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Note

Chemically bonded phases for liquid chromatography

Modification of silica with vinyl monomers

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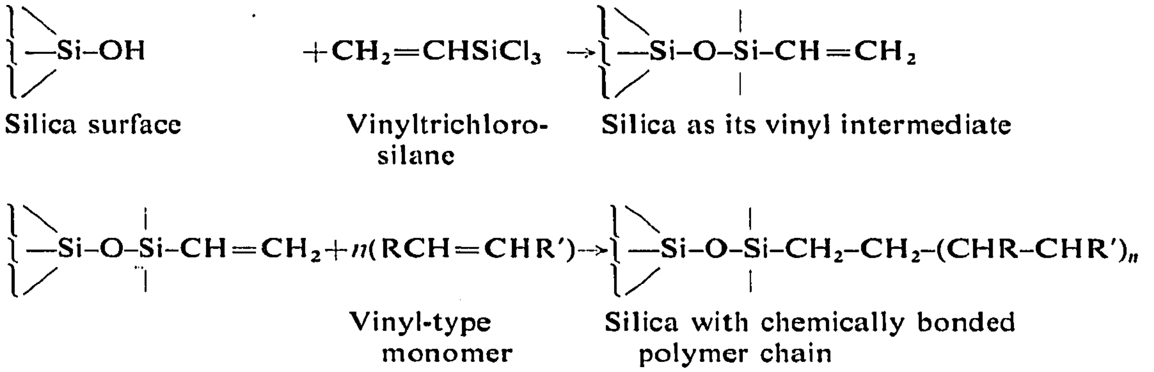
The use of chemically bonded stationary phases in liquid chromatography is now well established and has recently been the subject of review[1]. The most stable phases are formed by the reaction of organosilane compounds with the silanol groups present on silica surfaces, producing derivatives linked via a siloxane bond. Several useful bonded phases have been prepared in this way, but the range of organosilane intermediates available is somewhat limited.

Recent work in this laboratory has been concerned with bonding polar stationary phases to microparticulate silica, and one successful approach has involved the use of vinyl monomers. The basis of the procedure is to react vinyltrichlorosilane with silica to produce a reactive intermediate. Subsequent reaction of this intermediate with vinyl-type monomers, which are capable of polymerisation, yields a variety of packing materials displaying useful chromatographic properties. It is assumed that the polymerisation gives rise to chemically bonded chains (or bridges) at the silica surface. A representation of the postulated reaction is shown below.



$$\text{—Si–OH} + CH_2{=}CHSiCl_3 \rightarrow \text{—Si–O–Si–CH}{=}CH_2$$

$$\text{—Si–O–Si–CH}{=}CH_2 + n(RCH{=}CHR') \rightarrow \text{—Si–O–Si–CH}_2\text{–CH}_2\text{–(CHR–CHR')}_n$$

This study attempts to illustrate the potential of the reaction for the preparation of packing materials for liquid chromatography. The chromatography of a selection of phenols and benzyl alcohol on packings prepared with different vinyl monomers is described.

EXPERIMENTAL

Preparation of the vinyl-modified silica

15 g of microparticulate silica (Partisil 5 from H. Reeve Angel, Maidstone, Great Britain), 50 ml of isooctane and 25 ml of vinyltrichlorosilane were refluxed for 2 h. The modified silica was then washed several times with both isooctane and acetone and dried at 80°. Several batches of material were prepared and bulked to yield the starting material for further reaction.

Vinyl polymerisations

5 g of the vinyl-modified silica was placed in a round-bottomed flask. 25 ml of acetonitrile containing 2 g of a vinyl monomer were added and the mixture well dispersed. 25 ml of acetonitrile containing 0.2 g of benzoyl peroxide was then added, and the mixture was refluxed for 2 h. The vinyl monomers used were acrylonitrile, acrylic acid, butyl methacrylate, 2-hydroxypropyl methacrylate and diethylaminoethyl acrylate.

The products were Soxhlet extracted with acetonitrile, and then acetone, until no further removal of organic material occurred. In the case of the acrylic acid-modified silica, Soxhlet extractions with water were also carried out. The packing materials were dried at 80° before use. An indication of the level of organic loading achieved was made by measuring the weight loss of the materials on ashing at 600°.

Liquid chromatography

The packing materials were packed into 25-cm lengths of stainless-steel tubing (1/4 in. O.D., 4.9 mm I.D.) using the balanced density slurry technique[2]. Phenolic compounds were then chromatographed on the columns with tetrahydrofuran–isooctane (1:9) as the eluting solvent. The equipment used has been described elsewhere[3].

