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Journal of Chromatography A, 693 (1995) 79–88

JOURNAL OF  
CHROMATOGRAPHY A

# Preparation of 4-vinylpyridine and divinylbenzene porous-layer open tubular columns by in situ copolymerization

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First received 18 July 1994; revised manuscript received 4 October 1994; accepted 4 October 1994

## Abstract

A new type of polar porous polymer glass capillary column, named OPLOT-S, was prepared by in situ copolymerization of 4-vinylpyridine and divinylbenzene. Its chemical composition was found to be similar to that of Porapak S. The OPLOT-S columns performed very efficiently in analysing alcohols, hydrocarbons, nitriles, amines, polar and apolar mixtures and permanent gases. They can provide good separations of  $\text{NH}_3\text{-H}_2\text{O}$ ,  $\text{CH}_3\text{OH-H}_2\text{O}$  and  $\text{CO-CH}_4\text{-CO}_2$  in a relatively short time under general conditions. The polarities of capillary columns were evaluated by using the Rohrsneider and McReynolds constants.

## 1. Introduction

Organic porous polymers have been extensively utilized as column packing materials, since Hollis [1] reported the development of such polymers as stationary phases for GC. The very specific separation characteristics of the porous polymers were recognised [2–7]. They have the advantage that polar compounds are not absorbed by the column, but eluted as symmetrical peaks in comparison with alumina and molecular sieves. Moreover, they can provide conditions such that the retention of the column is not influenced by water. Porous polymer packings such as the Chromosorb and Porapak series have been commercially used in packed GC columns to analyse volatiles and gases including hydro-

carbons, alcohols, ketones, aldehyde, acids, esters, ethers, nitriles, amines and permanent gases.

Recently, the application of porous polymers in capillary GC has been developed owing to their unique separation characteristics [8–14]. It appears that they offer the advantages of porous polymer packings with the high resolution of a capillary column. De Zeeuw et al. [8,9] reported that a capillary column (PoraPLOTQ) coated with styrene and divinylbenzene was prepared by a two-step procedure. In the preparation process a porous polymer was formed and its stabilization on the inside of the capillary columns was achieved. Wang and Liu [13] introduced another apolar porous polymer capillary column coated with ethylvinylbenzene and divinylbenzene by in situ copolymerization and named it OPLOT-Q, since its chemical composition was found to be similar to that of Porapak Q. The preparation process was a one-step procedure in which

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stabilization of the porous polymer coating layer was achieved via a special additional reagent.

It is possible to prepare polar porous polymer capillary columns that possess particular properties and are suitable for the separation of different types of compounds. A suitable choice of monomers with special functional groups make it possible to obtain good separations for particular applications. In this paper, we describe the preparation of a new polar porous polymer capillary column coated with 4-vinylpyridine and divinylbenzene copolymerized in situ, named OPLOT-S. The reproducibility, thermal stability and retention characteristics of the OPLOT-S column are discussed in detail.

## 2. Experimental

### 2.1. Apparatus

GC measurements were carried out with a Hewlett-Packard (HP) Model 5890A gas chromatograph equipped with a flame ionization detector and an HP 3392 integrator–recorder. Nitrogen was used as the carrier gas at a velocity of ca. 20–25 cm/s. An HP 5880 gas chromatograph equipped with a thermal conductivity detector was used to analyse permanent gases and aqueous compounds and helium was used as the carrier gas.

A Shimadzu GDM-1B glass capillary drawing machine was used to draw glass capillaries with different inner diameters. Electron micrographs of the porous polymer coating materials were obtained with a JEOL JEM-1200EX/S electron microscope. The qualitative analysis of porous polymers was carried out with a Nicolet 10DX Fourier transform IR spectrometer.

### 2.2. Chemicals

All reagents used for GC were of chemical or analytical-reagent grade and used as received. Divinylbenzene (DVB) and 4-vinylpyridine (4VP) were purified by washing with 10% sodi-

um hydroxide to remove the stabilizer before use.

### 2.3. Preparation of the OPLOT-S columns

All glass capillary columns were treated with a special method before use. The leached surface of a glass capillary was dehydrated by filling 90% of its volume with 20% hydrochloric acid and heating at 180°C for 10 h. After heating, the capillary was rinsed with 10 ml of 0.5% hydrochloric acid, 10 ml of water and 10 ml of methanol and dried at 150°C for 5 h under a nitrogen flow. The capillary can acquire a highly active surface via silylation [13].

