SYNTHESIS, SOLID-STATE NUCLEAR MAGNETIC RESONANCE CHARACTERIZATION AND CHROMATOGRAPHIC EVALUATION OF A DIPHENYLPHOSPHINE–OCTADECYLSILANE HYBRID BONDED PHASE

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(First received October 5th, 1984; revised manuscript received December 11th, 1984)

SUMMARY

Mixed-mode bonded phases consisting of diphenylphosphinoethylsilane concurrently immobilized with octadecyldimethylsilane were synthesized. Elemental analysis and solid-state nuclear magnetic resonance (NMR) spectroscopy were employed in order to characterize the surface structure. Using the techniques of cross-polarization/magic angle spinning, ^{13}C, ^{31}P and ^{29}Si NMR spectra were obtained with a resolution approaching that usually obtained for liquids.

The novel diphenylphosphine–octadecylsilane (DPP–ODS) bonded phase was then evaluated for its chromatographic potential in the separation of a series of aromatic compounds. Preliminary results indicate that the column prepared from this material is a "hybrid", exhibiting reversed-phase character under hydroorganic eluent conditions, and polar character when the eluent is non-polar.

INTRODUCTION

Blended stationary phases recently have been prepared for high-performance liquid chromatography (HPLC). Crowther and Hartwick have synthesized a bonded phase which incorporates an ion exchanger embedded within a hydrophobic matrix[1]. The stationary phase features two dissimilar ligands chemically bonded to silica gel, and shows a selectivity different from that of ionic or hydrophobic packing materials[2]. Feibush *et al.* have immobilized a ligand exchange moiety on silica gel and then studied the effect of diluting the surface by adding polyether, *n*-butyl, *n*-decyl, or *n*-eicosyl functionalities. Capacity factors and enantioselectivities are much higher on the diluted phases relative to the concentrated phase[3].

We have immobilized a weak base, diphenylphosphinoethylsilane (DPP), and diluted it with octadecyldimethylsilane (ODS). Bonded DPP has never been used as a stationary phase in HPLC, although it has been used as an immobilizing ligand for heterogeneous catalysis[4,5]. The preparation of the DPP–ODS bonded phase extends

the previous work of Wahlund and Edlen, who developed stationary phases consisting of tri-*n*-octylphosphine oxide[6] or tributylphosphate[7] coated on alkyl-derivatized silica.

In order to understand clearly the nature of the chromatographic surface, we have systematically investigated the synthesis of new mixed-mode bonded phases of the type, DPP–alkylsilane. Using elemental analysis and solid-state NMR spectroscopy, we have obtained direct information on the mode of bonding of a triethoxysilylating reagent, the effect of endcapping and the effect of heating on the stability of the modified silica gels. Furthermore, we have developed a synthetic procedure for generating mixed-mode bonded phases, and have tried to determine the role of the proton scavenger in promoting surface coverage.

Using the cross polarization and magic angle spinning (CP/MAS) techniques, NMR spectra have been obtained which extend some of the recent work on the solid-state NMR of silica gel[8,9] and surface-derivatized silica gels[10–14]. The NMR spectra give a lucid picture of the character of the DPP immobilized on silica gel before and after reaction with trimethylchlorosilane and/or octadecyldimethylchlorosilane. Solid-state NMR data verify that the reaction of DPP-modified silica gel with an alkylsilylating reagent may be an effective procedure for the preparation of mixed-mode bonded phases.

Finally, the DPP–ODS bonded phase has been evaluated for use as a chromatographic adsorbent. The surface possesses a weak base functionality (diphenylethylphosphine) embedded within a hydrophobic matrix (octadecyldimethylsilane), and the combination should provide unique selectivity for the separation of proton-donating solutes. The separating ability of the DPP–ODS bonded phase has been evaluated by using a series of phenols. Further work is now in progress in order to develop fully applications for the new mixed-mode bonded phase.

EXPERIMENTAL

Instrumental procedures
The solid-state ^{29}Si NMR spectra were obtained at 39.75 MHz on a modified Nicolet NT-200 spectrometer. The solid-state ^{13}C and ^{31}P NMR spectra were obtained at 37.74 MHz and at 60.75 MHz respectively, on a modified Nicolet NT-150 spectrometer. Magic angle spinning was carried out at 3.5–4.0 kHz using bullet-type Kel-f or Delrin rotors containing 0.5 cm^3 of sample. A cross polarization contact time of 2 msec and a pulse repetition rate of 1 or 2 sec were employed.

The chromatographic system used was a Tracor, Model 985 solvent delivery system (Tracor Instruments, Austin, TX, U.S.A.), incorporating a Model 7125 automatic syringe-loading sample injector (Rheodyne, Berkeley, CA, U.S.A.), a Model 970A variable-wavelength detector with an 8-μl flow cell (Tracor), a Model 951 HPLC pump (Tracor), and a Model 3390A reporting integrator (Hewlett-Packard, Avondale, PA, U.S.A.). All bonded phases were slurry-packed into 150 × 3 mm I.D. glass-lined columns (Scientific Glass Engineering, Austin, TX, U.S.A.).

All solutes were prepared as concentrated solutions and then diluted to the desired mobile phase composition. Methanol (MCB Manufacturing, Cincinnati, OH, U.S.A.) was distilled, then aspirated through a 0.5-μm Millipore filter. Water was distilled and then aspirated through a 0.5-μm cellulose acetate filter. Iso-octane, etha-

nol and acetonitrile were filtered then used as is. The detector wavelength was set at 254 nm for all solutes injected.

