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## "BONDED PHASES" FROM CYCLIC ORGANOSILICONS FOR GAS AND LIQUID CHROMATOGRAPHY\*

WALTER A. AUE\* and PALITHA P. WICKRAMANAYAKE

5637 Life Sciences Building, Dalhousie University, Halifax, Nova Scotia (Canada)

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### SUMMARY

Non-extractable organic layers have been obtained by reacting typical organosilicon cyclics (siloxane or silazane rings) with supports common to both gas and liquid chromatography. The resulting phases performed well in both techniques.

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### INTRODUCTION

The so-called "bonded phases"<sup>1</sup> have measurably enriched analytical methodology. Research has been strong; not surprisingly so in an area where great utility is coupled with little knowledge. Making or using bonded phases still retains the flavor of an art. This, however, is helpful: it leaves the field open for future speculation and development.

That our understanding should be so limited comes as no surprise: by virtue of being "bonded", these phases lend themselves only to *in situ* structural investigation. (An exception to this statement is the interesting direct approach of Verzele *et al.*<sup>2</sup>, who dissolve bonded phases and determine the organosilicon fragments.)

From the beginning, researchers have differentiated between phases made from silicone monomers and those made from polymers—silicone or otherwise. The literature on *monomer*-derived layers is vast. Here, again, a distinction is made between materials made from monofunctional reagents ("monomeric" phases, "brushes") and those where di- or trifunctional silanes appear to have allowed the formation of polymeric structures. Whether these concepts are founded in reality is an open question.

In contrast, the literature on *polymer*-derived phases is rather scant. The major use of such layers has been deactivation in capillary gas chromatography (GC); they have also served in packed-column GC as separation media in their own right. In liquid chromatography nobody seems to have used them yet (save for our own group).

On the surface, there may seem to be a clear-cut distinction between phases

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\* Material taken from thesis work of P.P.W.

made from monomers and phases made from polymers. Under certain conditions this is reasonable, under others it becomes at least doubtful<sup>3</sup>. On one hand, traces of water, which may be around, can allow di- and trifunctional monomers to form polymers. Or, higher temperatures and the catalytic influence of the surface may bring about disproportionation of monofunctional reagents, in turn leading to polymers. On the other hand, ready-made polymers can depolymerize and the fragment monomers or oligomers react with the support<sup>4</sup>. Thermal energy and the presence of a catalyst (say an acidic or basic surface) may here, too, exert a deciding influence. The harsher the conditions of synthesis, the more questionable become arguments relating the structure of the bonded layer to the structure of the reagents that formed it. Furthermore, the bulk-phase processes to which one is accustomed, may not always be applicable to the typically 5–10 Å thin layers of modern high-performance liquid chromatographic (HPLC) packings —neither in a synthetic nor in a chromatographic context. It is also interesting to note that the procedures for making reversed phases have in recent years gone to higher and higher temperatures and, in certain cases, even required quite reactive chemical additives. All this tends to diminish the effects of functionally different starting materials.

Having included this cautionary paragraph we return to the distinction between monomers and polymers as starting substances for bonded phases. What seems to be missing here is an intermediate class —on first thought perhaps the oligomers or pre-polymers of molecular weights only a few times that of the monomer. Where do they fit? How do they react?

In polymer chemistry, of course, this sort of problem is old hat<sup>5</sup>. But there has been much less work associated with chromatographic phases. A decade ago we did fiddle around with pre-polymers, *i.e.*, short siloxane chains with reactive ends. We polymerized them further, in the flask or *in situ*, and subjected them to thermal treatments in order to change their molecular weight, diminish their extractability, etc. Various monomers were used by themselves or in mixture<sup>5,6</sup>.

Whereas we worked with packed GC columns, Madani and Chambaz<sup>7</sup> and Blomberg *et al.*<sup>8</sup> used this approach in capillary GC. The typical silicone pre-polymer, however, is not the only synthetic avenue that starts somewhere between monomer and polymer and leads to a chromatographically useful “bonded phase”.

