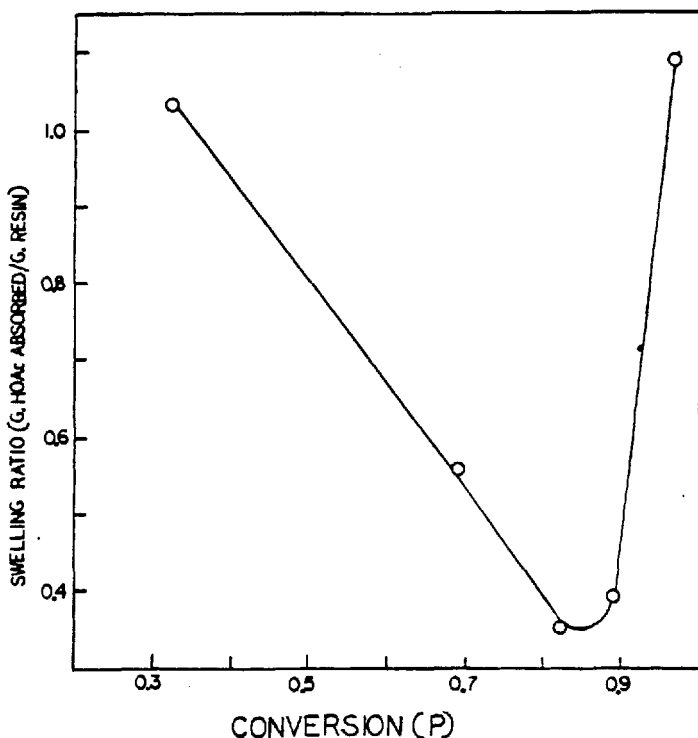
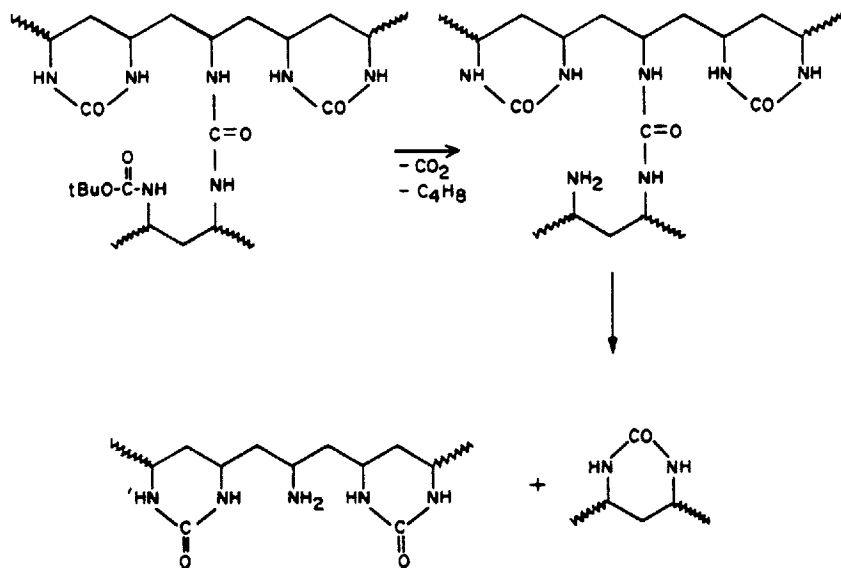


FIG. 4. Swelling of pyrolyzed poly(*t*-butyl *N*-vinyl carbamate) in glacial acetic acid as a function of degree of pyrolysis.

between "isolated" vinyl amine units and carbamate units. These linkages are less stable than cyclic urea units, and the latter are probably formed at the expense of the former during the final stages of the reaction. Thus reactions of the type shown below are believed to be responsible for the decrease in cross-link density at high conversions.

Resins for column separation studies were pyrolyzed to  $P = 0.85$ - $0.90$  to minimize effects of resin swelling on column flow rates.



Resins below  $P \approx 0.60$ , although possessing higher capacities, exhibited prohibitive swelling effects when converted from the free base to the salt form.

