

Design, Synthesis, and Characterization of Novel Hydrocarbon and Fluorocarbon Stationary Phases for Molecular Recognition in Liquid Chromatography

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Alkyl modified silica surfaces are the most commonly used and studied bonded phases in liquid chromatography. The chromatographic effects of phase length, ligand density, and column temperature have been investigated extensively and it has been found that longer alkyl chains, higher densities, and lower temperatures typically lead to improved separations of shape constrained geometric isomers such as polycyclic aromatic hydrocarbons and carotenoids. In this presentation the design, synthetic preparation, and initial chromatographic and spectroscopic characterization of two novel classes of stationary phases will be described.

The novel materials were originally designed to possess a high degree of alkyl chain conformational order thereby enhancing their molecular shape recognition properties. Perfluorinated phases were synthesized via linkage of perfluorinated carboxylic acids of various lengths to alkylamino-modified silica particles. Longer chain perfluorinated sorbents display enhanced shape selectivity properties, even at elevated temperatures (70 °C). A series of C₁₈ phases with various surface coverages were synthesized with deliberately introduced cavities through an initial reaction with a small monofunctional silane “spacer”, followed by reaction with octadecyltrichlorosilane via both solution- and surface-polymerization techniques. The presence of the spacer disrupts C₁₈ ligand ordering and enhanced shape selectivity is observed for surface polymerized sorbents only. Evidence of stationary phase conformational ordering via solid state ¹³C/²⁹Si CP/MAS NMR and suspended state ¹H HR/MAS NMR spectroscopy will also be presented.