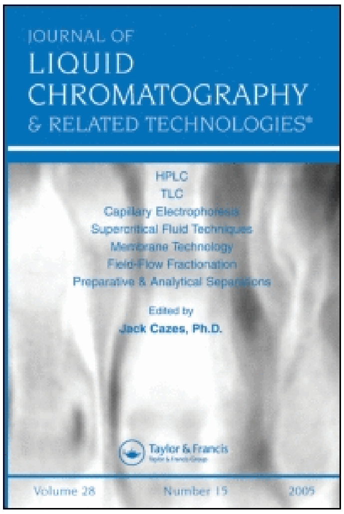


## Journal of Liquid Chromatography & Related Technologies

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

# Synthesis and Characterization of Liquid Crystal Type Stationary Phases on a Silica Hydride Surface

Joseph J. Pesek[a]; Maria T. Matyska[a]; Eric J. Williamsen[a]; Ruby Tam[a]; Zhuxu Wang[a]
[a] Department of Chemistry, San Jose State University, San Jose, CA, USA

**To cite this Article** Pesek, Joseph J. , Matyska, Maria T. , Williamsen, Eric J. , Tam, Ruby and Wang, Zhuxu(1998) 'Synthesis and Characterization of Liquid Crystal Type Stationary Phases on a Silica Hydride Surface', Journal of Liquid Chromatography & Related Technologies, 21: 18, 2747 — 2762

**To link to this Article: DOI:** 10.1080/10826079808003440

**URL:** http://dx.doi.org/10.1080/10826079808003440

J. LIQ. CHROM. & REL. TECHNOL., 21(18), 2747–2762 (1998)

# SYNTHESIS AND CHARACTERIZATION OF LIQUID CRYSTAL TYPE STATIONARY PHASES ON A SILICA HYDRIDE SURFACE

Joseph J. Pesek,* Maria T. Matyska, Eric J. Williamsen,
Ruby Tam, Zhuxu Wang

Department of Chemistry
San Jose State University
One Washington Square
San Jose, CA 95192, USA

## ABSTRACT

Two liquid crystal materials, 4-methoxyphenyl-4-allyloxybenzoate and cholesteryl-10-undecenoate, containing terminal olefin groups are bonded to a silica hydride surface via a metal complex catalyzed hydrosilation reaction. Bonding is confirmed by DRIFT, carbon-13 CP-MAS NMR and DSC. The effects of different catalysts, reaction temperature, catalyst to olefin ratio, and reaction time were studied to maximize the surface coverage. Chromatographic studies indicate that these bonded materials behave similarly to liquid crystal phases prepared by organosilanization. The hydrosilation method offers the possibility of bonding a wider variety of liquid crystal moieties in order to utilize the unique separation properties of these materials.

www.dekker.com

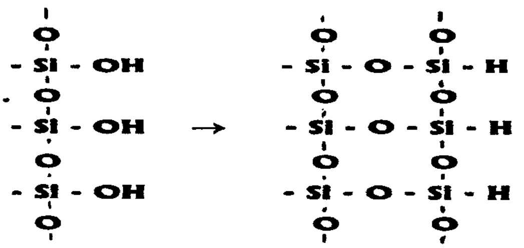
## INTRODUCTION

Specialty stationary phases with specific selectivities and/or applications have an important role in the usefulness of HPLC as a separation and analytical method. Some examples of such materials are chiral and ion-exchange phases that are suitable for the analysis of enantiomers and charged or polar species respectively. Within these broad categories the stationary phases are further subdivided into more specific materials that have an even narrower range of applications. For example, in chiral separations the stationary phase could be a Pirkle type, which is based on a three-point interaction mechanism, or a cavity type such as cyclodextrin, which has a specific pocket shape to resolve certain enantiomeric mixtures.

Separation of compounds in a mixture has been accomplished based on the shape of the molecule using structural features such as length to breadth ratio and planarity. While these differences are not as subtle as chirality, they offer a means of separation beyond the gross properties of hydrophobicity used in the reverse-phase mode or hydrophilicty used in the normal phase mode. For example, it was shown that polymeric $C_{18}$ phases were able to separate various polycyclic aromatic hydrocarbons (PAHs) better than monomeric phases as a result of greater discrimination based on molecular shape.[1,2] It has been concluded that the polymeric materials possess a high degree of ordering on the surface so that molecules which are more planar or have a large length to breadth ratio will be retained longer.[3] It has also been shown that $C_{30}$ bonded moieties are highly associated in reverse phase experiments[4] and therefore are effective for separations which are partially based on molecular shape. The effective separation of vitamin A acetate isomers[4] and carotenoid isomers[5] by $C_{30}$ columns has been attributed to bonded phase rigidity.

Bonded liquid crystals also appear to possess a high degree of association, perhaps even greater than polymeric $C_{18}$ phases, which results in enhanced selectivity based on the shape of the solute.[6-11] Solid state, cross-polarization magic-angle spinning (CP-MAS) NMR studies have been used to monitor the molecular motion of various organic moieties bonded to silica surfaces.[12] In comparison to a common stationary phase like $C_{18}$, two bonded liquid crystal materials, 4-methoxyphenyl-4-allyloxy benzoate (MPAB) and cholesteryl-10-undecanoate, displayed anomalies in the plots of spin-spin relaxation time ($T_2$) as a function of temperature (1/T). Instead of a relatively constant decrease in $T_2$ with respect to 1/T, plots for both liquid crystals had temperature ranges where increases occurred. This behavior was attributed to strong association between neighboring bonding moieties that resulted in "phase-like" transitions or significant changes in molecular ordering on the surface. Manipulation of these effects might provide a means for controlling chromatographic retention and selectivity.