RESULTS

Table I shows the weight loss of each packing material at 600°.

Table II shows retention time data of the various phenols on both silica and the modified silica columns. Fig. 1 shows chromatograms obtained with the same phenolic mixture being separated on each column under identical solvent conditions. The preparative procedures were found to be reproducible.

TABLE I
KEY TO COLUMNS

No.	*Description of packing material*	*% weight loss on ashing at 600°*
1	Silica (Partisil 5)	—
2	Vinyltrichlorosilane-treated silica	6.9
3	2 modified with diethylaminoethyl acrylate	11.4
4	2 modified with hydroxypropyl methacrylate	12.1
5	2 modified with acrylic acid	11.9
6	2 modified with acrylonitrile	9.1
7	2 modified with butyl methacrylate	10.9

TABLE II

RETENTION TIME DATA FOR PHENOLS ON COLUMNS PACKED WITH SILICA AND SILICA REACTED WITH VINYL MONOMERS

Columns: all 25 cm in length × 4.9 mm I.D.; packings, see Table I. Solvent: tetrahydrofuran–isooctane (1:9) at 1 ml/min. All the retention time data below are quoted relative to that of phenol (retention time = 100). The time shown in brackets beside phenol is its actual retention time in minutes.

Phenol	*Column*						
	1	*2*	*3*	*4*	*5*	*6*	*7*
Butylated hydroxytoluene	24	55	41	35	39	42	50
Pentachlorophenol	63	78	—	62	58	68	72
Thymol	64	79	69	65	69	69	76
m-Cresol	97	92	97	94	96	98	98
Phenol	100 (18.7)	100 (6.4)	100 (9.4)	100 (11.0)	100 (9.8)	100 (9.0)	100 (7.4)
p-Cresol	100	98	93	98	100	98	99
1-Naphthol	107	103	120	111	110	122	108
p-Chlorophenol	138	109	117	108	115	103	108
2-Naphthol	147	115	140	133	135	149	121
Benzyl alcohol	250	146	120	142	196	163	154
p-Nitrophenol	336	175	140	235	250	222	192

DISCUSSION

It is apparent from Fig. 1 that the packing materials prepared by the vinyl polymerisation process display useful properties. The columns prepared from these materials are efficient (HETP values based on the phenol peak at a solvent flow-rate of 1 ml/min range from 0.114 to 0.035 mm), and show significant differences in the separation of the various phenols. Marked de-activation of silica occurs after reaction with vinyltrichlorosilane (compare chromatogram A and B) and this leads to much shorter retention times for phenols and a drop in resolving power. Subsequent reaction of the vinyl-modified intermediate leads to packing materials displaying differing polarities. With the solvent system studied, the polarity of the packing material (assessed from the retention time of phenol) is dependent upon the monomer used for reaction, and increases in the order butyl methacrylate (G), acrylonitrile (F), diethylaminoethyl acrylate (C), acrylic acid (E), and 2-hydroxypropyl methacrylate (D). In all cases, however, phenols are less strongly retained than on a silica column of the same length. The elution sequence for phenols is roughly in order of increasing acidity, but variations in the relative retention time data indicate that significant interaction occurs between the bonded phases and the various phenols.

Proof that bonding of the type postulated actually occurs is not easy to produce, although the relatively high weight losses on ashing at 600° are significant since they indicate that organic material remains on the silica after prolonged Soxhlet extraction. This could, however, be attributed to physical adsorption of polymeric materials, but two factors suggest that this is not the primary mechanism of polymer