The OPLOT-S capillary columns were prepared by in situ copolymerization of 4VP and DVB in a mixed solution of polar and apolar reagents (octanol–heptane solvent system) as diluent and 0.5% azobisisobutyronitrile as initiator. The suspension obtained was forced by nitrogen pressure into a capillary column and the two ends were sealed with a flame, sustaining a pressure of ca. 49 kPa (0.5 kg/cm<sup>2</sup>), then reacted at 70°C for 10 h. After completion of the reaction, the capillary columns were washed with 10 ml of methanol and 10 ml of pentane and dried at 150°C for 5 h under a nitrogen flow. The OPLOT-S columns were evaluated with ethyl acetate at 150°C.

## 3. Results and discussion

The chromatographic characteristics of porous polymers differ with variation in the kinds of monomers and diluents, the concentration of cross-linking reagent and the reaction conditions. The kind of monomers used was the key factor for the selectivity of the porous polymers. Hollis [3] described the chemical compositions of a series of Porapak porous polymer packings. Porapak S is prepared from vinylpyridine and divinylbenzene. Fig. 1 shows the IR spectra of polymer coatings of OPLOT-Q and OPLOT-S columns. The spectrum of OPLOT-S differs from that of OPLOT-Q because there is a strong absorption peak at 1600 cm<sup>-1</sup> on curve 2.

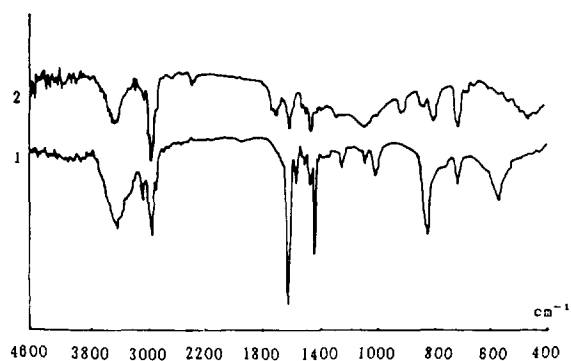


Fig. 1. IR spectra of (2) OPLOT-Q and (1) OPLOT-S porous polymer coatings (potassium bromide disc method).

This means that the OPLOT-S porous polymer has different functional groups to OPLOT-Q, the former being produced from 4VP.

In order to use optimized flow-rate conditions for practical analyses, we determined Van Deemter curves at different temperatures. The linear velocity of the carrier gas,  $u$ , was calculated from the relationship  $u = L/t_m$ , where  $L$  is the length of column and  $t_m$  is the retention time of methane. For the solute selected,  $H$  was calculated from the classical relationship

$$H = \frac{L}{5.54} \left( \frac{w_{1/2}}{t_R - t_m} \right)^2$$

where  $t_R$  is the retention time of the solute and  $w_{1/2}$  is the half-width of its chromatographic peak. Curves of the number of theoretical plates

( $H$ ) versus the mean linear velocity ( $u$ ) are shown in Fig. 2. Benzene, cyclohexane and 1-butanol were selected as the solutes, because they could provide different effects with the stationary phase, at column temperatures of 130 and 150°C. For benzene,  $H$  is not very temperature dependent, at least for  $u$  values higher than about 10 cm/s. The curves obtained with 1-butanol differed from those for benzene,  $H$  increasing markedly with increase in temperature. The curves for cyclohexane is slightly changed along with increasing of the temperature. For these three solutes the minimum  $H$  was obtained at  $u \approx 15\text{--}20$  cm/s. We therefore select  $u \approx 20\text{--}25$  cm/s as the optimum flow-rate for practical applications.

The concentration of cross-linking reagent was considered to change the size of the porous polymer bead and the pore structure [3]. Hollis reported that the size and rigidity of the pores of the polymer beads increased with increase in the content of cross-linking reagent. Three electron micrographs of porous polymer coatings with 4VP concentrations of 10, 20 and 30% are shown in Fig. 3. The size of the porous polymer is regular at 1–2  $\mu\text{m}$ . It is concluded that the size of the porous polymer beads decreased with increasing content of 4VP or decreasing content of DVB.