The other possible approach is through “cyclic polymers”, *i.e.*, cyclopoly-siloxanes or cyclopoly-silazanes<sup>3</sup>. Characteristically these are six- and eight-membered rings with (three or four)  $R_2SiO$  or  $R_2SiNH$  “monomer” units; although larger and smaller sizes are also known. Most of these compounds are easily synthesized from conventional monomers, *e.g.*,  $R_2SiCl_2$ . Some are also formed from typical silicone liquid phases in an undesirable effect known to gas chromatographers as column bleed<sup>9</sup>. In industry the reverse reaction, *i.e.*, polymerization to silicones, is their *raison d'être*. Hence they are often called “cyclic monomers”, even though each molecule contains a few of the segments that a chromatographer or a silicone chemist commonly thinks of as monomer units. For purpose of this paper, we shall call these reagents “cyclic polymers”.

A look at the chemistry of such cyclic polymers<sup>3</sup> shows that they might indeed be good candidates for bonded-phase synthesis. For instance, an acidic silica surface might induce them to rearrange and bond —although what sort of rearrangements and which type of bonds and how many, is open to speculation. It appears quite

logical, therefore, to introduce the cyclic polymers as one more piece of silicone chemistry to the chromatographic realm.

These thoughts did not guide us, however, in our first encounter with a cyclic. We had been charging our routine apparatus for making bonded phases with a motley collection of monomers and polymers—on the assumption that one ought to give Mother Nature a chance to show her kindness. One of the substances thrown into the pot was octaphenylcyclotetrasiloxane. Its success made us invest in other cyclic polymers. (A variety of these compounds is available from Petrarch Chemicals, Levittown, PA, U.S.A. The catalogue of this firm, incidentally, is a veritable bonanza for researchers interested in bonded phases—besides giving them an idea what colleagues may have already tried.)

Similar to the many other monomers that have served in silica treatments outside, and often prior to, chromatographic employment, at least one cyclic, octamethylcyclotetrasiloxane, has been tried before as a surface modifier<sup>10-12</sup>.

## EXPERIMENTAL

### *Phase synthesis*

The supports were prepared as follows: silica gel 62, 60–80 and 80–100 mesh, was extracted with 6 *N* HCl at boiling point in a modified Soxhlet (Kontes) for 2 days, then rinsed with excess distilled water and dried in vacuum at 110°C for 6 h. LiChrosorb Si 100, 10  $\mu\text{m}$ , was refluxed with 6 *N* HCl for 6 h, then washed with more warm HCl and rinsed with excess distilled water (on a fine-frit glass crucible) before being dried in vacuum like silica gel 62. Porasil F, 37–75  $\mu\text{m}$ , was similarly treated. Chromosorb W, 45–60 mesh, was treated like silica gel 62, except that about 6 days were necessary for the initial extraction until the color of a fresh portion of HCl had gone down to a very slight yellow.

"Acidic" or "basic" silica gel 62 was prepared from material treated as above, by steeping in HCl (pH 3) or NaOH (pH 10), and drying in vacuum at 110°C without water rinses.

The typical synthesis took place in a simple piece of glassware that we had used before to make bonded phases from (a) a variety of polymers based on carbon or silicon<sup>13</sup>, and (b) from silicon monomers<sup>14</sup>. Nitrogen purged the unit at all times, and hexadecane was used as the typical solvent. It should be mentioned that in this type of synthesis both nitrogen and hexadecane (or any other solvent) have to be free of deleterious contaminants: nitrogen was freed of oxygen, and hexadecane was freed of polar products (such as are formed in small amounts when alkanes stand around in the lab, especially in the light). The cyclosiloxane or silazane was used in excess: about 30% of the support weight in the case of silica gel, about 10% in the case of Chromosorb. The typical synthetic approach depended somewhat on whether the cyclic reagent was a solid or a liquid at room temperature.

In the former case, the support was mixed with hexadecane and the solid organosilicon placed into a little cup, suspended about 6 in. above the hexadecane level<sup>13</sup>. The nitrogen purge was turned on and, 30 min later, heating started. The heat input was sufficient to achieve reflux, but not strong enough to let the vapor reach the reagent cup. So, during 1 h of thus controlled reflux, water could be driven off the support and the glassware, prior to the bonding reaction taking place. This was done

to provide relatively arid and, it was hoped, fairly similar and reproducible conditions for all kinds of silicic supports.

After 1 h, heating was increased and the vapor reached the polymer, which melted and/or dissolved and dripped down into the boiling hexadecane. The mixture was kept at slow boil for 6 h. (Six hours was our standard time; it is not always necessary to cook that long.) The heat was adjusted such that it just kept the support in motion (with some help from the nitrogen purge), but did not lead to particle breakup.

