

SYMPOSIUM EE
Organic/Inorganic Hybrid Materials

November 29 - December 3, 2004

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* Invited paper

8:10 AM OPENING REMARKS 8:15 AM *EE1.1

Controlled Surface Nucleation of Latex Nuclei as Dissymmetrization Tool for Janus Nanoparticles.

Etienne Duguet¹, Stephane Reculosa², Franck Pereira¹, Adeline Perro^{1,2}, Serge Ravaine², Marie-Helene Delville¹, Elodie Bourgeat-Lami³, Christophe Mingotaud⁴ and Anne-Francoise Mingotaud⁴; ¹ICMCB, CNRS & University of Science and Technology of Bordeaux, Pessac, France; ²CRPP, CNRS & University of Science and Technology of Bordeaux, Pessac, France; ³LCP, CNRS & CPE, Villeurbanne, France; ⁴LIMRCP, CNRS & University Paul Sabatier, Toulouse, France.

The "Janus particles" term refers in Roman religion to Janus God who was usually represented with two heads placed back to back. Indeed, such objects may present original properties such as (i) an amphiphilic character if an hydrophilic face may be combined with an hydrophobic one, (ii) a giant dipole moment if the surface charges may segregate onto separate poles or (iii) a discriminatory reactive behavior if two types of chemical functions may be concentrated onto separate hemispheres. In a pioneering work, glass microspheres were deposited on a solid support covered with a cellulose varnish film of controllable thickness protecting one part of the spheres whereas the other one was treated with octadecyltrichlorosilane, which is commonly used to make a surface hydrophobic. After removal of the varnish that let the protected surface hydrophilic, amphiphilic particles were obtained. Although interesting for large particles, the technique is however unsuitable for nanoparticles, because the control of the varnish layer thickness below 1 micrometer would be rather difficult. In the most general case, Janus particles are prepared from symmetrical ones. Several dissymmetrization procedures, i.e. chemical or physico-chemical processes altering the symmetry elements of the precursor particles, have been investigated: partial contact with reactive media through Langmuir or Langmuir-Blodgett-derived techniques or toposelective surface chemical modification in directional fluxes and fields. Nevertheless, the low amount of produced Janus particles remains a limitation. That is why we are investigating and developing a new dissymmetrization technique derived from our experience of the controlled surface nucleation of polystyrene latex particles onto silica beads. This new concept is based on the nucleation of one latex particle per inorganic seed particle in order to obtain dumbbell-like hybrid particles. This route is successful if the nucleation step is favored at particle surface thanks to an adequate preliminary surface modification by PEO-based macromonomers for instance. Such hybrid particles are amphiphilic Janus particles, but more interestingly the polymer part may also act as a partial mask of the inorganic surface. Indeed, the non-protected hemisphere may be surface modified by a first reagent, then the mask is removed under the high shear of ultracentrifugation or ultrasonication and lastly the deprotected surface may be modified by a second type of reagents. This new method is an extension of the pioneering varnish technique without restriction concerning the amount and the size of the precursor particles (typically from 50 to 150 nm in diameter). The aim of this communication is to present this route in the context of those previously reported, to be more specific about the experimental conditions and to discuss the results and the expected applications of such new colloidal systems.

8:45 AM EE1.2

Novel Organosilanes for the Preparation of High Refractive Index Silicene Coatings. Pierre Maurice Chevalier¹ and Duan Li Ou²; ¹SISC, S&T, Dow Corning S.A., Senefte, Belgium; ²S&T, Dow Corning Ltd, Barry, United Kingdom.

In its continuing efforts to develop an in-depth understanding of the process-structure-property relationships, Dow Corning is investing, through the Surface and Interface Solutions Center (SISC), in innovative technologies from silanes to materials with improved properties towards current and future applications. As such, we wish to present herein the design and synthesis of novel organosilanes for the preparation of coatings having good dimensional stability and exhibiting higher refractive indices (RI), and thus for optical uses such as antireflective coatings for display devices, intra-ocular and optical lenses, optical amplifying fibers, or for hair care application. Two major approaches have been reported previously to enhance refractive index of silicone polymers, organic resins and glasses. The first approach involves blending of silica and organopolysiloxane with well-known RI enhancers e.g. titania and zirconia or by reacting silica precursors with titanium alkoxides. However, the RI of the final inorganic material is often much lower than the theoretical expected value because of in-homogeneity in the dispersion of the oxides particles (scattering effect). In addition, brittle glass or co-inorganic material does not always fulfill the processability and mechanical

requirements of specific applications. The second approach is focusing on the preparation of phenyl versus alkyl-containing silicones. Phenylalkylsiloxanes, allowing tunable RI from 1.43 to 1.55, for optical lenses and cosmetics have been described, confirming the importance of the organic group contribution onto the refractive indices. However, a need still remains for high refractive index, stable, curable and easily processable organo-modified silicone resins versus glasses or mixed metal oxides, having chemical resistance and well-balanced mechanical and thermal properties versus organic resins. Our current study is focusing on new synthetic routes to high refractive index curable polyaromatics and halogenated aromatic functional silicone resins with RI above 1.56 at 633 nm and ultimately with predictable and desired optical properties. Novel organosilanes containing anthracenylmethyl-, naphthylmethyl- and iodobenzyl-organic groups are synthesized and used as precursors for the preparation of stable and soluble aryl-functional silicone resins. Alternatively the direct iodination is also demonstrated onto preformed aromatic- functional resins. The curable resins are spin-coated onto silicon wafers, cured below 250°C and the refractive indices are measured by spectroscopic ellipsometry at 633 nm. To date we have demonstrated the preparation of silicone-based coatings with refractive index as high as 1.770. This is representing an RI enhancement of up to 0.21 as compared to traditional silicone and organic coatings, opening a new range of applications based upon improved thermo-mechanical and optical properties.

9:00 AM EE1.3

Polymerization on Surfaces of Nanoporous Silicas and Conversion of the Polymers to Nanoporous Carbons.

Michal Kruk¹, Bruno Dufour¹, Ewa B. Celer², Tomasz Kowalewski¹, Mietek Jaroniec² and Krzysztof Matyjaszewski¹; ¹Chemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania; ²Chemistry, Kent State University, Kent, Ohio.

The grafting of polymers on surfaces of nanoporous materials is very interesting from the point of view of basic research, and potentially highly important as a method to obtain nanomaterials with designed composition and surface properties, including those suitable as packings for HPLC. Atom transfer radical polymerization (ATRP) is known as an excellent method to form polymer layers of controlled composition and thickness on solid surfaces, but the opportunities of the use of this controlled polymerization method to introduce polymer layers on surfaces of nanoporous materials have been largely unexplored. To explore these opportunities, we studied the grafting of polyacrylonitrile (PAN) from surfaces of nanoporous silicas of different pore diameters. The obtained silica-PAN nanocomposites were converted to silica-carbon composites, and the carbons were isolated via dissolution of the silica matrix. The porous silicas used as the substrates for the polymerization, the silica-polymer nanocomposites, the silica-carbon nanocomposites and the carbons were extensively characterized using a variety of techniques, including nitrogen adsorption, thermogravimetry, transmission electron microscopy and powder X-ray diffraction. Moreover, the polymer formed on the silica surface was isolated and analyzed by size-exclusion chromatography. The amount of PAN formed in the nanopores was shown to depend on the polymerization time and the reaction mixture composition. The silica-PAN nanocomposites exhibited accessible porosity, as long as the silica nanopore diameter was sufficiently large and the amount of PAN introduced was significantly smaller than the amount necessary to fill the entire nanopore space. In these cases, there was evidence of the formation of fairly uniform polymer layer on the silica nanopore surface. The conversion of PAN to carbon via its stabilization by heating to 300°C under air and carbonization at 800°C under nitrogen was successfully achieved, and the dissolution of the silica substrate allowed us to obtain mesoporous carbons with high specific surface areas (300-1000 m² g⁻¹) and large pore volumes (0.8-2.4 cm³ g⁻¹). The carbons exhibited high adsorption capacity and yet very low microporosity, which makes these materials different from most mesoporous carbons reported to date, which exhibited significant microporosity or had quite low adsorption capacity. This study demonstrated the applicability of ATRP for the introduction of polymer films on nanoporous surfaces, and showed some remarkable opportunities in the conversion of surface-grafted polymer to nanoporous carbon.

9:15 AM EE1.4

One-Dimensional Assembly and Selective Orientation of Lander Molecules on an O-Cu Template.

Roberto Otero Martin¹, Yoshitaka Naitoh¹, Federico Rosei¹, Ping Jiang², Peter Thostrup¹, Andre Gourdon², Erik Laegsgaard¹, Ivan Stensgaard¹, Christian Joachim² and Flemming Besenbacher¹; ¹Department of Physics and Astronomy, University of Aarhus, Aarhus, Denmark; ²CEMES, CNRS, Toulouse, France.

Properly functionalized organic molecules are promising building blocks for nanoscale electronic circuits [1]. A major challenge is to develop a novel technology to assemble such molecular elements in a

planar conformation into a predetermined architecture with atomic-scale precision [2]. This requires the ability to create an ordered pattern for the molecular adsorption sites and to steer the adsorption orientation of the molecules into a geometry that will enable the interconnection of the molecules in a circuit. Here we demonstrate that the striped periodic supergrating created by a controlled oxidation of a Cu(110) surface [3] is a suitable nanoscale template for the assembly of individual molecular building blocks, such as the so-called "Lander molecules", into well-ordered arrays of long molecular chains. Furthermore, we show that by controlling the width of the nanotemplate we can select the adsorption orientation of the molecules, and thereby steer their alignment along the specific direction of the template [4]. [1] C. Joachim, J. K. Gimzewski, A. Aviram, *Nature* 2000, 408, 541-548 [2] F. Rosei, M. Schunack, Y. Naitoh, P. Jiang, A. Gourdon, E. Laegsgaard, I. Stensgaard, C. Joachim, F. Besenbacher, *Prog. Surf. Sci.* 2003, 71, 95-146 [3] K. Kern, H. Niehus, A. Schatz, P. Zeppenfeld, J. Goerge, G. Comsa, *Phys. Rev. Lett.* 1991, 67, 855-858 [4] R. Otero, Y. Naitoh, F. Rosei, Ping Jiang, Peter Thostrup, André Gourdon, Erik Laegsgaard, Ivan Stensgaard, Christian Joachim, and Flemming Besenbacher, *Angew. Chem. Intl. Ed.* 2004, 43, 2091

9:30 AM *EE1.5

Synthesis and Surface Functionalization of Cage-Like Mesoporous Silicas. Clemens Zapilko, Yucang Liang and Reiner Anwander; Anorganisch-Chemisches Institut, Technische Universität München, Garching b. München, Germany.