C, H, N analyses were performed either in-house using a Perkin-Elmer Model 240B elemental analyzer or by MicAnal Organic Microanalysis (Tucson, AZ, U.S.A.). Phosphorus analyses were performed by Industrial Testing Laboratories, Inc. (St. Louis, MO, U.S.A.). The silica gel samples for phosphorus analysis were digested with perchloric acid–nitric acid, then precipitated with Quimociac reagent. The method is based on the gravimetric determination of $(C_9H_7N)_3H_3PO_4 \cdot 12 MoO_3 \cdot H_2O$.

Syntheses

The silica gel used for surface modification for Samples 1–7 was LiChrosorb Si-60 (BET surface, $S_{BET} = 500$ m^2 g^{-1}; particle diameter, $d_p = 10$ μm). The silica gel used to prepare Samples 8–10 was Shandon Hypersil (BET surface, $S_{BET} = 170$ m^2 g^{-1}; particle diameter, $d_p = 5$ μm). The silica gels were dried for at least 18 h at 150°C prior to use.

Toluene was distilled over sodium and stored over 5 A molecular sieve prior to use. Pyridine was dried over magnesium sulphate. Proton Sponge [1,8-bis(dimethylamino)naphthalene] and trichlorosilane reducing agent were purchased from Aldrich. Diphenylphosphinoethyltriethoxysilane, octadecyldimethylchlorosilane and trimethylchlorosilane (silylating reagents) were all purchased from Petrarch.

Synthesis of DPP bonded phase (Samples 1–3). DPP (2.0 ml, 5.6 mmol) was added to 2 g of silica gel in 25 ml of dry toluene, and the suspension was refluxed under nitrogen for 2 h. The mixture was filtered and the precipitate washed with dry toluene.

Synthesis of DPP–TMS bonded phase (Sample 4). Trimethylchlorosilane (TMS; 2.0 ml, 16 mmol), pyridine scavenger (2.0 ml, 25 mmol) and dry toluene (25 ml) were added to 0.5 g of DPP bonded phase, Sample 1. The suspension was refluxed for 2 h and then washed with dry toluene.

Synthesis of DPP–TMS bonded phase (Sample 5). TMS (2.0 ml, 16 mmol), 1,8-bis(dimethylamino)naphthalene (2.0 g, 9.4 mmol) and dry toluene (50 ml) were added to 2.0 g of DPP bonded phase (Sample 2). The suspension was refluxed for 2 h and the precipitate washed with 100-ml portions of dry toluene, methanol, water and acetone.

Synthesis of DPP–ODS "endcapped" bonded phase (Samples 6 and 7). DPP (2.0 ml, 5.6 mmol) and pyridine (2.0 ml, 25 mmol) in 50 ml of dry toluene were added to 2 g of silica gel (LiChrosorb Si-60) and refluxed for 3 h under nitrogen. ODS (2.291 g, 6.60 mmol) in 25 ml of toluene was added and refluxed for 2.5 h. TMS (2.0 ml, 16 mmol; endcapping reagent) in 25 ml of toluene was added and the suspension refluxed for an additional 1 h. The modified silica gel (Sample 6) was filtered and then washed with 200 ml of toluene, methanol, water and acetone. Sample 7 was prepared by treating Sample 6 with trichlorosilane according to the method of Bemi et al.[15].

Synthesis of DPP–ODS–TMS bonded phase (Samples 8–10). DPP (2.56 g, 6.80 mmol) in 100 ml of dry toluene was added to 10 g of silica gel (Shandon Hypersil). The suspension was refluxed under nitrogen for 15 h, and the precipitate washed with successive 40-ml portions of toluene, methanol, water and acetone. The modified

silica gel was put in the oven to dry for 1.5 h at 140°C. A portion was then set aside for detailed characterization (Sample 8). The DPP bonded phase was subsequently treated with 2.36 g (6.80 mmol) of ODS and 3.03 g (14.1 mmol) of 1,8-bis(dimethyl-amino)naphthalene in 75 ml of dry toluene. The suspension was refluxed under nitrogen for 4 h. TMS (5 ml, 39.5 mmol), 1,8-bis(dimethylamino)naphthalene (3.02 g, 14.1 mmol) and dry toluene (15 ml) were added to the suspension and allowed to react for 20 h at room temperature. The mixture was filtered and the precipitate washed with 75-ml portions of dry toluene, methanol, water and acetone. A portion was set aside for further characterization (Sample 9). Diphenylethylphosphine oxide in Sample 9 was reduced by adding 25 ml (0.2476 mol) of trichlorosilane in 25 ml of toluene. The reaction was allowed to proceed at room temperature for 21 h, and the trichlorosilane was distilled and the precipitate washed with successive 50-ml portions of methanol, water and acetone (Sample 10).

RESULTS AND DISCUSSION

Elemental analysis data

Table I lists the results of elemental analyses for Samples 1–6. The silica derivatives were dried under vacuum at the temperatures given in the table prior to analysis. The surface coverage (determined from the elemental analyses) is expressed in μmoles of diphenylphosphinoethylethoxysilane per square meter of surface area. The calculations for Samples 1–3 are based on the method of Unger *et al.*[16], whereas the method outlined by Feibush *et al.*[3] is used for the mixed-mode bonded phases 4–6. The reaction schemes used for the preparation of Samples 1–7 are outlined in Fig. 1.

The reproducibilities of the reaction schemes are illustrated by a comparison of the results of elemental analysis (percent phosphorus) for Samples 1 and 2 and

TABLE I

LICHROSORB BONDED PHASES

Bonded phase	Sample number	%P	%C	Drying temp. (°C)	DPP coverage ($\mu mol\ m^{-2}$)	
					Based on %P	Based on %C
DPP	1	0.99	6.91	25	0.70	0.79
	2	1.12	7.63	25	0.81	0.90
	3	—	6.37	105	—	0.73
DPP–TMS	4	0.68	13.87	25	0.59	—
	5	0.74*	—	25	0.65	—
DPP–ODS "endcapped"	6	0.41	16.2	25	0.35**	

* Replicate analyses.
** Weight change on modification of silica gel assumed to be $+0.25$ g g^{-1} of silica gel. The true value is between 0.20 and 0.30 g g^{-1} of silica gel.