The chromatographic characteristics of the OPLOT-S column not only changed with variation in the concentration of the monomer, but

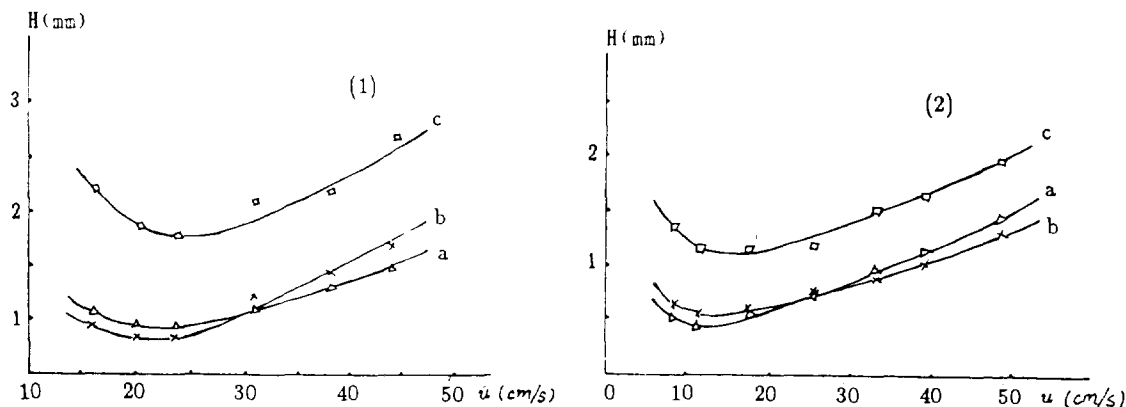


Fig. 2. Variation of  $H$  with the linear velocity,  $u$ , of the carrier gas ( $\text{N}_2$ ) at (1) 130°C and (2) 150°C for the solutes (a) benzene, (b) cyclohexane and (c) 1-butanol.

