CHROM. 23 102

Short Communication

Structural investigation of oligomeric *n*-octylsilyl reversed phases

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ABSTRACT

The structural characteristics of a series of oligomeric bonded phases prepared by the fluidised bed technique have been determined using ^{29}Si and ^{13}C CP-MAS-NMR spectroscopy. The porous properties of these materials were also investigated using GPC and it was shown that the size separation character-istics of the various oligomers were substantially the same irrespective of the carbon load.

INTRODUCTION

Surface modification of silica gels with organochlorosilanes has become pop-ular in reversed-phase high-performance liquid chromatography (RP-HPLC). De-pending on the functionality (chlorine atoms) of the silane reagent and the reaction conditions, the surface of the derivatized silica gel may vary from a bonded monolay-er to polymerized layers with a cross-linked structure of the silanizing agent on the silica surface [1,2].

The percentage carbon load of the modified silica gel is obtained by elemental analysis, and other parameters such as specific surface area, pore volume, particle size and size distribution are determined by BET nitrogen adsorption measurement, Coulter counter and other techniques [3,4]. However, none of these techniques pro-vides useful information about the surface structure of the bonded phases.

Solid-state ^{29}Si and ^{13}C cross-polarization and magic angle spinning nuclear magnetic resonance ($^{29}Si/^{13}C$ CP-MAS-NMR) spectrometry has proved to be a use-ful technique for a quantitative and qualitative description of the surface structure of chemically modified silica gels [2,5–12]. Such studies exploit the short relaxation time

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of ^{13}C and the ability of ^{29}Si–H cross-polarization to restrict detection to surface nuclei that are nearer the available protons of the hydroxyl groups. Hence the method is capable of differentiating the various binding sites on the silica surface.

As an extension of our previous work [13,14], this paper reports an investigation of the surface structure of oligometric n-octylsilyl reversed phase using ^{29}Si and ^{13}C CP-MAS-NMR spectrometry. In addition, the porous properties of the bonded phases were further examined by gel permeation chromatography (GPC).

EXPERIMENTAL

The bonded phases were prepared by the fluidized bed technique [15] and details of the original synthesis, physical characterization and column packing can be found in a previous paper [13]. The characteristics of the bonded phases are given in Table I.

Solid-state ^{29}Si and ^{13}C CP-MAS-NMR spectra of the unmodified and selected modified silica gels were obtained on a Bruker MSL-300 Fourier transform spectrometer. The $^{29}Si/^{13}C$ spectra were obtained at 59.60 and 75.47 MHz, respectively, using a zirconia rotor (7 mm I.D.) containing 100–200 mg of sample. To overcome excessive NMR line widths and overlapping lines, magic angle spinning was performed at 4 kHz. A cross-polarization contact time of 10 ms and a recycling time of 5 s were used. Chemical shifts were referenced to liquid tetramethylsilane.

Gel permeation chromatographic studies were performed on a chromatograph consisting of a Shimadzu LC-5A pump and SPD 2AM variable-wavelength UV detector (Shimadzu, Kyoto, Japan) operated at 254 nm. The columns were evaluated at ambient temperature using tetrahydrofuran (THF) (Fisons, Dorset, UK) as the mobile phase. Benzene (Fluka, Buchs, Switzerland) and polystyrenes (Waters Assoc. USA, and Polymer Labs., UK) of narrow molecular-mass distribution served as the standard test solutes. The solutes were made up singly in the mobile phase (ca. 1 mg/ml in THF) and injected into the column via a Rheodyne (Berkeley, CA, USA)

TABLE I

CHARACTERISTICS OF THE BONDED PHASES [13]

