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NEW POLAR SUBSTITUTED-PHENYL SILOXANE MONOMERS AND POLYMERS FOR CAPILLARY GAS CHROMATOGRAPHY

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SUMMARY

A series of polar substituted-phenylalkyl- (or phenoxyalkyl)dimethoxymethylsilanes has been prepared by the hydrosilylation of various phenyl-substituted alkenes. The disiloxane monomers were copolymerized with dimethoxydimethylsilane to prepare gums for testing as stationary phases for capillary column gas chromatography. Those phases which contained a phenoxypropyl unit were not stable at temperatures above 200°C. Phases having 3-phenylpropyl or 2-phenylethyl substituents were stable. The 4-methoxy- and 3,4-dimethoxyphenylethyl phases demonstrated different selectivities for polar solutes than could be obtained with other available stationary phases.

INTRODUCTION

The polysiloxanes generally have excellent thermal stabilities over wide temperature ranges which make them the materials of choice for stationary phases for capillary gas chromatography (GC). The methylpolysiloxanes (SE-30, OV-1, etc.) are the most popular phases because their coiled helical structures allow for a reasonably constant viscosity at both low and high temperatures[1]. The methylpolysiloxanes are used for most separations because of the high efficiency obtained with these phases; however, they are the least polar of the polysiloxane phases, and their limited selectivity is primarily due to weak non-polar dispersion forces[2].

Phenyl-substituted methylpolysiloxane phases have been studied extensively[3–6]. These phases have a higher intrinsic thermal stability than most other phases. The phenyl group is polarizable so that polar solutes are retained on the phase. The beneficial effect of the phenyl substituent has been shown to have an optimum at *ca.* 50% phenyl substitution[7,8]. The selectivity of the phenylpolysiloxanes is a result of the dipole-induced dipole interaction of the solute and stationary phase. Biphenyl- and naphthyl-substituted methylpolysiloxane phases are even more polarizable and exhibit still better selectivities for compounds with polar functionality[9,10].

The polarity and the polarizability of phenylmethylpolysiloxane phases can be increased by the substitution of polar groups onto the benzene ring. Miller and Lav-

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chik have shown an increase in the polarizability of toluene when substituted by cyano, nitro, certain halogen, and alkyl groups[11]. This paper describes the synthesis of new phenylmethylpolysiloxane phases in which the phenyl group contains methoxy, fluoro, cyano and nitro substituents. The phases were prepared from the corresponding polar-substituted phenylalkyl- (or phenoxyalkyl)-dimethoxymethylsilanes, which were synthesized for this study. Polymerization of dimethoxysilanes has proved to be a superior method to prepare polysiloxane phases[12]. The GC properties of the 3-(4-methoxyphenyl)propyl phase (prepared from monomer 7, Fig. 1) when coated on capillary columns have been reported[12]. The chromatographic properties of columns prepared from 2-(4-methoxyphenyl)ethyl and 2-(3,4-dimethoxyphenyl)-ethyl phases (prepared from monomers 8 and 9) are reported in this paper.

EXPERIMENTAL

Infrared (IR) spectra were obtained on a Beckman Acculab 2 spectrometer. Nuclear magnetic resonance (NMR) spectra were recorded by a JEOL FX90-Q spectrometer with methylene chloride or chloroform as the internal standard. Melting points were taken on a Thomas-Hoover melting point apparatus and are uncorrected. Carbon and hydrogen analyses were performed by MHW Labs., Phoenix, AZ, U.S.A. Chemicals were purchased from Aldrich (substituted phenyl compounds) or Petrarch