The family of cage-like mesoporous silicas comprise hexagonal SBA-2 ($P6_3/mmc$) and SBA-12 ($P6_3/mmc$) [1,2] as well as cubic KIT-5 ($Fm\bar{3}m$) [3], FDU-1 ($Fm\bar{3}m$) [4], SBA-16 ($Im\bar{3}m$) [2], and SBA-1 ($Pm\bar{3}n$) [1]. In addition, cage-like periodic mesoporous organosilicas, PMOs, such as hexagonal HMM-2 ($P6_3/mmc$) [5], cubic HMM-3 ($Pm\bar{3}n$) [6], and cubic PMO with $Im\bar{3}m$ space group [7] have been reported recently. It is assumed that their overall zeolite-like architecture, featuring an array of cages with diameters in the range of 3-10 nm, will produce superior materials for catalytic applications as well as for sorption/separation and sensing processes. The cages are three-dimensionally interconnected by smaller windows of uniform size, which can be tailored by carefully varying the synthesis conditions like temperature, pH-value, and the molar ratio of surfactant and silica precursor. Detailed information about the pore/cage architecture was obtained by (i) electron crystallography [1b], successfully applied by Ryoo et al. for the determination of the structural properties of SBA-1, SBA-6 and SBA-16, (ii) nonlocal density functional theory [8], (iii) chlorosilane-based surface silylation [9], (iv) combination of nitrogen and argon physisorption [10], and (v) investigation of the adsorption of bulky organic molecules on the silica surface [11]. Herein we report the synthesis and characterization of highly ordered two- and three-dimensional mesoporous silicas including a topologically new organosilica. Advanced organic-inorganic hybrid materials were obtained via surface functionalization using novel silylation reagents and by grafting of tailor-made metalorganic complexes. [1] (a) Huo, Q.; Leon, R.; Petroff, P. M.; Stucky, G. D. *Science* 1995, 268, 1324. (b) Sakamoto, Y.; Kaneda, M.; Terasaki, O.; Zhao, D.; Kim, J. M.; Stucky, G. D.; Shin, H. J.; Ryoo, Y. *Nature* 2000, 408, 449. [2] Zhao, D.; Huo, Q.; Feng, J.; Chmelka, B. F.; Stucky, G. D. *J. Am. Chem. Soc.* 1998, 120, 6024. [3] (a) Kleitz, F.; Liu, D.; Anilkumar, G. M.; Park, I.-S.; Solov'yov, L. A.; Shmakov, A. N.; Ryoo, R. *J. Phys. Chem. B* 2003, 107, 14296. (b) Matos, J. R.; Kruk, M.; Mercuri, L. P.; Jaroniec, M.; Zhao, L.; Kamiyama, T.; Terasaki, O.; Pinnavaia, T. J.; Liu, Y. *J. Am. Chem. Soc.* 2003, 125, 821. [4] Yu, C.; Yu, Y.; Zhao, D. *Chem. Commun.* 2000, 575. [5] Kruk, M.; Jaroniec, M.; Guan, S. Y.; Inagaki, S. *J. Phys. Chem. B* 2001, 105, 681. [6] Guan, S.; Inagaki, S.; Ohsuna, T.; Terasaki, O. *J. Am. Chem. Soc.* 2000, 122, 5660. [7] Guo, W.; Kim, I.; Ha, C.-S.; *Chem. Commun.*, 2003, 2692. [8] Ravikovitch, P. I.; Neimark, A. V. *Langmuir* 2002, 18, 9830. [9] Kruk, M.; Antochshuk, V.; Matos, J. R.; Mercuri, L. P.; Jaroniec, M. *J. Am. Chem. Soc.* 2002, 124, 768. [10] Kruk, M.; Jaroniec, M. *Chem. Mater.* 2003, 15, 2942. [11] Garcia-Bennett, A. E.; Williamson, S.; Wright, P. A.; Shannon, I. J. *J. Mater. Chem.* 2002, 12, 3533.

SESSION EE2: Mesoporous Films
Chair: Nicola Huesing
Monday Morning, November 29, 2004
Room 302 (Hynes)

10:30 AM *EE2.1

Evaporation-Induced Self-Assembly of Porous and Composite Hybrid Nanostructures. Jeffrey Brinker, Sandia National Laboratory/University of New Mexico, Albuquerque, New Mexico.

This talk discusses evaporation induced self-assembly as a means to organize simultaneously hydrophilic and hydrophobic precursors into

hybrid (organic/silica or metal/silica) nanocomposites that are optically or chemically polymerizable, patternable, or adjustable. For example, the co-self-assembly of amphiphilic photoacid generators with silica precursors results in photosensitive thin film mesophases in which the pore size, pore volume, surface area, and refractive index may be continuously varied over a range depending on the UV exposure time. Incorporation of switchable, hydrogel or azobenzene moieties provides a means to create nanostructures exhibiting chemo-, thermo- or opto-mechanical actuation. Biocompatible self-assembly, using phospholipids as the structure-directing agents, allows cell immobilization in a robust self-contained, self-sustaining environment of interest for stand-alone cell-based sensors. However, we observe that cells co-opt the EISA process, altering significantly the self-assembly pathway and creating a unique bio/nano interface. As a new direction in self-assembly, we have exploited mechanically-based re-assembly to create superhydrophobic, fractal silica surfaces mimicking those of the Lotus leaf and desert beetle. These surfaces are self-cleaning and fundamentally affect flow, making them of general interest for containerless fluidic microsystems.

11:00 AM *EE2.2

From Hybrid Films to Mesoorganized Multi-Metal-Oxide Meso-Organized Nanocrystalline Films (M3NF), Preparation and Characterization. Cedric Boissiere¹, David Grosso¹, Bernt Smarsly², Torsten Brezesinski², Sophie Lepoutre¹, Jose C. Valle Marcos¹, Lionel Nicole¹, Marcus Antonietti² and Clement Sanchez¹; ¹LCMC, UPMC, Paris, France; ²Max Planck Institute of Colloids and Interfaces, Potsdam, Germany.

The first Micellar Templated Structure (MTS) preparation of powders with periodically organized meso-ordered domains within alumina doped silica matrix was described in literature in 1992. Ever since, an increasing amount of time was dedicated to the research of new amphiphiles templates, inorganic compositions and their applications (heterogeneous catalysis, depollution, separation, etc). The preparation of MTS shaped as thin films was first reported in 1996. Their preparation by Evaporation Induced Self Assembly (EISA) is only possible via a precise and simultaneous control of the sol-gel chemistry and the evaporation process. These are promising materials for nanotechnology science attending that one can easily control their structure (separately tuned pore size, pore composition and inorganic wall composition) to modulate their chemical and physical properties. The present work is dedicated to a rapid summary of the micellar segregation and self-organisation that takes place during solvent evaporation within a surfactant / mineral polymerising hybrid medium. The present description was elaborated from results obtained mainly during meso-structured thin films preparation, but it approaches any system undergoing dynamic phase separation through rapid concentration in non volatile components. High quality and reproducible thin silica and non-silica mesoporous films were obtained with mono-oriented organised mesoporosity, fitting various space groups (i.e. $p6m$, $Pm\bar{3}n$, $Im\bar{3}m$, etc). The EISA mechanism was studied through in-situ time-resolved SAXS, interferometry and spectroscopic ellipsometry investigations during dip-coating. A Modulable Steady State (MSS) was found during which the system is in quasi-equilibrium with its environment and during which the final structure is formed. The corresponding Self-Assembly mechanism was found to be governed by a competition between evaporation, micellisation and condensation that depend on various critical chemical and processing parameters the influence of which have been summarized into directly usable phase diagrams. Calcined SiO₂ and TiO₂ mesoporous films structure (pore size and anisotropy, porous volume and surface) and mechanical properties (young modulus) were investigated by UV-Visible spectroscopic ellipsometry. Finally, thanks to a specially designed block copolymer, one further step was accomplished by achieving the dip coating and controlled nanocrystallisation of various metallic and multi-metal-oxides films (M3NF) of composition $CoxTi(1-x)O(2-x)$ with ilmenite or doped Anatase structure, and SrTiO₃ and MgTa₂O₆ with perovskite structure. Attending the well known magnetic, dielectric and catalytic properties of these structures, M3NF are highly compatible with high technology applications in microelectronic, energy transfer devices, spintronic, nano-mechanical adjustments, data storage, oxide fuel cells, etc

11:30 AM EE2.3

Templating with cross-linked block copolymer thin films. Ryan C. Hayward, Bradley F. Chmelka and Edward J. Kramer; Chemical Engineering, University of California, Santa Barbara, California.

Block copolymer templating of inorganic materials is an attractive route to the formation of mesostructured hybrid thin films. Typical approaches to the production of such materials rely on simultaneous assembly of an organic template and an inorganic sol-gel precursor into a hybrid mesostructure. While these techniques offer considerable control over local organization, the presence of the inorganic

component during the assembly process typically complicates efforts to manipulate the orientation and long-range ordering of the mesostructure. The ability to direct assembly of the block copolymer template independently from the incorporation of inorganic components promises significant advantages for improving morphological control over the resulting hybrid structures. We have investigated the use of polystyrene-block-poly(2-vinylpyridine) thin films as templates for the formation of organic/inorganic hybrid materials. Polymer films are pre-organized by thermal annealing and subsequently infiltrated with inorganic precursor solutions. Without cross-linking of the template film, microstructural rearrangement of the polymer takes place, leading to disorganized structures. The introduction of cross-links in the block copolymer film limits structural reorganization, thereby allowing replication of the polymer microstructure into a hybrid or porous inorganic film. At low cross-link densities, osmotic stresses are sufficient to cause distortion of the polymer structure, whereas at high cross-link densities only small amounts of inorganic material can be incorporated. In the intermediate regime however, it is possible to form high-fidelity inorganic replicas of the initial block copolymer structures. While we have focused on silica and titania as the inorganic components, we expect his approach can be generalized to a variety of inorganic species.

11:45 AM **EE2.4**

Synthesis and Characterization of Well-Ordered Distorted Cubic Phase Mesoporous Tin Oxide Thin Films.

Hugh W. Hillhouse and Vikrant Urade; Chemical Engineering, Purdue University, West Lafayette, Indiana.

The synthesis of ordered mesoporous silica [1] via the cooperative self-assembly of surfactants and silica oligomers defined a new synthesis route that has been extended to other sol-gel systems to yield novel nanostructured materials. As a result, high surface area mesoporous frameworks have been synthesized from many metal oxides. Further, the development of evaporation induced (or evaporation controlled) self-assembly techniques [2] to yield continuous thin films of these materials has opened up the possibility of new applications in sensors, nanowire synthesis, low-k dielectrics, electrode materials, and photovoltaics that may exploit the high surface area, ordered pore structure, present in these films. A host of mesoporous metal oxides thin films have been reported, including several elucidating in depth studies on the TiO₂ system [3]. However, despite the evolution of our understanding of these systems, well-ordered, thermally stable surfactant-templated mesoporous SnO₂ films has remained elusive. Previously, researchers have reported disordered mesoporous SnO₂ [4] as well as well-ordered non-porous mesostructures with p6m symmetry [5]. Here, we report the synthesis and characterization of highly ordered mesoporous tin oxide films having a distorted cubic mesostructure that results from the anisotropic contraction of a parent Im3m phase. Films are prepared by dip-coating dilute solutions of triblock copolymer surfactants and tin oxide precursors (from tin (IV) chloride). In contrast to SiO₂ and TiO₂ systems, the hybrid inorganic-organic films have no ordered mesostructure after dip-coating and are subsequently subjected to very high humidity at elevated temperatures. This delayed humidity treatment (DHT) induces the transition from a disordered amorphous hybrid to a highly ordered cubic mesostructure. The as-prepared films were then subjected to progressively higher temperatures to consolidate the inorganic framework. This thermal treatment is necessary to retain the mesostructure after surfactant removal and avoid structural collapse upon calcination. This method, although similar to that reported by Miyata and co-workers [5] differs in its use surfactant template and the controlled humidity and thermal treatments. By using this combination, we are able to both reach interface curvatures needed to form the cubic phase as well as condensation levels necessary for template removal. [1] Kresge, CT, et al. Nature 359, 1992, 710. [2] Brinker CJ, Lu YF, Sellinger A, Fan HY, Adv. Mater. 11 (7), 1999, 579. [3] Crepaldi, EL, et al., J. Am. Chem. Soc. 125(32), 2003, 9770. [4] Chen FL, Liu ML, Chem. Comm. 1999, 1829; Hyodo T, Shimizu Y, Egashira M, Electrochem. 71, 2003, 387; Qi LM, Ma JM, Cheng HM, Zhao ZG, Langmuir 14, 1998, 2579; Yuliarto B, Zhou HS, Yamada T, Honma I, Asai K. Chem. Lett. 32, 2003, 510. [5] Miyata H, Itoh M, Watanabe M, Noma T. Chem. Mater. 15, 2003, 1334.

SESSION EE3: Porous Materials by Templating
Chairs: John Bartlett and Jeff Brinker
Monday Afternoon, November 29, 2004
Room 302 (Hynes)

1:30 PM ***EE3.1**

Hierarchically Structured Silica Monoliths.

Nicola Karola Huesing¹, Doris Brandhuber¹, Christina Raab¹, Viktoria Torma¹ and Herwig Peterlik²; ¹Chemistry, Vienna University of Technology, Vienna, Austria; ²Physics, University of Vienna,

Vienna, Austria.