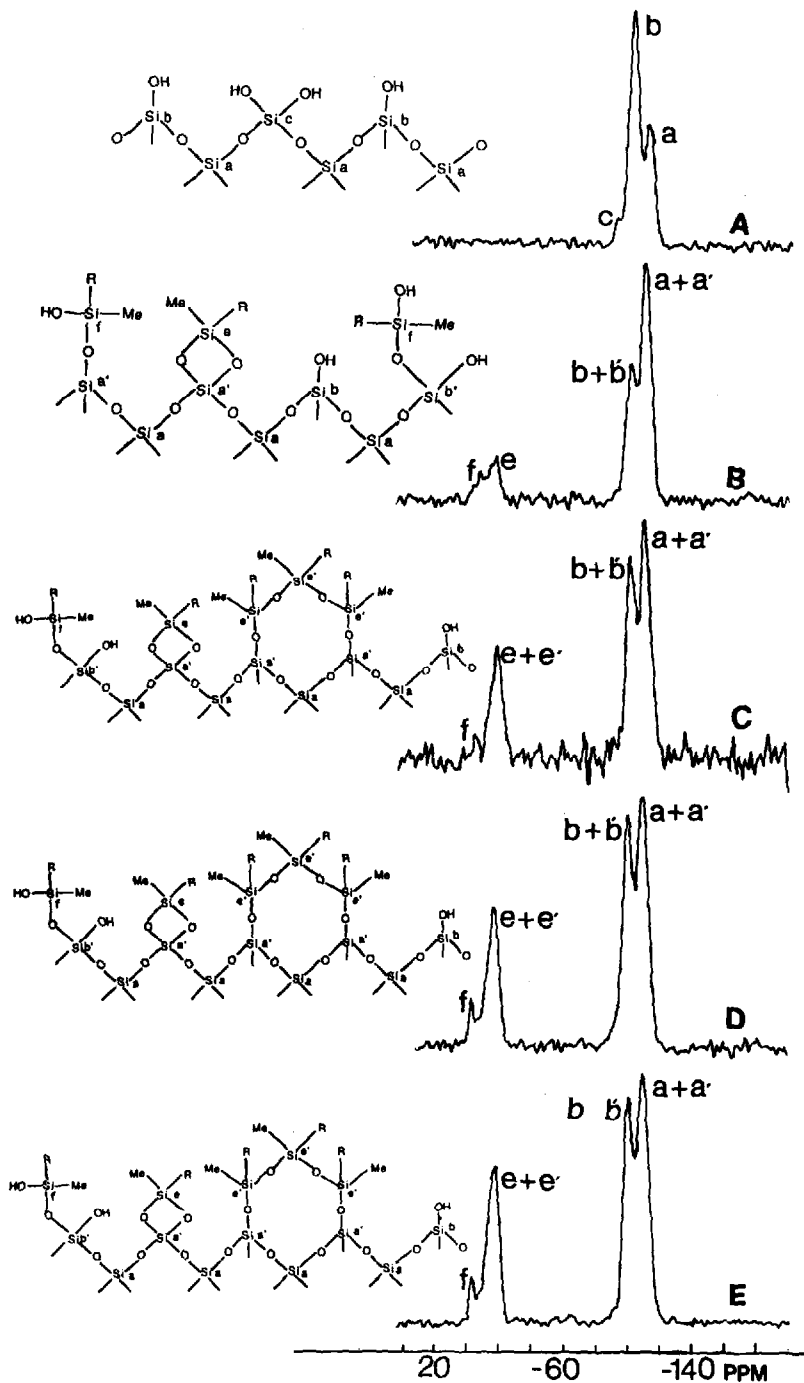| Column No.	C (%, w/w)	Surface area, S_{BET} (m^2 g^{-1})	Pore volume	
			$V_{P(N_2)}$ (cm^3 g^{-1})	$V_{P(GPC)}$ cm^3
Silica	–	250.00	1.00	0.87
1	7.58	153.04	0.82	0.76
2	9.69	144.99	0.71	0.65
3	11.14	132.69	0.60	0.58
4	12.18	126.59	0.63	0.56
5	12.69	118.64	0.59	0.54
6	14.43	115.97	0.59	0.53
–7	14.90	107.11	0.54	0.49
8	15.80	106.50	0.49	0.47
9	16.79	105.21	0.48	0.46
10	17.45	105.14	0.45	0.45

Fig. 1. ^{29}Si CP-MAS-NMR spectra of (A) silica after hydrothermal treatment at 200°C and of the bonded phases; (B) column 1; (C) column 3; (D) column 5; (E) column 10. Me = Methyl.