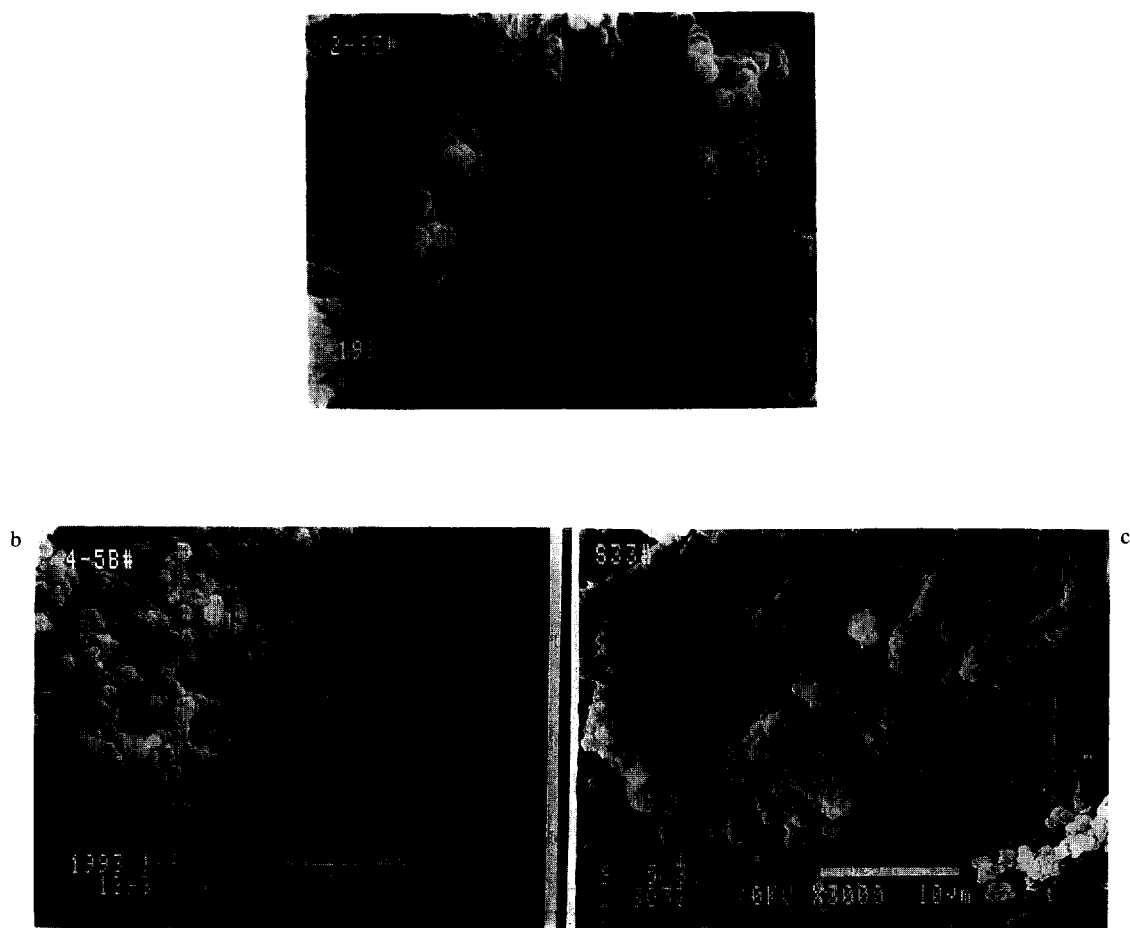


Fig. 3. Electron micrographs of porous polymer coatings with different 4VP concentrations. 4VP : DVB = (a) 1 : 9, (b) 1 : 4 and (c) 3 : 7.

was also influenced by the kind of diluent. The diluent used for the suspension solution for situ copolymerization must meet the following conditions: it must form a homogeneous mixture with the reactants and it must not swell the polymer beads after the in situ copolymerization reaction. Hence it is very important to select polar–apolar mixed solutions as diluents in order to produce polar porous polymer PLOT columns with high column efficiency. The OPLOT-S column was prepared using an octanol–heptane solvent system. The variation of the number of theoretical plates ( $H$ ) and with the ratio of polar and apolar diluent components ( $D$ ) is shown in

Fig. 4. It was found that the concentration of the polar diluent influenced the chromatographic characteristics of OPLOT-S. The selected range of polar diluent concentration become narrow with an increase in the content of 4VP.

The polarity of GC stationary phases is usually evaluated by using Rohrsneider and McReynolds constants [15,16]. Table 1 gives the retention indices of five different molecular types measured at 200°C on OPLOT-S and OPLOT-Q columns. The polarity of the OPLOT-S column is higher than that of the OPLOT-Q column, and the OPLOT-S column containing 30% 4VP shows the highest polarity because it