Hydrolysis and condensation reactions of alkoxysilanes such as tetramethoxy- or tetraethoxysilanes are the masterkey reactions in the synthesis of porous silica-based materials. However, the sol-gel process with these precursors is limited in its potential, especially when it comes to the synthesis of mesostructured monolithic materials due to the obligatory presence of the solvent as compatibilizing agent (typically an alcohol) and the catalyst to start the network forming reactions (acid or base). Diol- or polyol-modified silanes, such as tetrakis(2-hydroxyethyl)silane (EGMS) or the glycerol- and propane diol derivatives as precursors, have some distinct advantages since they can be condensed without a co-solvent, under neutral conditions (no catalyst is required to start the sol-gel reactions), and the diols/polyols released upon hydrolysis show a very good compatibility with lyotropic phases of surfactant molecules. In this work, we present the preparation of large mesostructured silica monoliths from diol/polyol modified silanes, which exhibit a highly regular arrangement of the mesopores within different macroporous matrices, e.g. a cellular scaffold. The material is directly prepared by true liquid-crystal templating (TLCT) from liquid-crystal like phases of block copolymer surfactants in water. The final materials structure shows a strong dependence on the choice of the precursor and template molecule as well as the concentration of the surfactant. Drying of large monoliths is often the most crucial step in the synthesis process, since surface tension, the evolution of capillary pressure and the removal of templates often results in large shrinkage or even destruction of the whole gel body. In this work, drying was performed via supercritical extraction with carbon dioxide, ethanol, methanol and acetone as well as under ambient conditions via surface silanization. In situ small angle X-ray scattering studies allowed to follow the evolution of the mesoscopically ordered structure during all processing steps starting from mixing the precursors, gelation, aging and supercritical or ambient pressure drying. With scanning and transmission electron microscopy (SEM,TEM) the porous periodically ordered structure of the final material was investigated from the nanometer to the micrometer length scale. Due to the choice of the solvent (diol or polyol and water) and the presence of the non-ionic surfactant molecules a second-level phase separation process is induced by spinodal decomposition leading to the formation of the macroporous cellular structure (in the case of EGMS and P123).

2:00 PM ***EE3.2**

Monolithic O/I-Hybrids with Hierarchically Ordered Meso- and Macropores. Kazuki Nakanishi^{1,3}, Yuki Kobayashi¹, Tomohiko Amatani¹, Kazuyuki Hirao¹ and Tetsuya Kodaira^{2,3}; ¹Material Chemistry, Kyoto University, Graduate School of Engineering, Kyoto, Kyoto, Japan; ²Nanoarchitectonics Research Center, National Institute of Science and Technology, Tsukuba, Ibaraki, Japan; ³PRESTO, Japan Science and Technology Agency, Kawaguchi, Saitama, Japan.

Monolithic silica and siloxane-based gels with well-defined co-continuous macropores and highly ordered mesopores have been synthesized from silicon alkoxides with an aid of structure-directing agent. While the macropores are formed by the concurrent phase separation and sol-gel transition induced by the polymerization reaction, the mesopores are templated by the self-organized assembly of the structure-directing agent. After drying and heat-treatment, gels with hierarchical and fully accessible pores in discrete size ranges of micrometer and nanometer were obtained. While the local alignment of the mesopores is confirmed by FE-SEM observation, the long-range mesoscale order over the whole sample is evidenced by X-ray diffraction measurements.

2:30 PM ***EE3.3**

Using Nanoscale Architecture to Control Functionality in Meso-structured Materials Produced Through Inorganic/Surfactant Co-organization.

Sarah H. Tolbert¹, Bradley Kirsch¹, Xu Chen², Vijay Gupta², Will Molenkamp¹, Andrew Clark¹, Dong Sun¹, Andrew Riley¹ and Scott Korlann¹; ¹Chemistry and Biochemistry, UCLA, Los Angeles, California; ²Mechanical and Aerospace Engineering, UCLA, Los Angeles, California.

Inorganic/surfactant co-organization is a powerful method for producing materials with complex and varied geometries on the nanometer length scale. Using a combination of self-assembly and host-guest chemistry, materials can be produced with a wide range of functionalities. More importantly, the nanoscale structure provides a simple route to tune this functionality. In this talk, we will explore a number of systems where materials properties can be tuned and new behavior can be created by control of structure on various length scales. In the first example, templated nanoporous materials are used to control the conformation and thus the optical properties of semiconducting polymers. In this way, new functionality, such as polarized or altered emission, can be created. If the nanoporous host is also an optically or electronically active material, the potential for

tuning materials properties is even greater. Thus, we next address the synthesis of new semiconducting frameworks and their combination with various polymeric guest species. Both bulk and new thin film systems will be addressed. Finally, on a structural level, we find that periodic inorganic/organic composites can be used to tune both stiffness and elasticity, creating materials with a unique combination of mechanical properties.

3:30 PM *EE3.4

Recent Progress in the Synthesis of Mesoporous Organosilicas with Crystal-like Pore-Walls. Shinji Inagaki, Mahendra P.

Kapoor, Yasutomo Goto and Kentaro Okamoto; Toyota Central R&D Labs., Inc., Aichi, Japan.

Periodic mesoporous organosilicas with integral organic functionality derived from bridged organosilanes [(R'O)3Si-R-Si(OR')3] in the presence of surfactant have homogeneous distribution of organic fragments and silica moieties within the framework (1). The materials have uniform pores, higher stability, and control on morphologies (2) and potential application in a variety of areas, including optoelectronics, sensing, enantioselective separation and catalysis. The main object of contemporary hybrid mesoporous materials synthesis is to control the geometry of a material at the molecular level of design. Changing the nature of the organic molecule in the hybrid mesoporous organosilicas are widely published and offer a wide range of opportunities to control the surface properties. Recently, we have described the surfactant-mediated synthesis of phenylene-silica hybrid mesoporous materials with precise control of the nanoarchitecture possessing well-oriented phenylene and silica fragments from 1,4-bis(triethoxysilyl)benzene (3). The material has a hexagonal array of mesopores as well as crystal-like pore walls exhibiting structural periodicity along the channel direction. This was the first synthesis of an ordered mesoporous material possessing a crystal-like periodic pore wall structure. The addition of crystallinity to the pore wall of mesoporous materials has long been sought after and is a most important development in this research field. Very recently, we have also reported the synthesis of ordered mesoporous 4,4'-biphenylene- (4) and 1,3-phenylene- (5) silicas hybrid materials with a crystal-like pore wall similar to that reported for 1,4-phenylene-silica material. We have also functionalized the mesoporous aromatic-silica hybrids by attaching functional groups such as sulfonic group (-SO₃H) for the applications of solid-acid catalysts and electrolyte for fuel cells (6,7). Here we describe the further extension of the crystalline mesoporous system to improve the framework functionality with physical and chemical properties. [References] (1) S. Inagaki, S. Guan, Y. Fukushima, T. Ohsuna, O. Terasaki, *J. Am. Chem. Soc.*, 121 (1999) 9611. (2) S. Guan, S. Inagaki, T. Ohsuna, O. Terasaki, *J. Am. Chem. Soc.*, 122 (2000) 5660. (3) S. Inagaki, S. Guan, T. Ohsuna, O. Terasaki, *Nature*, 416 (2002) 304. (4) M. Kapoor, Q. Yang, S. Inagaki, *J. Am. Chem. Soc.*, 124 (2002) 15176. (5) M. Kapoor, Q. Yang, S. Inagaki, *Chem. Mater.*, 16 (2004) 1209. (6) Q. Yang, M. Kapoor, S. Inagaki, *J. Am. Chem. Soc.*, 124 (2002) 9694. (7) M. P. Kapoor, Q. Yang, Y. Goto, S. Inagaki, *Chem. Lett.*, 32 (2003) 914.

4:00 PM EE3.5

Mesoporous and Homothetic Silica Capsules in Reverse Emulsion Micro-Reactors. Olivier Mondain-Monval¹, Philippe

David Poulin¹, Cecile Marceline Zakri¹, Stephane Stefanovitch Badaire¹, Renal Ronaldovitch Backov¹ and Giulia Juliette Fornasier²; ¹Centre de Recherche Paul Pascal - CNRS France, Pessac, France; ²LCMC, CNRS, Paris.

We present a simple process to synthesize silica mesoporous capsules. Mineralization, in this process, takes place at the oil-water interface of reverse emulsion droplets. A silica alkoxyde precursor (tetraethoxysilane - TEOS) is dissolved in the oil continuous phase whereas the dispersed aqueous phase is enriched with a water soluble surfactant. Shell thickness measurements as function of the capsule size shows an homothetic morphology. Simple scaling analysis reveals that mineralization takes place above a well defined hydrolyzed precursor concentration within the droplets. This behavior suggests that the system reaches a phase boundary, corresponding to the formation of a mesophase made of silica oligomers and surfactants, prior mineralization. In addition to serve as models for surfactant directed mineralization processes, such objects may find use in diverse encapsulation applications.

4:15 PM EE3.6

Air-Liquid Foams, Concentrated Direct Emulsions and Soft Chemistry Toward Hierarchically Organized Porous Monoliths. Renal Backov¹, Florent Carn¹, Annie Colin², Jacques

Livage³ and Nathalie Steunou³; ¹Chemistry, CRPP-CNRS UPR8641, Pessac, Gironde, France; ²Physical-Chemistry, LOF-UMR-CNRS Rhodia FRE2771, Pessac, 33607 Gironde, France; ³Inorganic Chemistry, LCMC-UMR-CNRS 7574, Paris, Paris, France.

Taking in account the extraordinary catalogue of shapes and

hierarchically organized matter that nature is providing, researchers are striving to reproduce those architectures in laboratories. One approach is based on combining soft chemistry or sol-gel process with soft matter and more precisely metastable thermodynamic systems such as air-liquid foams¹ or biliquid foams.² In a first strategy, by using air-liquid foams as macroscale pattern we were able to prepare macrocellular mesoporous metal oxide scaffolds where both Plateau-border lengths and widths as cell morphologies (i.e. spherical or polygonal shapes) can be tuned on demand while offering mesoporosity with vermicular templates. This dynamic approach based on the control of foam's liquid fraction during the mineralization process has been applied to the synthesis of SiO₂ and anatase or rutile TiO₂ as well as V₂O₅ monolith-type materials. In a second route we used concentrated direct biliquid foams to tune macroscale void spaces of silica monoliths while providing mesoporous texture with micellar templates. In this approach by increasing the oil volumic fraction we increase the emulsion viscosity. The increase of the viscosity enhances the shear stress applied to the oil droplets thus minimizing their sizes. Beyond the oil volumic fraction we did play with the pH conditions to tune the wall textures that connect two adjacent cells providing either only internal cell junctions (windows that connect two adjacent cells) or both internal and external cell junctions (nodes connecting four adjacent cells). Those strategies allow to develop materials with potential used as diffusers, membranes, cell promoters and chromatography. 1- Rational design of macrocellular silica scaffolds obtaining by a tunable sol-gel foaming process. Florent Carn, Annie Colin, Marie-France Achard, Herve deleuze, Zoubida Saadi and Renal Backov. *Adv. Mater.* 2004, 16, 140. 2- Inorganic monoliths hierarchically textured via concentrated direct emulsion and micellar templates. Florent Carn, Annie Colin, Marie-France Achard, Elisabeth Sellier, Herve Deleuze, Marc Birot And Renal Backov. *J. Mater. Chem.* 2004

4:30 PM *EE3.7

Synthesis and Application of Ordered Mesoporous Organic-Inorganic Hybrid Materials. Ferdi Schueth, Yanqin

Wang, Chia-min Yang, Anja Rumpelcker, Regina Palkovits and Bodo Zibrowius; MPI fuer Kohlenforschung, Muelheim, Germany.

Cocondensation of alkoxy silanes and functionalized alkoxy silanes in the presence of suitable surfactants or grafting of organic species on the surface of ordered mesoporous materials are methods to create surface functionalized ordered mesoporous materials with high surface area and regular porosity. The current focus of interest lies on the synthesis of functionalized ordered mesoporous materials synthesized with block copolymers, since these allow a higher degree of flexibility with respect to pore size and wall thickness compared to materials of the MCM-41 type. The contribution will highlight different pathways to synthesize such materials with various surface functional groups. The question of homogeneous distribution of the functional groups over the material will be addressed as well. From an application point of view, these materials offer many possibilities: They can be used as such, as for instance carboxylate functionalized materials in acid catalysis or ion exchange. Vinyl modified materials are very useful for the synthesis of other mesostructured functional oxides via the nanocasting pathway. It is thus possible to create ordered mesoporous Co₃O₄ or CoFe₂O₄. Another application field of organically functionalized silica is the reversible anchoring of molecular catalysts and other functional molecules to the surface which may offer advantages with respect to the recovery of such species after use. The contribution will cover various aspects of these application of ordered mesoporous organic-inorganic hybrid materials.