Samples 4 and 5. These do not vary by more than *ca.* 10%. The accuracy of the elemental analysis data is difficult to assess; however, the DPP surface coverage based on the percent phosphorus is within 10% of that based on the percent carbon (Samples 1 and 2). An average of the two values is probably the most reasonable coverage estimate, since the percent phosphorus may be low due to an incomplete hydrolysis of the modified silica gel in the analytical procedure, whereas the percent carbon may be high due to adsorbed toluene on the silica gel substrate.

If the modified silica gel is dried, a small loss in DPP-surface coverage (calculated from elemental analyses) results. Sample 1 when dried at 105°C for 1 h exhibits a 0.06 μmol m^{-2} loss in DPP surface coverage (originally 0.79 μmol m^{-2}, but afterwards 0.73 μmol m^{-2}). The loss is probably due to the removal of DPP molecules physically adsorbed on the surface but may also be due to the removal of adsorbed toluene. Heat treating tends to remove these molecules, while also pro-
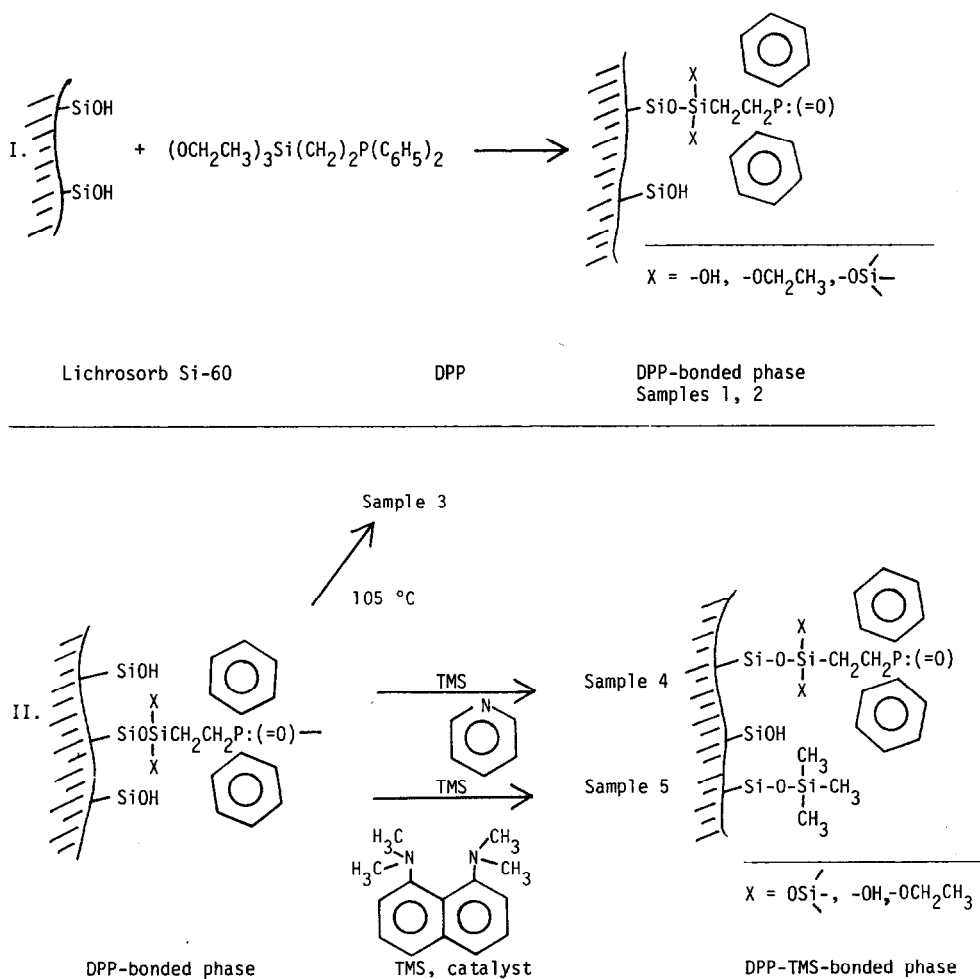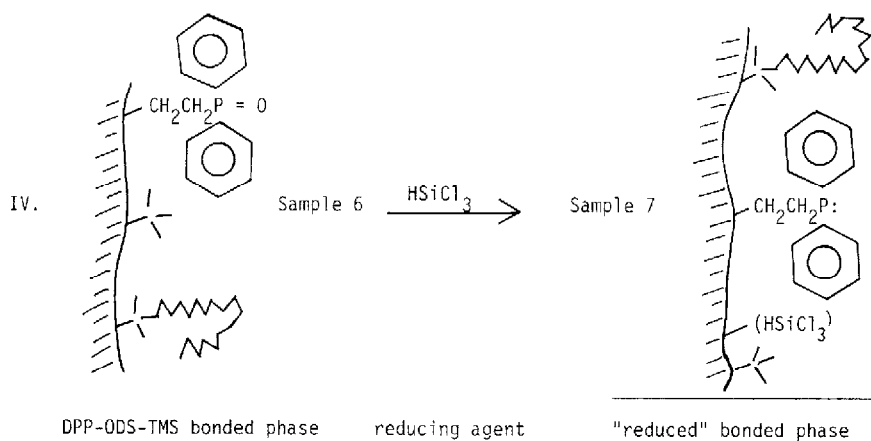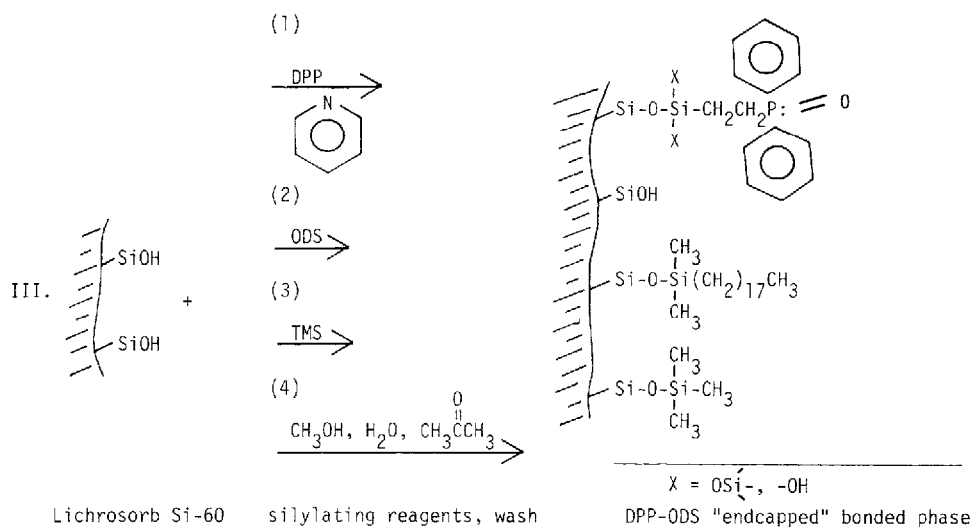