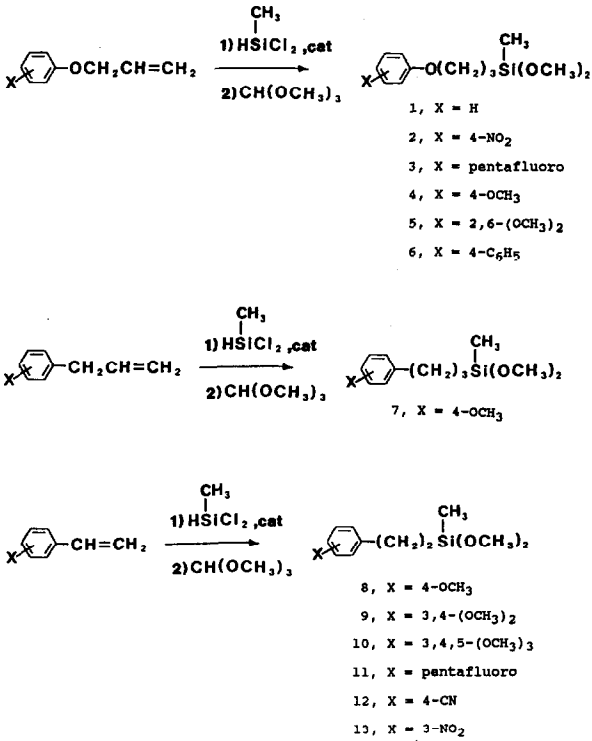

Fig. 1. New polar-substituted phenylsilane monomers.

Systems (silane compounds). The substituted phenylallyl ethers were prepared from the corresponding phenols and allyl bromide.

General procedure for the preparation of polar-substituted phenylalkyl- (or phenoxypropyl)dimethoxymethylsilanes (Fig. 1)

A mixture of the alkene and catalytic amounts of triphenylphosphine and hexachloroplatinic acid hexahydrate in 20% excess of dichloromethylsilane[13] was refluxed for 16 h. The resulting dichlorophenylalkyl- (or phenoxypropyl)silane was purified by distillation. The dichlorosilane material was refluxed for 16 h with 2.4 equivalents of trimethylorthoformate and catalytic amounts of methanol[9,14,15]. The dimethoxysilane product was distilled. Specific details are listed for each product.

3-Phenoxypropyldimethoxymethylsilane (1). 3-Phenoxypropene (12.74 g, 0.095 mole, b.p. 80–82°C/30 mmHg) was treated to give 15.54 g (66%) of the dichlorosilane (b.p. 86–110°C/2–5 mmHg). The dichlorosilane (15.37 g, 0.062 mole) was used to give 14.23 g (96%) of silane 1 (ref. 16) (b.p. 91–109°C/25 mmHg); NMR (δ): 0.20 (3H, s); 0.83 (2H, mult.); 1.93 (2H, mult.); 3.57 (6H, s); 3.98 (2H, t); 7.0 (3H, mult.); 7.3 (2H, mult.).

3-(4-Nitrophenoxy)propyldimethoxymethylsilane (2). 3-(4-Nitrophenoxy)-propene (20.48 g, 0.11 mole, b.p. 151–188°C/5 mmHg) was treated to give 33.16 g (99%) of the dichlorosilane. The crude dichlorosilane (33.16 g, 0.133 mole) was used to give 30.85 g (96%) of silane 2 (ref. 17) (b.p. 159–162°C/0.6 mmHg); NMR (δ): 0.14 (3H, s); 0.73 (2H, mult.); 1.88 (2H, mult.); 3.48 (6H, s); 3.96 (3H, t); 6.88 (2H, d); 8.12 (2H, d).

3-(2,3,4,5,6-Pentafluorophenoxy)propyldimethoxymethylsilane (3). 3-(2,3,4,5,6-Pentafluorophenoxy)propene (7.01 g, 0.031 mole, b.p. 62–63°C/30 mmHg) was treated to give 6.83 g (64%) of the dichlorosilane (b.p. 92–98°C/0.2 mmHg). The dichlorosilane (6.61 g, 0.02 mole) was used to give 5.89 g (91%) of silane 3 (b.p. 82–87°C/0.2 mmHg); NMR (δ): 0.15 (3H, s); 0.76 (2H, mult.); 1.82 (2H, mult.); 3.53 (6H, s); 4.13 (2H, t). Analysis for $C_{12}H_{15}F_5O_3Si$: calculated C, 43.63; H, 4.59; found, C, 43.41; H, 4.58.