SESSION EE4: Self-assembly Approaches
Chairs: Cedric Boissiere and Sarah Tolbert
Tuesday Morning, November 30, 2004
Room 302 (Hynes)

8:30 AM *EE4.1

Hybrid Materials and Self-Assembling Phases. Samuel I. Stupp, Materials Science, Chemistry, and Medicine, Northwestern University, Evanston, Illinois.

Most mineralized structures in nature such as bone and exoskeletons are hybrid materials in which proteins or other macromolecules nucleate and mediate the growth of inorganic phases. The organic content in these hybrids is typically nanostructured in forms such as fibrils or macromolecules occluded in crystalline lattices. These biogenic structures often have organic-inorganic epitaxial relationships or energy dissipating capacity under stress which are difficult to emulate in synthetic materials. Our laboratory has previously reported one biomimetic example where an apparent epitaxial relationship is established between self-assembling nanofibers of peptide amphiphiles and the hydroxyapatite crystals they nucleate. We report here on three hybrid systems in which two-dimensional or

one-dimensional self-assembling phases template the formation of mineral structures. In one example silica is nucleated in periodic structures of electronically conjugated molecules that exhibit strong fluorescence and energy transfer. In two other examples, biomolecular nanofibers can template one-dimensional semiconducting phases if their surfaces bind precursors ions to the inorganic phase.

9:00 AM *EE4.2

Self-Assembly of Organic/Inorganic Hybrid Nano Building Blocks: Molecular Design Rules from Simulation.

Sharon C. Glotzer, Departments of Chemical Engineering and Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan.

Remarkable new materials are now possible in which organic and inorganic components are organized on nanometer scales. One such class of materials is comprised of inorganic nanocrystals and nanostructured molecules functionalized by organic tethers. By controlling the type, number and placement of the tethers on the surface of these inorganic building blocks, it is possible to construct hybrid organic/inorganic amphiphiles with a natural tendency towards self-assembly, but whose complex geometry and topology, as well as size, rival that of simple organic surfactants [1]. Using simulation, we seek to develop an intuitive framework for predicting the self-assembled structures that result from these shape amphiphiles. In this talk, we present new results of molecular and mesoscale simulations of tethered inorganic nanocrystals and polyhedral oligomeric silsesquioxanes (POSS) and their self-assembly into complex ordered structures [1,2,3]. We show how tuning thermodynamic parameters and architectural features of model tethered building blocks such as nanospheres, nanocubes, and nanorods can control key features of the self-assembled materials. In particular, we describe simulations of self-assembly of mono-tethered [2], tetra-tethered [3], and diblock-monotethered [4] POSS using a coarse-grained model developed in collaboration with several groups [5]. We map phase diagrams for several representative cases of the neat and solvated system, and explore how the multifunctional and cubic nature of the POSS molecule controls both the local and mesoscale ordering of nanostructured phases. [1] Z.L. Zhang, M.A. Horsch, M.H. Lamm and S.C. Glotzer, Tethered nano building blocks: Toward a conceptual framework for nanoparticle self-assembly. *Nano Letters*, 2003. 3(10): p. 1341-1346. [2] X. Zhang and S.C. Glotzer, preprint. [3] E.R. Chan, X. Zhang, A.S. Keyes, C-Y Lee, M. Neurock and S.C. Glotzer, preprint. [4] L. Ho, E.R. Chan, X. Zhang and S.C. Glotzer, preprint. [5] T. Ionescu, X. Zhang, E.R. Chan, C-Y Lee, H.C. Li, P. Cummings, J. Kieffer, C. McCabe, M. Neurock and S.C. Glotzer, preprint. This work is supported by grants from the National Science Foundation (DMR-0103399) and the U.S. Department of Energy (DE-FG02-02ER46000).

9:30 AM *EE4.3

Nanostructured Hybrids: Transcription of Supramolecular Organisation into Organic/Silica Gels. Joel J. E. Moreau, Ecole Nationale Supérieure de Chimie, Montpellier, France.

The combination of organic and inorganic substructures in silsesquioxane hybrids offers unique possibilities for designing new synthetic routes to nanostructured materials. The creation of hybrids with well-ordered mesopore structure was obtained by use of external organic surfactant templates as it was first reported in the synthesis of silica mesophases. The surfactant control of phase was extended to amphiphilic molecules with covalent bond between the silicate and the surfactant tail and led to organic-inorganic layered materials. Hybrids have even larger potentialities since the organic component can itself exhibit diverse self-assembly properties and may direct the formation of the three-dimensional hybrid network in a self-organization process. We already reported the use of supra-molecular interactions, based on the association properties of urea groups by H-bond or on the hydrophobic properties of long hydrocarbon chains, between precursor molecules during the hydrolysis and condensation of $(RO)_3Si-R'-Si(OR)_3$. The self-assembly properties which can be assigned to the organic units, led to helical fibers or layered hybrids. We wish to report here the creation of hybrids showing medium long range ordered structure and a variety of morphologies (fibers, lamellae, spherical or rod like particules, or hollow tubes) according to the structure of the molecular precursor and the nature of the reaction conditions. The mechanism of the transcription of the supramolecular architecture of the assemblies of precursor molecules into the hybrid three dimensional network will be discussed.

10:30 AM *EE4.4

Structural Engineering of Self Assembled Nanohybrids via π - π and H-bonding Interactions. Gerard Calleja¹, Inna Karatchevtseva¹, David J. Cassidy¹, Dunbar P. Birnie², Bruno A. Latella¹ and John R. Bartlett¹, ¹Materials and Engineering Science, ANSTO, Menai, New South Wales, Australia; ²Department of Ceramics and Materials Engineering, Rutgers University, Piscataway,

New Jersey.

Applications of nanohybrid coating in optics, photonics and as sensors requires precise control of the size and spatial orientation of organic and inorganic domains, to enable the properties of the materials to be modulated. Organic groups capable of self assembling by exploiting well-defined interactions such as H-bonding, π - π interactions and/or size exclusion can be used to control the structural evolution of nanohybrids, leading to control of the size and spatial orientation of organic and inorganic domains within the nanohybrids. This study investigates the structural evolution of a series of nanohybrid powders and coatings incorporating self assembling organic species based on complexes between aromatic carboxylic acids (e.g. benzoic (BZA) and trimesic (TZA) acid) and amine functionalised alkyltrialkoxysilanes (e.g. aminopropyltriethoxysilane and N-(3-trimethoxysilyl)propylethylenediamine). The structural evolution of conventional (non self assembling) nanohybrids based on methyltrimethoxysilane was also investigated for comparison. Self assembly in solution prior to initiating formation of the inorganic network was studied by Raman and FT IR spectroscopy, NMR, light scattering and small angle X ray scattering (SAXS), while the nanostructure and properties of the corresponding thin films and nanopowders were investigated by XRD, AFM, TEM, SAXS, and Raman spectroscopy. The mechanical properties of selected coatings were examined using nanoindentation and tensile testing. Coating solutions prepared by hydrolysing MTMS:TMOS mixtures at pH 2, with a $H_2O:Si(IV)$ mole ratio of 10 and equivalent SiO_2 concentration of 5 wt%, exhibited weak, flat SAXS patterns, consistent with the presence of small, structurally diverse species in solution. In contrast, the corresponding solutions prepared from the acid/amine complexes exhibited scattering patterns consistent with larger, more structurally defined species, suggesting that self assembled moieties were forming in solution prior to deposition of coatings and/or precipitation of nanopowders. Raman spectra indicated that the self assembled moieties remained intact during hydrolysis of the methoxy groups and evolution of the inorganic network. AFM and TEM images revealed the presence of well defined domains in the self assembled coatings (with dimensions of 20 to 100 nm), whereas the corresponding coatings produced from the MTMS:TMOS mixture were smooth and featureless. Tensile testing revealed that the self assembled nanohybrid coatings were well adhered to the substrates. These results clearly highlight the structure directing role of the self assembling organic species in such novel nanohybrid precursors that exploit H-bonding and/or π - π interactions, leading to well defined nanosegregation of organic and inorganic domains. Methods for tailoring the structure of these organics to modulate the size and spatial orientation of the domains will be discussed.

11:00 AM *EE4.5

Solid state NMR investigation of interactions between surfactant molecules and walls in mesostructured organosilicas. Niki Baccile and Florence Babonneau; Chimie de la Matière Condensée, UPMC/CNRS, Paris, France.

A large variety of periodic mesostructured organosilicas can be prepared by co-condensation of trialkoxysilane, $RSi(OR)_3$ and tetraalkoxysilane, $Si(OR)_4$ in the presence of surfactants. We have previously demonstrated that the nature of the R group can strongly influence the structure of the self-assembled materials. In the presence of phenyl groups with cetyltrimethylammonium bromide as surfactant, 2d-hexagonal as well as cubic Pm3n phases can be obtained. The formation of this cubic phase suggests that the phenyl groups may play an active role in the self-assembly process by specifically interacting with the polar head groups of the surfactant. Silicas and organosilicas with phenyl, vinyl and methyl groups have been prepared with cationic surfactants with C16 aliphatic chains and various polar head groups. In order to characterize the location of the various organic entities with respect to each other, a high resolution 1H solid state investigation has been conducted, using one of the most sensitive NMR experiments to probe dipolar couplings in solids, and thus spatial proximity: the double-quantum (DQ) NMR experiment under fast Magic Angle Spinning. These DQ experiments using the Back-to-Back recoupling sequence have clearly shown the existence of coherences between the CTAB molecules and the aromatic protons, in the case of the phenyl-functionalized samples. A detailed analysis of these experiments on the various samples will be presented, which can lead to a precise localization of the organic entities at the silica/surfactant interface.

11:30 AM *EE4.6

Silica and Hybrid Silica Gels Revisited: New Insight by Solid State Nuclear Magnetic Resonance. Christian Bonhomme, Lydie Camus and Florence Babonneau; Laboratoire de Chimie de la Matière Condensée, Université P. et M. Curie, Paris, France.

Since the beginning of the 80's, silica gels have been systematically studied by ²⁹Si solid state NMR, using both MAS and CP MAS

techniques (see Maciel et al.). However, a "paradox" is often claimed in the literature: MAS and CP MAS experiments do not lead to comparable results in terms of quantification of the various species present in the gels. In this presentation, we show that this paradox can be solved by a careful analysis of the cross polarization data (CP) and that the published data, though "experimentally correct", are misinterpreted! This approach is extended to a large number of hybrid silica gels involving organics components. Criteria related to "quantitative CP experiments" are established. We show also that 1H solid state NMR gives valuable informations concerning the H networks, by using the most recent developments in high resolution proton NMR (decoupling by multipulses, Lee-Goldburg decoupling under very fast MAS). Under Lee-Goldburg decoupling, the CP process is oscillatory in nature, allowing the direct measurement of H-Si distances by solid state NMR! The behaviour of crystalline (cubane shaped silsesquioxanes), as well as amorphous gels are examined. It is shown that molecular motion in the gels leads to the drastic averaging of the homonuclear H-H interactions, leading to strong dipolar oscillations. Such oscillations are even observed in the case of weakly coupled spins, encountered in Si-CH3 groups.

SESSION EE5: Nanoparticles
Chairs: S. Glotzer and Joel Moreau
Tuesday Afternoon, November 30, 2004
Room 302 (Hynes)

1:30 PM **EE5.1**

Living-Anionic Polymerization Terminated to Nanoparticle Surface and Its Influence on Structure and Dynamics of PI/silica hybrids. Qiang Zhang and Lynden A. Archer; Cornell University, Ithaca, New York.