Fig. 1.

Fig. 1. Reaction scheme for the preparation of bonded phases on LiChrosorb Si-60.

moting "permanent" chemical bond formation between the alkylsilylating reagent and the surface[17].

Endcapping of the DPP-bonded phase with trimethylchlorosilane results in a more substantial loss in DPP-surface coverage. On endcapping Sample 1 with TMS the percent phosphorus drops from 0.99% to 0.68% (see Table I). The loss may be due to the cleavage of siloxane linkages by hydrogen chloride which is evolved during the endcapping sequence[14]. Alternatively, the proton scavenger, pyridine, may be reacting directly with the surface, forcing the hydrolysis of the DPP moiety. A sterically hindered amine [1,8-bis(dimethylamino)naphthalene] was employed in order to diminish the potential for surface interaction; however, this amine did not seem to prevent a 25% loss in DPP coverage. The TMS coverage for Sample 4, DPP–TMS

bonded phase, is 7.2 μmol m^{-2}. The coverage density that has been reported for trimethylchlorosilane is *ca.* 4.0 μmol m^{-2} (ref. 18). The high value obtained (7.2 μmol m^{-2}) in the present work indicates that the trimethylchlorosilane has reacted not only with available surface hydroxyl groups, but also with hydroxyls associated with the diphenylphosphinoethylsilane. This point is discussed below with the NMR data.

In order to increase the DPP surface coverage, the silica gel used as a substrate was changed from LiChrosorb Si-60 (60 Å pore size) to Shandon Hypersil (100 Å pore size). Evidence suggests that the pore size may have a substantial effect on synthetic efficiency[19,20]. As the pore size is increased, a bulky silylating reagent has a higher probability of reacting with the substrate, since it can penetrate more fully into all the available pores. An alternative justification for using Shandon Hypersil instead of LiChrosorb Si-60 is that the alternative substrate may have different surface properties which might enhance the diphenylphosphine surface coverage. The time of reflux was increased from 2 h to 15 h, and the sample was "heat-cured" in order to promote surface bonding. Table II lists the results of analysis for Samples 8–10. The DPP coverage after heat curing was 1.25 μmol m^{-2}, after reaction with ODS and TMS 1.18 μmol m^{-2}, and after reduction with trichlorosilane, 1.14 μmol m^{-2}. The results indicate that DPP bonded phase is very stable after heat curing and that subsequent silylations do not significantly reduce the surface coverage. Apparently, since diphenylphosphinoethyltriethoxysilane is a trisilylating reagent that can form multiple bonds to the silica substrate, heat-curing promotes multiple bond formation, thus making DPP bonded phase more impervious to acid hydrolysis. The subsequent additions of monochlorosilylating reagents and Proton Sponge, 1,8-bis-(dimethylamino)naphthalene, do not significantly affect the DPP-surface coverage.

TABLE II

SHANDON HYPERSIL BONDED PHASES

Bonded phase	Sample number	%P	%C	DPP coverage (μmol · m^{-2})
DPP	8	0.62*	–	1.25
DPP–ODS–TMS	9	0.56	6.35	1.18**
"Reduced"	10	0.54	5.99	1.14**

* Sample oven dried at 140°C.
** The DPP coverage assumes a weight change on modification of $+0.10$ g g^{-1} of silica gel. The true value lies between 0.08 and 0.11 g g^{-1} of silica gel.

NMR data

Fig. 2 illustrates all the possible types of silicon present on silica gel after silanization. The corresponding ^{29}Si NMR chemical shift (relative to the external standard, 85% H$_3$PO$_4$) is given next to the identifying letter; the chemical shift correlations are based on refs. 10, 12, and 14.