3-(4-Methoxyphenoxy)propyldimethoxymethylsilane (4). 3-(4-Methoxyphenoxy)propene (19.3 g, 0.12 mole, b.p. 121–123°C/30 mmHg) was treated to give 31.1 g (94%) of the dichlorosilane (b.p. 110–128°C/0.5 mmHg). The dichlorosilane (30.6 g, 0.11 mole) was used to give 28.2 g (95%) of silane 4 (b.p. 115–136°C/0.5 mmHg); NMR (δ): 0.17 (3H, s); 0.76 (2H, mult.); 1.86 (2H, mult.); 3.54 (6H, s); 3.77 (3H, s); 3.88 (2H, t); 6.88 (4H, s). Analysis for $C_{13}H_{22}O_4Si$: calculated, C, 57.73; H, 8.22; found, C, 58.00; H, 8.27.

3-(2,6-Dimethoxyphenoxy)propyldimethoxymethylsilane (5). 3-(2,6-Dimethoxyphenoxy)propene (32.2 g, 0.17 mole, b.p. 140–142°C/30 mmHg) was treated to give 44.7 g (87%) of the dichlorosilane (b.p. 137–155°C/0.5 mmHg). The dichlorosilane (43.5 g, 0.14 mole) was used to give 41.5 g (98%) of silane 5 (b.p. 145–155°C/0.5 mmHg); NMR (δ): 0.14 (3H, s); 0.77 (2H, mult.); 1.87 (2H, mult.); 3.54 (6H, s); 3.84 (6H, s); 3.97 (2H, t); 6.57 (2H, mult.); 6.97 (1H, mult.). Analysis for $C_{14}H_{24}O_5Si$: calculated, C, 55.96; H, 8.07; found, C, 55.79; H, 7.82.

3-(4-Phenylphenoxy)propyldimethoxymethylsilane (6). 3-(4-Phenylphenoxy)-propene (3.3 g, 0.016 mole, m.p. 81–83°C) was treated to give 4.8 g (94%) of the dichlorosilane (b.p. 140–150°C/0.1 mmHg). The dichlorosilane (4.7 g, 0.015 mole)

was used to give 3.9 g (85%) of silane 6 (b.p. 140–148°C/0.05 mmHg); NMR (δ): 0.24 (3H, s); 0.82 (2H, mult.); 1.94 (2H, mult.); 3.60 (6H, s); 4.00 (2H, t); 7.00 (2H, d); 7.50 (5H, mult.); 7.57 (2H, d). Analysis for $C_{18}H_{24}O_3Si$: calculated, C, 68.30; H, 7.66; found, C, 68.50; H, 7.55.

3-(4-Methoxyphenyl)propyldimethoxymethylsilane (7)[12]. 3-(4-Methoxyphenyl)propene (5.0 g, 0.034 mole) was treated to give 8.17 g (92%) of the dichlorosilane (b.p. 87–97°C/0.1 mmHg). This dichlorosilane (8.08 g, 0.031 mole) was used to give 7.01 g (90%) of silane 7, (b.p. 85–103°C/0.1 mmHg); NMR (δ): 0.14 (3H, s); 0.68 (2H, mult.); 1.71 (2H, mult.); 2.61 (2H, t); 3.52 (6H, s); 3.80 (3H, s); 6.81 (2H, d); 7.10 (2H, d). Analysis for $C_{13}H_{22}O_3Si$: calculated, C, 61.36; H, 8.73; found, C, 61.19; H, 8.53.

2-(4-Methoxyphenyl)ethyldimethoxymethylsilane (8). 4-Methoxystyrene (2.51 g, 0.019 mole) was treated to give 4.1 g (88%) of the dichlorosilane (b.p. 77–83°C/0.1 mmHg). The dichlorosilane (4.1 g, 0.017 mole) was used to give 3.8 g (96%) of the silane 8 (b.p. 85–95°C/0.1 mmHg); NMR (δ): 0.14 (3H, s); 0.98 (2H, mult.); 2.67 (2H, mult.); 3.54 (6H, s); 3.80 (3H,s); 6.80 (2H, d); 7.14 (2H, d). Analysis for $C_{12}H_{20}O_3Si$: calculated, C, 59.95; H, 8.40; found, C, 59.94; H, 8.29.