In case the cyclic polymer reagent was a *liquid* at room temperature, it was injected into the apparatus through a rubber septum fitted to the condenser top. The support in hexadecane had been conditioned before by a 1-h reflux as described above, and allowed to come to room temperature for the injection. As with the solid reagent, a 6-h standard reaction time was allowed at slow reflux.

After letting the reaction mixture cool to manageable temperatures, the support was shortly washed with toluene and transferred to a high-speed, continuous extractor<sup>15</sup>, where it was washed with toluene close to boiling point temperature for 10 h (again a standard time with wide safety-margin). The only exception to the sole use of toluene was an additional extraction with methanol for 5 h, to check for hydrolytic stability of a silazane-based material.

Aside from standard-type syntheses, reaction conditions were changed in certain cases to establish, on a spot basis, which treatments were and which were not necessary. For instance, synthesis with  $(\text{Ph}_2\text{SiO})_4$  (Ph = phenyl) —a compound that was tested first and served as a well-performing “standard” from then on—was carried out with tetradecane, hexadecane and octadecane as solvents; with reflux in hexadecane for 3, 6 and 12 h; with subsequent extraction by toluene for 1 h, 10 h and 1 week; and, once, without the preliminary 1-h conditioning of the support.

As a reaction medium, refluxing hexadecane was judged slightly better than either tetradecane or octadecane by chromatographic performance of the resulting phase. There was no such preference associated with the different reflux and extraction times. Three hours and 1 h, respectively, were long enough. Also, the initial removal of moisture by a 1-h reflux had no noticeable effect. When spent hexadecane was worked up, crystals separated. These were shown by a mixed melting point determination to be unchanged octaphenylcyclotetrasiloxane.

### *Phase testing*

All phases were sent for C, H and, where appropriate, N analysis. Those based on silica gel 62 and Chromosorb W were tested systematically by *gas* chromatography in standard columns with standard procedures and solutes. The temperature-programmed runs involved four sample mixtures: straight-chain alkanes with odd carbon numbers from 7 to 13; a solution of aromatics including benzene, toluene, *m*-xylene and *p*-cymene; the long-chain, primary alcohols with 5, 6 and 7 carbons; and the short-chain ones methanol, ethanol and propanol. For a special purpose, acidic and basic solutes such as phenol, aniline and pyridine, were also used.

One phase (made from octaphenylcyclotetrasiloxane and 10- $\mu\text{m}$  LiChrosorb Si 100) was packed by the conventional balanced-density technique into a short (9 cm) column, and tested in both regular and reversed-phase HPLC modes.

## RESULTS AND SPECULATIONS

In GC tests, the bonded phase produced by  $(\text{Ph}_2\text{SiO})_4$  on an acidified silica gel surface performed well, the one on the "neutral" surface did almost or just as well. However, treatment of the surface with NaOH led to a somewhat inferior phase. This, and the fact that unchanged octaphenylcyclotetrasiloxane could be recovered from the regular reaction mixture, indicates that breaking of the ring may be a surface reaction, likely induced by the "acidic" nature of silica gel. Whether other cyclic polymers react similarly was not investigated.

Table I lists some cyclic polymers and characteristics of the phases derived from them. Synthesis was usually successful, even though the same routine procedure was followed throughout, and optimization was not attempted. For instance, no attention was paid to the fact that the boiling points of some reagents fell below that of hexadecane. The synthetic conditions were essentially the same that led to successful bonded phases either from typical silicon monomers<sup>14</sup> or from various polymers of different structure and molecular weight, including some popular gas-liquid chromatographic (GLC) silicone liquid phases<sup>13</sup>.

As is commonly encountered in the history (but less commonly admitted in the literature) of bonded phases, we do not know the precise structure of the organic layer. Have the rings opened and do they stick with one or with both ends to the surface? Have they split into smaller units or even unzipped to monomers? And, if so, precisely how are these bonded? Each to two silanol groups or, in some average ratio, both to silanol groups and to each other? Or perhaps there occurs little conventional "bonding" and instead, longer chains with some cross-links are formed? And could not different cyclics, different reaction conditions, different surfaces favor one over the other bonding mechanism?

