*Journal of Chromatography*, 178 (1979) 71–78

CHROM. 12,093

# POROUS VINYLPYRIDINE POLYMERS AS COLUMN PACKINGS FOR GAS CHROMATOGRAPHY

ATSUSHI SUGII and KUMIKO HARADA
*Faculty of Pharmaceutical Sciences, Kumamoto University, 5-1 Oe-honmachi Kumamoto City, Kumamoto 862 (Japan)*
(Received May 7th, 1979)

## SUMMARY

Three porous vinylpyridine polymers (I–III), cross-linked with divinylbenzene and having different surface properties, are presented as column packings in gas chromatography. Primarily by separating mixtures of amines, the efficiency of these columns is compared with that of Chromosorb 103. Polymer II is suitable for the separation of lower boiling aliphatic amines, whereas for rapid analyses of higher boiling amines and aminoalcohols polymer III can be used successfully and with less tailing.

## INTRODUCTION

A variety of porous polymers having different chromatographic properties have been used as column packings in gas chromatography (GC). Dave[1] has reported the evaluation of twelve kinds of commercially available porous polymers as column packings for GC and has presented detailed data for many classes of compounds to aid users in selecting the appropriate packing for specific separations.

The porous vinylpyridine polymers are presumed to be suitable as column packing for the separation of amines because of their basicity. Recently, Komers *et al.*[2] have presented a porous 4-vinylpyridine–divinylbenzene copolymer having large pore diameter, which is synthesized by the usual suspension copolymerization method in the presence of *n*-heptane, as column packing for GC. Although they have determined the separation of N-substituted anilines by using this polymer, no detailed chromatographic properties with other compounds are reported.

It is well known that the surface properties of the polymer, such as surface area and pore diameter, affect the column efficiency in gas chromatography[3,4]. This paper deals with the evaluation of porous vinylpyridine polymers, with various surface properties, as column packing for GC. The applicability of the polymers mainly to the separation of amines is discussed, and their ability to separate amines is compared with that of Chromosorb 103 which gives good separation of alkylamines[1].

## EXPERIMENTAL

### *Reagents and materials*

All reagents used for GC were reagent grade and used without purification. 4-Vinylpyridine (4VP) and 2-vinylpyridine (2VP) were purified before use by distillation. Commercially available divinylbenzene (DVB) solution (50–55%) was purified by the washing with 5% sodium hydroxide to remove the stabilizer. Chromosorb 103 (Johns-Manville, Denver, Colo., U.S.A.) was obtained from the Wako (Osaka, Japan).

### *Preparation of the porous vinylpyridine polymers*

The polymers were prepared by the usual suspension copolymerization of 4VP or 2VP with DVB in an aqueous solution of 0.2% hydroxyethyl cellulose containing 10% sodium chloride and 0.4% sodium hydroxide in the presence of toluene or isooctane as diluent and benzoyl peroxide as initiator at 70–80°. The products were washed with a large quantity of hot water and methanol. After drying in a vacuum desiccator, a fraction of 60–80 mesh was collected.

### *Determination of surface properties*

The specific surface area and pore volume of the polymers were measured with a Sorptomatic 1800 apparatus (Carlo Erba, Milano, Italy) by the BET method using nitrogen at the temperature of liquid nitrogen. The average pore diameter was calculated from:

$$\text{Average pore diameter (nm)} = \frac{\text{Pore volume (cm}^3\text{/g)}}{\text{Specific surface area (m}^2\text{/g)}} \cdot 4 \cdot 10^3$$

### *Thermal analysis*

Thermogravimetric analysis was carried out on Shimadzu Thermoflex apparatus, DT-20B and TG-20, in a dynamic nitrogen atmosphere and at a heating rate of 10°/min.

### *Gas chromatography*

The GC measurements were carried out with Shimadzu GC-4APF equipped with dual hydrogen flame-ionization detectors. The columns used were 1 m × 4 mm I.D. glass columns unless otherwise noted and nitrogen was employed as the carrier gas at a flow-rate of 60 ml/min.

The asymmetry of the peaks was defined as the ratio of the intercepts cut out from a peak at one tenth of its height by a perpendicular line drawn from the maximum of the peak to the zero line[5].

The values of height equivalent to a theoretical plate (HETP) were calculated from

$$\text{HETP} = \frac{L}{5.54}\left(\frac{w_{1/2}}{t}\right)^2$$

where $L$ is the column length, $w_{1/2}$ is the width of the peak at half-height and $t$ is the retention time at the peak maximum[6].