2-(3,4-Dimethoxyphenyl)ethyldimethoxymethylsilane (9). 3,4-Dimethoxystyrene (2.5 g, 0.015 mole) was treated to give 3.5 g (83%) of the dichlorosilane (b.p. 98–105°C/0.1 mmHg). The dichlorosilane (3.5 g, 0.013 mole) was used to give 3.2 g (97%) of silane 9 (b.p. 100–110°C/0.1 mmHg); NMR (δ): 0.17 (3H, s); 1.03 (2H, mult.); 2.71 (2H, mult.); 3.57 (6H, s); 3.80 (3H, s); 3.90 (3H, s); 6.77 (3H, s). Analysis for $C_{13}H_{22}O_4Si$: calculated, C, 57.73; H, 8.22; found, C, 57.80; H, 8.05.

2-(3,4,5-Trimethoxyphenyl)ethyldimethoxymethylsilane (10). 2,3,4-Trimethoxystyrene (4.6 g, 0.024 mole, b.p. 116–123°C/0.1 mmHg), prepared by the procedure of Greenwald *et al.* from 3,4,5-trimethoxybenzaldehyde[18], was treated to give 3.6 g (49%) of the dichlorosilane (b.p. 122–129°C/0.1 mmHg). This dichlorosilane (3.6 g, 0.012 mole) was used to give 2.2 g (64%) of silane 10 (b.p. 112–126°C/0.1 mmHg); NMR (δ): 0.13 (3H, s); 0.96 (2H, mult.); 2.65 (2H, mult.); 3.52 (6H, s); 3.81 (3H, s); 3.84 (6H, s); 6.43 (2H, s). Analysis for $C_{14}H_{24}O_5Si$: calculated, C, 55.96; H, 8.07; found, C, 55.81; H, 7.87.

2-(2,3,4,5,6-Pentafluorophenyl)ethyldimethoxymethylsilane (11). 2,3,4,5,6-Pentafluorostyrene (5.0 g, 0.026 mole) was treated to give 5.2 g (65%) of the dichlorosilane (b.p. 65–75°C/0.1 mmHg). The dichlorosilane (5.1 g, 0.016 mole) was used to give 4.77 g (97%) of silane 11 (b.p. 55–65°C/0.1 mmHg); NMR (δ): 0.14 (3H, s); 0.92 (2H, mult.); 2.74 (2H, mult.); 3.51 (6H, s). Analysis for $C_{11}H_{13}F_5O_2Si$: calculated, C, 43.99; H, 4.37; found, C, 44.00; H, 4.47.

2-(4-Cyanophenyl)ethyldimethoxymethylsilane (12). 4-Cyanostyrene (0.84 g, 6.5 mmole) was used to give 1.17 g (74%) of the dichlorosilane (b.p. 102–110°C/0.05 mmHg). The dichlorosilane (1.04 g, 4.26 mmole) was used to give 0.92 g (92%) of silane 12 (b.p. 95–99°C/0.1 mmHg); NMR (δ): 0.12 (3H, s): 0.92 (2H, mult.); 2.71 (2H, mult.); 3.49 (6H, s); 7.25 (2H, d); 7.50 (2H, d). Analysis for $C_{12}H_{17}NO_2Si$: calculated, C, 61.23; H, 7.29; found, C, 60.96; H, 7.04.

2-(3-Nitrophenyl)ethyldimethoxymethylsilane (13). 3-Nitrostyrene (1.89 g, 0.013 mole) was treated to give 1.14 g (34%) of the dichlorosilane (b.p. 120–135°C/0.1 mmHg). This dichlorosilane (0.93 g, 3.5 mmole) was used to give 0.73 g (81%) of silane 13 (b.p. 105–130°C/0.1 mmHg); NMR (δ): 0.11 (3H, s); 0.95 (2H, mult.); 2.75

(2H, mult.); 3.51 (6H, s); 7.40 (2H, mult.); 8.00 (2H, mult.). Analysis for $C_{11}H_{17}NO_4Si$: calculated, C, 51.73; H, 6.72; found, C, 51.63; H, 6.59.

