

## **Synthesis of chemically bonded liquid crystals for high-performance liquid chromatography**

### **New phases via the organochlorosilane pathway**

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#### **ABSTRACT**

Two bonded nematic liquid crystal stationary phases for use in high-performance liquid chromatography were prepared by reacting the silanized forms of [4-(allyloxy)benzoyl]biphenyl and 4-([4-(allyloxy)benzoyloxy]-4'-methoxybiphenyl with the surface of silica. The diffuse reflectance infrared Fourier transform and carbon-13 cross-polarization magic angle spinning NMR spectra of the two bonded phases confirmed that the reaction was successful. Carbon elemental analysis indicated a high loading of the liquid crystal on the surface. Van 't Hoff plots using polyaromatic hydrocarbons as the solutes in an acetonitrile-water mobile phase indicated that phase transitions are occurring. The relative retention of anthracene and phenanthrene as a function of temperature is also sensitive to changes in the stationary phase morphology and reveals that more than a single transition is occurring over the temperature range studied.

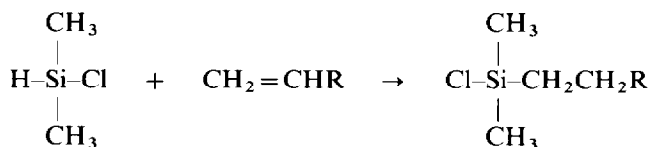
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#### **INTRODUCTION**

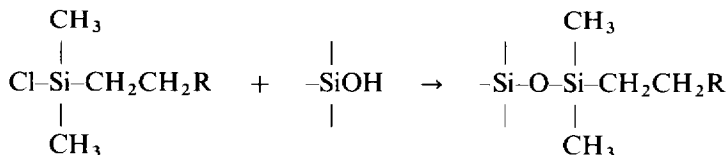
Since the introduction of liquid crystals as stationary phases more than 25 years ago [1,2], many applications have been developed for gas chromatography (GC) [3]. More recently, it has been shown that liquid crystals are suitable stationary phases for supercritical fluid chromatography (SFC) [4,5]. However, the same properties that make these materials desirable as stationary phases in GC and SFC also make them potentially just as useful in high-performance liquid chromatography (HPLC). These properties include phase transitions which can be controlled by experimental conditions in order to change the retention mechanism. It has now been demonstrated that liquid crystal materials can be synthesized and bonded to porous silica [6] so that they possess properties which are clearly different than those of ordinary reversed-phase materials for HPLC [7,8].

The previous studies have all utilized a material which was shown to have liquid crystal properties when bonded to a polysiloxane backbone [9]. Because the preliminary results on this material suggest a phase that might possess unique capabilities for HPLC, it is now necessary to verify further the synthetic approach for the original material and the resulting physical and chromatographic properties.

The successful pathway originally chosen involves the synthesis of a liquid crystal silane reagent using standard hydrosilylation chemistry [10]. It involves a reaction between a terminal olefin, which is a liquid crystal for one compound in this study, and dimethylchlorosilane to produce the silane reagent:



The silane reagent is then reacted with the silica surface to produce the bonded phase:



The same reaction pathway was utilized in this study in order to determine its general usefulness and to characterize further the resulting chromatographic properties that bonded liquid crystals possess as stationary phases in HPLC.

## EXPERIMENTAL

### *Materials*

All chemicals used in the synthetic procedures and the chromatographic characterizations were of analytical-reagent grade. Solvents in the HPLC experiments were of chromatographic grade. All liquid reagents and solvents used in moisture-sensitive reactions were distilled and collected over type 4A molecular sieves. All solid materials used in moisture-sensitive reactions were dried at 110°C for 24 h prior to the start of the experiment. The dried solids were then cooled to 25°C over Drierite in a vacuum desiccator. The solid support was Nucleosil 300-10. Deuterated chloroform was used as the solvent for proton NMR spectra.