The ^{29}Si CP/MAS NMR spectrum of DPP bonded phase (Sample 3) is given in Fig. 3(a). The sample on which the spectrum was obtained had been oven-dried at 105°C for 2 h. Chemical shifts of -107 and -99 ppm can be attributed to silicon atoms already on the surface. Additional absorbance peaks appear at -49 and -55
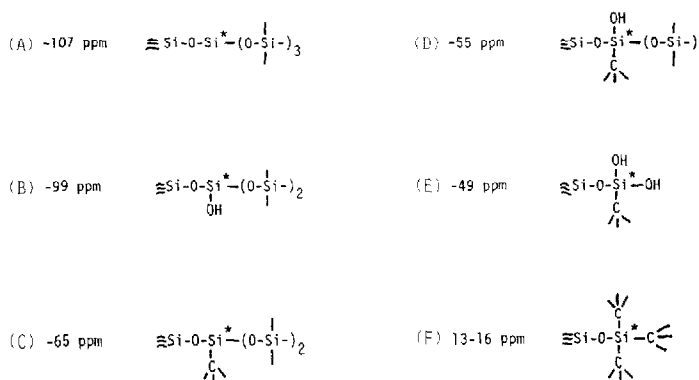
(A) ~107 ppm $\equiv$Si-O-Si*-(O-Si-)$_3$ (D) -55 ppm $\equiv$Si-O-Si*-(O-Si-)
                                                                       OH
                                                                       C
                                                                      /|\

(B) -99 ppm $\equiv$Si-O-Si*-(O-Si-)$_2$ (E) -49 ppm $\equiv$Si-O-Si*-OH
                         OH   OH
                                                                       C
                                                                      /|\

(C) -65 ppm $\equiv$Si-O-Si*-(O-Si-)$_2$ (F) 13-16 ppm $\equiv$Si-O-Si*-C$\leq$
                         C   C
                        /|\   /|\

Fig. 2. Silicon functionalities at the surface of bonded phases.

ppm; these are due to diphenylphosphinoethylsilicon immobilized on the surface. The peak at −49 ppm is due to the reaction of one Si–ethoxy group with the surface. The second peak at −55 ppm is consistent with the reaction of two Si–ethoxy groups either with the surface hydroxyl or with another SiOH moiety associated with the derivitizing agent. Since there is no peak at −65 ppm there is no appreciable amount of DPP silicon that has a tridentate linkage to other silicons. The results indicate that cross-linked polymerization does not occur under anhydrous conditions[21], and that the use of trialkoxysilylating reagents does not always lead to a "polymeric" stationary phase.

The ^{29}Si CP/MAS NMR spectrum for DPP–ODS "endcapped" bonded phase (Sample 6) is illustrated in Fig. 3(b). The ^{29}Si NMR data indicate that both an alkyldimethylsilicon (Peak 6), and the diphenylphosphinoethylsilicon (peaks C, D and E) have been attached to the surface. The diphenylphosphinoethylsilicon yields three peaks, attached to the silicon. Peaks C, D, and E are weak in intensity, but this is expected since the sample has only 0.35 μmol of phosphorus per square meter.

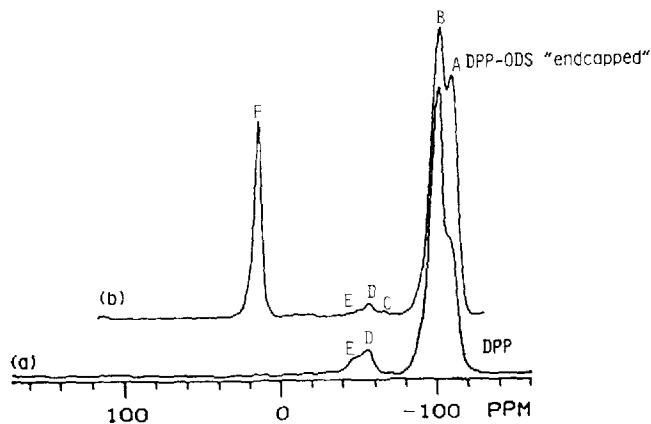Fig. 3. ^{29}Si CP/MAS NMR spectra of DPP and DPP–ODS "endcapped" bonded phases. Samples 3 and 6.
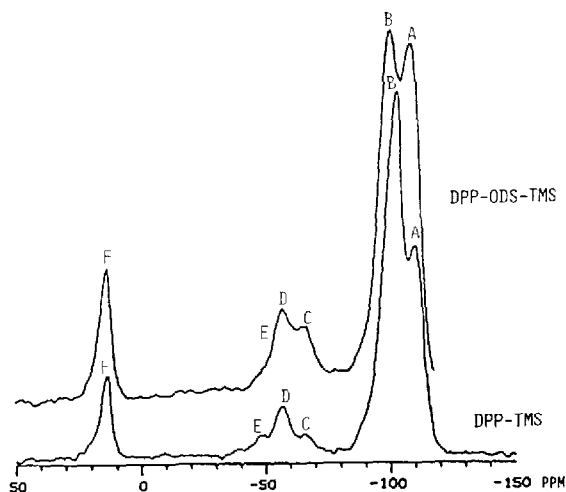
Fig. 4. ^{29}Si CP/MAS NMR spectra of DPP–TMS and DPP–ODS–TMS bonded phases. Samples 5 and 9. Sample 9 is a modified Shandon Hypersil bonded phase.