The earlier studies of bonded liquid crystal stationary phases involved materials made by conventional organosilanization. A potentially more versatile approach for attaching such moieties to oxide supports is through the use of the silanization/ hydrosilation method for modifying surfaces.[13-15] In this reaction sequence the first step involves formation of a hydride layer by controlled deposition of triethoxysilane (TES) as shown below for a silica surface:

I).


The organic moiety is then attached to the hydride surface via a hydrosilation reaction as follows:

II). $-Si-H + CH_2 = CH-R \xrightarrow{Catalyst} -Si-CH_2-CH_2-R$

While terminal olefins are the most common functionality used in these reactions,[16] a number of other unsaturated groups such as alkynes, carbonyls, nitriles, and isocyanates are also possible. Liquid crystal compounds with all of these functional groups are available commercially or can be synthesized from examples in the literature. The materials described in this study are the result of attaching a liquid crystal compound possessing a terminal olefin group to a silica hydride surface. In addition to the syntheses, some preliminary chromatographic data on these stationary phases will also be presented.

## EXPERIMENTAL

### Materials

One liquid crystal, which could be bonded to a silica hydride surface, cholesteryl-10-undecenoate, was purchased from Sigma (St. Louis, MO, USA) and used as received. The second compound, 4-methoxyphenyl-4-allyloxybenzoate, was synthesized according to the method of Apfel et al.[17] Chloroplatinic acid hexahydrate (Strem Chemical, Newburyport, MA, USA) in isopropanol (J.T. Baker, Phillipsburg, NJ, USA), chlorotris(triphenylphosphine)-rhodium in benzene (J.T. Baker), or 1,2-bis(diphenyl-phosphino) ethane nickel (II) chloride (Strem Chemical) in benzene were used for catalyst solutions in the hydrosilation reaction. Triethoxysilane (United Chemical Technologies, Bristol, PA, USA) was used for the synthesis of the silica hydride. Silica (6.5 μm particle diameter, 380 Å mean pore size and 106 $m^2/g$) was obtained from The Separations Group (Hesperia, CA, USA). Two polycyclic aromatic hydrocarbon test mixtures (SRM 869 and SRM 1647c) were obtained from the National Institute of Standards and Technology (Gaithersburg, MD, USA). Other solutes for chromatographic testing were obtained from Aldrich (Milwaukee, WI, USA) in the highest purity available and were dissolved in the appropriate solvents without further purification. HPLC grade solvents (Burdick & Jackson Laboratories, Muskegon, MI, USA) were filtered before use and water was purified by a Milli-Q™ system (Millipore Corp., Bedford, MA, USA).

## Bonded Phase Synthesis

The silica hydride intermediate was prepared according to a previously described procedure.[13] Addition of the olefin via hydrosilation required the following process in both cases for a five gram batch of product. About 1.5 mmol of olefin was placed in a dry three-necked 250 mL round-bottom flask containing 75 mL of distilled toluene and equipped with a condenser, a thermometer, and a glass stopper. The solution was stirred well for several minutes and then the appropriate amount of catalyst was added so that the catalyst:olefin ratio was $2 \times 10^{-3}$. The solution was heated and maintained at 70° for about one hour. Then about 5 g of silica hydride was added slowly to the mixture, the flask was flushed with nitrogen, the temperature was raised to 100° and reaction was allowed to proceed for 96 hours. Upon completion of the synthetic period, the product was divided into four equal amounts and centrifuged followed by washing with toluene four times, methylene chloride twice, and ether twice. Between washings the product was centrifuged and the supernatant liquid was removed followed by addition of the next wash solvent. After the final portion of ether was removed, the material was dried at room temperature overnight followed by 24 hours in a vacuum oven at 110°.

## Spectroscopic and Thermal Characterization

Infrared spectra were acquired in the diffuse reflectance mode (DRIFT) on a Perkin-Elmer (Norwalk, CT, USA) Model 1800 spectrometer. Spectra were acquired in the single beam mode from 4000-450 $cm^{-1}$ with 2 $cm^{-1}$ resolution using a deuterated triglycine sulfate (DTGS) detector. The sample was mixed with pure KBr in a 1:1 ratio. A background spectrum of KBr was used as a reference. Solid state NMR spectra were acquired on a Bruker (Billerica, MA,