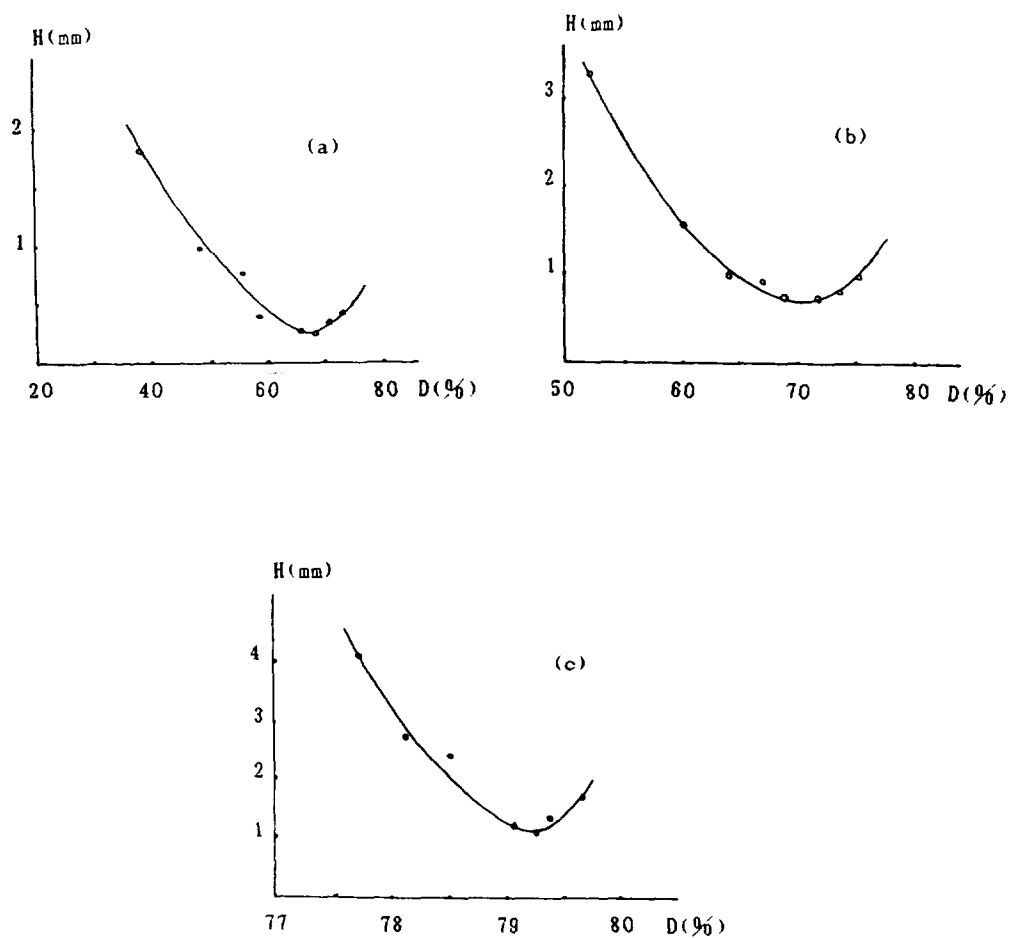


Fig. 4. Curves for selecting polar diluents for OPLOT-S columns. 4VP : DVB = (a) 1 : 9, (b) 1 : 4 and (c) 3 : 7. Solute = ethyl acetate.

Table 1  
Comparison of the retention indices on OPLOT-Q and OPLOT-S columns for different molecular types, measured at 200°C

Column	Benzene	1-Butanol	3-Pentanone	2-Nitropropane	Pyridine
OPLOT-Q	611	555	644	628	640
OPLOT-S (10% 4VP)	620	597	667	666	684
OPLOT-S (20% 4VP)	631	625	686	696	704
OPLOT-S (30% 4VP)	642	649	704	725	724

has the highest 4VP content. This investigation shows that the overall selectivity of the OP-PLOT-S column differs from that of the OP-PLOT-Q column.

The following equation was used for calculating the retention indices,  $I$ :

$$I = 100 \left[ n + z \left( \frac{\log t'_n - \log t'_x}{\log t'_{n+z} - \log t'_n} \right) \right]$$

where  $n$  and  $n + z$  correspond to alkanes with  $n$  and  $n + z$  carbon atoms, respectively, and  $x$  corresponds to a solute the retention time of which is between that of  $n$  and  $n + z$  alkanes and  $t'_n$ ,  $t'_x$  and  $t'_{n+z}$  are the relative retention time of  $n$ -pentane, solute and  $n$ -octane, respectively; the gas hold-up time of the column is obtained using methane.

Table 2 gives the reproducibility of preparing OP-PLOT-S columns. It was found that the column efficiencies were all above 1500 theoretical plates per metre as evaluated with ethyl acetate. When the reactant concentration ( $C$ ) increases, the capacity factor increases. This means that capillary columns with different coating layer thicknesses can be prepared for particular applications by controlling the reactant concentration by in situ copolymerization.

Table 2  
Reproducibility of OP-PLOT-S columns

No.	Column (m × mm I.D.)	$C$ (w/w)	$N/m$	$k$	$\alpha$
1	15.5 × 0.49	5.98	1675	1.48	1.82
2	15.5 × 0.49	5.98	1653	1.51	1.83
3	15.5 × 0.49	7.08	1698	1.65	1.84
4	15.5 × 0.49	5.98	1682	1.65	1.84
5	15.5 × 0.48	7.68	1818	1.78	1.84
6	15.5 × 0.48	7.68	1875	1.83	1.84
7	15.5 × 0.47	8.38	1781	2.00	1.83
8	15.5 × 0.47	8.38	1774	2.10	1.83
9	15.5 × 0.50	8.45	1856	2.01	1.84
10	15.5 × 0.50	8.45	1856	1.99	1.82
11	15 × 0.49	9.24	1982	2.23	1.82
12	15 × 0.49	9.24	1862	2.23	1.82
13	15 × 0.49	9.24	1845	2.21	1.82
14	15 × 0.49	9.24	1980	2.24	1.83

Column temperature, 150°C. Solutes: ethyl acetate (for  $N/m$  and  $k$ ) and 1-propanol-*sec.*-butanol (for  $\alpha$ ).