Questions of this sort concern not only the organic structure of the layer, but also the (chromatographically important) number of residual silanol groups on the silica surface. To know the latter number would, in turn, help to define the bonded layer. A detailed study of the inorganic-organic interphase is beyond the limited objectives of this paper, however, and we shall therefore restrict ourselves to mentioning a few, fairly obvious structural implications of the analytical and chromatographic results.

The maximum amount of silanol groups on a fully hydroxylated surface is often assumed to be about five per  $100 \text{ \AA}^2$  or  $8 \mu\text{moles}/\text{m}^2$ . If so, then one could compare the latter number, 8, with the  $\mu\text{moles}$  of eventually bonded monomer units,  $\text{R}_2\text{SiO}$  or  $\text{R}_2\text{SiNH}$ , per square metre. From the phase from  $(\text{Me}_2\text{SiO})_3$  ( $\text{Me} = \text{methyl}$ ) on silica gel 62 this number computes as 4.8, from  $(\text{Et}_2\text{SiO})_3$  ( $\text{Et} = \text{ethyl}$ ) as 3.5, from  $(\text{PhMeSiO})_3$  as 4.2, from  $(\text{Me}_2\text{SiNH})_4$  as (the highest) 6.8, etc. So this value, which is often called " $\alpha_{\text{exp}}$ ", is lower in each case than 8. (A cautionary note:  $\alpha_{\text{exp}}$  is not, as commonly assumed, independent of surface area<sup>14</sup>.) This agrees, in general, with the behavior of monomeric conventional reagents such as  $\text{R}_2\text{SiCl}_2$ ; although the value for the silazane is somewhat on the high side. In some cases it is possible to imagine one monomer unit reacting with two silanol groups. Other models, of course, are allowed as well. As alluded to before, the true number of residual (surface, inorganic) silanol groups—as well as the number of siloxy groups potentially capable of forming such silanols—would be of interest in this context.

TABLE I  
SYNTHESIS AND GAS CHROMATOGRAPHIC TESTS OF BONDED PHASES DERIVED FROM CYCLIC ORGANOSILICON POLYMERS  
Solvent hexadecane (b.p. 287°C), except for last case when it was dodecane (b.p. 215°C).

Cyclic polymer	B.p.* (°C)	Support (surface area, m <sup>2</sup> /g)	%C (%N)**	Gas chromatography††† (retention temperature, °C***)				Kováts' indices <sup>b</sup>					
				Alkane (C-13)	Aromatic (p-cymene) (C-7)	Long-chain alcohols (C-7)	Short-chain alcohols (C-3)	Hepta-p-Cy-nol	Pyridine	Phenol	Aniline		
(Me <sub>2</sub> SiO) <sub>4</sub>	175 (760)	Silica gel 62 (300)	2.20	Good (180)	Good (170)	Fair (240)	Fair (172)	1550	1200				
(Me <sub>2</sub> SiO) <sub>3</sub>	134 (760)	Silica gel 62 (300)	3.21	Good (158)	Good (138)	Good (185)	Fair/poor (140)	1550	1145	1430	1300	1360	
(Et <sub>2</sub> SiO) <sub>3</sub>	117 (10)	Silica gel 62 (300)	4.60	Good (185)	Good (157)	Good/fair (209)	Fair/poor (164)	1500	1090				
(PhMeSiO) <sub>3</sub>	160-190 (0.5)	160-190Silica gel 62 (300)	9.17	Good (210)	Good (170)	Good/fair (200)	Fair (150)	1250	1040				
(Ph <sub>2</sub> SiO) <sub>4</sub>	330 (1)	Silica gel 62 (300)	6.19	Good (240)	Good (11)	Not eluted	Good/fair (195)	1130	1390	1230	1350		
		Chromosorb W (45-60 mesh (1)	0.12										
		LiChrosorb Si-100, 10 μm (400)	8.36										
		Porasil F (10)	0.53										
(Me <sub>2</sub> SiNH) <sub>2</sub> 225		Silica gel 62 (300)	4.27 (0.99)	Good (170)	Good (122)	Good (122)	Poor	975	840	935	930		
		Silica gel 62 (300)	3.91 (0.31)††	Good (155)	Good (111)	Good (138)	Fair/poor (90)	1160	980	1055	820	840	
		Silica gel 62 (300)	3.75 (0.93)	Good (158)	Good (112)	Good (121)	Poor	1040	985				

\* Petracch Systems Catalog; pressures (mmHg) are in parentheses.