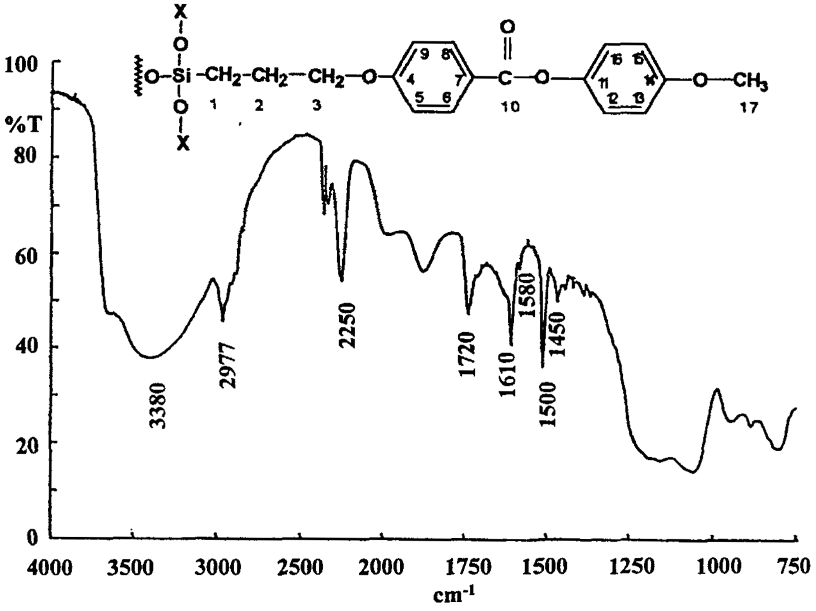


Figure 1. DRIFT spectrum of MPAB bonded to a silica hydride surface.

USA) MSL 300 spectrometer. Details of the experimental conditions are given elsewhere.[12] Differential scanning calorimetry data were obtained on a Perkin-Elmer Model DSC-7 instrument using uncovered platinum pans. The analysis was done in air over a temperature range of 50-600°C using an empty sample pan as a blank. Analyses for carbon were determined on a Perkin-Elmer Model 240C Elemental Analyzer.

## HPLC Measurements

The bonded materials were packed by a pneumatic amplification method into 150 x 4.6 mm stainless steel tubes as a slurry in 90:10 chloroform/methanol using methanol as the driving solvent. Mobile phases were degassed with helium for at least 10 min before use. The void volume was measured by means of a potassium nitrate peak.

A Model 1050 HPLC system from Hewlett-Packard (Palo Alto, CA, USA) consisting of a quaternary pump, a multi-wavelength absorbance detector, and an autosampler was used for all chromatographic experiments. The system was controlled by an HP Vectra 05/20 computer via an HP 35900 interface.

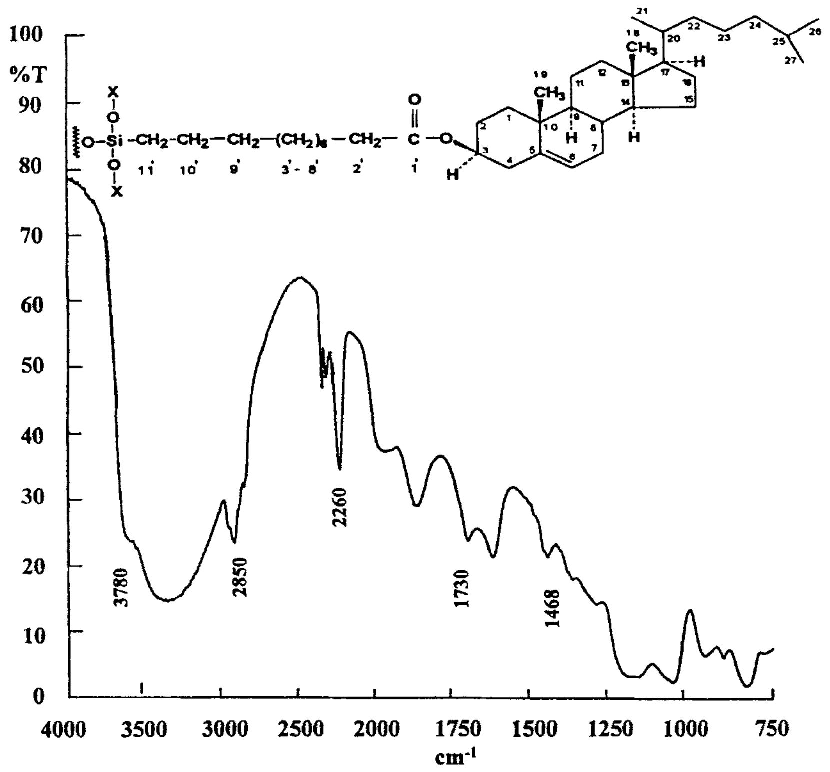


Figure 2. DRIFT spectrum of cholestryl-10-undecenoate bonded to a silica hydride surface.

## RESULTS AND DISCUSSION

Success of the bonding process can be easily monitored via DRIFT spectra, which provide information about the key functional groups, attached to the silica hydride surface. Figure 1 shows the DRIFT spectrum after the reaction of silica hydride with 4-methoxyphenyl-4-allyloxybenzoate (MPAB). The essential features of the spectrum are the carbon-hydrogen stretching bands near 3000 cm$^{-1}$, a peak for residual Si-H groups at 2250 cm$^{-1}$, the carbonyl stretching band at 1720 cm$^{-1}$ and aromatic bending bands at 1610, 1580, 1500, and 1450 cm$^{-1}$. Figure 2 shows the DRIFT spectrum of the product from the reaction of silica hydride with cholesteryl-10-undecenoate. The bonded material can be identified by bands near 3000 cm$^{-1}$ for carbon-hydrogen stretching, a peak 1730 cm$^{-1}$ for the carbonyl stretch, and an unsaturated carbon-hydrogen bending band at 1468 cm$^{-1}$. The spectrum also has a peak at 2250 cm$^{-1}$ which is due to the unreacted