Fig. 4 illustrates the ^{29}Si CP/MAS NMR spectra for DPP–TMS (Sample 5) and DPP–ODS–TMS (Sample 9) bonded phases. On bonding trimethylchlorosilane to DPP bonded phase, two new peaks appear at $+14$ ppm and -65 ppm. The peak at $+14$ ppm is assigned to trimethylsilicon, while the peak at -65 ppm is attributed to a silicon bonded to a carbon and three siloxanes. The reduction in signal intensity of peak E (compare Figs. 3 and 4) and the appearance of peak C after "endcapping" indicate that the trimethylchlorosilane has reacted with hydroxy groups associated with diphenylphosphinoethyldihydroxysilane and diphenylphosphinoethylhydroxysilane to produce TMS-silylated DPP moieties. Fig. 5 summarizes the reaction schemes.
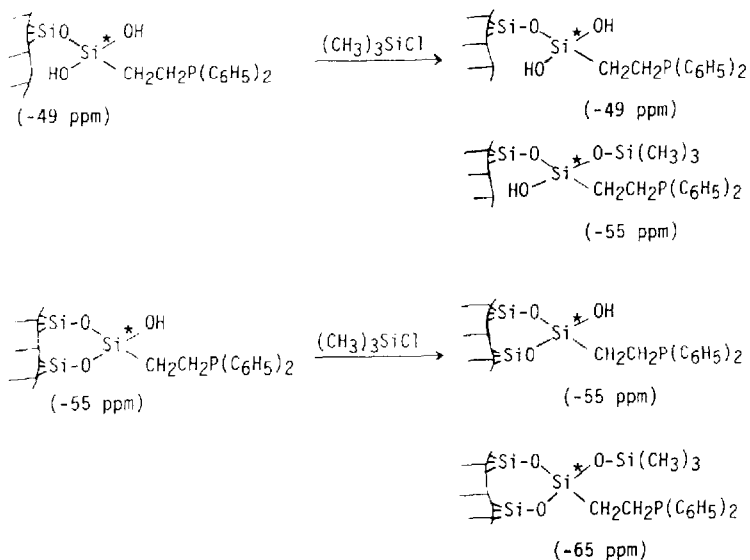

Fig. 5. Endcapping reactions for diphenylphosphinoethylsilane bonded phase.

When octadecyldimethylchlorosilane and trimethylchlorosilane are reacted with DPP bonded phase, the height of the peaks at -107 ppm and $+15$ ppm increase relative to the height of the peak at -99 ppm (see Figs. 3 and 4). An increase in the peak at -107 ppm indicates the presence of additional silicons with four siloxane linkages. This would be a direct result of alkylsilylation which converts silanols (-99 ppm) to siloxanes (-107 ppm)[12]. An increase in the peak intensity at $+15$ ppm can be attributed to the addition of either octadecyldimethylsilicon or trimethylsilicon; the two peaks produced cannot be distinguished in these spectra[14].

The ^{31}P NMR spectrum of DPP–ODS–TMS bonded phase (Sample 9) is given in Fig. 6(a). The NMR spectrum reveals the presence of the following structural moieties which have been identified on the basis of previously reported ^{31}P NMR chemical shifts[15]: (1) phosphine (-10 ppm); (2) phosphine oxide ($+35$ ppm). The data indicate that the synthetic route adopted for immobilizing the diphenylphosphinoethylsilane results in some oxidation of the phosphine moiety producing a heterogeneous stationary phase. Both the phosphine and the phosphine oxide are produced for Samples 1, 3 and 9.
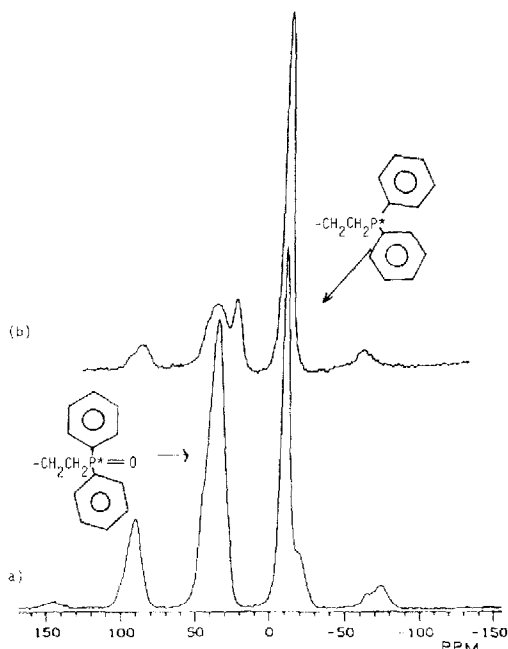

Fig. 6. ^{31}P CP/MAS NMR spectra of DPP–ODS–TMS bonded phase before and after reduction. Samples 9 and 10. Extra peaks are due to spinning side-bands.

The ^{31}P NMR spectrum of reduced DPP–ODS–TMS bonded phase (Sample 10) is given in Fig. 6b. A comparison of the two spectra in Fig. 6 indicates that the trichlorosilane reduction procedure is effective and that the ratio of phosphine oxide to phosphine on the surface is diminished, producing a more homogeneous diphenylphosphine stationary phase.

Fig. 7. ^{13}C CP/MAS NMR spectra of DPP, DPP-TMS and DPP-ODS-TMS bonded phases. Samples 3, 5, and 9.

Fig. 7 gives the ^{13}C CP/MAS NMR spectra for DPP, DPP-TMS and DPP-ODS-TMS bonded phases. Fig. 8 lists the ^{13}C CP/MAS NMR data for the DPP-ODS-TMS bonded phase. The ^{13}C NMR chemical shift (relative to external tetramethylsilane) is given below the corresponding carbon atom. The assignments are based on data from analogous compounds[14].

Fig. 8. ^{13}C CP/MAS NMR assignments for DPP-ODS-TMS bonded phase.

The ^{13}C NMR data indicate that the concurrent immobilization of diphenyl-phosphinoethyltriethoxysilane and octadecyldimethylchlorosilane produces a mixed-mode bonded phase with carbons that are readily distinguishable. The methylene carbons in a long chain ($+31$ ppm) can only be attributed to the octadecyldimethylsilane moiety, whereas the phenyl carbons (129–133 ppm) are a direct result of the immobilization of diphenylphosphinoethyltriethoxysilane. The data also indicate that the methyl carbons associated with TMS and the two methyl carbons attached to silicon in ODS cannot be distinguished.