The general procedure followed in preparing the resins involved pyrolysis of the carbamate polymer, grinding and sizing of the product, preparation of the resin column, treatment of the resin column with the  $\text{HBr}/\text{HOAc}$  reagent, and conversion of the treated resin to a form appropriate for subsequent studies.

### Ion Exchange Characteristics

By use of the above procedures it was possible to prepare resins having capacities ranging from 2 to 5 meq/g (based on pyrolyzed, untreated resin). The resins were very stable, exhibiting reproducible capacities on repeated cycling. Table 1 shows results obtained with resins derived from polymers pyrolyzed to various extents. The capacities observed are close to those predicted by

$$\text{Resin capacity (meq/g)} = 1000(1 - P + Z) / [143(1 - P) + 56(P - Z) + 43Z] \quad (3)$$



TABLE 1. Column Exchange Studies

Resin	A	B	C	D	E	F
W	0.274	0.400	0.480	0.522	~0.60	~0.60
P	0.45	0.65	0.786	0.854	1.000	1.000
Z	0.00	0.01	0.028	0.046	0.135	0.135
Resin form	Capacity <sup>a</sup> (meq/g)					
-NH <sub>3</sub> <sup>+</sup>	4.75	3.43	3.44	2.74	2.20	2.48
-NH <sub>2</sub>	5.30	3.43	3.41	2.45	1.99	2.24
-NH <sub>3</sub> <sup>+</sup>	5.33	3.62	3.34	2.69	2.14	2.40
-NH <sub>2</sub>	5.30	3.52	3.28	2.75	2.02	2.28
-NH <sub>3</sub> <sup>+</sup>	5.20	3.59	3.46	2.83	2.11	2.37
-NH <sub>2</sub>	-	-	3.35	2.69	-	-
-NH <sub>3</sub> <sup>+</sup>	5.30	-	-	-	2.28	2.58
Theoretical capacity <sup>a</sup>	5.30	4.17	3.25	2.82	2.49	2.49

<sup>a</sup>Resin capacities are calculated for pyrolyzed but unhydrolyzed resin. Theoretical capacities are calculated using Eq. (3).

### Amino Acid and Peptide Separation Studies

In contrast to other weak base resins (e.g., diethylaminoethyl cellulose), the resins derived from poly(*t*-butyl *N*-vinyl carbamate) showed no tendency to "bleed" amine containing products when cycled through extremes of pH. Thus, near zero base lines were obtained when the columns were used for amino acid or peptide separations. Ninhydrin-sensitive materials are apparently not released by the columns.

Neutral amino acids were not adsorbed by the resins and could not be separated. Acidic amino acids were adsorbed, however, and could be separated from mixtures containing neutral amino acids. Mixtures of acidic amino acids were resolved into their components by the use of elution development techniques. Figure 5 shows the separation obtained when an alanine/tyrosine/glutamic acid/aspartic acid mixture