### *Apparatus*

All glassware for moisture-sensitive synthetic work was dried at 110°C for 24 h prior to use and assembled hot with a nitrogen purge. Infrared spectra were obtained in the diffuse reflectance infrared Fourier transform (DRIFT) mode on a Perkin-Elmer (Norwalk, CT, USA) Model 1800 spectrometer. Proton NMR spectral studies were performed on a Varian (Palo Alto, CA, USA) EM 390 spectrometer. Carbon-13 cross-polarization magic angle spinning (CP-MAS) NMR spectra were obtained on a Bruker (Billerica, MA, USA) MSL 300 spectrometer operated in the TOSS mode to eliminate sidebands. Elemental analyses were done at the University of California Berkeley Micro Lab. Differential scanning calorimetric (DSC) measurements were made on a Perkin-Elmer Series 7 thermal analysis system. Surface area measurements (BET) were made on a Micromeritics (Norcross, GA, USA) Model ASAP 2400

analyser. Chromatographic studies were done with a Dionex (Sunnyvale, CA, USA) Model GPM-2 gradient pump module, a Dionex VDM-2 detector, a Pickering (Mountain View, CA, USA) Model CHX 650 column heater and a Spectra-Physics (San Jose, CA, USA) Model SP8875 autosampler.

*Synthesis of [4-(allyloxy)benzoyl]biphenyl [9]*

To a two-necked, 250-ml, round-bottomed flask equipped with a 50-cm reflux condenser, a Teflon septum with a nitrogen line, a magnetic stirring bar and an oil-bath, 4.93 g of 4-phenylphenol dissolved in 50 ml of dry pyridine were added under nitrogen. Next, 6.13 g of 4-(allyloxy)benzoyl chloride were added with stirring. The mixture was stirred for 3 h at 25°C and then heated at 60°C for an additional 2 h. After the reaction mixture had cooled to 25°C, 200 ml of acidic (20% HCl) deionized water were added. The resulting precipitate was collected by vacuum filtration and washed with 200 ml of cold deionized water. The crude product was recrystallized from acetone-ethanol (1:1) yielding 8.45 g (88%), m.p. 138–140°C.

*Synthesis of 4-{[4-(allyloxy)benzoyl]oxy}-4'-methoxybiphenyl [9]*

A 400-ml volume of 10% sodium hydroxide solution cooled to 0°C was placed in a three-necked, 1000-ml, round-bottomed flask equipped with a self-equalizing addition funnel, a 50-cm reflux condenser, a Teflon septum with a nitrogen line, a magnetic stirring bar and an ice-bath. Next, 75.50 g of 4,4'-dihydroxybiphenyl were added with vigorous stirring. To this 48.64 g of dimethyl sulphate were added with vigorous stirring over a 1-h period. After the addition was complete, the resulting precipitate was recovered by vacuum filtration with a sintered-glass filter and was redissolved in 400 ml of 10% sodium hydroxide solution. The solution was heated briefly to boiling and was allowed to cool for filtration. The solid was placed in 200 ml of water and was heated to boiling and filtered while hot. The filtrate was then heated to 70°C and acidified with 20% hydrochloric acid, causing crude 4-hydroxy-4'-methoxybiphenyl to precipitate. The product was recrystallized twice from ethanol.

The recrystallized material (3.62 g), dissolved in 100 ml of dry pyridine and under a nitrogen blanket, was placed in a three-necked, 250-ml, round-bottomed flask equipped with a 100-ml self-equalizing addition funnel, a 50-cm reflux condenser, a magnetic stirrer and an oil-bath. Then 4.19 g of 4-(allyloxy)benzoyl chloride dissolved in 20 ml of dry pyridine were added with stirring over a 1-h period. The reaction mixture was stirred for an additional 3 h at 25°C and then heated at 60°C for a further 2 h. The reaction mixture was cooled to 25°C and 400 ml of water were added. The solution was acidified with 20% hydrochloric acid. The precipitate was recovered by vacuum filtration and washed with 400 ml of saturated sodium hydrogencarbonate solution and then with 400 ml of deionized water. The crude product was recrystallized twice from acetone yielding 4.27 g (84%) with the following melting points: crystalline to nematic, 147°C, and nematic to isotropic liquid, 249°C.

