A Chemically Bonded Liquid Crystal as a Stationary Phase for High Performance Liquid Chromatography. Synthesis on Silica via an Organochlorosilane Pathway

J. Pesek* / Teresa Cash

Department of Chemistry, San Jose State University, San Jose, CA 95192, USA.

Key Words
Column liquid chromatography
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Summary
A compound which becomes a liquid crystal when bonded to a polysiloxane was reacted with dimethylchlorosilane to produce a reagent suitable for bonding to a silica surface. After the silanization reaction was complete, the product was characterized by elemental analysis, diffuse reflectance Fourier transform Infrared Spectroscopy (DRIFT), CP/MAS carbon-13 NMR and differential scanning calorimetry (DSC). Preliminary chromatographic testing was done by retention index measurements using the alkylarylketone homologous series and by measuring the separation factor, α, for anthracene/phenanthrene at two different mobile phase compositions.

Introduction
Liquid crystals were first reported as stationary phases in gas chromatography 25 years ago [1, 2]. They are useful in both packed [3] and capillary [4] columns. The properties and many applications of liquid crystals as stationary phases in gas chromatography have been reviewed [5].

In contrast to the extensive literature references in gas chromatography, there are only two reports [6, 7] concerning liquid crystals as stationary phases for HPLC. This might be explained by the fact that liquid crystals are readily adaptable as stationary phases for GC. They are generally of high molecular weight and low volatility since they are an intermediate between a solid and a true isotropic liquid. These oriented liquid phases usually occur much above room temperature which significantly reduces or eliminates column-bleed and the need for chemical bonding. These properties also explain their adaptability for use in either packed or capillary columns. However, the tremendous versatility for achieving difficult separations exhibited by liquid crystal stationary phases in GC [5] should be an indicator of their potential in HPLC. Already studies [8–10] have shown that liquid crystals bonded to polysiloxane polymers do retain properties (phase transitions) which can be ascribed to a state intermediate between a solid and ordinary liquid. Therefore, similar behavior might be possible for a liquid crystalline molecule bonded to silica. These molecular orientations are a function of surface type and solvent [11] so therefore could be controlled in a typical liquid chromatographic experiment. In liquid chromatography the net result would be two different ways of controlling liquid crystal phase changes: first by temperature as in gas chromatography and second by mobile phase composition.

The earlier studies [6, 7] on liquid crystals as stationary phases in HPLC are very incomplete. Both present a few separations based on liquid crystals which are physically coated on the solid support. Obviously this method leads to short column lifetimes due to the prolonged exposure to various solvents and high pressure (shear forces) which could remove the stationary phase. The one attempt [6] to bond a liquid crystal to silica was probably unsuccessful because the synthetic route chosen exposed the product to high NaOH concentrations for a long time. Therefore, a concerted effort should be made to find suitable methods for bonding liquid crystals to chromatographic surfaces. When such phases have been synthesized it will be possible to determine if liquid crystal properties are present and then to test whether the effects of surface structure, temperature, and mobile phase composition can be used to control chromatographic separations on these materials. This paper presents the first attempt to synthesize a bonded liquid crystal stationary phase by a convenient reaction pathway.

Experimental
Synthesis of Bonded Liquid Crystal Phase
The precursor used in this study, [4-(allyloxy)benzoyl]-4-methoxyphenyl (Figure 1), was synthesized with a yield of
This compound was converted into a silanization reagent by reaction with dimethylchlorosilane to produce a silanization reagent (Fig. 1). This mixture was heated at 65°C and stirred for 7 days. The solvents were removed by vacuum and the remaining solid was kept under nitrogen. A small amount of the solid was removed and checked with proton NMR. The spectrum displayed a large peak near 0 ppm due to the presence of =Si(CH3)2 indicating that the reaction had been successful.

The final product was made by adding 20 mL of freshly distilled toluene, 5 g of silica and 0.5 mL of pyridine to the flask containing the silanization reagent. This mixture was maintained at 40°C for 2 days. The solid was then filtered, washed with 100 mL of toluene followed by 100 mL of methanol and finally dried at 100°C under vacuum.

**Materials**

The silica used was Nucleosil 300-10 with a surface area of approximately 100 m²/g. The silica was dried at 120°C for 24 hours before use. The materials for the liquid crystal synthesis are identical to those used by Apfel [10]. The dimethylchlorosilane (Petrarch) was used as received. Toluene and methanol were reagent grade (Baker). Water for the chromatographic testing was prepared on a Millipore apparatus. The alkylarylketone standards were purchased as a kit (Sigma).

**Bonded Phase Evaluation**

Elemental analysis was obtained from Chemical Analytical Services (Berkeley, CA). The FTIR spectra were done on a Perkin-Elmer Model 1800 spectrometer and DSC measurements were performed on a Perkin-Elmer Model 7 Series Thermal Analysis System. Proton NMR spectra were done on a Varian EM-390 Spectrometer and carbon-13 CP/MAS spectra were run on a Bruker MSL-400 Spectrometer (Catalytica, Mountain View, CA). BET (m²/g) was estimated from the adsorption of the copper amine complex on the silica [13]. The final product was packed into a 150 x 4.6 mm stainless steel column using a Haskel pneumatic amplification pump. The chromatographic testing with the alkylarylketone series was done according to Smith [14] using 60:40 methanol-water as the mobile phase. The chromatographic system consisted of a Beckman 421 controller, two Beckman 110A pumps, an Altex injector equipped with a 20 µL sample loop, a Beckman Model 160 detector and a Hewlett-Packard Model 3390 integrator. The void volume was measured by injection of nitrate.

The production of chemically bonded stationary phases via organochlorosilane chemistry is well-established and is used in the synthesis of virtually all commercially available nonpolymer bonded materials [15]. Therefore, the bonding chemistry is likely to be successful if a liquid crystal silanization reagent can be synthesized. However, since there are several types of liquid crystals (nematic, smectic, and cholesteric) and hundreds of known compounds in each type [16], it is impossible to predict a priori which molecules might retain or produce liquid crystalline properties after bonding to silica. We chose to begin with the compound 4-(allyloxy)benzoyl-4-methoxynaphthalene because it has been shown that liquid crystalline properties are generated when it is bonded to polysiloxane and used as a stationary phase in gas chromatography [10]. In addition, it can be reacted with dimethylchlorosilane to produce a silanization reagent because it has a terminal double bond. The overall synthetic approach is shown in Figure 1.

The success of the first step, production of the silanization reagent, is illustrated by the IR spectra in Figure 2. It is quite clear that all of the essential spectral features of the starting compound are present in the product. In particular the three strong bands between 1500 and 1750 cm⁻¹ are quite evident in each spectrum. Small differences are seen in the carbon-hydrogen stretching region around 3000 cm⁻¹ due to the presence of the two methyl groups (=Si(CH3)2) in the product material. Other differences can be ascribed to the presence of silicon-carbon and silicon-chlorine vibrational modes not present in the original material. The OH stretch near 3500 cm⁻¹ is quite evident in each spectrum. Small differences are seen in the carbon-hydrogen stretching region around 3000 cm⁻¹ due to the presence of the two methyl groups (=Si(CH3)2) in the product material. Other differences can be ascribed to the presence of silicon-carbon and silicon-chlorine vibrational modes not present in the original material. The OH stretch near 3500 cm⁻¹ has no particular importance since this is due to a variable amount of adsorbed water in either sample and the partial or complete hydrolysis of the chlorine on the silanization reagent after it has been removed from the dry nitrogen atmosphere.

**Results and Discussion**

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