Surface initiated anionic polymerization has been the common approach to tether long polymer chains to silica nanoparticles. In this study, the opposite approach was adopted: living polyisoprene (PI) chains were terminated and tethered to silica nanoparticles. Sec-BuLi was used to initiate the anionic polymerization of PI in a cyclohexane solvent. Silica surface was grafted with a layer of organosilane oligomers whose open ends were functionalized with chrolosilane groups under anhydrous conditions in the next step. Finally, living PI chains were terminated by these chrolosilane groups and therefore chemically attached to silica nanoparticles. Hairy particles with various PI molecular weight and narrow molecular weight distributions were synthesized. These hairy particles were characterized by gel permeation chromatography, thermogravimetric analysis, dynamic light scattering, atomic force microscopy, etc. The relaxation dynamics of tethered chains were studied by dielectric spectroscopy and structure and dynamics of hybrid materials containing linear PI chains and such particles were investigated using rheometry.

1:45 PM **EE5.2**

One-step Hydrothermal Synthesis of Metal Oxide Nanoparticles whose Surface is Covalently Bound with an Organic Monolayer. Seiichi Takami, Teruyuki Sato, Tahereh Mousavand, Satoshi Ohara, Mitsuo Umetsu and Tadafumi Adschiri; Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, Miyagi, Japan.

We report one-step hydrothermal synthesis of a hybrid nanomaterial where a metal oxide nanoparticle was covalently covered with an organic monolayer. The organic monolayer can be tuned to alter the surface properties of metal oxide nanoparticles. Our method relies on the dehydration between an organic molecule and a hydroxyl group on the growing surface of metal oxide nanoparticles under hydrothermal conditions. We note that organic reagents become miscible with water at higher temperature due to decreased dielectric constant of water. Therefore, metal oxide nanoparticles can be tethered with longer alkyl chains that are not miscible with water at room temperature. We synthesized iron oxide nanoparticles that were modified with C₁₀ alkyl chains. The end of alkyl chains was changed to -CH₃, -NH₂, and -COOH, controlling the surface properties of the oxide nanoparticles. We also successfully attached peptides on the surface of metal oxide nanoparticles. We confirmed that the similar approach is effective for various metal oxides including TiO₂, Co₂O₃, NiO, and Ce₂O₃.

2:00 PM ***EE5.3**

Nanoparticle-Polymer Nanocomposites prepared by the Incorporation of Organically Surface-Functionalized Metal and Metal Oxide Nanoparticles into Polymers.

Guido Kikelbick and Dieter Holzinger; Institute of Materials Chemistry, Vienna University of Technology, Vienna, Austria.

Nanocomposites formed via the incorporation of inorganic nanoparticles into organic polymers offer many interesting applications in fields like optics, electronics, magnetic materials, etc.

Major challenges in the preparation of these materials are to avoid agglomeration and phase separation and to obtain a good chemical link between inorganic and organic moiety. Probably the most promising method to get homogeneous nanocomposites is the surface functionalization of the inorganic nanoparticles with organic groups that act as both, compatibilizers and linkers that covalently bind to the organic polymer matrix via polymerizable or initiating groups. In this contribution we present the controlled preparation of metal (Au) and metal oxide (MO_x; M = Ti, Zr, V, Fe, Sn, Y) nanoparticles and nanorods and their organic functionalization via post synthetic treatment or via in situ surface modification. Goal of all synthetic procedures was the controlled preparation of both, the inorganic particles and the organic polymers. Gold nanoparticles and nanorods were surface-modified with thiol groups or a silica shell that was further modified and incorporated into various polymers. The optical properties of the final materials revealed that the inorganic nano building blocks were homogeneously distributed in the polymer matrix and the materials respond to environmental, such as mechanical, changes. Metal oxide nanoparticles were prepared in microemulsions using either metal alkoxides or metal salts as precursors. Their surface was functionalized during synthesis via an *insitu* approach using modified alkoxides that contained bidentate ligands or via the use of silane coupling agents after synthesis. Applying these approaches initiator groups for atom transfer radical polymerization (ATRP) were attached to the surface and various polymers were grafted from the surface of the thus obtained macroinitiators resulting in inorganic-organic core-shell nanoparticles.

2:30 PM **EE5.4**

Characterization of Metal-Polymer Interfaces in Nanocomposites and the Implications to Mechanical Properties. Rina Tannenbaum, Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia.

The properties of nanocomposites are dominated by the large interfacial area created when nanoparticles are embedded in a polymer matrix. A strong interaction between the polymer and the nanoparticles will result in a flat conformation of the polymer on the surface and lead to a compact interface. On the other hand, a weak interaction will result in the extension of the adsorbed polymer chains into the bulk polymer matrix, leading to a diffuse interface. This work examines the properties of the interfacial region between cobalt oxide (and other metal oxide) nanoparticles embedded in poly(methyl methacrylate) (PMMA) and in poly(styrene) (PS) matrices, two polymers having functional groups with different reactivities. The thickness and structure of the polymer layer adsorbed on the nanoparticles will be determined by coupling transmission electron microscopy (TEM) experiments with thermo-gravimetric analysis (TGA) and infrared spectroscopy (FTIR). Our results indicate that the interfacial region between the cobalt oxide particles and PMMA is denser and more compact than that formed with PS, due to the strong adsorption of PMMA on the surface of the cobalt oxide particles. Nanoindentation experiments show that the characteristics of the interface strongly influence the mechanical properties of the nanocomposites.

2:45 PM **EE5.5**

Core-shell Nanocapsules and Drug Detoxification on Myocyte/Microelectrode Array Devices. Randy S. Duran¹, Aleksa Jovanovic¹, Mark Pottet², Christiane Thielemann², Jorge Chavez¹ and Wolfgang Knoll²; ¹Chemistry, Univ of Florida, Gainesville, Florida; ²Max Planck Institute for Polymer Research, Mainz, Germany.

Polymerizable alkoxysilane compounds find broad use in applications ranging from self-assembly to sol-gel materials. We are interested in synthesizing core-shell nanocapsules from these compounds for eventual drug detoxification applications. Specifically, we have investigated the chemical polymerization of these compounds confined to a free surface of a microemulsion droplet. By varying conditions, monodisperse nanocapsules over a large range of sizes can be obtained. Drug uptake results probed by neonatal myocytes plated over microelectrode array devices will be discussed.

3:30 PM **EE5.6**

Encapsulation and Controlled Release of Bioactive Molecules from Sol-Gel Nano-Particles. Chris J. Barbe, Linggen Kong, Hu Qiang Lin, Kim Finnie, Scott McNiven, Mark Blackford and David Cassidy; Materials & Engineering Science, ANSTO, Menai, New South Wales, Australia.

We present a generic approach to the synthesis of sol-gel silica matrices for encapsulating bioactive species, and controlling their subsequent release over periods ranging from hours to months. The bioactive species are incorporated into the matrix during gelation at, or near, ambient temperature, and remain entrapped until the gels are immersed in solution. The release profile can be tailored by

controlling the internal structure of the gels (pore volume, size and tortuosity, and surface chemistry). In turn, the gel structure can be precisely tailored by varying such sol-gel processing parameters as the water-to-alkoxide ratio, pH, alkoxide concentration, ageing, drying time and temperature. Hence, the release rate of the encapsulated species is controlled by adapting the structure of the internal pore network to the physico-chemical properties of the drug molecule. Combining emulsion synthesis with sol-gel technology enables the carrier to be produced in the form of mono-dispersed spherical particles, with an average size that can be varied from 50 nm to 50 microns. The particle diameter is determined by the size of the reverse micelles, which is controlled by the hydrophile-lipophile balance between the surfactant, aqueous phase and non-polar solvent. The release rate of the encapsulated species is controlled by the internal nanostructure of the spheres, which can be tailored (as in bulk gels) by varying the sol-gel chemical parameters. The ability to independently control the release rate and particle size renders this technology particularly attractive for passive, in-vivo targeting of different organs and tumours. Preliminary in-vivo bio-distribution results, as well as comparisons with alternative controlled-release carriers based on polymers and liposomes, will also be presented.

3:45 PM **EE5.7**

Bioconjugation of CdTe Nanoparticles & Nanowires and Au Nanoparticles: Plasmon-Exciton Interaction. Jaebeom Lee¹, Nicholas A. Kotov¹ and Alexander O. Govorov²; ¹Chemical Engineering, University of Michigan, Ann Arbor, Michigan; ²Physics and Astronomy, Ohio University, Athens, Ohio.

Photoluminescence (PL) enhancement of CdTe nanoparticles (NPs) and nanowires (NWs) is presented from the bioconjugation of hybrid semiconductor-metal supermolecules system. D-biotin and streptavidin for bioconjugation were utilized to connect NPs and NWs in solution. In the presence of metallic nanoparticles, excitonic light emission of nanoparticles is strongly enhanced. The enhancement effect is explained in terms of plasmon-assisted absorption of incident light and plasmon-induced increase of nanoparticles dipole moments. This supermolecules and bioconjugates system can be useful to build further efficient photonic devices and biological sensors.

4:00 PM **EE5.8**

The Effects of Surface Modification on the Electronic Properties of Metal Nanoparticles. Jess Patrick Wilcoxon, Billie L. Abrams and Eugene L. Venturini; 1122, Sandia National Laboratories, Albuquerque, New Mexico.

Nanoparticles with sizes in the range of 1-3 nm have between 50 and 90% of all their atoms at surface positions, so surfactant adsorption modifies the electron density as well as the interatomic distances. This changes the electronic properties of the nanoparticles such as optical absorption and magnetic susceptibility. We report studies of the effect of binding of organic ligands or surfactants to metal clusters of Au, Ag and Au/Ag and Co. These nanoparticles were investigated using size-exclusion chromatography, (SEC), to separate clusters by size, and chemical affinity chromatography, (CAC), to investigate the effect of ligand binding to the cluster surface. We demonstrate that addition of alkyl thiols to metal clusters results in etching of the cluster surface producing especially stable sizes with narrow size dispersion. We find that the length of the thiol determines the etching rate, with the shortest chains, which actually bind most weakly to the cluster surface, having the largest effect on the size dispersion. We also show that deposition of Ag onto the surface of Au clusters weakens the binding of thiols to the surface while alloying the surface of Ag with Au strengthens the bond. In the case of 1.8 nm Co particles in dilute solution we show that the magnetic response depends strongly on the surfactant deposited onto the surface, with alkyl amines producing a nearly linear response at high fields, but not altering the low field susceptibility. Studies of the deposition of magnetic atoms onto the surface of Co clusters reveal an initial quenching of the moment followed by recovery of the magnetic response due to redistribution of the atoms on the cluster surface. Acknowledgments: Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

4:15 PM **EE5.9**

Tunable Electronic Behavior of Ligand-coated Metal Nanoparticles. Gretchen A. DeVries, Kathy Li and Francesco Stellacci; Materials Science and Engineering, MIT, Cambridge, Massachusetts.

Metal nanoparticles hold promise for many scientific and technological applications, including single electron transistors, sub-diffraction limit waveguides, and bio-chemical sensors. Understanding and controlling the behavior of these nanoparticles is essential for the development of reliable devices. Here, we study the electronic and optical properties of metal nanoparticles stabilized by a dense monolayer of organic

ligands. Modulation of both ligand and core parameters can influence the behavior of the nanoparticles. The synthesis procedure for these nanoparticles allows for easy variation of such parameters, providing a straightforward method to produce nanoparticles with desired properties. We present a systematic analysis of the role of several parameters, including the dielectric constant (ϵ) and the electron affinity of the ligand shell, the composition of the core, and the radius of the nanoparticle, on the electro-optical characteristics of the nanoparticles. Specifically, we investigate the optical absorption of nanoparticles in solution, the $I(V)$ characteristics of individual nanoparticles, and the electron mobility across films of nanoparticles as a function of the above parameters. For example, we show that by solely varying the ratio of low- ϵ to high- ϵ molecules in the ligand shell, it is possible to tune the position of the optical absorption resonance, as predicted by Mie theory. Additionally, controlling the composition (and hence the dielectric properties) of the ligand shell can cause the position of the Coulomb blockade on the $I(V)$ curve to shift by as much as 0.5 V. Via this analysis, we demonstrate the ability to easily and controllably tune the electronic and optical behavior of ligand-coated metal nanoparticles.