7125 valve fitted with a 20-μl loop. Benzene and polystyrene standard (molecular mass $1.2 \cdot 10^6$) were used to determine the void or mobile phase volume V_o and the exclusion volume V_{ex}, respectively. The relative retention R and the solute probe diameter $\varnothing$ were calculated by [16]

$$R = [(V_e - V_{ex})/(V_o - V_{ex})]100$$
$$\text{and } \varnothing = 0.62 \, (MW)^{0.59}$$

where V_e is the retention volume of the test solute.

RESULTS AND DISCUSSION

Fig. 1 shows the ^{29}Si CP-MAS-NMR spectra of the unmodified and modified silica gels. The NMR data were obtained by on-line computer acquisition and processing. The chemical shifts (labelled a–f) were assigned according to the literature [6,7,10]. The proposed surface structure of the bonded phases are given beside each figure. The chemical shifts and the structural environment of the silicon atom of interest (Si*) are given in Table II.

As shown in Fig. 1A, the ^{29}Si spectra showed the dominant silica resonances at -110 (peak a = a'), -100 (peak b = b') and -90 (peak c) ppm, and these has been assigned to the surface silicon, $(\equiv SiO)_4Si^*$, single hydroxyl sites, $(\equiv SiO)_3Si^*OH$, and geminal hydroxyl sites, $(\equiv SiO)_2Si^*(OH)_2$, respectively. The weak absorbance at -90 ppm indicates that the silica contains a relatively small amount of geminal silanols.

The ^{29}Si spectra of the representative packings (columns 1,3,5 and 10) are shown in Fig. 1B–E. The absence of peak c in these spectra suggests that the geminal hydroxyls are more reactive, although present in smaller proportion. In general, there is a rapid transfer of intensity between adjacent peaks with increase in carbon load due to an increase in the formation of secondary siloxane bonds, $i.e.$, bonds labelled a', b' and e'. The resonance at -19 ppm (peak e) in Fig. 1B is assigned to silane molecules characterized by two siloxane bonds formed via a 1:2 reaction with the silanols. The presence of peak f, assigned to a silicon atom bonded to siloxane bond and a hydroxyl group, indicates that the silane reagent also undergoes a 1:1 reaction with the silanols and the hydroxyl groups arises from the hydrolysis of the unreacted chlorine atom of the reagent. Consequently, it can be concluded that the silane reagent undergoes mixed reactions with the silica surface, $i.e.$, 1:1 and 1:2 stoichiometry.

TABLE II

STRUCTURAL ENVIRONMENT OF Si* ATOM

Chemical shift (ppm)	Peaks	Species
-110	a(a')	$Si^*(OSi\equiv)_4$
-101	b(b')	$HOSi^*(OSi\equiv)_3$
-91	c	$(OH)_2Si^*(OSi\equiv)_2$
-19	e(e')	$-O-Si^*(CH_3)(R)-O-$
-8 to -4	f	$HO\ Si^*(CH_3)(R)-O-$