\*\* Guelph Chemical Laboratories.

\*\*\* Of last eluting member of series.

† Approximate — from temperature-programmed runs. Also: isotherms may be non-linear.

†† After 5 h additional extraction with methanol.

††† Of groups of compounds in a standard temperature program. Grading: good, fair, poor.

In the case of one particular bonded phase, however, further speculation was possible even without information on silanol groups. To understand why, one needs to recall that the bonds to the surface formed by a cyclosiloxane likely contain the linkage (inorganic)Si-O-Si(organic). Whether the oxygen link has been contributed by the surface or by the reagent is not known. It is also not known whether there are many linkages with short, perhaps monomeric appendages, or whether there are but a few anchor points with longer chains attached. With a silazane, however, the situation is different: nitrogen can be easily determined by elemental analysis.

The phase from  $(\text{Me}_2\text{SiNH})_4$ , toluene extracted, contains 4.27% C and 0.99% N. That means that for about every five monomer units bound (as judged by the carbon content), only two nitrogen atoms remain. One could be tempted to calculate an average chain length on the basis, but to do so would mean to assume answers to a couple of important questions: are bonds to the surface formed via oxygen or via nitrogen, and in what form and/or combination? Has some liberated ammonia been chemisorbed by the silica surface?

Because it was easy to do, we secured additional experimental evidence in this case of a silazane-based phase. It is well known that silazanes hydrolyze (or methanolize) much easier than siloxanes. Hence we extracted the phase, which had already been extracted with toluene for 10 h, with (close to boiling) methanol for a further 5 h. This decreased its carbon content by a small amount, from 4.27 to 3.91%; but dropped its nitrogen content drastically, from 0.99 to 0.31%. The latter number means that now there remains only one nitrogen for every seven to eight  $(\text{CH}_3)_2\text{Si}$  units.

And that indicates, of course, that most surface bonds are Si-O-Si, not Si-NH-Si. Furthermore, it favors the model of bound, single monomer units (except that NH in the original  $\text{R}_2\text{SiNH}$  unit has now been largely replaced by oxygen), rather than the model of longer silazane chains (which would have retained more of the original nitrogen).

Whether the validity of speculation on a silazane-derived phase extends to phases made from siloxanes, is not known. The  $\alpha_{\text{exp}}$  values for siloxane-bonded material are considerably lower than 8 and comparable to conventional literature data. That supports, or at least does not rule out, a similar model of bonded monomer units. (For comparison, a dense population of bonded oligomeric chains would have given  $\alpha_{\text{exp}}$  values above 8, owing to our use of the monomer unit as the basis for calculation.)

Chromatographic evidence also seems to support the bonded-monomer or bonded-short-segment model. If longer chains were involved, there would remain on the surface a proportionately larger number of free silanol groups. The fact that some phases allowed even lower alcohols to elute (in contrast to neat silica gel, which does not) suggests that the number of free hydroxyls was considerably reduced.

Thus, in general, the chromatographic "success" of a synthesis was reflected by the resulting phase's carbon content. The higher the carbon content the better usually GC response to the test mixture. Alkanes, of course, always give good chromatography—even on bare silica gel 62. So do the aromatics. But already the long-chain alkanols begin to vary in behavior on different phases, and these variations become pronounced for the lower alcohols. Some phases, incidentally, will not even allow elution of the latter group of compounds—at least not with shapes that could qualify as *bona fide* peaks. Fig. 1 shows gas chromatography [or closer defined:

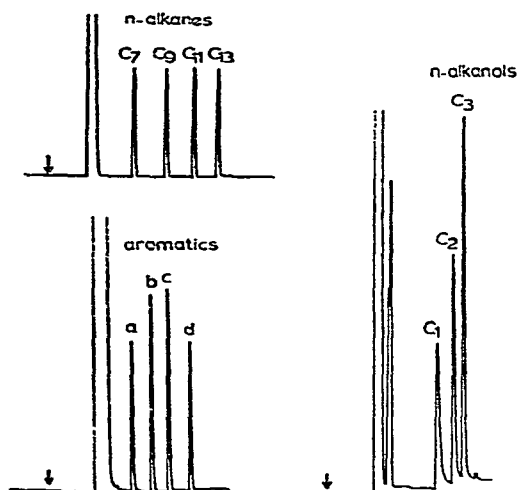


Fig. 1. Test gas chromatograms of a bonded phase derived from  $(\text{Ph}_2\text{SiO})_4$  and silica gel 62. Carbon numbers as indicated. Peaks: a = benzene; b = toluene; c = *m*-xylene; d = *p*-cymene. Standard temperature program:  $8^\circ/\text{min}$  from 40 to  $220^\circ\text{C}$  (if necessary up to  $250^\circ\text{C}$ ).

