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FINAL REPORT

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CHEMICAL ENGINEERING OF SYNTHESIS SOLUTIONS FOR
MULTICOMPONENT INORGANIC POLYMERS AND CERAMICS

ALON MCCORMICK

DEPARTMENT OF CHEMICAL ENGINEERING AND MATERIALS SCIENCE

UNIVERSITY OF MINNESOTA

421 WASHINGTON AVE SE

MINNEAPOLIS, MN 55455

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unlimited.
RECENT HIGHLIGHTS OF PROJECT ACCOMPLISHMENTS

Multicomponent Sol to Gel Systems for Coating and Other Applications

While there have been several studies reported in the literature of the structure and properties of organic/inorganic hybrid materials prepared by “sol-gel” chemistry, less is known about how solution conditions influence copolymerization kinetics and material nanostructure. We are developing kinetic polymerization models for structure development of this class of materials. We use $^{29}$Si nuclear magnetic resonance spectroscopy to monitor the concentrations of differently hydrolyzed and connected silicon sites, and fit integrated sets of differential equations to these concentrations to quantify kinetic trends as monomers and solution conditions are varied.

Related Work Elsewhere:

How Ours is Different:
Models are quantitative and predictive; appropriate simplifications allow us to understand kinetics of large sets of reactions; we use reaction transients to engineer materials. Hydrolysis pseudoequilibrium demonstrated and utilized; first shell substitution effects on condensation reactivity found for several monomers; copolymerization quantified.

Controlling Precipitation in Sol-to-Gel Coating Systems

The appearance of nanometer scale particles is an important feature in most sol-to-gel reactive coating operations. The size distribution of these particles generally plays a critical role in all performance properties of the coating. We investigate the roles of particle formation and growth steps on the final particle size distribution. Using $^{29}$Si NMR, SEM, TEM, conductimetry, and photon correlation microscopy, we monitor the effect of reactor composition on intermediate concentration and
final size distribution. To date we have found that increasing reaction rates sharpens the final size distribution and that a balance between nucleation and growth rates must be struck to achieve self-sharpening growth.

Related Work Elsewhere:

How Ours is Different:
Kinetic modeling using $^{29}$Si NMR to trace the role of nucleation profile.

**Optimization of sol/gel processes by programmed chemical kinetic transients**

Given that most sol/gel applications are in coating processes, we design and test chemical kinetic transients to take place after coating in order to regulate the development of molecular architecture and so influence film microstructure and properties. We both: 1) "precondition" the coating fluid so as to provide post-coating kinetic transients and 2) to deliberately manipulate post-coating process parameters that govern kinetics. Liquid and solid state NMR of $^{29}$Si and of $^{13}$C provides our major means of monitoring chemical kinetics transients and identifying specific molecular architectures, such as small rings and cages.

Related Work Elsewhere:
Union Cabide, Dow Corning, GE, Dow Chemical, Bell Labs, Phillips, 3M, Eastman Kodak, R. A. Assink (Sandia), W.G. Klemperer (U of Illinois), J. Livage (Université Perrie et Marie Curie, France), F. Devreux (Ecole Polytechnique, France), B. Cabane (CNRS, France) J.J. van Beek (U of Utrecht, The Netherlands), H.C. Marsmann (Universität Paderborn, Germany)

How Ours is Different:
The novelty of our approach is in designing deliberately programmed kinetic transients and assembling thermodynamic and kinetic models with no empirical assumptions.
PUBLICATIONS RESULTING FROM THIS PROJECT

Support for this work has been leveraged with several fellowships for graduate student support. These papers include specific acknowledgement of ONR support.


GRADUATE STUDENTS, POSTDOCS, VISITING SCIENTISTS, AND COLLABORATORS

Graduate students and postdoctoral associates supported by this grant

Li Voon Ng and Steve Rankin - Transport and kinetic non-idealities in inorganic polymerization and Sol gel copolymerization.

Li Voon and Steve were also partially supported by fellowships from the National Science Foundation.

Jan Sefcik -- Thermodynamics and kinetics of silicates and aluminosilicates in zeolite synthesis. Design and testing of chemical kinetic transients to regulate the development of molecular architecture and so influence film microstructure and properties.

Kangtaek Lee -- Sol gel particle synthesis.

Kangtaek's work was also partially supported by a grant from Oak Ridge National Labs.

Gary Pozarnsky - Intermediates in multicomponent sol/gel reactions. Now with Clarkson University, Potsdam, NY.

Jorge Sanchez - Kinetics of SiO2 sol/gel reactions. Now with AT&T Bell Labs, Murray Hill, NJ

Gary and Jorge were also partially supported through fellowships from the Center for Interfacial Engineering at the University of Minnesota.

Odile Zarembowitch (visiting scientist from Universite Pierre et Marie Curie) - multicomponent vanadate preparation.

As is sometimes the case in academics, some funds had been used to support students who successfully completed NEITHER their degree nor any publications: Jianchong Yang, Enrico Westenberg

Collaborators

Mike Harris (Oak Ridge National Labs) - sol gel synthesis of particles.

Gary Wieber (Dow Corning) - sol gel synthesis of inorganic/organic hybrid copolymers.