The peak at $+59$ ppm in the ^{13}C NMR spectrum of DPP can be attributed to the CH$_2$ group of the Si–OCH$_2$CH$_3$ functionality[14]. Apparently all the ethoxy groups associated with DPP have not been hydrolyzed even after heating in the oven at 150°C for 2 h. Subsequent alkylsilylations eventually result in the disappearance of this peak, as seen by comparing the three spectra of Fig. 7.

Chromatography

In order to evaluate the potential of a mixed-mode bonded phase containing both hydrophobic and weak base functionalities, the DPP–ODS–TMS "reduced" bonded phase (Sample 10) has been chosen for use as a chromatographic adsorbent. This bonded phase has been well characterized, is stable and features a DPP surface coverage approaching 1.25 μmol m^{-2}. Diphenylmethylchlorosilane on reaction with silica gel yields[18] a maximum surface coverage of 2.6 μmol m^{-2}. Since diphenyl-
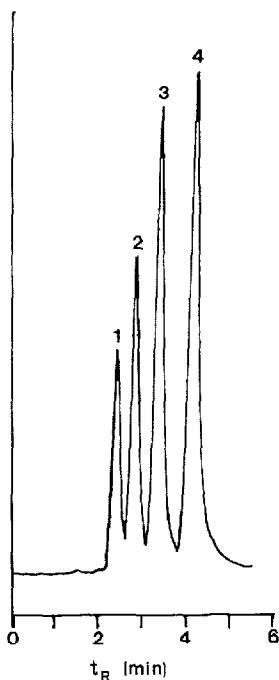

Fig. 9. Reversed-phase separation of substituted aromatics on DPP–ODS–TMS bonded phase (Sample 10). Column, 150 × 3 mm I.D. "glass-lined"; mobile phase, acetonitrile–water (50:50); flow-rate, 0.50 ml/min; detection, UV 254 nm. Peaks: 1 = phenol, 0.15 ppt; 2 = acetophenone, 0.1 ppt; 3 = nitrobenzene, 0.03 ppt; 4 = toluene, 1.0 ppt.

phosphinoethyltriethoxysilane also has two large phenyl groups, the accessibility of the surface should be similar for both silylating reagents. If the maximum coverage is assumed to be 2.5 μmol m^{-2}, then the extent of DPP surface coverage is *ca.* 50%. The remainder of the accessible surface is covered by octadecyldimethylsilyl and trimethylsilyl groups, as verified by ^{13}C NMR.

Fig. 9 is a chromatogram obtained using Sample 10. The chromatogram illustrates the separation of a mixture of (1) phenol, (2) acetophenone, (3) nitrobenzene and (4) toluene. The order of elution of the solutes is the same as for an octadecylsilyl bonded phase (Shandon Hypersil ODS) under similar eluent conditions. The number of theoretical plates for toluene ($k' = 1.35$) is 1750. This translates to an effective plate height of 8.57 · 10^{-3} cm.

Fig. 10 illustrates the effect of varying the solvent composition. There appears to be a linear correlation between the log capacity factor (log k') and the percent organic modifier. As the concentration of water in the binary solvent mixture increases, retention time also increases. The data indicate that the DPP–ODS–TMS bonded phase, though possessing a surface that has been only partially coated with octadecylsilyl groups, still maintains sufficient hydrophobic character so that the chromatographic properties are very similar to those of ODS bonded phases[18].
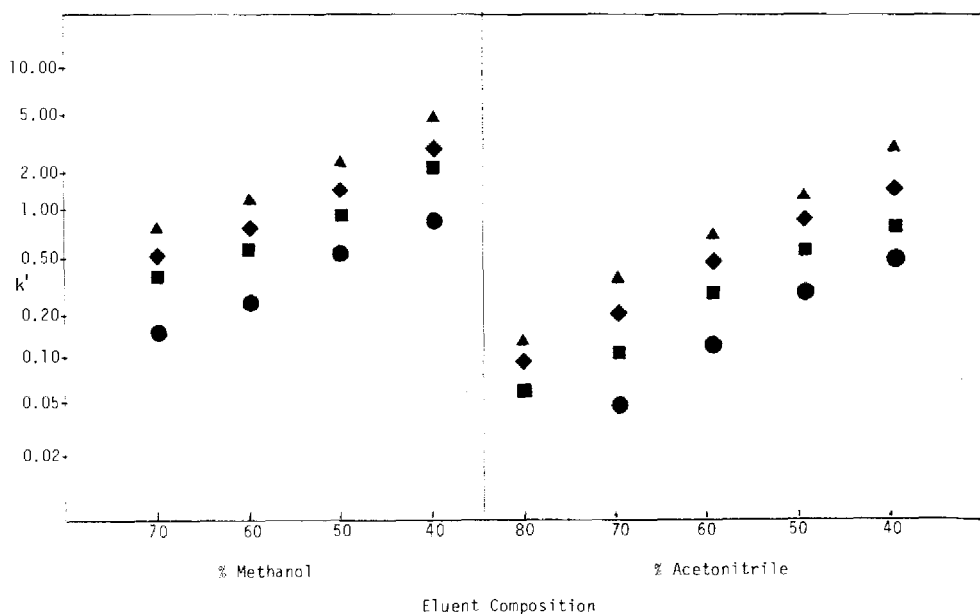

Fig. 10. Capacity factor, k', as a function of eluent composition. ● = Phenol, ■ = acetophenone, ◆ = nitrobenzene, ▲ = toluene.