gas-solid chromatography (GSC) on a modified surface] of three GC test mixtures eluting from a bonded phase made from octaphenylcyclotetrasiloxane and silica gel 62.

If the alkanes are used to determine chromatographic efficiency, the results are satisfactory in the context of GSC. Reduced plate heights between 2 and 3 were often measured on the silica gel-bonded phases. (We only tested one Chromosorb phase; it did not perform as well.)

"Deactivation" is also quite good as shown by the acceptable chromatography of the lower alkanols—considering the fact that one deals with a silica gel of some  $300 \text{ m}^2/\text{g}$  with only a nominal  $3 \text{ \AA}^{14}$  layer of siloxane "bonded" to a surface that contains, in addition, an unknown number of silanol groups. (The alcohol peaks, in fact, suggest that the latter number is not too large.)

Table I lists some selected retention temperatures and (very approximate) Kováts' indices. Now, we do realize that the chromatographic phase under study is not a proper one for the measurement of these indices (and the image of "polarity" they convey). However, the results are sufficiently interesting to justify a bit of misuse. It turns out that the retention of polar solutes on the silazane-derived phase is less than on phases synthesized from siloxane rings. Is the cause a different layer structure, the effect of residual organic nitrogen, the chemisorption of ammonia, the shielding or replacement of silanol groups, the relatively high load? We don't know, but the fact that the cyclosilazane yielded a "less polar" phase is possibly important. Furthermore, that behavior does not change too drastically with the additional methanol extraction.

Microparticulate bonded phases based on silicone monomers are currently much en vogue, and suggest testing by liquid chromatography. A short (9 cm) column was packed for that purpose. As Fig. 2 shows, the standard material based on  $(\text{Ph}_2\text{SiO})_4$  does give a reversed-phase type separation of an aromatic mixture, benzene to *p*-cymene (similar to the one used in the GC trials).



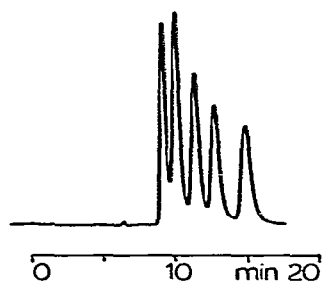


Fig. 2. Liquid chromatography on a bonded phase derived from  $(\text{Ph}_2\text{SiO})_4$  and LiChrosorb Si 100,  $10 \mu\text{m}$ . Peaks according to increasing retention time: (air); benzene; toluene; ethylbenzene; cumene; *p*-cymene. Column:  $9 \times 0.41 \text{ cm}$  I.D. Solvent: methanol-water (60:40) at  $0.2 \text{ ml/min}$ .

It has been known for some time that bonded phases lend themselves well to liquid chromatography with all kinds of additives. Here we have used long-chain alcohols<sup>16</sup> to demonstrate such an effect on our packing. Table II shows the resolution of two pairs of peaks and the reduced plate height. The latter does not change, while the added alcohol produces a large increase in retention and, for the chosen pairs, in resolution. This was to be expected. One could probably characterize such conditions as being closest to liquid-liquid chromatography.

TABLE II

HPLC EFFICIENCY, AND RESOLUTION OF SELECTED SOLUTE PAIRS, ON ADDITION OF ALCOHOL

	<i>Mobile phase</i>			
	<i>Methanol-water</i> (60:40)	<i>Methanol-water</i> (60:40) +0.5% <i>heptanol-1</i>	<i>Methanol-water</i> (60:40) +5% <i>heptanol-1</i>	<i>Methanol-water</i> (60:40) <i>saturated with</i> <i>dodecanol-1</i>
<i>R</i> (cumene/ <i>p</i> -cymene)	2.1	2.6	2.8	6.8
<i>R</i> (phenanthrene/pyrene)	2.5	2.7	2.8	7.4
<i>h</i> (cumene)*	3.2	3.1	3.0	3.3

\* Reduced plate height,  $\text{HETP}/d_p$  ( $d_p = 10 \mu\text{m}$  nominal).