4:30 PM **EE5.10**

Formation and Reaction of Metal-containing Nanoparticles in Organic/Inorganic Hybrid Aerogels. Chunhua Yao and William Risen; Chemistry, Brown University, Providence, Rhode Island.

Synthesis of hybrid aerogel materials that contain both selectively reactive nanoparticles and nanoparticles with appreciable magnetic susceptibilities will be reported. This has been achieved by first synthesizing silica-biopolymer hybrid aerogels, then incorporating metal ions sequentially, and finally carrying out photolytically induced chemical reductions or decompositions. Thus, for example, silica-chitosan hybrid gels were prepared, Au(III) ions were coordinated to the chitosan, and, after forming the Au(III)-silica-chitosan aerogel by SCL extraction, UV photolysis afforded gold nanoparticles of controlled size in the aerogel. Following absorption of a volatile organometallic compound, such as iron carbonyl itself or its compounds with Co, into the aerogel, additional UV photolysis affords reduced metal decomposition products. The organic/inorganic hybrid products obtained by this approach and several of their size (TEM), optical and magnetic properties will be discussed. In addition, reactions with thiol and disulfide compounds with the metal nanoparticles in the aerogels will be discussed.

4:45 PM **EE5.11**

Jet Blowing of Polymer Micro and Nanofiber Composites with Inorganic Materials. John V. Badding, Ayusman Sen, Sachin Borkar and Bin Gu; Chemistry, Pennsylvania State University, University Park, Pennsylvania.

We have developed a jet-based technique, which we call jet-blowing, that is useful for the fabrication of micro and nanofibers of difficult to process polymers such as polytetrafluoroethylene. The technique is well suited to the preparation of composites composed of fibers and inorganic nanomaterials. Physical blending or in-situ oxidation of metal carbonyls has been used to load inorganic phases such as palladium nanoparticles and metal oxide nanoparticles into the precursor polymer powder. The composite materials have been characterized by electron microscopy, Raman spectroscopy, X-ray diffraction, differential scanning calorimetry, and BET surface area measurements. Preliminary results suggest that the resulting composites have high surface areas and may be suitable as catalytic materials.

SESSION EE6: Structural Characterization

Chair: Florence Babonneau

Wednesday Morning, December 1, 2004

Room 302 (Hynes)

8:15 AM ***EE6.1**

In situ SAXS/XRD Investigations of the Formation of Mesoscopically Ordered Surfactant-Silica Mesophases.

Mika Linden^{1,2}, Cilaine V. Teixeira¹, Heinz Amenitsch³, Viveka Alfredsson⁴ and Freddy Kleitz²; ¹Dept. Phys. Chem., Abo Akademi University, Turku, Finland; ²Department of Heterogeneous Catalysis, Max-Planck Institute for Coal Research, Muelheim/Ruhr, Germany; ³Austrian Academy of Sciences, Graz, Austria; ⁴Physical Chemistry 1, Lund University, Lund, Sweden.

The formation of a variety of different surfactant-silicate mesophases has been studied by in situ synchrotron SAXS/XRD. The syntheses were carried out having the surfactant, the pH of the solution and the temperature as parameters, resulting in the formation of hybrid materials having a 2D hexagonal or one of several cubic structures. Careful analysis of both the scattering and diffraction patterns allows

the different stages of the formation to be described in some detail. The results are compared with literature data (if available) obtained with complementary techniques. It is shown that the formation mechanism is drastically different depending on the initial structure of the surfactant aggregates in solution. Thus, new synthesis approaches can be foreseen that allow the structure of the final hybrid mesophase to be rationally controlled.

8:45 AM *EE6.2

The Use of Multinuclear Solid State NMR for the Characterization of Sol-Gel Derived Hybrid Nanocomposites. Christel Gervais¹, Beatriz Julian^{1,2}, Eloisa Cordoncillo², Purificacion Escribano², Mark E. Smith³, Florence Babonneau¹ and Clement Sanchez¹; ¹Chimie de la Matiere Condensee CC174, Universite Pierre et Marie Curie, Paris, France; ²Departamento de Quimica Inorganica, Universitat Jaume I, Castellon, Spain; ³Department of Physics, University of Warwick, Coventry, United Kingdom.

Properties of hybrid materials in which organic and inorganic components are combined in the nanometer range are strongly dependent on the extent and the nature of the interface between the constituents. Considering for example siloxane-metal-oxo nanocomposites prepared through hydrolysis and condensation of $\text{MxSi}(\text{OEt})_{4-x}$ (with $0 < x < 2$) and $\text{M}(\text{OR})_n$ alkoxides ($\text{M} = \text{Ge}(\text{IV}), \text{Ti}(\text{IV}), \text{Zr}(\text{IV}), \text{Nb}(\text{V}), \text{Ta}(\text{V})$), the degree of homogeneity of the final materials depends on the ability to favour hetero-condensation reactions between the precursors. The siloxane component can be characterized through vibrational spectroscopy and ²⁹Si NMR, and the size or the average distance between metal-oxo nanodomains can be deduced from SAXS analysis. However, the characterization of the interface is not a direct task. Evidence of the Si-O-M linkages may be obtained from FTIR measurements but the attribution of asymmetric Si-O-M stretching mode is not straightforward. For hybrid elastomers based on poly(dimethylsiloxane), ²⁹Si MAS and CP-MAS NMR experiments permit to distinguish and quantify mobile siloxane units from the rigid ones directly linked to the metallic atoms [1]. Such experiments give indirect information about the hybrid interface. ¹⁷O NMR experiments appear as a very straightforward tool to characterize the structure of these materials by probing directly and quantifying the different types of oxo-bridges (M-O-M of oxide network, Si-O-Si of siloxane chains and Si-O-M siloxane-MxOy interface) of the nanocomposites and determining the influence of the functionalization of the silicon alkoxides[2] and the nature of the MxOy oxides[3] on the extent of the Si-O-M interface. Moreover, a complementary NMR approach is to examine the metallic atoms: ^{47,49}Ti has been shown to give useful information about Ti-based oxides[4] despite the intrinsic difficulty of observing these nuclei. Both isotopes magnetically active ⁴⁹Ti ($I = 7/2$) and ⁴⁷Ti ($I = 5/2$) have a low natural abundance, small gyromagnetic ratios and moderately large quadrupole moments resulting in very large lineshapes. These factors combine to produce relatively low intrinsic detection sensitivity. Despite these problems, titanium NMR has a great potential for characterising titano-siloxane hybrid systems. An overview of the use of such advanced NMR techniques for the characterization of hybrid materials and their interfaces will be presented. [1] B. Julian, C. Gervais, E. Cordoncillo, P. Escribano, F. Babonneau, C. Sanchez Chemistry of Materials, vol 15, 3026-3034 (2003) [2] C. Gervais, F. Babonneau, M.E. Smith Journal of Physical Chemistry B, vol 105, 1971-1977 (2001). [3] B. Julian, C. Gervais, M.-N. Rager, J. Maquet, E. Cordoncillo, P. Escribano, F. Babonneau, C. Sanchez Chemistry of Materials vol 16, 521-529 (2004) [4] C. Gervais, M.E. Smith, A. Pottier, J.-P. Jolivet, and F. Babonneau Chemistry of Materials vol 13, 462-467 (2001)

9:15 AM *EE6.3

High Resolution Solid State NMR, a Tool for Characterization of Complex Hybrid Materials. Dominique Massiot and Bruno Alonso; CRMHT-CNRS, Orleans Cedex 2, France.

Over the last years, solid state NMR has undergone significant developments both on the methods and hardware points of view. These developments lead improved sensitivity and resolution improvements, which open the way to new experiments able to probe the structure of complex materials at different length scales. These experiments include homo and heteronuclear correlations, mediated by through bond or through space interactions. Illustration will be given with studies of mesoporous or hybrid or bioinvolved materials[1,2]. In the case of spray-dried mesoporous silica spheres, we have been able to identify and to locate at the interface the remaining alkoxy groups. Moreover, the relative amount of these groups has been measured and related to the textural properties of the mesoporous spheres [3]. Current ¹H solid-state NMR experiments focussed on hybrid mesoporous organosilica spheres is shown to be also particularly useful for the knowledge of self-assembly processes. [1] B. Alonso and D. Massiot, J. Magn. Reson., 163, 347-352 (2003). [2] Advanced Materials, in press [3] B. Alonso, A. Douy, E. Veron, J. Perez, M.-N. Rager and D. Massiot, J. Mater. Chem., 14, 2006-2016 (2004).

SESSION EE7: Polymer-Clay Hybrids
Chair: Mika Linden
Wednesday Morning, December 1, 2004
Room 302 (Hynes)

10:00 AM *EE7.1

Potential for polyolefin-clay hybrid. Arimitsu Usuki, Toyota CRDL, Aichi, Japan.

We have been synthesized nylon 6 clay hybrid (NCH) in 1989. In the clay gallery, ϵ -caprolactam is polymerized; the silicate layers were dispersed in nylon 6 to give a NCH. This is the first example of an industrial clay-based polymer nanocomposite. The modulus of NCH increased to 1.5 times that of nylon6, the heat distortion temperature increased to 140 degree from 65 degree, and the gas barrier effect was doubled at a low loading (2 wt. %) of clay. However, polyolefin clay hybrid could not be synthesized easily because polyolefin is hydrophobic and has poor miscibility with clay silicates. Octadecyl ammonium ion was used as a modifier for the clay and a maleic anhydride modified polyolefin was used so that the clay became more compatible. Thus polyolefin was directly intercalated into the clay gallery. There is also a direct-intercalation process in which polyolefin is modified using maleic anhydride, followed by melt compounding. It is a useful process from an industrial standpoint. Ethylene propylene rubber-clay hybrid (EPR-CH) are prepared by melt-compounding maleic anhydride modified EPR (EPR-MA) with organophilic clay, and their properties are examined. Silicate layers of organophilic clay are found to exfoliate and homogeneously disperse into the nanometer level in the hybrid by transmission electron microscopy observation. EPR-CHs exhibit higher tensile modulus compared to EPR-MA and composites containing conventional fillers such as carbon black and talc. The storage modulus of EPR-CHs is also higher than those of EPR-MA and the conventional composites. Creep resistances of EPR-CH are much improved compared for EPR-MA. Degree of swelling in hexadecane is remarkably restricted. Improvement of these properties is caused because dispersed silicate layers have much large interface with the EPR matrix and are thought to strongly restrain the EPR polymer chains. Nanocomposite technology using small amount of silicate layers is useful to improve properties of thermoplastic elastomer. Various kinds of thermoplastic elastomers are expected to be produced by loading of silicate layers with or without conventional fillers.

10:30 AM EE7.2

Modification of Metal Alkoxide Precursors by Organofunctional Bidentate Ligands: Chemical Problems and Chances for Materials Syntheses. Ulrich Schubert, Ulrike Bauer, Michael Puchberger, Helmut Fric and Claudia Visinescu; Institute of Materials Chemistry, Vienna University of Technology, Wien, Austria.

Complexing ligands are often used to slow down the reactivity of metal alkoxides in sol-gel processes. Substitution by appropriate organic groups allows, in principle, to introduce organic functionalities in metal oxide-based sol-gel materials. However, there are some chemical problems associated with the preparation of organofunctional metal alkoxides, which are mainly caused by the Lewis-acidic character of the metal alkoxides. This will mainly be discussed for single-source precursors of the type $(\text{RO})_3\text{Si}(\text{CH}_2)_3\text{X-M}(\text{OR})_n$ ($\text{M} = \text{Al}, \text{Ti}, \text{etc.}$), where X is a coordinating ligand.

10:45 AM EE7.3

Controlling Morphological Behavior in Polymer-Clay Hybrids using Very Low Surfactant Loadings. Rick Beyer¹, Mary Kurian^{2,3}, Arnab Dasgupta^{2,4} and Mary E. Galvin²; ¹Army Research Laboratory, Aberdeen Proving Ground, Maryland; ²Materials Science & Engineering, University of Delaware, Newark, Delaware; ³Air Products & Chemicals, Inc., Allentown, Pennsylvania; ⁴Indium Corporation of America, Utica, New York.