The value for the mutual resolution[7] ($R$) between amine peaks was defined by

$$R = \frac{(t_2 - t_1)}{(w_2 + w_1)} \cdot 2$$

where $t_1$ and $t_2$ are retention times and $w_1$ and $w_2$ are the distances on the base line between the points where the two tangents to the points of inflection of the peaks intersect the base line.

## RESULTS AND DISCUSSION

Three kinds of vinylpyridine polymers with different surface properties were prepared by changing the kinds of monomers and diluents and the degree of cross-linking. Table I shows the composition and physical properties of the vinylpyridine polymers (I–III) used in this study. The physical properties of Chromosorb 103, which is used as a control substance, are also shown in this Table. The surface properties of Chromosorb 103 are different from our vinylpyridine polymers, especially in pore diameter. Although the chemical structure of Chromosorb 103 is not clear, it contains no nitrogen.

TABLE I

CHARACTERIZATION OF THE POROUS VINYLPYRIDINE POLYMERS AND CHROMOSORB 103

4VP = 4-Vinylpyridine; 2VP = 2-vinylpyridine; DVB = divinylbenzene solution (50%).

| *Polymer* | *Composition of monomers (g)* | | | *Diluent (g)* | | *Analysis N (%)* | *Specific surface area ($m^2/g$)* | *Pore volume ($cm^3/g$)* | *Average pore diameter (nm)* |
|---|---|---|---|---|---|---|---|---|---|
| | *4VP* | *2VP* | *DVB* | *Isooctane* | *Toluene* | | | | |
| I | 120 | – | 30 | – | 37.5 | 10.8 | 7.8 | 0.024 | 12.3 |
| II | 105 | – | 70 | – | 140 | 8.5 | 62.9 | 0.091 | 5.8 |
| III | – | 105 | 70 | 105 | – | 8.2 | 12.4 | 0.035 | 11.3 |
| Chromosorb 103* | – | – | – | – | – | 0 | 15–25 | – | 350.0 |

* See ref. 1.

The thermal stability of polymers I–III was determined by thermal gravimetric analysis, and the data are shown in Fig. 1. Polymer I is stable up to 250° in a nitrogen atmosphere, and the higher cross-linked polymers II and III are stable up to 290°.

The polarities of the polymer are evaluated by using the McReynolds constants as well as the method of Komers *et al.*[2]. As is shown in Table II, the polarities of the vinylpyridine polymers are higher than that of Chromosorb 103. Among the polymers I–III, polymer I shows the highest polarity because of a higher pyridine content per polymer unit.

The column efficiency and the extent of tailing of chromatographic peaks were expressed as the HETP and the peak asymmetry, respectively. The data at a constant column temperature and flow-rate are shown in Table III. The HETP of

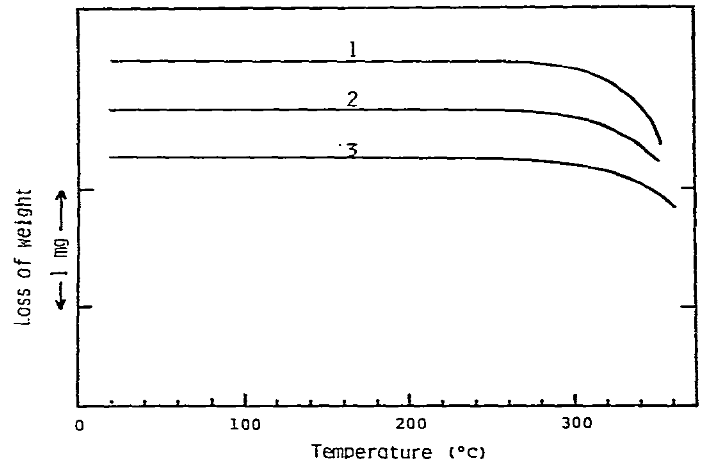

Fig. 1. Thermograms of the porous polymers in a nitrogen atmosphere. 1 = Polymer I (sample weight, 7.4 mg); 2 = polymer II (8.1 mg); 3 = polymer III (7.1 mg).

TABLE II

McREYNOLDS CONSTANTS AT A COLUMN TEMPERATURE OF 140°

The absolute values of the retention indices observed on the squalane column at 140° are as follows: benzene, 653; 1-butanol, 686; 2-pentanone, 750; 1-nitropropane, 686; pyridine, 790.

| *Solute* | *McReynolds constant* | | | |
|---|---|---|---|---|
| | *Polymer I* | *Polymer II* | *Polymer III* | *Chromosorb 103* |
| Benzene | 697 | 109 | 214 | 20 |
| 1-Butanol | 1006 | 232 | 281 | 13 |
| 2-Pentanone | 692 | 97 | 129 | −36 |
| 1-Nitropropane | 1078 | 285 | 350 | 99 |
| Pyridine | 912 | 125 | 262 | −24 |

polymers II and III are superior to that of Chromosorb 103. Kiselev[8] has shown that the HETP increases with decreasing pore diameter. Although the pore diameter and specific surface area of polymer I are nearly equal to those of polymer III, polymer I shows a higher HETP than polymer III. This may be explained on the basis of differences of the polarity and the pore distribution of the polymers.