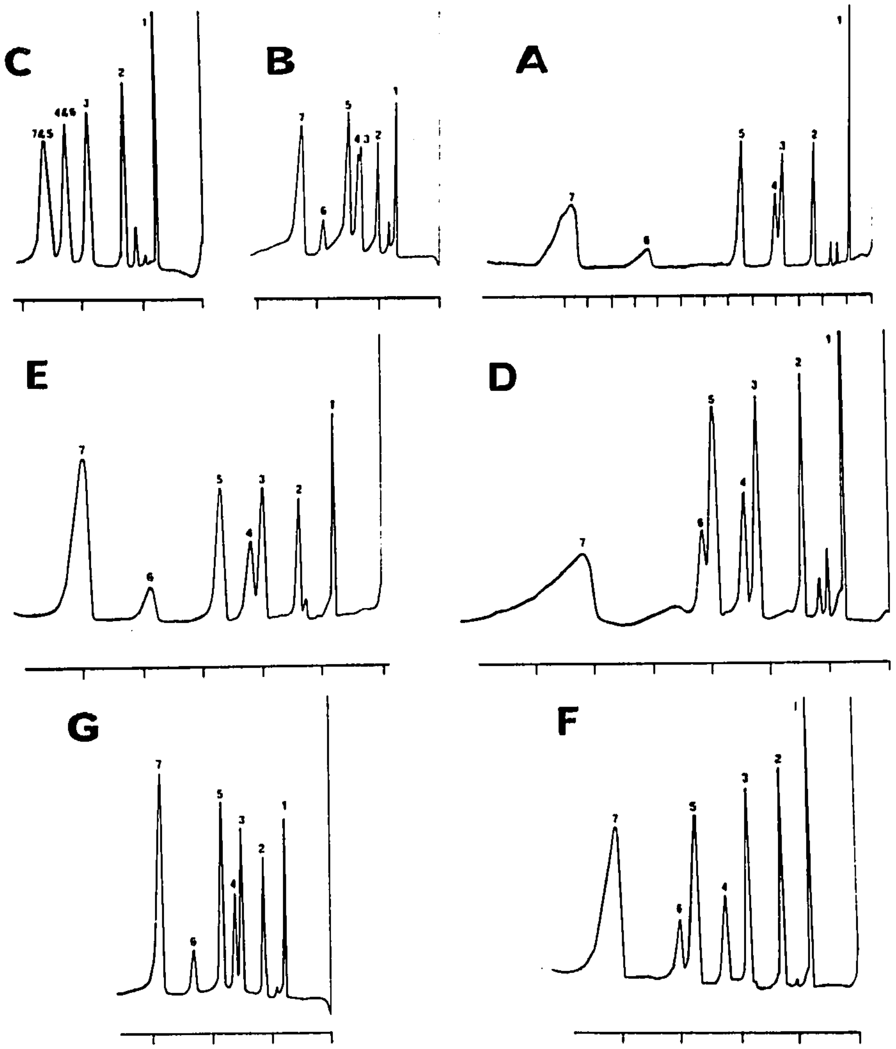


Fig. 1. Separation of phenols on silica and vinyl-modified silicas using tetrahydrofuran–isooctane (1:9) as the eluting solvent. (A) Silica (Partisil 5); pressure drop at 1 ml/min, 300 p.s.i. (B) Silica modified with vinyltrichlorosilane; 750 p.s.i. (C) B modified with diethylaminoethyl acrylate; 600 p.s.i. (D) B modified with 2-hydroxypropyl methacrylate; 750 p.s.i. (E) B modified with acrylic acid; 600 p.s.i. (F) B modified with acrylonitrile; 500 p.s.i. (G) B modified with butyl methacrylate; 500 p.s.i. 1 = Butylated hydroxytoluene; 2 = thymol; 3 = phenol; 4 = 1-naphthol; 5 = 2-naphthol; 6 = benzyl alcohol; 7 = *p*-nitrophenol. Time intervals of 5 min are marked on the chromatograms.

retention. The first is the stability of the packings, which is apparent from the reproducible chromatographic characteristics when used with a wide range of solvents of different polarity. The second indication is given by experiments in which butyl methacrylate was polymerised in the presence of silica (rather than the vinyltrichlorosilane treated silica used to prepare all the other packings). After prolonged Soxhlet extraction of the resulting material it was found to give a weight loss of 3.2%

after ashing at 600°. This is appreciably lower than the weight loss for the "chemically bonded" packings. It was also found that the chromatographic properties of the material were virtually identical with those of silica.

The most interesting feature of the technique described in this paper is its potential. There are large numbers of vinyl-type monomers available for study, *viz.* acrylates, methacrylates, vinyl compounds, allyl compounds, etc. These are all relatively low priced chemicals and are available with a wide range of functional groups. It should be possible to prepare a very diverse selection of bonded stationary phases from these materials capable of achieving a wide range of separations based both on liquid–liquid partition and ion exchange. The versatility of the reaction could be further extended by carrying out chemical modifications after the primary bonding reaction has taken place.

REFERENCES

1 A. Pryde, *J. Chromatogr. Sci.*, 12 (1974) 486.
2 R. E. Majors, *Anal. Chem.*, 44 (1972) 1722.
3 B. B. Wheals, C. G. Vaughan and M. J. Whitehouse, *J. Chromatogr.*, 106 (1975) 109.