As can be seen from Fig. 1B–E, the intensity of peak e increased with increasing carbon load whereas that of peak f remained relatively unchanged between Fig. 1A and B and Fig. 1C and D, respectively. As it becomes more difficult for the silane molecules to react with the surface silanols owing to steric hindrance on increasing the reaction step, therefore, the above phenomena indicate that further silanization occurred on the newly formed silanols. Consequently, the increase in siloxane peak intensity (peak e) suggests a possible 1:2 reaction mechanism between the silane molecules and the hydroxyl groups of two adjacent siloxane bonds (labelled e'), that is, the
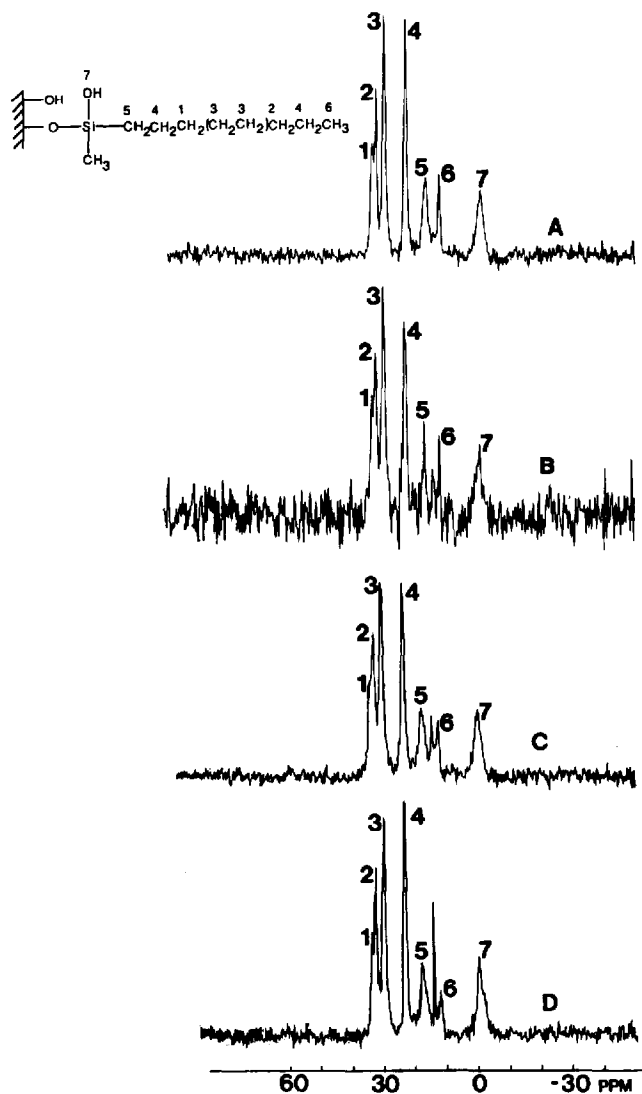

Fig. 2. ^{13}C CP-MAS-NMR spectra of the bonded phases: (A) column 1; (B) column 3; (C) column 5; (D) column 10.

newly formed silanols. This is further confirmed by the absence of the silicon peak at −47 ppm associated with one ≡Si–O–group, two hydroxyl groups and an alkyl group [2].

Fig. 2 shows the ^{13}C CP-MAS-NMR spectra of the representative packings and the chemical shifts (labelled 1–7) were assigned according to the literature [7,11,17]. The resonances at 34 and 32 ppm are assigned to methylene carbons 1 and 2, respectively, owing to their slower cross-polarization rate than methylene carbon 3 in the same chemical environment [10].

The dominant peaks at 22 and 29 ppm can be identified with the methylene groups adjacent to the terminal methyl C (peak 4) and internal methylene carbon atom (peak 3) of the hydrocarbon chain, respectively. The absorption at 17, 12 and −0.56 to −1.04 ppm are assigned to the methylene carbon atom attached to Si atom (peak 5), terminal methyl C (peak 6) and the methyl carbon attached to Si atom (peak 7), respectively.

In general, the chemical shifts of the carbon atoms were affected by their chemical environments and not the carbon load, except the carbon atoms near the silica surface (peak 7), which cross-polarize faster with increasing carbon load. The lower field shift in carbon 7 resonances with increasing carbon load further substantiate the polymeric nature of the bonded phases and consequent increase in steric interaction between the methyl groups possibly with the silica surface and/or the other attached silane moieties. The gradual decrease in the intensities of peaks 5 and 6 may be attributed to the short relaxation time of carbon atoms near the silica surface.
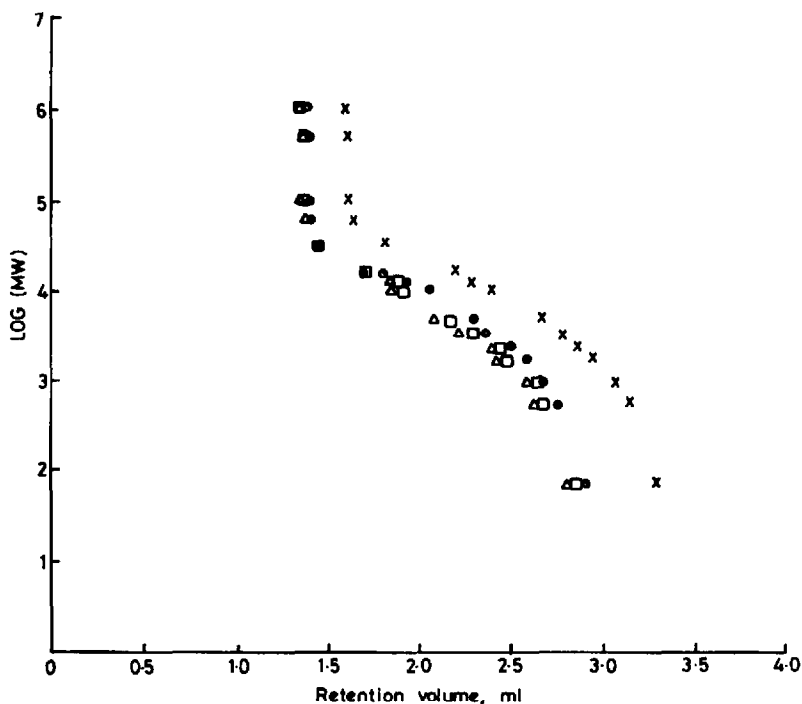