Lukas *et al.*[9] showed that the symmetry of the peaks of the polar compounds on less polar sorbents was greater than that of non-polar compounds and the symmetry of the peaks of the non-polar compounds on polar sorbents was greater than that of the polar compounds. In this study, the peak asymmetry was independent of the polarity of the polymers and no serious tailing was observed. Polymer I is not suitable as column packing because of poor resolution and low column efficiency. The data shown in Table III suggest that polymers II and III are useful in GC. Retention indices and peak resolution data for some amines are shown in Tables IV and V.

The elution of the primary amines having the same carbon number, such as the isomers of butylamines, occurs in accordance with their boiling points. In general,

TABLE III

HEIGHT EQUIVALENT TO A THEORETICAL PLATE (A)* AND PEAK ASYMMETRY (B) OF SELECTED COMPOUNDS ON POROUS VINYLPYRIDINE POLYMERS AND CHROMOSORB 103

Temperature, 150°; flow-rate of carrier gas, 60 ml/min.

| *Compound* | | *Polymer I* | *Polymer II* | *Polymer III* | *Chromosorb 103* |
|---|---|---|---|---|---|
| Ethylamine | (A) | 180.2 | 4.2 | 3.8 | 12.8 |
| | (B) | 0.51 | 0.78 | 0.71 | 0.67 |
| Diethylamine | (A) | 240.9 | 5.8 | 5.9 | 13.4 |
| | (B) | 0.52 | 0.32 | 0.48 | 0.57 |
| Triethylamine | (A) | 650.0 | 38.0 | 36.0 | 58.8 |
| | (B) | 0.13 | 0.45 | 0.46 | 0.43 |
| Pyridine | (A) | 168.0 | 3.3 | 4.6 | 7.1 |
| | (B) | 0.55 | 0.25 | 0.52 | 0.50 |
| Heptane | (A) | 794.0 | 8.7 | 20.8 | 23.0 |
| | (B) | 0.25 | 0.34 | 0.57 | 0.54 |
| Ethanol | (A) | 98.0 | 3.1 | 6.7 | 10.1 |
| | (B) | 0.59 | 0.45 | 0.70 | 0.53 |
| 2-Aminoethanol | (A) | 99.0 | 3.2 | 2.9 | 14.7 |
| | (B) | 0.58 | 0.25 | 0.50 | 0.13 |

* HETP (mm).

the retention indices of polymer III were larger than those of polymer II. In the case of the aromatic amines, such as anilines and pyridine, appreciable differences in retention indices between polymers II and III were found. Polymer II, having relatively small pore and large surface area, is superior to polymer III in the separation of low boiling amines. However, polymer III, with a smaller surface area than polymer II, is suitable for the separation of higher boiling amines because of their short retention time. For example, the retention times of *n*-hexylamine at a column temperature of 150° are 5.83 and 2.50 min on polymers II and III, respectively. According to Dave[1], Chromosorb 103 is not suitable for the analysis of glycols, however, polymer III showed high column efficiency and symmetrical peaks for the glycols.

As is shown in Table III, polymer III is also conveniently applicable to the analysis of aminoalcohols. The chromatographic separation of aminoalcohols using a polymer III column is shown in Fig. 2 and compared with the behaviour of Chromosorb 103. Polymer II is useful for the separation of primary, secondary and tertiary amines; typical chromatograms are shown in Fig. 3.

In order to examine the effect of basicity of column packings in the separation of amines, polymer II impregnated with potassium hydroxide (0.5%) was used for the separation of the aliphatic amines. However, no appreciable improvement in the separation of the amines was observed by the alkaline treatment of the polymer. Polymers II and III are also adaptable to an aqueous solution. Even in the presence of 99% of water, no significant effect was observed on the resolution of the mixed sample shown in Fig. 3.