Table 3  
Thermal stability data on OP-PLOT-S column with 10% 4VP

Heating temperature (°C)	Heating time (h)	$N/m$	$k$	$\alpha$
240	3	1982	2.19	1.78
	6	1924	2.39	1.78
	20	1990	2.55	1.79
250	3	1919	2.49	1.80
	6	1990	2.56	1.81
	20	1724	2.63	1.79
260	3	1724	2.63	1.79
	7	1724	2.63	1.76
270	3	1463	2.66	1.76
	12	1351	2.66	1.76

Conditioner as in Table.

Column temperature 150°C. Solutes: ethyl acetate (for  $N/m$  and  $k$ ) and 1-propanol-*Sec.*-butanol (for  $\alpha$ ).

The thermal stability of OP-PLOT-S columns was determined by heating for different times at different temperatures in a nitrogen flow. The results are given in Tables 3–5. It is clear that the OP-PLOT-S column can be conditioned at 250, 230 or 210°C when the 4VP concentration is 10, 20 or 30%, respectively.

A number of applications are illustrated in Figs. 5–12. Hydrocarbons can be separated on an OP-PLOT-S column (Fig. 5). Temperature programming allows most  $C_7$  hydrocarbons to be separated. Fig. 6 shows the separation of a

Table 4  
Thermal stability data on OP-PLOT-S column with 20% 4VP

Heating temperature (°C)	Heating time (h)	$N/m$	$k$	$\alpha$
210	3	1742	3.12	1.75
	10	1756	3.15	1.76
220	3	1784	3.13	1.79
	10	1776	3.19	1.80
	20	1758	3.24	1.76
230	3	1772	3.25	1.75
	10	1486	3.29	1.73
	20	1378	3.38	1.70

Conditions as in Table 3.

Table 5  
Thermal stability data on OPLOT-S column with 30% 4VP

Heating temperature (°C)	Heating time (h)	<i>N/m</i>	<i>k</i>	$\alpha$
190	3	1964	1.85	1.65
	7	2058	1.83	1.66
	20	1993	1.88	1.68
200	3	1908	1.90	1.68
	10	1964	1.94	1.66
	20	1908	1.94	1.66
210	3	1751	1.94	1.66
	10	1658	1.94	1.65

Conditions as in Table 3.

mixture of alcohols. These types of compounds elute with slightly tailing because of the polarity of the stationary phase in comparison with the OPLOT-Q column [13].

The OPLOT-S column also can be used

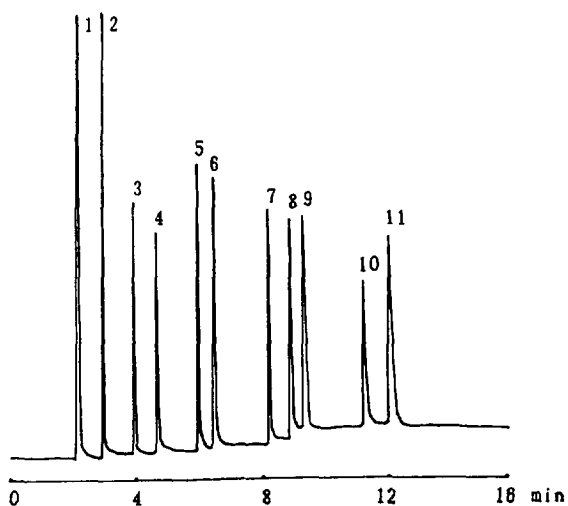


Fig. 6. Separation of a mixture of alcohols. Column, 22 m  $\times$  0.35 mm I.D. OPLOT-S; temperature, increased from 120 to 220°C at 10°C/min. Peaks: 1 = methanol; 2 = ethanol; 3 = 2-propanol; 4 = propanol; 5 = isobutanol; 6 = *sec.*-butanol; 7 = 1-butanol; 8 = isopentanol; 9 = 1-pentanol; 10 = 2,3-dimethyl-3-pentanol; 11 = 2-methylpentanol.