The promise of lightweight yet very strong and tough hybrid materials based on simple combinations of polymer matrices and layered silicate clay fillers has not come to fruition as once hoped. A significant reason for this continues to be difficulty controlling dispersion of individual silicate layers during fabrication of the hybrid material. Typically, immiscibility between hydrophilic clays with hydrophobic organic materials limits formation of exfoliated nanocomposites by in situ synthetic processes, solution processing, or melt blending. In cases where in situ synthesis is possible, the addition of clay to the reaction mixture affects the molecular weight distribution and reaction kinetics, leading to the formation of a potentially undesirable product. Where melt processing is used to forcibly destroy silicate tactoids and disperse the individual silicate layers, the matrix polymer is also at risk of damage. Clays are typically modified using surfactants to compatibilize them with their polymer matrices prior to

processing; if this process could be used to facilitate dispersion, hybrid materials would be more likely to become a reality. It has been predicted that control over the equilibrium dispersion of the silicate layers may be found in the enthalpic interactions between the silicate, surfactant, and homopolymer. These same models also found an effect of surfactant length on equilibrium morphology. This project has examined these predictions using a model polystyrene/montmorillonite (PS/MMT) system. Low polydispersity, quaternary amine terminated PS surfactants were synthesized with a variety of molecular weights and used to modify MMT in different ways. These experiments showed that a low loading of surfactant, around 17 %, helps the silicate naturally disorder in a PS matrix ($\chi = 0$) with simple annealing (direct melt intercalation). The identical experiment with much higher surfactant loadings resulted in no change in silicate morphology. Surprisingly, using poly(vinylmethylether) ($\chi < 0$) did not cause an increase in dispersion under these conditions, but samples made with poly(methylmethacrylate) ($\chi > 0$) did not show a change in silicate dispersion. These experiments showed that the shortest surfactants provided the most change in morphology upon annealing. Although longer surfactants might enhance the disruption of the clay tactoids through their entropic benefit to any intercalating polymer molecule, this is only observed experimentally for short surfactants. Several situations provide reasonable explanations for this observation; to distinguish between surfactant molecular weight and surfactant coverage as causes of this behavior, a set of samples have been fabricated at only 5 % surfactant loading and characterized. These results and their implications will be presented here.

11:00 AM *EE7.4

Inorganic-Organic Hybrid Materials From Layered Double Hydroxide Structure and Their Subsequent Carbonaceous Repliqua. Fabrice Leroux¹, El M. Moujahid¹, C. Roland¹, L. Vieille¹, C. Taviot-Gueho¹, J. P. Besse¹, E. Raymundo-Pinero² and F. Beguin²; ¹Materials Chemistry, Universite Blaise Pascal, Aubiere, France; ²CRMD, Orleans, France.

Under specific conditions, some organic molecules and polymers once confined into a host structure give rise to carbonaceous materials associated to a large microporosity. It has been illustrated by several examples such as clay materials, but also with 3D host structures such as MCM-48. In this idea, various monomers and/or polymers have been incorporated between the sheets of layered double hydroxide (LDH) (hydroxalite and hydrocalumite-type) materials. In this contribution, we will focus on a biopolymer (alginate) and two monomers, sulfopropylmethacrylate (SPMA) and vinylbenzenesulfonate (VBS), as the organic moiety. In a first step, the synthesis of the inorganic - organic hybrid materials will be described, and the interaction between the host structure and the guest molecule will be discussed according to the preparation pathway. For vinyl and acrylate-based interleaved monomers, the reaction of in-situ polymerization will be characterized, and the behavior in temperature will be presented. In a second step, the textural properties of the carbonaceous materials obtained after a charring process of the former hybrid materials will be discussed in term of porosity and specific surface area and related to the preparation mode. Specific surface area up to 2300 m²/g may be reached for samples prepared initially via the monomer intercalation and its subsequent in-situ polymerization. In addition, the carbonaceous materials have been tested as electrochemical supercapacitors in sulfuric acid medium (1M) by means of galvanostatic and potentiostatic techniques and also by complex impedance spectroscopy. Some of the studied materials present interesting capacitances (up to 160 F/g) associated to a good behavior upon cycling.

11:30 AM *EE7.5

Graphite Nanoplatelets: A Nanoreinforcement Capable of Modifying Mechanical, Thermal and Electrical Properties of Polymer Composites. Lawrence T. Drzal^{1,2}, Hiroyuki Fukushima^{1,2} and Kiriaki Kalaitzidou^{1,2}; ¹Composite Materials and Structures Center, Michigan State University, East Lansing, Michigan; ²Dept of Chemical Engineering and Materials Science, Michigan State University, East Lansing, Michigan.

Nanocomposites composed of polymers reinforced with exfoliated clays and carbon nanotubes are being considered for applications such as interior and exterior accessories for automobiles, structural components for portable electronic devices, and films for food packaging. While most nanocomposite research has focused on exfoliated clay platelets and carbon nanotubes, the same nanoreinforcement concept can be applied to another layered material, graphite, to produce nanoplatelets and nanocomposites. Graphite is the stiffest material found in nature (Young's Modulus = 1060 MPa), having a modulus several times that of clay, but also having excellent electrical and thermal conductivity. With the appropriate surface treatment, exfoliation and dispersion in a thermoset or thermoplastic polymer matrix results in a composite

with excellent mechanical, electrical and thermal properties, opening up many new structural applications as well as non-structural ones where electromagnetic shielding and high thermal conductivity are requirements as well. In this presentation, the mechanical, thermal and electrical properties of exfoliated nanographite platelet reinforced polymer composites (epoxy, polypropylene and nylon) will be presented, including modulus, strength, coefficient of thermal expansion, as well as electrical and thermal properties. The results will be compared and contrasted with the same polymer matrices reinforced with nanoclay, vapor grown carbon fibers and particulate graphite. The results show that when nanographite platelets are added to a polymer, the resulting composite can have three times the modulus of nanoclay platelet reinforced composites. With the proper surface treatment of the nanographite, little reduction in composite tensile strength was detected compared to the neat matrix. Impedance measurements have shown that these platelets percolate at below 3 volume percent and exhibit a 10 order of magnitude reduction in impedance at these concentrations.

SESSION EE8: Hybrid Polymers
Chairs: Guido Kiekelbick and Rick Laine
Wednesday Afternoon, December 1, 2004
Room 302 (Hynes)

1:30 PM EE8.1

Kinetic Stability of the Well-Dispersed or Exfoliated State of Polymer Nanocomposites Made by a Novel Process Method. Kosmas Kasimatis¹ and John M. Torkelson^{1,2}; ¹Chemical & Biological Engineering, Northwestern University, Evanston, Illinois; ²Materials Science & Engineering, Northwestern University, Evanston, Illinois.

Polymer nanocomposites have the potential to yield materials that are "lighter, stronger, and harder" or that possess enhanced barrier properties, electrical conductivity, and thermal and dimensional stability. These enhancements rely on the achievement of exfoliation or dispersion of the nanofiller. Unfortunately, the production of well-exfoliated or well-dispersed polymer nanocomposites has proven challenging, especially when the polymer is nonpolar, or has a high melt temperature or a limited thermal stability. While there has been some success in producing well-dispersed nanocomposites by in situ polymerization in the presence of nanofiller, this is less desirable from a technological standpoint than an approach allowing for direct mixing of polymer and nanofiller. However, melt mixing, e.g. twin-screw extrusion (TSE), has proven unable to yield substantial dispersion or exfoliation for many polymer-nanofiller hybrids. Here we report both on the use of a novel process method that yields well-exfoliated or well-dispersed polymer nanocomposites and on the long-term kinetic stability of the dispersion or exfoliation during subsequent melt processing into a final product. The process is called solid-state shear pulverization (SSSP) and has the virtue, as does TSE, of being a solventless, continuous process that is well suited for commercial application. However, unlike TSE, SSSP produces well-exfoliated nonpolar/organoclay nanocomposites, e.g. well-exfoliated polypropylene (PP)/clay nanocomposites result without using maleic anhydride-modified PP as the matrix. SSSP uses a twin-screw extruder that is specially modified so that processing occurs in the solid state, yielding a powder or particulate that can be subsequently melt processed into a final product. During SSSP, the system undergoes many fragmentation and fusion steps, resulting in intimate mixing and excellent dispersion. The achievement of the exfoliated state of PP/organoclay nanocomposites made by SSSP is evidenced by several methods: transmission electron microscopy (TEM), x-ray diffraction (XRD), and differential scanning calorimetry (DSC). The TEM, XRD, and DSC results contrast sharply with similar characterization done on PP/organoclay hybrids made by twin-screw extrusion which exhibit little exfoliation. Furthermore, the well-exfoliated state is maintained after 2 hr of annealing above the melt transition of PP. Thus, even though the PP/organoclay system is thermodynamically incompatible, the exfoliated state achieved via SSSP is apparently kinetically stable in the melt state over times that are long in comparison to melt processing times. This indicates that SSSP can yield a variety of polymer nanocomposites that cannot be made in a well-dispersed state by melt mixing. Further examples of this will be detailed including nanocomposites involving other polymers with organoclay as nanofiller and nanocomposites involving other nanofillers, such as carbon nanotubes.

1:45 PM EE8.2

Fabrication of Nanocomposite Thin Film of Hydroxyapatite and Polyvinylalcohol and its Ionic Conductive Properties. Toshihiko Takaki¹, Kazuyuki Fukuda¹ and Yoshiro Tajitsu²; ¹Interfacial Science group, Material Science Laboratory, Mitsui Chemicals, Sodegaura-shi, Chiba, Japan; ²Graduate School of Engineering, Kansai University, Suita-shi, Osaka, Japan.

A great deal of research interest is being invested in the fabrication and characterization of nanocomposite films as key materials of the application to the new optical and electrical devices. The interface between the polymer and inorganic particle has the different property from the bulk material. Inorganic particle size decreased to nanometer size, so the increase of surface-to-bulk ratio enhances the unique property. We investigated the preparations and characterizations of hydroxyapatite (HAP) polymer nanocomposites because HAP has unique chemical and physical properties. The HAP-PVA nanocomposite was prepared by reacting Ca(OH) with H₃PO₄ in the presence of polyvinylalcohol (PVA) having calboxyl groups and the HAP particles were commonly formed in the shape of spindles (long axis ca. 80 nm and short axis ca. 25 nm). The reactant was stable and formed transparent films by casting method. The cross-sectional TEM image of the films revealed that the HAP particles with nanometer size were uniformly dispersed in PVA matrix. The composite films can be drawn to 300-500% even if the content of HAP is higher (weight ratio of PVA:HAP =1:1). The HAP-PVA composite films had better He gas barrier properties than the neat PVA film. Generally, it is difficult to obtain a polymer film in which the ion transport is stable and dc conductivity is high. At present, polymer film with high conductivity is in great demand. For the realization of such high conductivity, the HAP-PVA film containing Li⁺ was designed as a solid polymer electrolyte. The HAP colloidal solution was stable when the LiN(CF₃SO₂)₂ aqueous solution was poured. The PVA nanocomposite films containing lithium salt were casting from the HAP colloidal solution with LiN(CF₃SO₂)₂. The transparent and flexible films were obtained. Besides, it is possible to draw the nanocomposite film. These characteristics are very unique as compared with traditional composite film. The ionic conductivity of the film (PVA:HAP =1:1) with the 35wt % content of LiN(CF₃SO₂)₂ is about 10⁻⁷ S/m at room temperature. The ionic conductivity of the drawn film increased. Its value reached to 10⁻³ S/m. In order to investigate the effect of HAP particles on the enhancement of ionic conductivity, we prepared the silica-PVA nanocomposite films and measured the ionic conductivity. The value of ionic conductivity of cationic silica-PVA nanocomposite was 10⁻³ S/m at room temperature. On the other hand, the value of ionic conductivity of anionic silica-PVA nanocomposite was lower than that of cationic silica-PVA nanocomposite. Now, we speculate that, the realization of the high ionic conductivity of these films is because, the anion of lithium salt is trapped by inorganic nanoparticles such as HAP or silica particles, and as a result, the free lithium ions increase at the surface of the inorganic nanoparticles. Finally, the high conductivity in the HAP-PVA composite film might be realized.