*Synthesis of silane reagents and silica bonding [6,10]*

The organic moiety dissolved in 20 ml of dry toluene was placed in a two-necked, 100-ml, round-bottomed flask equipped with a 50-cm reflux condenser, a Teflon septum with a nitrogen line, a magnetic stirrer and an oil-bath. Next, 11.8 mmol of dimethylchlorosilane were added to the reaction flask while stirring and purging with

nitrogen. After 5 min, 8 mg of hexachloroplatinic acid were added. The reaction mixture was heated to 65°C and stirred for 10 days under nitrogen. Then 20 ml of freshly distilled toluene were added followed by 6.5 g of silica (Nucleosil 300-10) and 0.5 ml of dry pyridine. The reaction mixture was stirred for 10 days at 40°C under nitrogen. The solid was then collected and washed with 60 ml of toluene followed by 60 ml of ethanol. The washing procedure was repeated six times.

## RESULTS AND DISCUSSION

Fig. 1 depicts the structures of the starting liquid crystals and the silane reagents which were used to bond the material to porous silica. Each of these materials was characterized by both IR and proton NMR spectra. Compound **a** displayed peaks in the IR region at 3072  $\text{cm}^{-1}$  for the C-H stretch of the terminal alkene, at 1647  $\text{cm}^{-1}$  for the C=C double bond stretch, at 1608 and 1511  $\text{cm}^{-1}$  for aromatic C-H bending, at 1731  $\text{cm}^{-1}$  for the C=O stretch, at 1260 and 1169  $\text{cm}^{-1}$  for the C-O ester stretch and also peaks between 3072 and 3017  $\text{cm}^{-1}$  representing aromatic C-H stretching and between 2980 and 2893  $\text{cm}^{-1}$  representing aliphatic C-H stretching.

The essential features of the proton NMR spectrum include a complex pattern centered at 7.50 ppm due to the aromatic hydrogens (thirteen from integration data), a multiplet at 6.10 ppm due to a single vinyl hydrogen, another multiplet at 5.45 ppm due to two vinyl hydrogens and a doublet at 4.75 ppm which is assigned to the methylene protons of the =CHCH<sub>2</sub>O segment of the molecule.

The IR spectrum of compound **b** contains the same essential features as that of compound **a** as the structures are very similar. The proton NMR spectrum of **b** also has

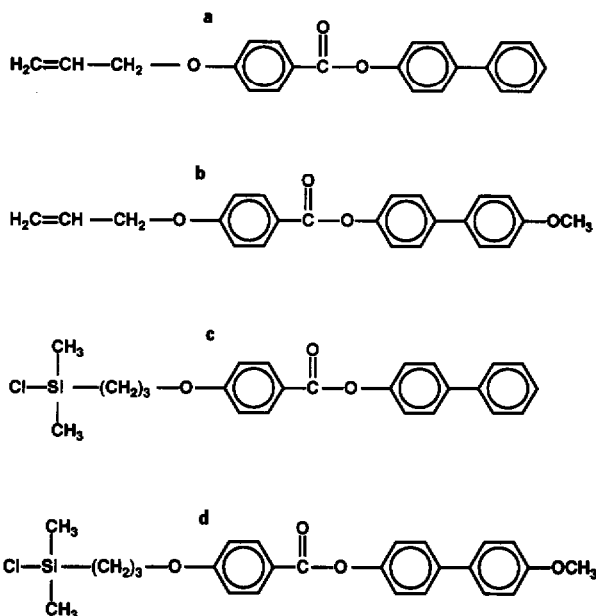


Fig. 1. Structures of (a) 4-(allyloxy)benzoylbiphenyl, (b) 4-([4-(allyloxy)benzoyloxy]-4'-methoxybiphenyl, (c) silane reagent of compound **a** and (d) silane reagent of compound **b**.

the same peaks as observed for **a** and an additional peak (singlet) at 3.80 ppm. This peak corresponds to the methoxy group and represents the only major structural difference between the two compounds.