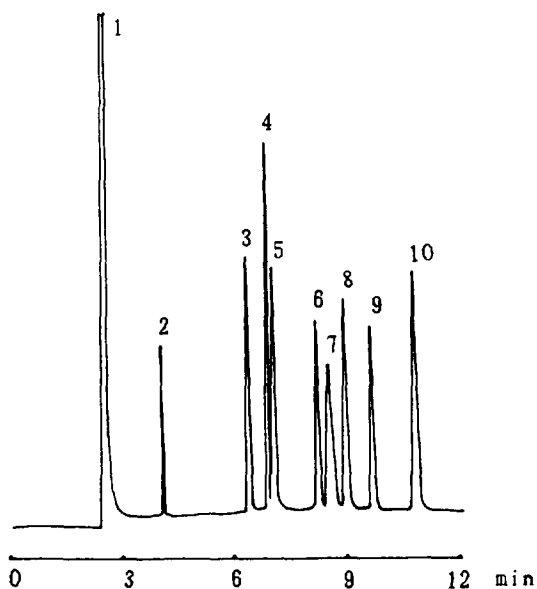


Fig. 5. Separation of a mixture of C<sub>7</sub> hydrocarbons. Column, 25 m  $\times$  0.41 mm I.D. OPLOT-S; temperature, increased from 130 to 180°C at 8°C/min. Peaks: 1 = methanol; 2 = pentane; 3 = hexane; 4 = benzene; 5 = cyclohexane; 6 = 2,4-dimethylpentane; 7 = 2,2,3-trimethylbutane; 8 = 2-methylhexane; 9 = heptane; 10 = toluene.

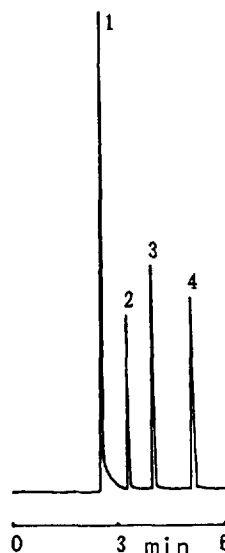


Fig. 7. Separation of a mixture of nitriles. Column, 22 m  $\times$  0.35 mm I.D. OPLOT-S; temperature 150°C. Peaks: 1 = methanol; 2 = acetonitrile; 3 = acrylonitrile; 4 = propionitrile.

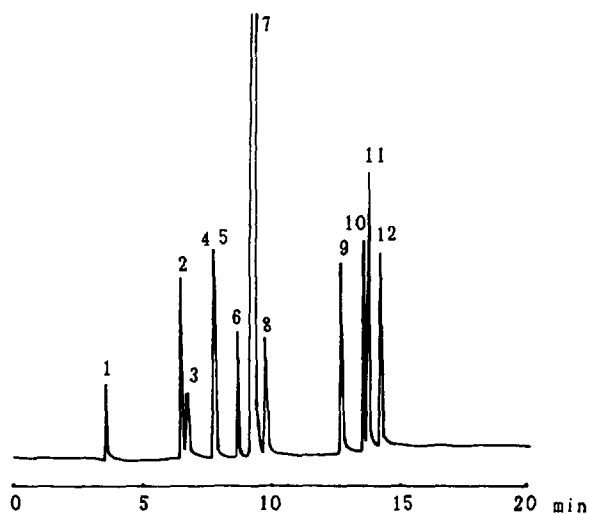


Fig. 8. Separation of a mixture of polar and apolar compounds. Column, 22 m  $\times$  0.35 mm I.D. OPLOT-S; temperature, isothermal for 5 min at 100°C, then increased at 8°C/min to 200°C. Peaks: 1 = methanol; 2 = acetonitrile; 3 = ethanol; 4 = acetone; 5 = dichloromethane; 6 = methyl acetate; 7 = pentane; 8 = 2-propanol; 9 = ethyl acetate; 10 = hexane; 11 = benzene; 12 = cyclohexane.

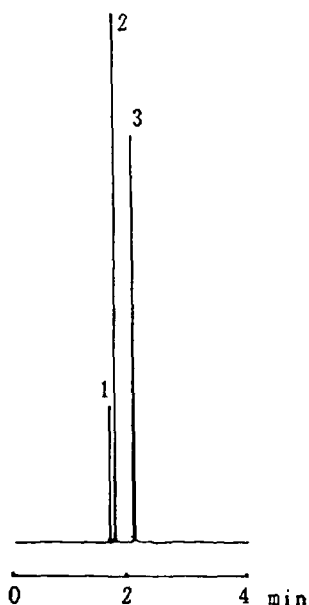


Fig. 9. Separation of CO, CH<sub>4</sub> and CO<sub>2</sub>. Column, 36 m  $\times$  0.36 mm I.D. OPLOT-S; temperature, 50°C. Peaks: 1 = CO; 2 = CH<sub>4</sub>; 3 = CO<sub>2</sub>.