The changes that the alcohol brings about—after some time of equilibration but otherwise without too much trouble—are shown in Figs. 3 and 4. The former represents liquid chromatography of *n*-alkyl benzenes on a 9-cm column. Fig. 4 then plots their retention, in alcohol-free and alcohol-saturated systems, and compares it with that of some aromatics. It is satisfying to see how the alkylbenzenes are pulled apart by the presence of the alcohol.

Also, how the retention behavior of compound groups changes against one another. If we may abuse Kováts' indices and the polarity concept once more, and assign benzene the index 0, toluene 100, ethylbenzene 200, etc., then biphenyl, for instance, changes its index with the addition of dodecanol from 400 to 270. The stationary phase has become "less polar". Not that there is much new about that—it is simply included here to demonstrate the phase's behavior.

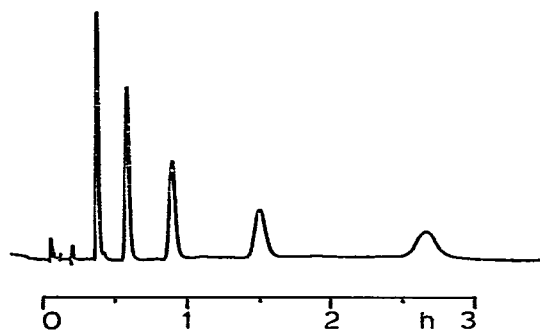


Fig. 3. Liquid chromatography on the same column as used for Fig. 2. Elution sequence of peaks: (air); benzene; toluene; ethylbenzene, *n*-propylbenzene; *n*-butylbenzene. Solvent: methanol-water (60:40) saturated with dodecanol-1, at 0.2 ml/min.

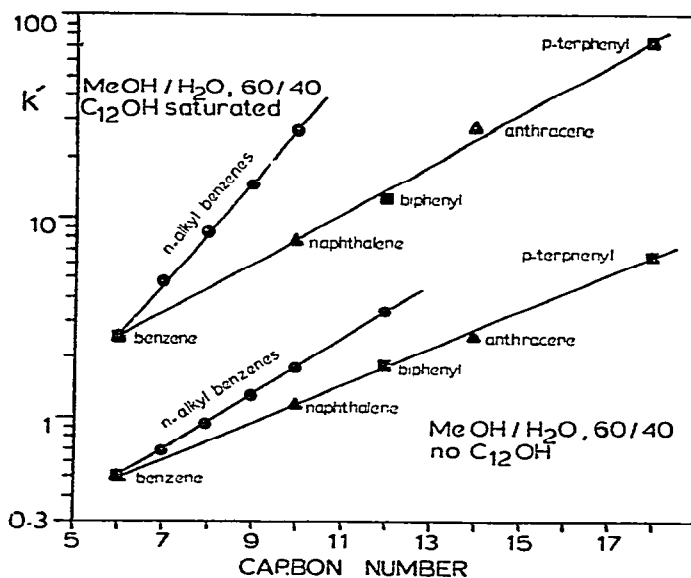


Fig. 4. HPLC capacity ratios for various test compounds with solvent free of, or saturated with, dodecanol. See Figs. 2 and 3 for typical chromatograms.

What the particular advantages and disadvantages of such "cyclic polymer" phases are, is difficult to define at present. The reagents are relatively stable and easy to handle and we have certainly not noticed any poorer chromatography because of their (only potentially) "polymeric" structure. In fact, we obtained comparable chromatographic performances from supports treated (a) with silicone monomers, (b) with cyclic organosilicon polymers and (c) with long-chain silicones (as well as with certain long-chain carbon polymers). Whether this is due to layers being just a few Ångströms thin; or to monomers polymerizing and (more likely) polymers depolymerizing; or to a combination of these plus perhaps some as yet unrecognized effect, is up for discussion.

It is clear, however, that bonded phases of good chromatographic quality for both GC and LC can be produced from cyclic organosilicon polymers by simple and inexpensive laboratory techniques. And that may be helpful to the practicing chromatographer.

#### ACKNOWLEDGEMENT

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