Polymer II is also effective for the separation of alcohols, hydrocarbons, ketones and carboxylic acids. Fig. 4 shows the relation between carbon numbers and the logarithm of retention volumes of the homologous series of *n*-alkanes, *n*-alcohols,

TABLE IV

RETENTION INDICES ON POLYMERS II AND III AT A COLUMN TEMPERATURE OF 170°

| *Compound* | *Retention index* | |
|---|---|---|
| | *Polymer II* | *Polymer III* |
| Methylamine | 409 | 486 |
| Ethylamine | 517 | 587 |
| *n*-Propylamine | 632 | 677 |
| *n*-Butylamine | 740 | 823 |
| *n*-Hexylamine | 966 | 1023 |
| Isopropylamine | 551 | 587 |
| Isobutylamine | 702 | 751 |
| Isoamylamine | 827 | 876 |
| Dimethylamine | 485 | 528 |
| Diethylamine | 614 | 692 |
| Di-*n*-propylamine | 818 | 857 |
| Di-*n*-butylamine | 1009 | 1051 |
| Trimethylamine | 445 | 435 |
| Triethylamine | 706 | 740 |
| Tri-*n*-propylamine | 937 | 937 |
| Tri-*n*-butylamine | 1131 | 1168 |
| *sec.*-Butylamine | 676 | 718 |
| *tert.*-Butylamine | 603 | 617 |
| *tert.*-Amylamine | 736 | 771 |
| Ethylenediamine | 938 | 1022 |
| 1,3-Propanediamine | 1058 | 1150 |
| Aniline | 1373 | 1538 |
| N-Methylaniline | 1406 | 1580 |
| N-Ethylaniline | 1428 | 1587 |
| N,N-Dimethylaniline | 1308 | 1490 |
| Pyridine | 979 | 1117 |
| 2-Aminoethanol | 1109 | 1186 |
| 3-Aminopropanol | 1249 | 1313 |
| 1-Amino-2-propanol | 1102 | 1156 |

TABLE V

PEAK RESOLUTION OF ALIPHATIC AMINE PEAKS AT A COLUMN TEMPERATURE OF 150°

| *Peaks of alkylamines* | *Peak resolution* | |
|---|---|---|
| | *Polymer II* | *Polymer III* |
| $nC_1$–$nC_2$ | 0.91 | 0.44 |
| $nC_2$–$nC_3$ | 1.48 | 0.53 |
| $nC_3$–$nC_4$ | 1.84 | 1.25 |
| $isoC_3$–$isoC_4$ | 1.70 | 0.91 |
| $isoC_4$–$isoC_5$ | 1.64 | 0.88 |

methyl *n*-alkyl ketones and carboxylic acids. The experimental data show linear plots except for $C_1$ in the *n*-alcohol series. In the case of methanol, the deviation from the straight line was also found on a porous polymer, Polysorbate-2 column[10].

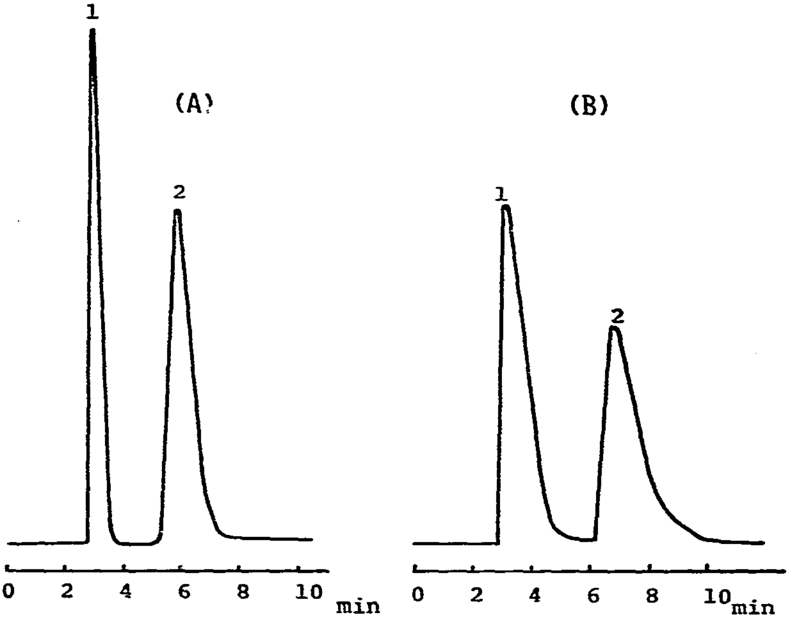

Fig. 2. Separation of aminoalcohols on polymer III (A) and Chromosorb 103 (B). Column, 1 m × 4 mm I.D.; temperature, 150°. Peaks: 1 = 2-aminoethanol; 2 = 3-aminopropanol.

