SEPARATION AND CHARACTERIZATION OF CLOSED FUNCTIONALIZED
DOUBLE-DECKER SHAPED SILSESQUIOXANES

By: David Felipe Vogelsang Suarez

Advisor: Andre Lee

Stoichiometric reaction of tetrasilanol octaphenyl double-decker shaped silsesquioxanes (DDSQ-(Ph)₈(OH)₄) with difunctional dichlorosilanes (R₁R₂SiCl₂) provided a new class of model hybrid organic-inorganic compounds. These model compounds (DDSQ-2(R₁R₂)) have a dimensionally well-defined closed inorganic Si-O core, eight phenyl groups for thermo-oxidative stability and compatibility to aromatic organics, and well-specified R₁ and R₂ for possible further chemical reactions. However, these compounds contain cis and trans conformations about the DDSQ if R₁ and R₂ are different.

Separation of cis and trans isomers by liquid chromatography was proposed as the alternative technique to the more tedious fractional crystallization for isolation of pure compounds. It was found polar nature of the R group enables the separation by adsorption chromatography. In contrast, partition chromatography allows separation of isomers of a larger solubility difference. Results of HPLC also provided quantitative measure of the isomer ratio in a cis and trans DDSQ-2(R₁R₂) mixture with deviations better than ±5%. In contrast, the current quantification of the isomer ratio by ²⁹Si-NMR has been reported to have ±10% deviation from the real value.

HPLC separation was extended to analyze resolution of the elution for DDSQ mixtures with polarity differences. Reaction of DDSQ-(Ph)₈(OH)₄ with R₁R₂SiCl₂ and (CH₃)SiCl₃ mixture
followed by hydrolysis, lead to a mixture of DDSQ compounds with zero, one, and two hydroxyl groups. Well separation of the three expected products was made by LC. Characterization by NMR and mass-spectroscopy allowed identification of each separated product. An asymmetric structure about the DDSQ core with one hydroxyl group (DDSQ-(R1R2)((CH3)(OH))) was obtained.

Scale-up of HPLC separation for the mixture containing zero, one, and two hydroxyl groups was simulated in ASPEN chromatography. Linear adsorption isotherm parameters were obtained by frontal analysis. A correlation between HPLC stationary phase adsorption parameters and preparative stationary phase LC adsorption parameters was obtained. These parameters permitted satisfactory prediction of the column efficiency, the resolution of the elution, and total collection time in a column separation verified with a 5g-scale. In the scale of preparative-LC, fractions collected were of high purity as verified by 29Si NMR. Additionally, for DDSQ-2(R1OH) a highly cis concentrated fraction and a nearly-pure trans fraction were also successfully isolated.

DSC experiments were performed for nearly-pure cis and trans DDSQ-2(R1R2), and for DDSQ-2(R1R2) mixtures of varying cis-to-trans compositions. R1 was fixed as methyl, and for R2 aryl groups were selected. It was found trans isomer had a higher melting temperature than cis isomer and as the size of R2 increases the melting temperatures of nearly-pure isomers decrease. Interesting cis and trans structures are not miscible in the solid state and form binary eutectic. Binary cis and trans eutectic temperature and composition can be predicted using the ideal binary assumption.