The IR spectrum can be used to confirm the success of the hydrosilylation reaction to produce compound **c**. It displays increased intensity in the aliphatic C-H stretching region due to the two methyl groups and a disappearance of the bands at  $3072\text{ cm}^{-1}$  from the C-H olefinic stretch and at  $1647\text{ cm}^{-1}$  from the C=C double bond stretch. The proton NMR of **c** has no peaks in the vinyl region and a large singlet at 0.25 ppm which corresponds to the two methyl groups attached to silicon. Similar results are observed in both the IR and NMR spectra of compound **d**. Therefore, as in the previous study [6], spectral data confirm the success of the syntheses of both starting materials and the liquid crystal silane reagents.

Once the silane reagent has been synthesized, the bonding chemistry to the silica surface is identical with that used for the production of all commercially available monomeric stationary phases. Again, both IR and NMR can be used to verify the success of the bonding reaction. Fig. 2 (top) shows the DRIFT spectrum of the product from the reaction of compound **c** and silica (phase 1). Significant aromatic and

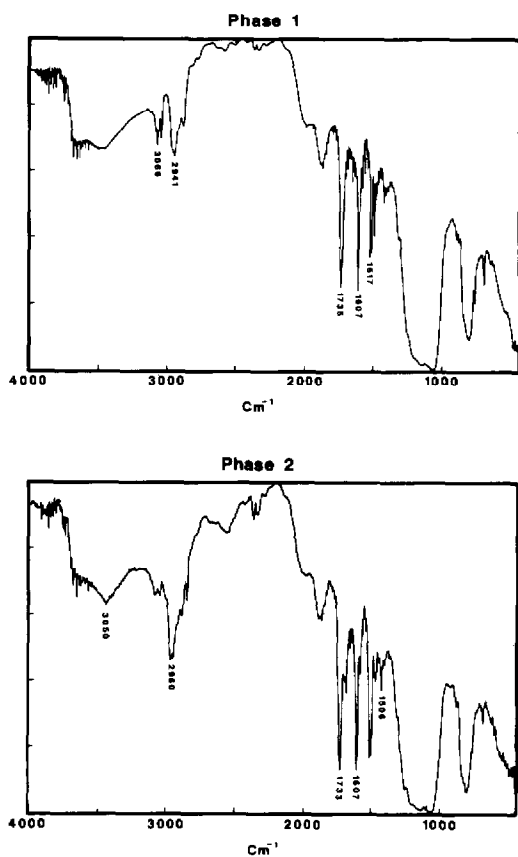


Fig. 2. DRIFT spectra of phase 1 and phase 2 on silica.

aliphatic C–H stretching is observed, in addition to three peaks (1735, 1607 and 1517  $\text{cm}^{-1}$ ) which correspond approximately to bands observed in both the liquid crystal starting material and liquid crystal silane reagent as described above. Fig. 2 (bottom) shows the DRIFT spectrum for the product from the reaction of compound **d** and silica (phase 2). As expected, its spectrum is similar to that of phase 1 with the same essential features as described above.

The carbon-13 CP-MAS spectrum of phase 1 is shown in Fig. 3 (top). The large peak at 0 ppm is due to the two methyl groups attached to the silicon of the silane reagent, the peaks between 10 and 30 ppm are the methylene groups, the peak near 70 ppm is the  $\text{OCH}_2$ -carbon, the peaks between 100 and 150 ppm are the aromatic carbons and the peak near 163 ppm is the carbonyl carbon. The spectrum of phase 2 shown in Fig. 3 (bottom) is essentially the same as phase 1 except for the peak at 57 ppm, which is the result of the methoxy carbon. An additional peak near the carbonyl may be due to incomplete suppression of the sidebands. However, it is clear from both the DRIFT and carbon-13 CP-MAS spectra that the bonding reactions were successful so that chromatographic characterizations could be done with the assumption that the stationary phase consisted of a bonded liquid crystal material.