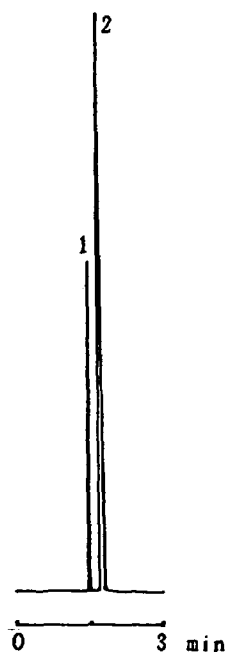


Fig. 10. Separation of water and methanol. Column, 18 m  $\times$  0.36 mm I.D. OPLOT-S; temperature, 130°C. Peaks: 1 = water; 2 = methanol.

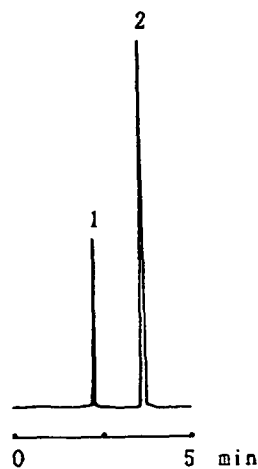


Fig. 11. Separation of ammonia liquor. Column, 18 m  $\times$  0.36 mm I.D. OPLOT-S; temperature, 100°C. Peaks: 1 = ammonia; 2 = water.

advantageously for analysing nitriles with symmetrical peaks (Fig. 7).

One of the unique retention characteristics of the porous polymer is shown in the separation of



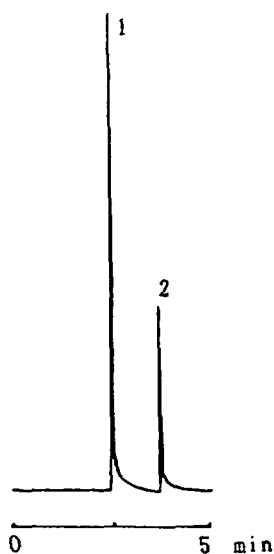


Fig. 12. Separation of amines. Column, 22 m  $\times$  0.35 mm I.D. glass OPLOT-S; temperature, 200°C. Peaks: 1 = diethylamine; 2 = triethylamine.

polar and apolar volatile mixtures, as high-polarity compounds cannot be eluted from alumina and molecular sieves, which means they cannot be analysed together with light hydrocarbons or permanent bases. The OPLOT-S column can provide a good separation of such mixture (Fig. 8).

Separation of carbon dioxide from air had to be performed with a porous polymer stationary phase as  $\text{CO}_2$  is absorbed by alumina and molecular sieves. Fig. 9 shows the separation of permanent gases at 50°C under isothermal conditions. At this temperature there is baseline resolution among carbon monoxide, methane and carbon dioxide.

Water is a problematic analysis on most GC column, but it can be achieved by using a porous polymer. Fig. 10 shows the separation of water from methanol at 130°C and Fig. 11 shows the separation of ammonia liquor at 100°C, detected with a micro thermal conductivity detector.

Owing to the basic pyridine functional group of the OPLOT-S column, it can be applied to basic nitrogen compounds, such as ammonia, diethylamine and triethylamine (Figs. 11 and 12). These compounds cannot be analysed on

other types of capillary column because of absorption.

#### 4. Conclusions

The OPLOT-S column can be prepared with good reproducibility. The method of in situ suspension copolymerization should be applicable to preparing different porous polymer PLOT columns in the future. The OPLOT-S column performed very efficiently in analysing volatile compounds and gases. It provides good separations of  $\text{NH}_3\text{-H}_2\text{O}$  and  $\text{CO-CH}_4\text{-CO}_2$  in a short time under general conditions. It was found that the content of 4VP affected the polarity and selectivity of the OPLOT-S column. Electron micrographs of the columns showed that the size of the polymer beads decreased with increasing content of 4VP or decreasing content of DVB. The OPLOT-S column is different from other porous polymer capillary columns as basic nitrogen compounds can be separated with high resolution.

#### Acknowledgement

This work was supported by the National Natural Science Foundation of China.

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