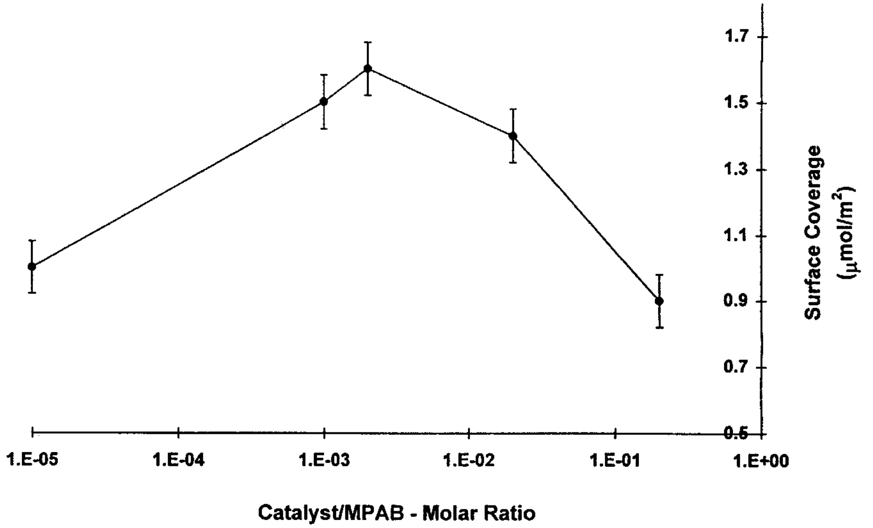


**Figure 3**. Surface coverage (μmol/m$^2$) vs. catalyst to olefin ratio for the bonding of MPAB to silica hydride using hexachloroplatinic acid as the catalyst.

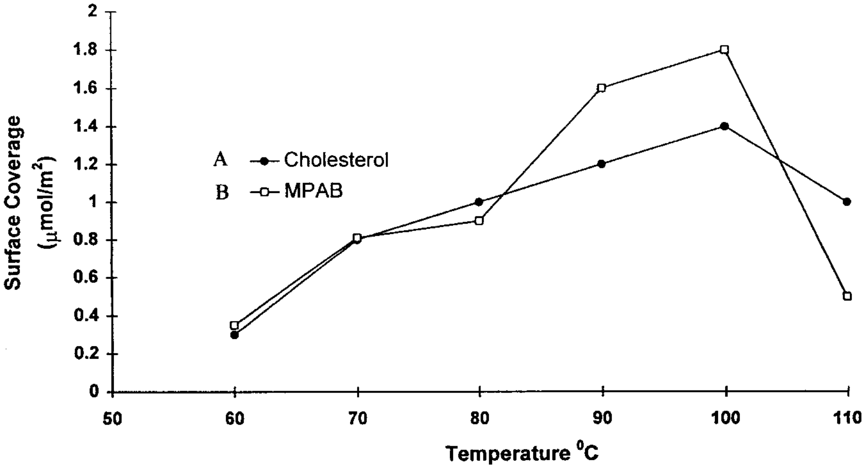


**Figure 4**. Surface coverage (μmol/m$^2$) vs. temperature for the bonding of the two liquid crystals to a silica hydride surface using chlorotris-(triphenylphosphine) *rhodium as the* catalyst. A) cholestery 10-undecenoate and B) MPAB.

hydride groups. These bonded materials have also been characterized by $^{13}C$ CP-MAS NMR and have been reported previously[12]. The solid state NMR spectra also confirm the bonding of the two liquid crystals to the silica hydride surface via hydrosilation.

Due to the large size and unusual nature of the bonded moieties, it was necessary to study the reaction conditions in order to maximize the amount of ligand attached to the surface. First, a number of catalysts were tested and two were found to consistently produce the highest yields: hexachloroplatinic acid which has been used in all of the previous hydrosilation studies on silica hydride surfaces[15] and chlorotris(triphenyl-phosphine)-rhodium. Second, an appropriate catalyst:olefin ratio was determined in previous studies[13] to be an important factor in achieving adequate bonding. A typical study for the liquid crystal MPAB using hexachloroplatinic acid is shown in Figure 3. Both catalysts generally gave a maximum yield of bonded phase at a ratio of catalyst to olefin about 2 x $10^{-3}$ for MPAB and cholesterol. Figure 4 shows the effect of temperature on the bonding of both liquid crystals to silica hydride at the optimum catalyst to olefin ratio. It is clear that maximum yield occurs near 100°C.

A study of reaction time using both catalysts on each liquid crystal resulted in continuously increasing yield up to about 96 hours with little improvement at longer times. According to these results bonding of the liquid crystal materials used for column studies was done at 100° for 96 hours. Under the optimum conditions developed above, a third catalyst, 1,2-bis(diphenylphospino)ethane Nickel (II) was also tested. Yields for a single test on each liquid crystal resulted in 1.5 $\mu$mol/m$^2$ for cholesterol and 2.03 $\mu$mol/m$^2$ for MPAB. Clearly it appears from the limited studies here that other transition metal complexes in addition to Spier's catalyst are applicable to the hydrosilation of olefins on silica hydride surfaces.