General procedure for preparing polysiloxane phases from the corresponding monomers

A mixture of 1 equivalent of the phenyl-substituted dimethoxymethylsilane, 1.4 equivalents of dimethoxydimethylsilane, 2% of diethoxymethylvinylsilane and 1% of 2,2,5,5-tetramethoxy-2,5-disilahexane were dissolved in 5 ml of acetonitrile and 5 ml of water. Five drops of a 10% solution of tetramethylammonium hydroxide in methanol were added, and the mixture was stirred for 2–4 days at room temperature to effect hydrolysis. Methylene chloride (5 ml) was added, and the phases were separated. The aqueous phase was extracted with two 5-ml portions of methylene chloride. Five drops of the base catalyst solution were added to the combined methylene chloride fractions. The methylene chloride solution was polymerized under a stream of argon gas in an oven that was heated from 40°C to 115°C at 0.5°C min^{-1}. The upper temperature was maintained until the polymer was quite viscous (several hours or more). More base catalyst could be added to increase the viscosity. The resulting polymer was dissolved in methylene chloride, small amounts of a 1:3 mixture of chlorodimethylvinylsilane and hexamethyldisilazane were added, and the resulting solution was stirred overnight at room temperature to effect endcapping. The solution was washed three times with 5-ml portions of water, and the polymer was precipitated with 3–5 ml of methanol except for the polymer made from 10 where hexane was used. In the latter case, water had to be removed after the hexane was added and then the solvents were evaporated and the residue was dissolved in methylene chloride and precipitated with hexane. The mixture was centrifuged, and the supernatant solvents were discarded. The polymer was again dissolved in methylene chloride and precipitated with methanol a total of seven more times. The polymer was then dissolved in methylene chloride and filtered through a 2-μm TFE millipore filter. The solvent was evaporated, and the polymer was dried under vacuum. Polymer

TABLE I

POLYSILOXANE YIELDS AND COMPOSITIONS

Monomer	*Hydrolysis time (days)*	*Polymerization time (h)*	*Yield (%)*	*Aromatic (%)*
1	3	5	26	28
2	2	5	36	36
3	4	24	44	37
4	2	7	10	31
5	3	4.5	21	34
6*	–	–	–	–
7	4	24	32	35
8	4	24	37	33
9	3	4	56	37
10	4	3	12	30
11	3	5	22	30
12	3	3	25	35
13	3	2	9	29

* Polymer was a solid.

TABLE II

CHROMATOGRAPHIC PROPERTIES FOR POLAR AND POLARIZABLE SOLUTES ON THE METHOXYPHENYLETHYL PHASES (FROM 8 AND 9)*

Stationary phase	*Before cross-linking*				*After cross-linking*				*Rinseout (%)*
	I_{BiPh}	k	*Plates* m^{-1}	I_{ol}	I_{BiPh}	k	*Plates* m^{-1}	I_{ol}	
4-Methoxy	1569	16.9	3920	1622	1565	15.3	4460	1619	5.4
3,4-Dimethoxy	1637	17.7	3690	1703	1634	16.0	3950	1704	9.3
4-Methoxy**	1544	13.2	3900	1599	1539	12.0	4210	1680	8.5
3,4-Dimethoxy**	1629	16.8	4190	1700	1626	15.5	4240	1693	4.5

* Kováts retention indices, capacity ratios, and efficiencies measured for biphenyl (I_{BiPh}) and Kováts retention indices for dodecanol (I_{ol}) at 80°C.

** Deactivated with cyanopropylhydrosiloxane[19].

composition was determined by a careful NMR analysis. Specific details are given for each polymeric phase in Table I.

Testing of stationary phases in capillary GC

Fused-silica capillary columns (10 m × 0.20 mm I.D.; Hewlett-Packard, Avondale, PA, U.S.A.) were purged with dry nitrogen gas at 250°C for 5 h before use in