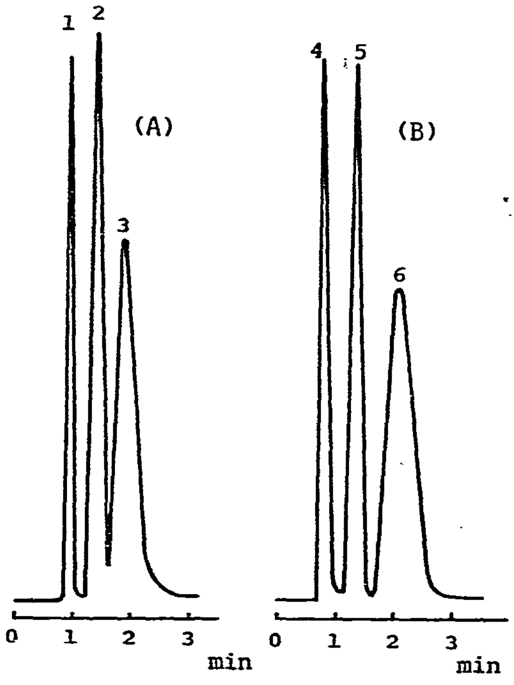

Fig. 3. Separation of primary, secondary and tertiary amines on polymer II. Column, 2 m × 4 mm I.D. Temperature: 170° (A); 200° (B). Peaks: 1 = ethylamine; 2 = diethylamine; 3 = triethylamine; 4 = *n*-propylamine; 5 = di-*n*-propylamine; 6 = tri-*n*-propylamine.

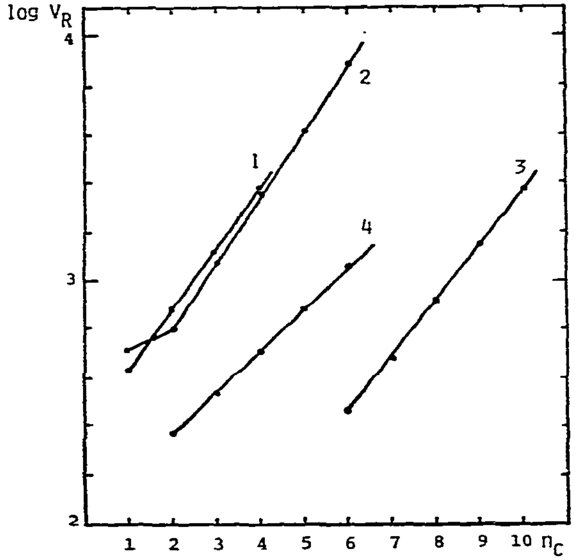

Fig. 4. Dependence of the logarithm of corrected retention volume upon the number of carbon atoms in the molecules on polymer II. Curves: 1 = methyl *n*-alkyl ketones; 2 = *n*-alcohols; 3 = *n*-alkanes; 4 = *n*-carboxylic acids. Column temperature: 120° (1–3); 200° (4).

It is concluded that polymer II is useful for the separation of lower boiling amines as well as Chromosorb 103. The column efficiency for amines, alcohols and hydrocarbons is better than that of Chromosorb 103. Polymer III is suitable for the analysis of higher boiling amines and aminoalcohols.

## ACKNOWLEDGEMENTS

The authors thank Miss C. Kawanishi and T. Sasaoka for technical assistance. Thanks are also due to the members of the Central Research Laboratory, Sumitomo Chemical Co., Osaka, Japan, for measurements of surface properties of the polymers.

## REFERENCES

1 S. B. Dave, *J. Chromatogr. Sci.*, 7 (1969) 389.
2 R. Komers, H. Kopecká and M. Kraus, *J. Chromatogr.*, 148 (1978) 43.
3 A. V. Kiselev, Yu. S. Nikitin, R. S. Petrova, K. D. Shcherbakova and Ya. I. Yashin, *Anal. Chem.*, 36 (1964) 1526.
4 M. Kraus and H. Kopecká, *J. Chromatogr.*, 124 (1976) 360.
5 T. A. Gough and C. F. Simpson, *J. Chromatogr.*, 51 (1970) 129.
6 J. E. Oberholtzer and L. B. Rogers, *Anal. Chem.*, 41 (1969) 1590.
7 A. B. Littlewood, *Gas Chromatography*, Academic Press, New York, 2nd ed., 1970, p. 162.
8 A. V. Kiselev, *Advan. Chromatogr.*, (1967) 173–196.
9 J. Lukas, J. Hradil, M. Křiváková and J. Čoupek, *J. Chromatogr.*, 114 (1975) 335.
10 K. I. Sakodynsky and L. I. Panina, *J. Chromatogr.*, 58 (1971) 61.