The carbon content of phase 1 as determined by elemental analysis was 9.69%. This corresponds to a surface coverage [11] of  $3.55 \mu\text{mol}/\text{m}^2$ . The values for phase 2 were 12.75% carbon with a coverage of  $4.74 \mu\text{mol}/\text{m}^2$ . These results can be compared with the *ca.*  $3.5 \mu\text{mol}/\text{m}^2$  obtained in a previous study [6]. Both the phase used in the previous work (ABMP) and phase 1 in this study involve materials that only become liquid crystals when bonded to a polysiloxane backbone. Phase 2, however, is a true liquid crystal when in the form of compound **b**. This might account for the higher loading obtained, as a higher degree of ordering is already present when the bonding occurs. Even the  $3.5 \mu\text{mol}/\text{m}^2$  realized with the other two phases is high considering the size of the molecules. Phase 1 is approximately equivalent in chain length to a normal  $\text{C}_{18}$  alkyl but is considerably bulkier. The bonding density is better than the  $3.3 \mu\text{mol}/\text{m}^2$  achieved with monomeric  $\text{C}_{18}$  phases [11].

DSC measurements are the simplest means for detecting phase transitions in

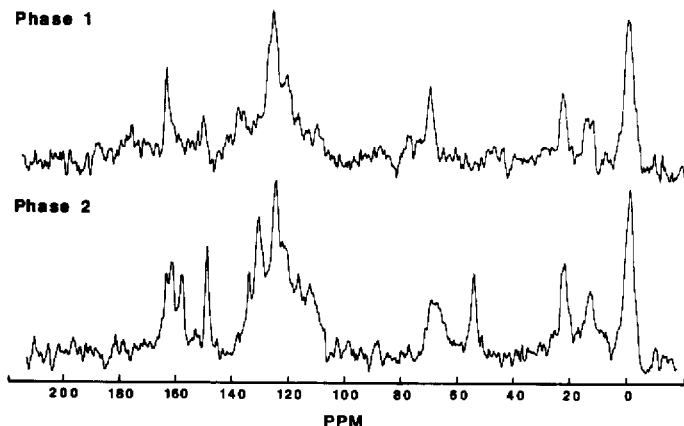


Fig. 3. Carbon-13 CP-MAS-NMR spectra of phase 1 and phase 2 on silica.

liquid crystals. However, the previous study [6] showed only a very broad, positive heat flow rather than a sharp transition that is expected with pure materials. Indeed, compound **b** gave such a sharp transition at 147°C, which agrees with the literature value [9], for the crystalline to nematic phase change. However, no sharp transitions were observed in the DSC data for either phase 1 or phase 2 on silica. A comparison of the DSC measurements for bare silica, phase 1 and phase 2 over the temperature range 300–425°C gave slopes of 0.088, 0.109 and 0.120 mW/°C, respectively. This increased positive heat flow is similar to that observed in the early study and indicates a broad transition temperature (probably nematic to isotropic) due to the variable contact between adjacent molecules that reflects the irregular nature of the porous silica surface.

Some preliminary chromatographic testing has been initiated on phase 1 in order to ascertain if its properties are similar to those observed for the ABMP phase in the previous study [6]. Fig. 4 is the Van 't Hoff plot for phenanthrene and anthracene in acetonitrile–water (50:50). A distinct transition is observed near 65°C for both solutes. This compares with the 55°C transition temperature observed for the ABMP phase. A higher transition temperature for phase 1 would be expected as it exhibits higher values than ABMP when bonded to polysiloxane [9].

Another perspective on the behavior of the bonded phase is seen in Fig. 5, which is a plot of the relative retention of anthracene and phenanthrene ( $k'_2/k'_1$ ) vs. temperature. While the Van 't Hoff plots for these compounds show a single transition, this plot indicates that the bonded phase behavior may be more complex. Certainly the general trend to less discrimination between the two molecules as temperature increases is reasonable. The order in the phase becomes less so that the slot model proposed [12] becomes less likely to exist under these conditions. As the order in the