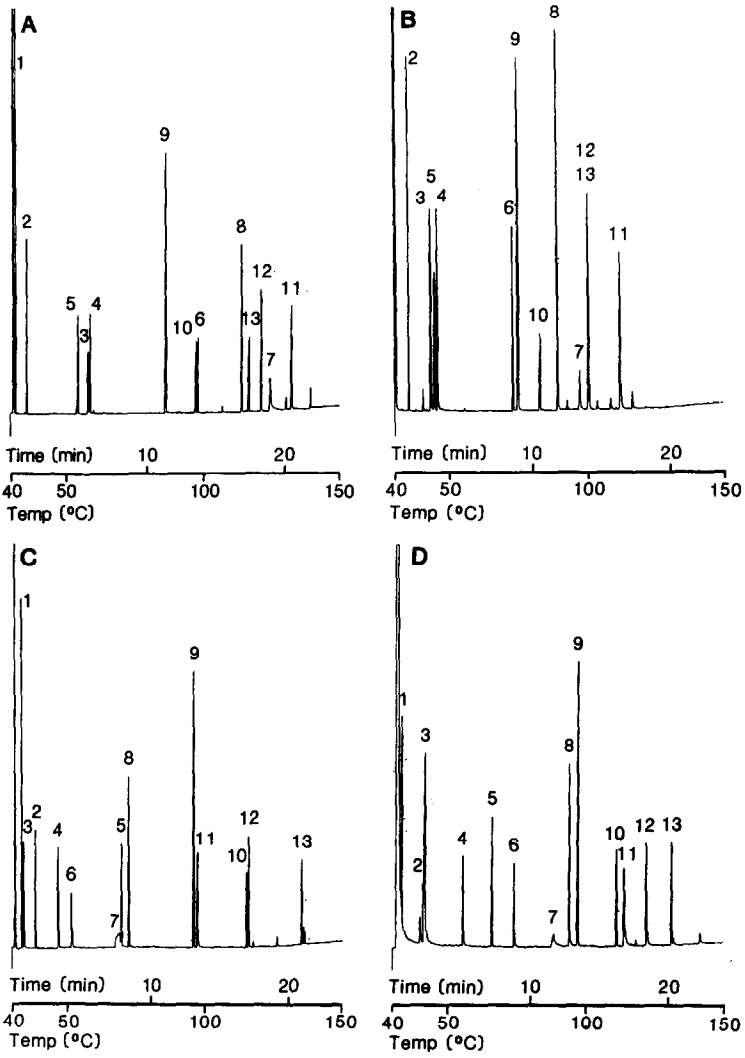

Fig. 2. Gas chromatogram of an alcohol and normal hydrocarbon standard mixture on (A) Carbowax 20M, (B) 50% cyanopropyl-, (C) 33% 4-methoxyphenylethyl-, and (D) 37% 3,4-dimethoxyphenylethyl-polysiloxane stationary phases. Chromatographic conditions: 10 m × 0.20 mm I.D. fused-silica columns; columns B, C and D were deactivated with cyanopropylhydrosiloxane deactivation; split injection at 40°C; temperature programmed from 40°C to 150°C at 5°C min^{-1}, after an initial time of 2 min. Peaks: 1 = *n*-decane; 2 = 2-octanone; 3 = 2,3-butanediol; 4 = 1-octanol; 5 = *n*-tetradecane; 6 = phenol; 7 = glycerine; 8 = 4-ethylphenol; 9 = methyl dodecanoate; 10 = octadecane; 11 = 1,8-octanediol; 12 = 1-tetradecanol; 13 = *n*-eicosane.

order to remove acidic residues from the synthetic material. Several capillaries were deactivated before coating using a cyanopropylhydrosiloxane deactivation procedure[19]. All phases were dissolved in methylene chloride and filtered through a 2-μm metalfrit filter before they were statically coated on the capillary wall. Cross-linking of the stationary phases was accomplished by purging each column with azo-*tert.*-butane at room temperature for 1 h, sealing the ends, and heating the column from 40°C to 220°C at 4°C min^{-1}, and holding the upper temperature for 40 min. After cross-linking, all columns were rinsed with 2 ml of methylene chloride and conditioned by programming from 40°C to 270°C at 1°C min^{-1} and holding at 270°C for 10 h. The columns were tested using an HP 5890 gas chromatograph equipped with a split injector and a flame ionization detector. Hydrogen was used as carrier gas at a linear velocity of 50 cm s^{-1}. The columns were tested for polarity and efficiency before and after cross-linking by calculating the retention indices and plates per metre for biphenyl and dodecanol at 80°C (see Table II).

Thermostabilities of the stationary phases were determined by measuring the bleed at increasing temperatures. The ability of the phase to cross-link was measured by the average percentage decrease in the capacity factor of normal hydrocarbons, C_{16}, C_{17} and C_{18}, after cross-linking, conditioning and rinsing the column. A standard mixture of various alcohols and hydrocarbons was used to study the selectivity of these new stationary phases (see Fig. 2).