In addition to the DRIFT and CP-MAS characterization described above, both bonded liquid crystal materials were analyzed by differential scanning calorimetry (DSC). Figure 5A shows the DSC thermogram of the hydride surface with a single peak near 450°C representing the oxidation of the Si-H group to silanols. After bonding, the DSC thermogram undergoes noticeable change. In the case of the cholesterol compound, two peaks are seen in the thermogram (Figure 5B). It is apparent that the presence of the bonded moiety effects the properties of the hydride species since there no longer is a peak at 450°C but peaks at 407°C and 380°C.

Both DRIFT and $^{29}Si$ CP-MAS NMR spectra confirm the presence of hydrides on the surface after bonding of the liquid crystals. Therefore, it is likely that one of the peaks represents residual hydrides on the surface but

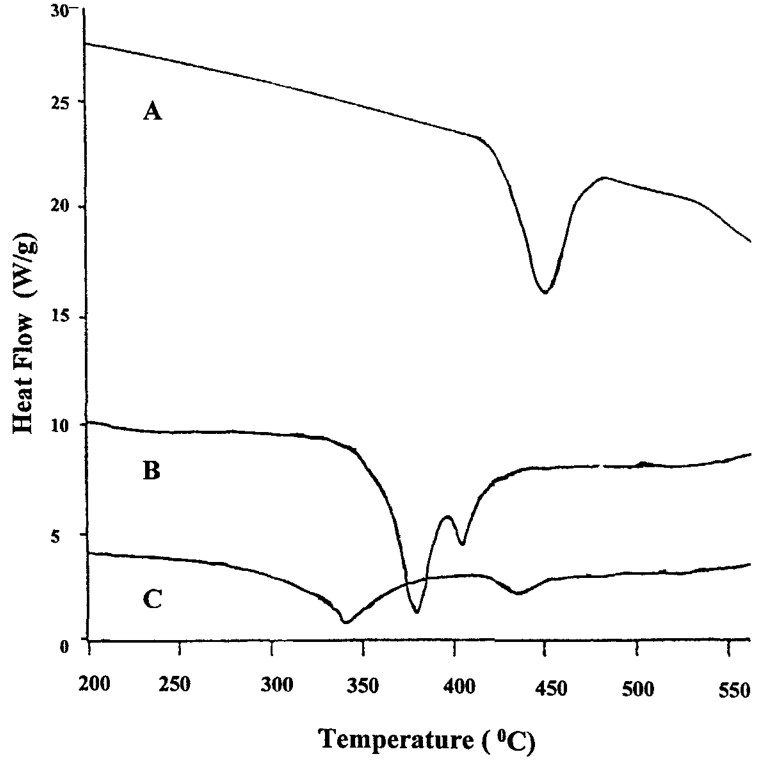


**Figure 5.** DSC thermograms of modified silica materials. A) silica hydride, B) silica hydride after modification with cholestery 10-undecenoate, and C) silica hydride after modification with MPAB.

shifted from the original position for a pure hydride surface while the other is due to oxidation of the bonded organic moiety. A similar result is obtained for the bonded MPAB material (Figure 5C) but with peaks at 340°C and 440°C. These results support the conclusions of the spectroscopic studies which indicate that the liquid crystals are bonded to rather than physically coated on the surface.

In order to test the hydrolytic stability of the bonded liquid crystal materials, about 300 mg of each phase was placed in 100 mL of pH 2 and 8 solutions. A small aliquot from each of the continuously stirred four samples was removed daily and an elemental analysis for carbon was obtained for the isolated solids. The percent carbon was then converted to surface coverage, expressed as $\mu mol/m^2$, according to a modified form[13] of the equation developed

