Diffusion and Adsorption of Single Dendrimers for Gas Hydrate Prevention

Principle Investigator: Pu-Chun Ke, Assistant Professor

Department of Physics and Astronomy, Clemson University, Clemson, SC 29634-0978

Introduction

Dendrimers are hyper-branched, nonlinear macromolecules that have well-defined structure and high density of end groups that allow for chemical conjugation. The applications of dendrimers range from drug delivery, therapeutics, to cosmetics, polymer science, and engineering.[1] One recent discovery has found that dendrimers and other hyper-branched polymers can effectively prevent the formation of ice crystals in oil pipelines, a problem which costs the petroleum industry over 1 million dollars a day.[2] To unravel the underlining mechanism of this application, we have conducted a single-molecule fluorescence study using squalane, an aliphatic hydrocarbon molecule, and G3-PAMAM, a generation 3 poly(amidoamine) dendrimer as a model system.

Materials and Methods

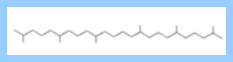
- **Instrument:**

Single-molecule total-internal reflection (TIR) fluorescence microscope (CCD camera: Roper Cascade 512B, excitation by a Nd^+:YAG laser at 532 nm)

- **Samples:**

G3-PAMAM (Dendritech) labeled with TRITC (Anaspec)

Squalane (Sigma): Aliphatic hydrocarbon kit 18, MW 422 g/mol



- **Spectrophotometry:**

0.25% w/w of labeled G3-PAMAM with 0.405 mg/mL Squalane

- **Transmission Electron Microscopy (TEM):**

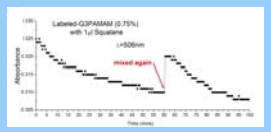
0.25% of TRITC-labeled G3-PAMAM with 2,000X Squalane (0.806 mg/mL)

- **Total Internal Reflection Microscopy:**

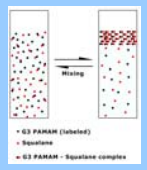
26 nM of labeled G3-PAMAM spin-coated on a glass slide at 6,000 RPM for 1 min.

Experiments

- **Spectrophotometry**

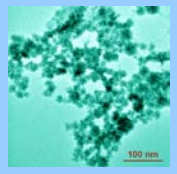


Time dependence of G3-PAMAM-Squalane interaction



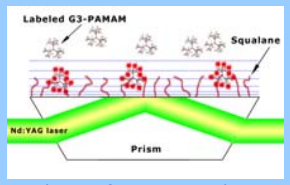
Model for G3-PAMAM-Squalane binding

- **TEM imaging**

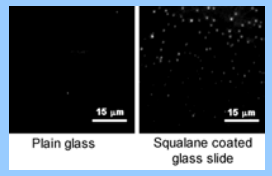


G3-PAMAM-Squalane

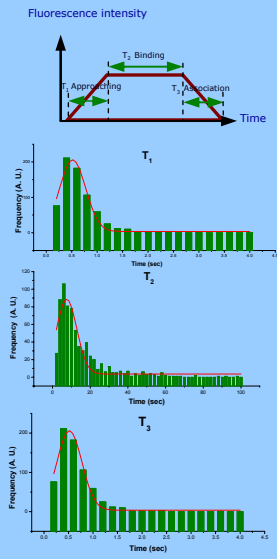
- **Single-Molecule TIR Fluorescence3**



Detection scheme of PAMAM-Squalane interaction



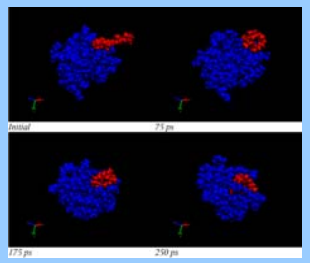
Fluorescence of PAMAM-Squalane binding



Histograms of single-molecule kinetics of PAMAM-Squalane interaction

- **Molecular Dynamics Simulations**

(In collaboration with Dr. Monica Lamm at Iowa State University)



Snapshots of PAMAM and Squalane in solvent simulation with solvent removed from visualization. The PAMAM is in blue and the Squalane in red.

Conclusion

The binding of dendrimers and hydrocarbons is attributed to the entrapment of hydrocarbons by the branches of dendrimers through hydrophobic-hydrophobic interaction. Using combined experimental techniques of spectrophotometry, TEM, and single-molecule fluorescence imaging and molecular dynamics we have shown the approaching, binding, and dissociation kinetics of dendrimers with respect to immobilized hydrocarbons. In addition we are conducting studies on the dependences of PAMAM and Squalane interaction on the pH and the salt strength of the solution. Our research is relevant to understanding the reptation of entangled star-branched polymers and has significant value to the cost saving of the petroleum industry.

Acknowledgment

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References

1. B. Helms, E.W. Meijer, "Dendrimers at work", *Science* 313, 929-930, 2006.
2. P. Froehling, "Development of DSM's Hybrane Hyperbranched Polyesteramides", *J. Poly. Sci. A* 42, 3110, 2004.
3. K. Pasupathy, J. Ching, A. Jones, Q. Lu, M. Lamm, P.C. Ke (manuscript in prep for *J. Phys. Chem. B*).