RESULTS AND DISCUSSION

The aryldimethoxymethylsilane monomers used in this study were prepared by the two-step process shown in Fig. 1. The first step is the hydrosilylation of the relevant alkene using Speier's catalyst[13]. The resulting dichlorosilane was not completely purified but was treated with trimethyl orthoformate to obtain the dimethoxysilane monomer[9,14,15]. The dimethoxysilanes were used in all polymerization reactions because the by-product methanol can be readily removed from the reaction mixture. It is instructive to note that Birchall *et al.* had difficulty preparing polymers from dichloro-2-(pentafluorophenyl)ethylmethylsilane, the dichloro analog of compound 11[20]. The polymers were synthesized from mixtures of dimethyl- and the polar-substituted aryldimethoxymethylsilanes designed to give *ca.* 25% of the polar-substituted phenyl substituent in the final polymer. As is listed in Table I, the percentage of aromatic substitution was always greater than 25%. Evidently, a fraction of the lower boiling dimethyl monomer was lost during the hydrolysis or polymerization steps. All polymers except that prepared from monomer 6 were gums, which is required for efficient coating of capillary columns. Table I lists the polymers that were prepared along with hydrolysis and polymerization times used in polymer preparation.

The polysiloxane prepared from monomer 7 proved to be an excellent stationary phase for the GC separation of selected nitrogen heterocycles and isomers of the methylphenanthrenes[12]. Unfortunately, similar phases using methoxyphenyl polymers prepared from monomers 4 and 5 were not stable at temperatures above 200°C. Indeed, all phases containing the polar-substituted phenoxypropyl group (polymers from 1–5) were not stable at high temperatures. It is possible that the oxygen atom three carbons away from the siloxane chain attacks the chain and causes cleavage.

On the other hand, phases containing liquid-crystalline side groups attached to the polysiloxane chain through an oxypropyl link were stable at relatively high temperatures[21,22]. In the latter case, the ordered long rod-like liquid-crystalline side groups could keep the oxygen atom from approaching the polysiloxane chain. Polysiloxane phases prepared from monomers 8–13 were stable at temperatures above 200°C.

Stationary phase film rearrangement caused by a drop in viscosity at increasing temperatures is a common problem when large groups are substituted onto a polysiloxane chain. Immobilization of methoxyphenyl stationary phases prepared from monomers 8 and 9 on the capillary wall was therefore necessary. The amount of stationary phase that could be rinsed out of the column after cross-linking was only 5% (see Table II). These gum phases, coated as smooth films on the capillary wall, gave high column efficiencies of *ca.* 4000 plates m^{-1}, and they were found to be thermally stable to 280°C after cross-linking.

Dipole induced-dipole interactions dominate when a biphenyl solute is retained on the methoxyphenyl stationary phases. The retention indices (Table II) for a biphenyl solute were similar before and after cross-linking of the phases, which means that the polarizabilities of the phases were unchanged by immobilization. Hydrogen bonding properties were also unaffected by cross-linking, as can be seen from the consistent retention indices for the alcohol solute.

A mixture of several alcohols, alkanes and a methylated fatty acid was used to demonstrate the selectivity on the methoxyphenyl stationary phases compared with two commercially available polar phases. Fig. 2 shows the separation of this test mixture on fused-silica columns coated with 35% 4-methoxyphenyl, 33% 3,4-dimethoxyphenyl, Carbowax 20M and 50% cyanopropyl stationary phases. Carbowax 20M and the 50% cyanopropyl phase showed the highest retention indices for alcohols when these stationary phases were compared. From Fig. 2 it is clear, however, that alkanes and aliphatic alcohols are selectively retained on the methoxyphenyl phases compared with the retention of phenols, diols and glycerol. The use of retention indices to describe selectivity for aliphatic alcohol solutes is, in this case, misleading since the resolution of these alcohols is highest on the methoxyphenyl phases and lowest on the Carbowax 20M phase. These observations suggest the presence of strong dispersion forces in addition to moderate polarity in the methoxyphenyl stationary phases which leads to unique selectivities that cannot be achieved with the use of other available stationary phases.

The chromatographic properties shown by the two stationary phases tested in this study demonstrate the successful approach of using polar-substituted phenyl groups attached by a two-carbon spacer to a polysiloxane backbone as stationary phases in high resolution chromatography. Substitution of polar groups on the bonded phenyl functionality results in increased dipole moments in the substituents. This opens new possibilities for stable phases of increased polarity.

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