Fig. 11 is a chromatogram obtained under normal phase conditions for the same column. The order of elution is (1) toluene, (2) nitrobenzene, (3) *o*-nitroaniline, (4) *m*-nitroaniline, (5) *p*-nitroaniline. The selectivity differs from that obtained on a silica gel column (Shandon Hypersil) because *m*-nitroaniline elutes before *p*-nitroaniline. The steric requirements imposed by either the bulky phenyl groups associated
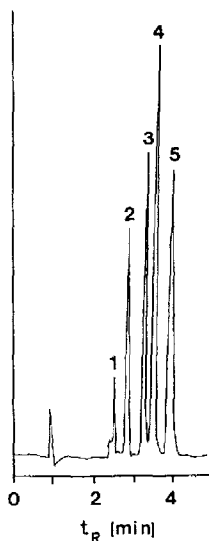
Fig. 11. Normal phase separation of aromatics on DPP–ODS–TMS bonded phase (Sample 10). Column, 150 × 3 mm I.D. "glass-lined"; mobile phase, isooctane–ethanol–water (85:14.5:0.5); flow-rate, 1 ml/min; detection, UV 254 nm. Peaks: 1 = toluene; 2 = nitrobenzene; 3 = *o*-nitroaniline; 4 = *m*-nitroaniline; 5 = *p*-nitroaniline.

with the DPP moiety or the long chain octadecyl functionality may cause a reversal in the order of elution.

The column exhibits the same affinity as an octadecylsilyl column for non-polar solutes, but concurrently exhibits the potential for polar interactions when used in the normal phase mode. This ability to function either in the normal or reversed phase modes is similar to that of other columns such as the amino or cyano-bonded phases. However, if the selectivity of the DPP–ODS–TMS bonded phase is compared with that of an amino column (IBM Amino (NH$_2$) column), the order of elution differs. For a mixture of toluene, acetophenone, *m*-dinitrobenzene and diethylphthalate, using the DPP–ODS–TMS column, the *m*-dinitrobenzene elutes before the diethylphthalate, which is the reverse of the behavior of the amino column.

Finally, Fig. 12 shows the separation of a mixture of phenols on the DPP–ODS–TMS bonded phase. Resorcinol, phenol, *m*-nitrophenol, *p*-ethylphenol, 2-naphthol, and 1-naphthol are completely resolved. To a first approximation the solutes elute in order of increasing carbon number; however, secondary steric constraints also dictate the order of elution, since 2-naphthol is resolved from its geometric isomer, 1-naphthol.

The stability of the DPP–ODS–TMS bonded phase was evaluated by running acetonitrile–water (35:65) through the column for *ca*. 4 h. No perceptible loss of efficiency was observed. The column was then equilibrated overnight with the same eluent composition. A chromatogram generated after 16 h demonstrated increased band broadening and peak tailing (27% loss of efficiency). On regenerating the column with 50 column volumes of acetonitrile, the initial chromatographic efficiency was restored. Repeated use and regeneration of the column over a period of two weeks resulted in no permanent loss of efficiency.
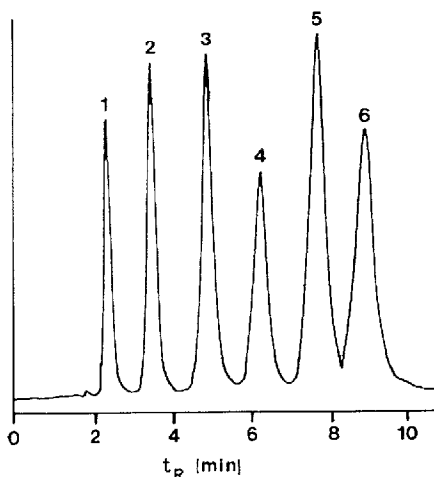
Fig. 12. Reversed-phase separation of phenols on DPP–ODS–TMS bonded phase (Sample 10). Column, 150 × 3 mm I.D. "glass-lined"; mobile phase, acetonitrile–water (35:65); flow-rate, 0.50 ml/min; detection, UV 254 nm. Peaks: 1 = resorcinol, 0.08 ppt; 2 = phenol, 0.08 ppt; 3 = m-nitrophenol, 0.04 ppt; 4 = p-ethylphenol, 0.16 ppt; 5 = 2-naphthol, 0.08 ppt; 6 = 1-naphthol, 0.12 ppt.

Further work is now in progress to develop other applications for the DPP–ODS–TMS bonded phase. Some promising avenues of research include using the oxidized form of DPP as a bonded phase, and using DPP as an immobilizing ligand for the retention of metal complexes. Metal-coated DPP bonded phase may have some interesting applications as a ligand-exchange packing or as an immobilized heterogeneous catalyst. Further research in these areas as well as on the uses of neat DPP bonded phase is now in progress.

CONCLUSIONS

A mixed-mode phase consisting of diphenylphosphinoethylsilane concurrently immobilized with octadecyldimethylsilane has been synthesized. Elemental analysis data indicate that *ca.* 50% of the original hydroxyls have been engaged in linkages to the diphenylphosphinoethylsilyl moiety. ^{29}Si NMR data indicate that the functionality has been immobilized by the reaction of at most two ethoxy groups with the surface sites. ^{13}C NMR data show that both the octadecyldimethylsilyl and diphenylphosphinoethylsilyl moieties have been immobilized. ^{31}P NMR data indicate that the surface is heterogeneous, containing both phosphino and phosphine oxide moieties. The phosphine oxide groups are readily reduced by using trichlorosilane as a reducing agent.

Preliminary chromatographic data show that the diphenylphosphineoctadecylsilane (DPP–ODS) bonded phase is useful for the separation of phenols. The results indicate that the column is a "hybrid", exhibiting reversed-phase character under hydro-organic eluent conditions, and polar character when the eluent is non-polar.

ACKNOWLEDGEMENTS

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