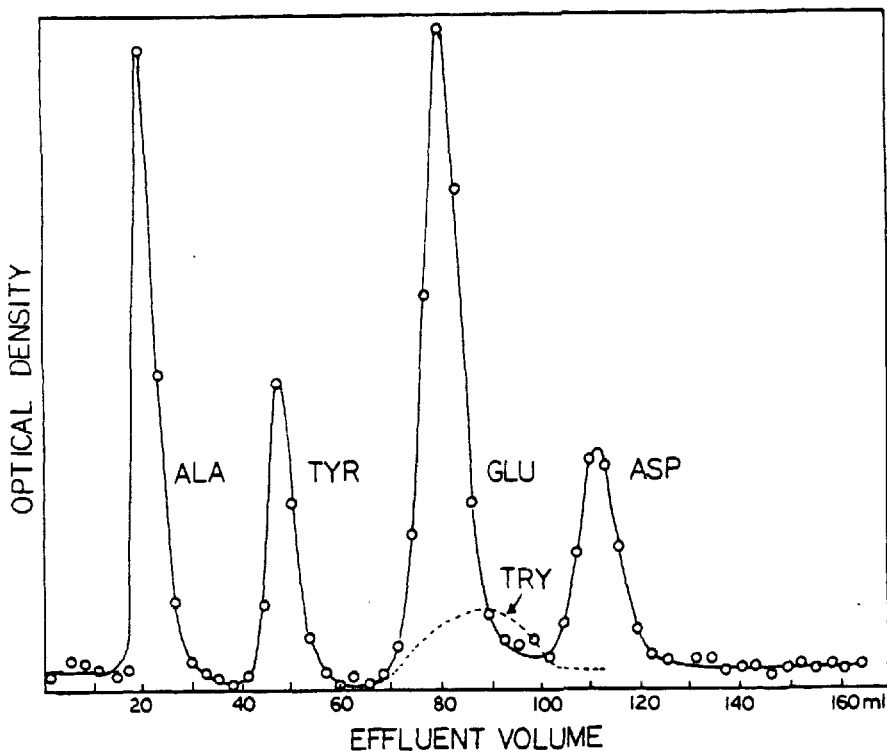


FIG. 5. Separation of a mixture of alanine, tyrosine, glutamic acid, and aspartic acid. The mixture was eluted with 0.46 M acetate buffer (pH = 5.0). The dotted line shows the elution behavior of tryptophan under the same conditions.

was eluted from a column ( $P = 0.88$ ) using 0.46 M sodium acetate buffer (pH = 5.0). The order of elution of the amino acids corresponded to their relative  $pK_3$ 's. Under these conditions, tryptophan and glutamic acid were eluted together. However, these two amino acids were separated when the buffer concentration was reduced to 0.23 M (Fig. 6). A mixture of tyrosine and glutamyl-tyrosine was easily separated by elution with 0.46 M sodium acetate buffer (pH = 5.0).

To obtain good resolution, it was necessary that 100-200 mesh resin be used. Incomplete resolution was obtained with 50-200 mesh resin.

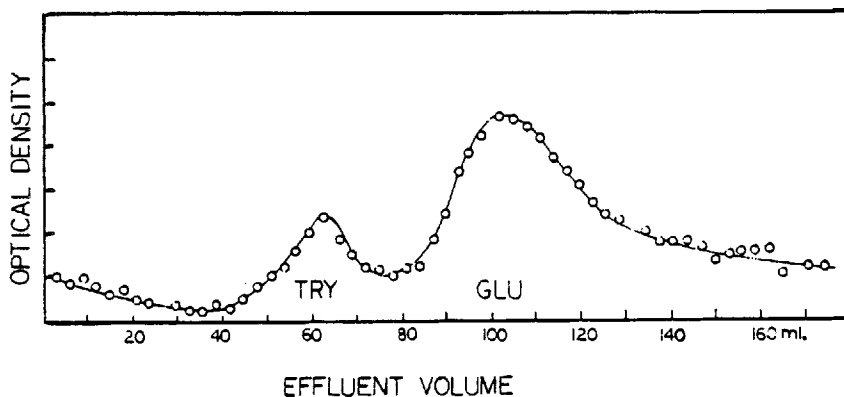


FIG. 6. Separation of a mixture of tryptophan and glutamic acid. The mixture was eluted with 0.23 M acetate buffer (pH = 5.0).

### Metal Ion Separations

By analogy to the results of Storch and Manecke [10] with chemically cross-linked poly(vinyl amine), primary amine groups present on resins derived from poly(*t*-butyl *N*-vinyl carbamate) were expected to function as ligands for metal ions and thereby be useful for their chromatographic separation. The free base form of the column had a strong affinity for  $Zn^{+2}$ ,  $Cu^{+2}$ ,  $Co^{+2}$ ,  $Ni^{+2}$ , and  $Fe^{+2}$  ions, but  $Na^+$  and  $Mg^{+2}$  were not retained by it. Cupric and cobalt ions formed characteristic blue-green complexes with the resins. By eluting with solutions of decreasing pH, it proved possible to separate the various ions (Fig. 7). It did not prove possible to separate  $Co^{+2}$  from  $Ni^{+2}$ , however. Nickel and cobalt ions were not retained by the resin below pH 7. Zinc ion was not retained at pH's below 5.8, but was strongly retained at pH 7. Copper ion was strongly retained by the resin at pH's above 3. Thus the selectivity series for the resin was  $Cu^{+2} \gg Zn^{+2} > Ni^{+2} \sim Co^{+2} \gg Na^+ \sim Mg^{+2}$ . This order is in agreement with the results of Storch and Manecke [10], except that  $Zn^{+2}$  and  $Ni^{+2}$  are interchanged.