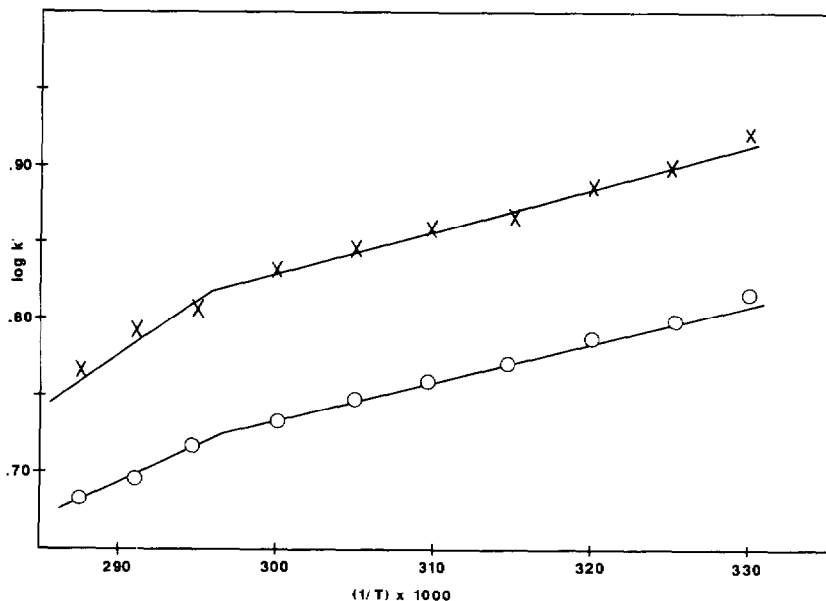


Fig. 4. Log  $k'$  vs.  $1/T$  (K) for (○) phenanthrene and (×) anthracene on phase 1.

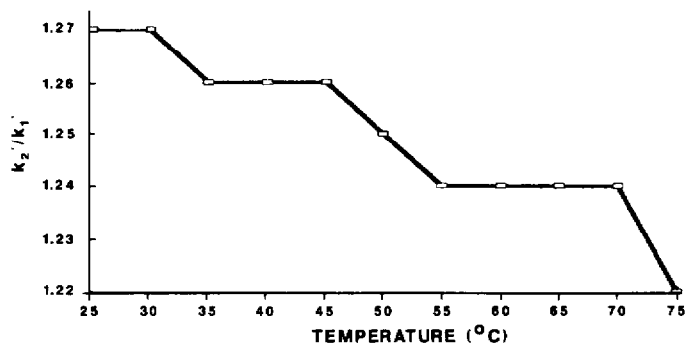


Fig. 5. Plot of  $k'_2$  (anthracene)/ $k'_1$  (phenanthrene) vs. temperature on phase 1.

phase decreases, the ability to discriminate on the basis of molecular shape (length-to-width ratio) also begins to decrease. The relative retention plot also indicates that the nature of the transition may not be uniform as three separate changes in the ratio take place over the temperature range studied. Because the surface is not homogeneous it is expected that there would be variable contact between the adjacent bonded moieties. This may account for the variations observed in relative retention as the order in the bonded liquid crystal is not being disrupted uniformly. As these changes are small, it appears that the relative retention is more sensitive to the subtle variations in bonded phase structure not seen in the normal Van 't Hoff plot.

Finally, it should be noted that the relative retention for anthracene and phenanthrene at 25°C (1.27) is very close to that measured for ABMP (1.29) at the same temperature but with a slightly different mobile phase composition (30:70). According to previous results [7], the relative retention might increase as the amount of water in the mobile phase increases owing to the tendency of all hydrophobic phases, especially alkyls, to aggregate under these conditions. This would ensure that a greater fraction of a liquid crystal phase would be in a slot-like configuration. In addition, no measurable changes were recorded in  $k'$  values during the course of the characterization experiments, indicating that the phase was stable and that changes in phase morphology induced by temperature and/or solvent composition were reversible.

## CONCLUSIONS

It has been shown that the organochlorosilane pathway is a useful method for bonding liquid crystals to silica surfaces. Preliminary results indicate that these new materials possess the same type of behavior that was identified in an earlier study and that these characteristics are consistent with liquid crystal behavior. Further chromatographic measurements must be done on these and other materials to understand fully their behavior and potential as stationary phases for HPLC. Additional synthetic work and extensive chromatographic characterization are currently being undertaken in our laboratory as well as at a number of other collaborating institutions.



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