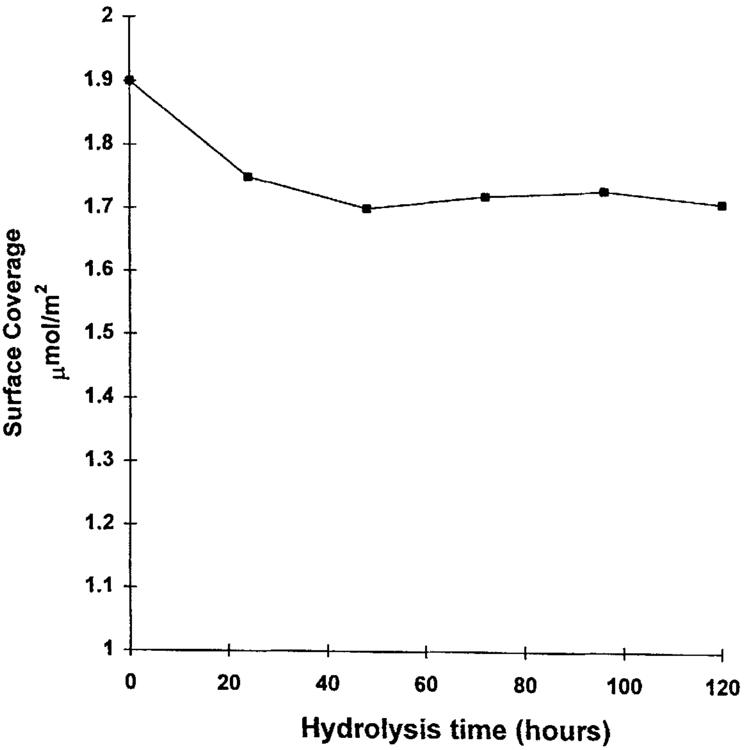


**Figure 6.** Surface coverage (μmol/m$^2$) vs. hydrolysis time for cholesterol phase at pH 8.

by Berendsen and De Galan.[18] The results obtained over five days for the cholesterol phase at pH 8 are shown in Figure 6. Results for the cholesterol material at pH 2 and the bonded MPAB at both pH 2 and 8 are similar to the data in Figure 6, i.e. a rapid initial decrease in the surface coverage followed by little change in the amount of carbon determined by elemental analysis. Since the results seem independent of pH and the type of bonded moiety, the most likely explanation is the hydrolysis of residual ethoxy groups from TES, which are present when the hydride intermediate is formed on Vydac silica.[19] This explanation is supported by the carbon-13 CP-MAS NMR spectrum of the hydrolyzed cholesterol material after 5 days at pH 8 shown in Figure 7. In comparison to the spectrum of the bonded phase after synthesis,[11] the peaks for the ethoxy group at 17 and 60 ppm have almost completely disappeared. Therefore, it appears that the bonded liquid crystals are both stable for reasonable periods of time at pH 2 and 8 so that chromatographic testing can be used to further characterize the materials.

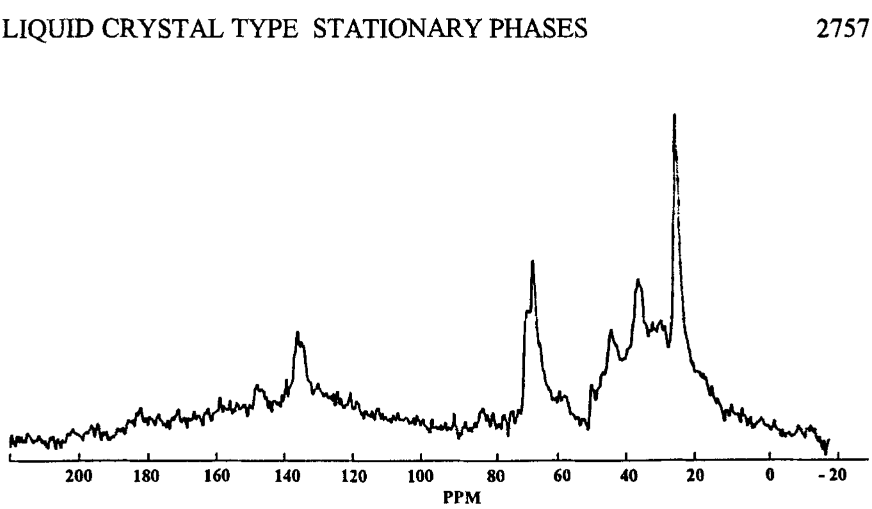


**Figure 7.** Carbon-13 CP-MAS NMR spectrum of cholesterol phase after hydrolysis for five days at pH 8.

The mixtures used for chromatographic testing were reference materials of polycyclic aromatic hydrocarbon (PAH) mixtures from the National Institute of Standards and Technology (NIST). The first, SRM 869, has been developed to classify bonded stationary phases according to whether they are monomeric or polymeric in nature.[3] Figure 8A shows the chromatogram of this three component mixture on the cholesterol bonded phase. The pattern is typical of one observed for stationary phases classified as intermediate. These materials are often highly loaded monomeric materials and it has been demonstrated in past studies that bonded liquid crystal phases seem to fall into this category as well.[8-10] This is probably due to the high degree of association of adjacent ligands which makes them different from other monomeric phases.[12] The bonded phases in this study are in reality monomeric materials since there is only a single point of attachment between the organic moiety and the silica surface. Further confirmation of the intermediate classification is obtained from the relative retention between two of the solutes, 1,2:3,5,6:7,8-tetrabenzonaphthalene (TBN) and benzo[a]pyrene (BaP). The relative retention, $\alpha_{TBN/BsP}$, calculated for the cholesterol phase is 1.48. The values for polymeric phases are between 0.62 and 1.33 while those for monomeric phases are between 1.78 and 2.12. Figure 8B shows the same mixture on the MPAB column and the pattern is still typical of an intermediate column but closer to a monomeric phase. This result is confirmed by the value of $\alpha_{TBN/BaP}$ which is 1.68. Therefore, both the retention patterns and the relative retentions of the two test solutes in this mixture confirm that the cholesterol and MPAB liquid crystal phases on hydride surfaces are similar to those made via an organosilane process.