Fig. 3. Polystyrene calibration graphs for (×) silica gels, (○) column 1, (□) column 3 and (△) column 5 by GPC.
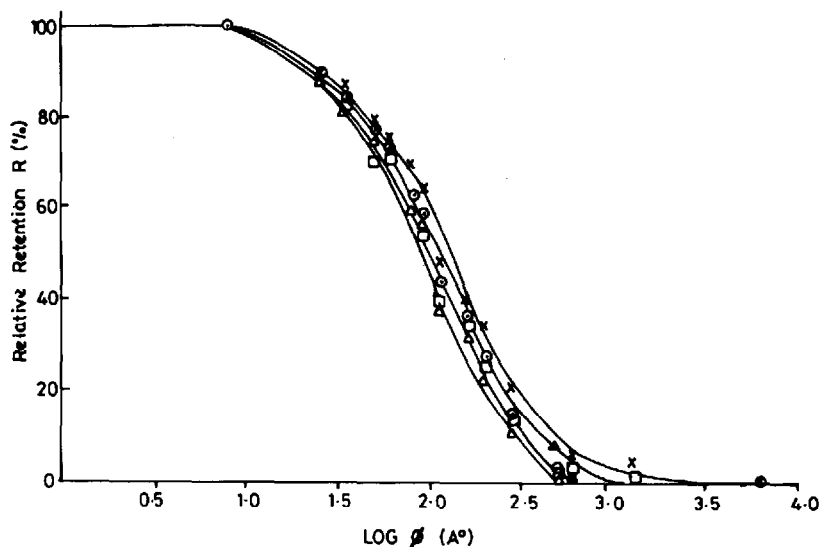
Fig. 4. Pore-size distribution by GPC. Symbols as in Fig. 3.

Considering the resonance pattern in Fig. 1 and 2, it is proposed that the bonded phases consists essentially of cyclic structures of the type $(-Si-O-Si(CH_3)-(R)-O-)_n$ and $[(-Si-O-Si(CH_3)(R)-O-)_2Si(CH_3)(R)]_n$, where n is the number of siloxane units and R is the alkyl chain length (C_8).

The molecular mass calibration graphs of the packings, as illustrated in Fig. 3, are substantially the same except that of the unmodified silica gels. This further confirms the retention properties of the phases in the reversed-phase mode as reported in an earlier paper [13]. The shift in the calibration graphs reflects the effect of surface modification on the size-exclusion properties of silica gels and possible operation of a mixed retention mechanism [18]. Irrespective of the carbon load and the shift in the calibration graphs, the bonded phases have the same molecular mass separation range (molecular mass 580–68 000) and similar pore-size distribution as illustrated in Fig. 4.

Whilst the effect of surface modification on surface area and pore volume $[V_{p(N_2)}]$ has been explained earlier [13], it is further observed that the GPC experiments produced lower pore volumes than the BET nitrogen adsorption isotherm as shown in Table I. The differences in the pore volumes measured by the two methods may be ascribed to possible alteration of the pore structure by the mobile phase (THF) or the penetration of the micropores by nitrogen [18].

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