## EXPERIMENTAL

### *t*-Butyl *N*-Vinyl Carbamate

*t*-Butyl *N*-vinyl carbamate was prepared from vinyl isocyanate and *t*-butanol according to the method of Hart [6]. After purification by

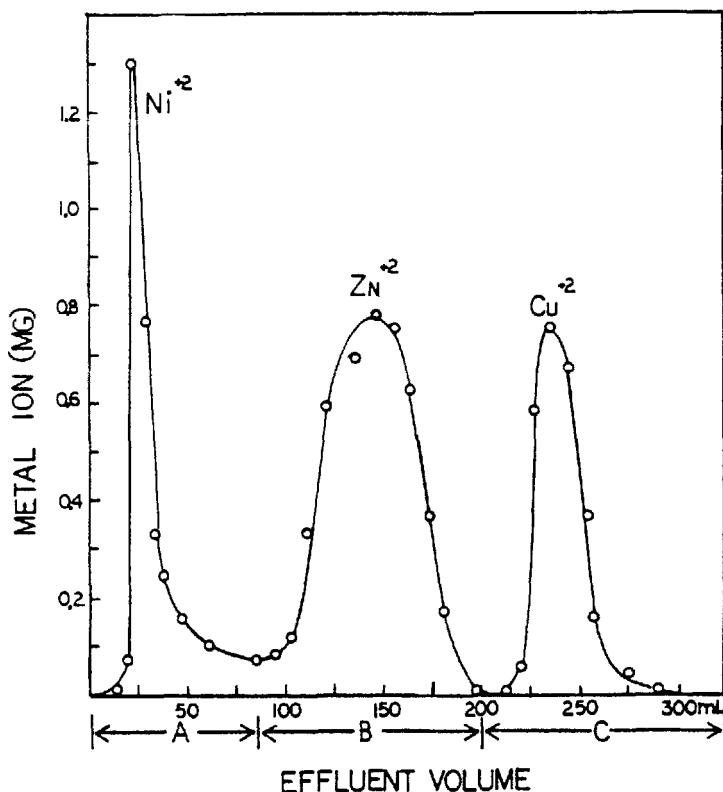


FIG. 7. Separation of a three-component metal ion mixture. A = 0.1 M NaOAc. B = 0.1 M acetate buffer, pH = 4.2. C = 0.5 N HCl.

sublimation at 50° (3 mm) the material melted at 66-67° and was soluble in hexane to the extent of 3 g/100 ml. Calculated for C<sub>7</sub>H<sub>15</sub>NO<sub>2</sub>: C, 58.80; H, 9.08; N, 9.78; O, 22.38. Found: C, 58.81; H, 9.10; N, 9.60; O, 22.23.

t-Butyl N-vinyl carbamate was obtained on some occasions as a viscous semisolid upon precipitation in water and was soluble in hexane to the extent of 35 g/100 ml. Sublimation of this semisolid yielded pure monomer with the lower hexane solubility.

#### Poly(t-butyl N-Vinyl Carbamate)

Poly(t-butyl N-vinyl carbamate) was prepared in hexane solution at 60° initiated by AIBN, as previously described [17] ( $\bar{M}_n = 160,000$ ).

### Pyrolysis Rates

Pyrolysis rates were obtained by following the weight loss of 50-60 mg polymer samples when heated, under nitrogen, in  $0.6 \times 3.7$  cm glass tubes at  $200 \pm 2^\circ$ . These were used to estimate heating times for large-scale preparations.