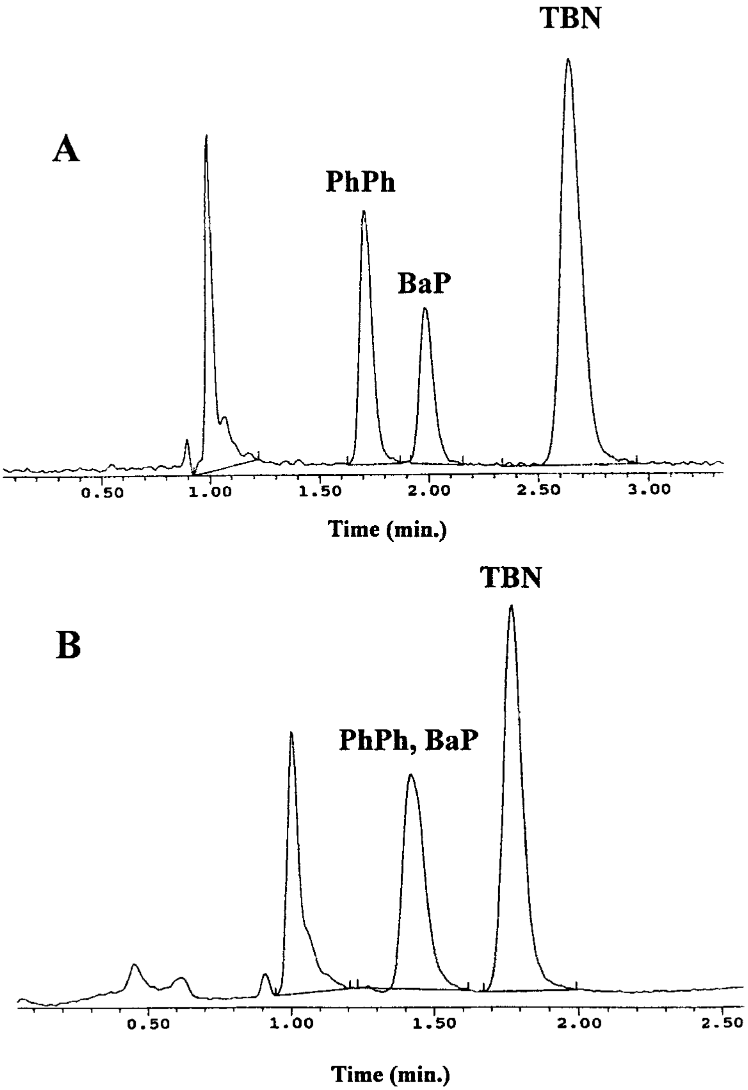


**Figure 8**. Chromatograms of three component PAH mixture (SRM 869) used for classification of stationary phase. A) cholesterol phase and B) MPAB phase. Mobile Phase: 85:15 acetonitrile/water. UV detection at 254 nm and flow rate = 2.0 mL/min. Solutes: PhPh = phenanthro[3,4-c]phenanthrene; BaP = benzo[a]pyrene; and TBN = 1,2:3,4:5,6:7,8-tetrabenzonaphthalene.

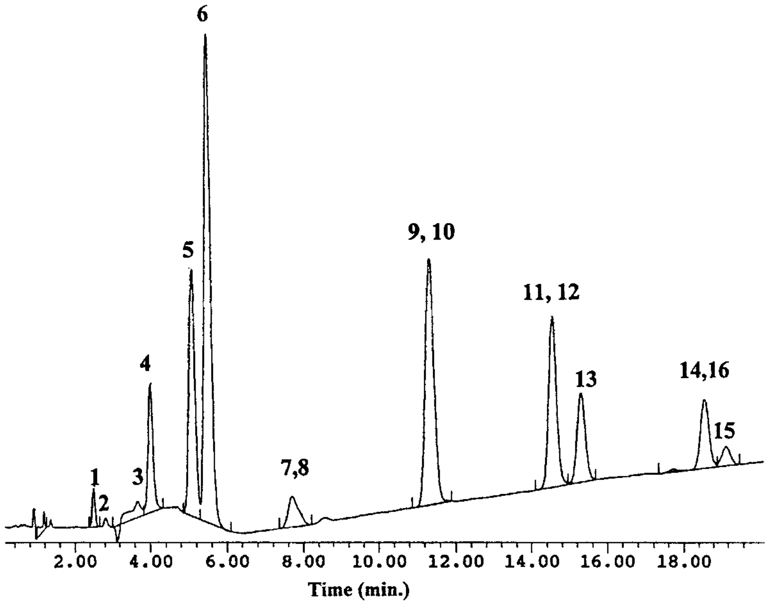


**Figure 9.** Chromatogram on cholesterol phase of 16 component PAH mixture (SRM 1647c) for testing molecular shape discrimination. Mobile phase: gradient of acetonitrile in water from 40%-70% in 15 min. UV detection at 254 nm and flow rate = 2.0 mL/min. Solutes: 1 = naphthalene; 2 = acenaphthylene; 3= acenaphthene; 4 = fluorene; 5 = phenanthrene; 6 = anthracene; 7 = fluoranthene; 8 = pyrene; 9 = benz[a]anthracene; 10 = chrysene; 11 = benzo[b]fluoranthene; 12 = benzo[k]fluoranthene; 13 = benzo[a]pyrene; 14 = dibenz[a,h]anthracene; 15 = benzo[ghi]perylene; 16 = indeno[1,2,3-cd]pyrene.

The second reference material, SRM 1647c, consists of sixteen PAHs which can be used to classify the stationary phase according to its ability to separate based on molecular shape, i.e. size, length to breadth ratio, and planarity. The comparison is made between the new phase and typical monomeric or polymeric octadecyl bonded materials using an acetonitrile/water gradient as the mobile phase. The chromatogram of this mixture for the cholesterol bonded phase is shown in Figure 9. The number of peaks refers to their elution order on a typical polymeric $C_{18}$ phase.[1] There are twelve peaks, although the one at 7.7 min has a shoulder, so that four pairs of compounds are incompletely resolved under these conditions. The basic pattern is similar to that obtained for intermediate phases with several notable exceptions. First peaks 3 and 4, acenaphththene and fluorene, are better resolved than on an intermediate phase and in fact closer to the resolution obtained on a polymeric phase. There is a large difference in the length to breadth ratio (L/B) between these compounds indicating that the liquid crystal material has good discrimination capabilities based on this property. Second, peaks 7 and 8, fluoranthene and pyrene, are only partially resolved similar to the result obtained for a monomeric stationary phase. The L/B ratio and Mol. Wt. of these two compounds are almost identical. The next group of peaks, 11,12, and 13, appear similar to an intermediate phase except that peak 13 is better separated from the other two compounds on the cholesterol material. The main difference between compound 13 in comparison to 11 and 12 is that it has a much greater degree of planarity than the other two. In the last group of three compounds it is again the most planar structure, benzo[ghi]perylene, that is the last eluted compound. The results for the MPAB phase are similar to the cholesterol material for the first 10 compounds. In the last two groups compounds 11,12 and13 are better separated on MPAB than cholesterol but the last group, 14,15 and 16 are not resolved at all.

These results indicate that while both phases are liquid crystal materials, they are not identical and have separation properties which are different. Therefore, bonding of different liquid crystal compounds could lead to other separation capabilities that might offer advantages for solving specific separation problems.

## CONCLUSIONS

It appears that liquid crystal bonded phases can be successfully synthesized on hydride surfaces via a terminal olefin containing compound. These results are supported by DRIFT and CP-MAS spectroscopic data as well as thermal analysis measurements. The chromatographic data support earlier results[8-10] that liquid crystal bonded phases have an ability to selectively retain solutes based on molecular shape. The use of the hydrosilation reaction for attachment of the organic moiety opens up greater possibilities for bonding a wider variety of liquid crystals, particularly those containing a cyano group, and exploiting their unique properties. The selective retention could be enhanced by temperature as well as solvent effects. Studies are currently underway exploring both the synthetic aspects of hydrosilation using functionalities other than olefins as well as the potential for enhancing separations via thermal and solvophobic effects on the liquid crystal bonded material.

## ACKNOWLEDGMENTS

The authors wish to thank the National Science Foundation (CHE 9612710) for partial support of the research reported here and The Separations Group for donation of the Vydac silica.

## REFERENCES

1. S. A. Wise, L. C. Sander,. J. High Resolut. Chromatogr. Chromatogr. Commun., **8**, 248 (1985).

2. L. C. Sander, S. A. Wise, J. High Resolut. Chromatogr. Chromatogr. Commun., **11**, 383 (1988).

3. L. C. Sander, S. A. Wise, Anal. Chem., **61** 1749 (1989).

4. M. Pursch, S. Strohschein, H. Handel, K. Albert., Anal. Chem., **68** 386 (1996).

5. L. C. Sander, K. Epler Sharpless, N. E. Kraft, S. A. Wise, Anal. Chem., **66**, 1667 (1994).

6. J. J. Pesek, A. M. Siouffi, Anal. Chem., **61**, 1928 (1989).

7. J. J. Pesek, Y. Lu, A. M. Siouffi, F. Grandperrin, Chromatographia, **31**, 147 (1991).

8. K. Jinno, Y. Saito, R. Malhan nee Chopra, J. J. Pesek, J. C. Fetzer, W. R. Biggs, J. Chromatogr., **557**, 459 (1991).

9. K. Jinno, H. Mae, Y. Saito, J. J. Pesek, J. C. Fetzer, W. R. Biggs, J. Microcol. Sep., **3**, 417 (1991).

10. Y. Saito, K. Jinno, J. J. Pesek, Y.-L. Chen, G. Luehr, J. Archer, J. C. Fetzer, W. R. Biggs, Chromatographia, **38**, 295 (1994).

11. C. Delaurent, V. Tomao, A. M. Siouffi, Chromatographia, **45**, 355 (1997).

12. J. J. Pesek, M. T. Matyska, E. J. Williamsen, R. Tam, Chromatographia, **41**, 301 (1995).

13. J. E. Sandoval, J. J. Pesek, Anal. Chem., **63**, 2634 (1991).

14. C.-H.Chu, E. Jonsson, M. Auvinen, J. J. Pesek, J. E. Sandoval, Anal. Chem., **65**, 808 (1993).

15. J. J. Pesek, M. T. Matyska, J. E. Sandoval, E. J. Williamsen, J. Liq. Chromatogr., & Rel. Technol., **19**, 2843 (1996).

16. B. Marciniec, **Comprehensive Handbook on Hydrosilylation**, Pergamon Press, Oxford, 1992.

17. M. A. Apfel, H. Finkelmann, G. M. Janini, R. J. Laub, B. H. Luhmann, A. Price, W. L. Roberts, T. L. Shaw, C. A. Smith, Anal. Chem., **57**, 651 (1985).

18. G. E. Berendsen, L. De Galan, J. Liq. Chromatogr., **1**, 561 (1978).

19. J. J. Pesek, M. T. Matyska, E. Soczewinski, P. Christensen, Chromatographia, **39**, 520 (1994).

Received September 1997
Accepted October 16, 1997
Manuscript 4620