### Swelling Measurements

Samples of polymer (20-30 mg) pyrolyzed to various extents were swollen in glacial acetic acid (25 ml) for 24 hr in glass stoppered weighing dishes. The swollen resins were then transferred to fritted glass filter crucibles and the excess acetic acid was removed by rapid filtration. The swollen polymers were then rapidly transferred to tared weighing dishes and were weighed accurately. The contents were then dried in vacuo for 24 hr and reweighed. The loss in weight was taken as a measure of the solvent content of the gel.

### Resin Preparation

Samples (2 - 6 g) of poly(*t*-butyl *N*-vinyl carbamate) were heated at  $200 \pm 3^\circ$  under nitrogen in a resin kettle. The polymer was distributed over the floor of the kettle to insure uniform heat transfer to the polymer during the reaction. The pyrolyzed resin was then weighed and the weight loss was used to calculate the exact extent of pyrolysis by means of Eqs. (1) and (2).

For ion-exchange studies the resin was ground and a weighed sample was placed in a buret over a small quantity of glass wool. The resin was then swollen in glacial acetic acid. A 2-M solution of HBr in acetic acid was then passed slowly through the resin to hydrolyze *t*-butyl carbamate units. The HBr/HOAc reagent was then displaced with fresh HOAc, which was in turn displaced by water. The resin was then treated with dilute NaOH solution, followed by distilled water until the washings were neutral. Capacities of the resins toward acid were determined by passing a known excess of acid through the resin, followed by washing with water and titration of the unconsumed acid. Capacities of the protonated resins toward base were determined by passing excess base through the resin, followed by washing with water and titration of the unconsumed base.

Resins used for chromatographic separations were swollen in glacial acetic acid and were then ground in a Waring Blender. The resin particles were collected, washed with water, and screened while wet through U.S. Standard Mesh Sieves. Oversize particles were re-ground and resieved until the proper size range was obtained. Extreme!

fine particles which impeded column flow rates were removed by stirring the resin in a large volume of water, followed by decantation of the fines which settled slowly. Columns were prepared from particles of 50-200 mesh and 100-200 mesh. The latter were necessary for amino acid separations, but their use required pressurized columns.

Columns were prepared from the resins and were treated with 2 N HBr in HOAc to remove residual carbamate units. After being washed with water, the resins were converted to the free base form by passing 1 N NaOH through them until the effluents were basic. The columns were then washed with water until the effluents were neutral.

### Amino Acid Separations

Prior to amino acid separations studies, the column (1 × 45 cm, containing 14.5 g of 100-200 mesh resin,  $P = 0.88$ ) was equilibrated with buffer solution (generally 0.46 NaOAc-HOAc buffer, pH = 5.00) until the influent and effluent streams were within  $\pm 0.05$  pH units. One milliliter of an amino acid or peptide solution (0.4-0.6 g/liter) in buffer was then introduced at the top of the resin column and was eluted with buffer solution at 4.5 ml/hr under 15 psi pressure. Effluent fractions (3 ml) were then collected and analyzed by the photometric ninhydrin procedure of Yemm and Cocking [18]. Individual peaks were identified by comparison of elution volumes with those of pure materials. Nearly quantitative recovery of the amino acids from the column was obtained in all cases.

### Metal Ion Separations

Metal ion separations were conducted using a 1 × 30 cm column containing 6.4 g (dry weight) of 50-100 mesh resin ( $P = 0.90$ ) equilibrated with 0.1 M sodium acetate. One milliliter of a metal salt mixture (1 g/100 ml) was added to the column, followed by elution with the desired reagents to effect separation: 0.1 M NaOAc for  $\text{Ni}^{+2}$  or  $\text{Co}^{+2}$ ; 0.1 M NaOAc buffer, pH 4.2 for  $\text{Zn}^{+2}$ ; and 0.5 N HCl for  $\text{Cu}^{+2}$ . Conventional photometric or titrimetric techniques were utilized in analyzing the column effluents for sodium [19], magnesium [20], copper [21], cobalt [22], nickel [23], and zinc [24]. Nearly quantitative agreement was obtained in all cases between the amounts of metal ions in the sample and in the effluent fractions.

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