2:00 PM **EE8.3**

Nanostructured Organosilicates from Mixtures of Amphiphilic Copolymers and Polyorganosilicates.

Ho-Cheol Kim, James L. Hedrick, Eric Drockenmuller, Teddie Magbitang, Victor Lee, Philip Rice and Robert D. Miller; IBM Almaden Research Center, San Jose, California.

Self-assembled periodic structures of organic copolymers have been used to direct inorganic nanostructures. Selective chemical reaction using precursors or preferential interaction with specific domains is commonly used to localize inorganic materials, hence to create controlled nanostructures. We report the generation, structure-property correlations of thin films of organosilicates containing nanoscopic structures. Binary mixtures of amphiphilic copolymers and organosilicates were used to create the nanostructured organosilicates. A variety of molecular architectures of amphiphilic copolymers including linear, radial and linear-dendritic block copolymers were used to direct the nanostructures. Ordered spherical, cylindrical and lamellar morphologies were characterized using atomic force microscopy (AFM), electron microscopy (TEM), and small angle x-ray scattering (SAXS). A laser excited surface acoustic wave spectroscopy (SAWS) was used to determine mechanical properties of the nanostructured organosilicates, which will be discussed in correlation with morphologies of the thin films.

2:15 PM **EE8.4**

Polymer-Layered Silicate Nanocomposites: New Synthetic Methodologies and Materials Using Living Radical Polymerizations.

Devon Shipp, Nuha Salem, Mahesh Thopasridharan, Stacey R. Reeder, Brendan P. Farrell and Hanying Zhao; Department of Chemistry, Clarkson University, Potsdam, New York.

Composites comprised of a polymer matrix and inorganic fillers are one of the most important and significant materials in today's society. Examples include the use of glass fibers dispersed throughout a polymer matrix. Such materials are of great interest because they usually display significant improvements in mechanical properties, and often other properties such as barrier and fire-retardancy, over and above that of the pure polymer. One of the most significant

developments in the past decade or so has been nanocomposite materials in which at least one component has nano-scale dimensions. Perhaps the best example of these nanocomposites is polymer-layered silicate nanocomposites (PLSNs) that consist of well-dispersed silicate (clay) layers within the polymer matrix. In these materials the large surface to volume ratios of the inorganic component, inter alia, leads to significant improvements in properties, and perhaps most importantly, the tradeoffs in physical properties often observed in macroscopic filled composites may be avoided in the nanocomposites. The work presented in this paper examines the use of in situ living radical polymerization to produce PLSNs that have well-defined molecular weights and polydispersities. Furthermore, using this method one can control the grafting of polymer chains to the surface of the silicate layer, make statistical and block copolymers, and potentially create a large range of polymer architectures in order to examine structure-property relationships encompassing a broad range of materials yet with a high degree of definition. Three living radical polymerization methods have been used: nitroxide-mediated polymerization (NMP), atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain transfer (RAFT) polymerization. Each typically gives pre-determinable molecular weights, low polydispersities and chain-end functionality. We have shown that ATRP can be achieved from initiators that are tethered between the silicate layers. Various homopolymers and block copolymers have been made through this approach. NMP and RAFT polymerizations have been applied to silicates that have been modified with a polymerizable surfactant. In most cases a significant amount of exfoliation is observed. Furthermore, block copolymer-PLSNs exhibit tunable surface properties.

2:30 PM ***EE8.5**

Polymer Approaches to Nanostructured Multifunctional Hybrids. **Ulrich Wiesner**, MS&E, Cornell University, Ithaca, New York.

The study of polymer based self-assembly ("bottom-up") approaches to multifunctional polymer-inorganic hybrid materials is an exciting emerging research area interfacing solid state and soft materials and offering enormous scientific and technological promise. By choice of the appropriate synthetic polymers as well as ceramic precursors unprecedented morphology control down to the nanoscale is obtained. Tailoring of the polymer-inorganic interface is of key importance. The structures generated on the nanoscale are a result of a fine balance of competing interactions, a typical feature of complex biological systems. The potential for new multifunctional materials lies in the versatility of the polymer chemistry as well as that of the inorganic chemistry that can be exploited in the materials synthesis. In the present contribution the synthesis and characterization of nanostructured hybrid materials will be presented with potential applications ranging from microelectronics to nanobiotechnology. In all cases cooperative self-assembly of organic and inorganic species is induced by amphiphilic macromolecules. Besides amorphous and crystalline oxide materials novel systems toward high temperature SiCN and SiC structures are introduced. Examples will include the preparation of mesoporous materials and superparamagnetic mesoporous materials with pore sizes ranging from 5-50 nm for separation technology and catalysis, solid hybrid polymer electrolytes for battery applications, the synthesis of nanoparticles with controlled shape, size, and composition for applications in the life sciences, as well as thin film materials with potential applications in microelectronics and nanobiotechnology.

3:30 PM **EE8.6**

Inorganic-Organic Hybrid Materials with Surface-Modified Metal Oxide Cluster as the Inorganic Component. **Yu Gao**, Franz Rene Kogler, Myhedini Jupa, Michael Puchberger and Ulrich Schubert; Institute of Materials Chemistry, Vienna University of Technology, Vienna, Austria.

Inorganic-organic hybrid materials have extraordinary properties due to the synergism between properties typical of both components. Pre-formed transition metal oxide clusters having suitable organic groups bonded to their surface are prepared by carefully controlled hydrolysis and condensation of carboxylate-substituted transition metal alkoxide. The clusters are then polymerized in the presence of organic co-monomers by various polymerization techniques to form inorganic cluster-reinforced polymers. The properties of the cluster-crosslinked hybrid polymers are distinctly different to those of the parent polymers.

3:45 PM ***EE8.7**

Structural Control and Characterization of Organic-Inorganic Hybrid Materials. **Plinio Innocenzi**¹, Giovanna Brusatin³, Florence Babonneau², Bruno Alonso⁴, Dominique Massiot⁴ and Tongjit Kidchob¹; ¹Architecture and Planning, University of Sassari, Alghero (SS), Italy; ²Chemistry of Condensed Matter, University of Paris 6, Paris, France; ³Dipartimento di Ingegneria Meccanica, settore

materiali, University of Padova, Padova, Italy; ⁴CRMHT, CNRS, Orleans, France.

Structural control in organic-inorganic hybrids is a crucial step to fabricate highly performing materials with functional properties. A combination of different characterization techniques is necessary to reach a better understanding of the structure in order to address the synthesis as a function of the required applications. An example of different organic-inorganic materials, studied by high resolution solid state nuclear magnetic resonance (NMR) and infrared spectroscopies in the middle and near infra-red range, will be presented. In particular have been studied hybrid materials obtained employing organically modified alkoxides containing polymerizable organic functional groups. The extent of the reactions involving the functional group in the solid state is the main parameter to be controlled to obtain a highly homogeneous structure at a nanometric scale. The residual mobility of the organic chains has allowed the use of NMR techniques initially developed for liquids that have brought to a better understanding of the hybrid structure. Two-dimensional ¹H and ¹³C NMR correlations have been employed to unambiguously assign ¹H and ¹³C signals of the organic groups.

4:15 PM **EES.8**

Synthesis and Characterization of Imide-Oligosiloxanes Hybrid Nanocomposite (Imide HYBRIMER) by Reaction of Nano Amine Modified Oligosiloxane and Dianhydride.

Tae-Ho Lee, Jeong Hwan Kim, Ji Hoon Ko and Byeong-Soo Bae; Department of Materials Science and Engineering, Korea Advanced Science and Technology, Daejeon, South Korea.

Imide-oligosiloxanes hybrid nanocomposites (Imide HYBRIMER) were synthesized and their unique properties were examined in this study. Imide HYBRIMER is made by reaction with nano-sized amine modified oligosiloxane (AMO) and dianhydride, where oligosiloxane moieties are cross-linked by imide bondings to form three-dimensional nanocomposite. Each AMO unit has more than three amine groups so that the structure of Imide HYBRIMER is a three-dimensional network. Incorporation of oligosiloxane or silica into polyimide has been known to have advantageous properties, such as higher thermal stability, higher mechanical strength, higher transparency and lower birefringence compared to conventional organic polyimides. Since the AMO has high compatibilities with polyimides, high concentrations of AMO can be added. It is easy to tailor properties of oligosiloxanes by controlling species and amounts of alkoxy silane precursors, therefore properties of Imide HYBRIMER can simply be controlled to be optimized. Nano AMO resins were synthesized by condensation reaction with aminopropyltrimethoxysilane (APTS) and diphenylsilanediol (DPSD) under base catalysts without water and solvents. Nanostructures of AMO were controlled by changing DPSD contents and catalysts and were investigated by ²⁹Si nuclear magnetic resonance spectroscopy (NMR), Fourier transformation infra-red spectroscopy (FT-IR), matrix-assisted laser desorption/ionization-time of flight (MALDI-TOF) and small angle neutron scattering (SANS). The sizes of AMO measured by SANS were from 1 to 5 nm. More three-dimensional shapes and higher condensed structures were obtained with increase of DPSD contents in resins. Their molecular weights were about 600–1000. The preparation of Imide HYBRIMER was completed through the thermal imidization process of amic acids, which were formed by reaction with amine groups in AMO and dianhydrides.

5-(2,5-dioxotetrahydrofuryl)-3-methyl-cyclohexene-1,2-dicarboxylic anhydride (DODCA) as alicyclic dianhydride and pyromellitic dianhydride (PMDA) as aromatic dianhydride were used. The formations of amic acids and imide groups in Imide HYBRIMER were confirmed by FT-IR and the typical vibration peaks of imide were clearly observed. 5% mass loss temperatures measured by thermogravimetric analysis (TGA) were above 400°C and thermal expansion coefficients measured by thermomechanical analysis (TMA) were varied from 33 to 80 ppm/°C. According to dynamic mechanical analysis (DMA), their storage modulus were about 1.6–2.1 GPa. They became larger and decreases of the modulus at glass transition temperature were reduced by increasing DPSD contents in AMO. Higher thermal stabilities and mechanical strengths could be obtained by incorporating siloxane moieties in hybrid nanocomposites. Imide HYBRIMER could induce low birefringence about 0.003, which was lower than that of linear typed polyimides and optical transparency in visible region became larger by 5–10% after adding of AMO.

4:30 PM **EES.9**

Microcellular Organic/Inorganic Hybrid Polymers from High Internal Phase Emulsions. Michael S. Silverstein and Huiwen Tai; Department of Materials Engineering, Technion - Israel Institute of Technology, Haifa, Israel.

Microcellular organic/inorganic hybrid polymers were prepared from styrene (S), divinylbenzene (DVB) and methacryloxypropyltrimethoxysilane (MPS) by polymerizing the

monomers and crosslinking comonomer in the continuous but minor (10%) phase of a high internal phase emulsion (polyHIPE). The morphologies of these polyHIPE were investigated using scanning electron microscopy (SEM), the thermal properties were investigated using differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA) and thermogravimetric analysis (TGA) and the dynamic and static mechanical properties were investigated using the DMTA. The hybrid polyHIPE have cell structures typical of polyHIPE, cells 2 to 10 μm in diameter whose walls were perforated with pores 0.5 to 2 μm in diameter. Increasing the MPS concentration reduced the interfacial tension and produced a marked reduction in cell diameter. The high temperature modulus and thermal stability of the polyHIPE were dramatically increased through the formation of an inorganic polysilsesquioxane network through the hydrolytic condensation of the trimethoxysilyl groups. In the presence of DVB crosslinking this results in the formation of organic/inorganic interpenetrating networks reminiscent of interpenetrating polymer networks (IPN). The modulus at temperatures above the T_g was increased by up to two orders of magnitude through the formation of this inorganic network. The formation of a dense inorganic network is limited at low MPS content and, therefore, the thermal stability is higher for polyHIPE containing DVB crosslinking. The formation of a dense inorganic network would be constrained by the presence of a DVB network at high MPS contents and, therefore, the thermal stability is higher for polyHIPE without DVB crosslinking. Novel microcellular high temperature materials can, therefore, be prepared through the synthesis of organic/inorganic hybrid polyHIPE.

4:45 PM **EES.10**

The Synthesis and Characterization of Energy-Conducting Polymers with Pendant Inorganic Chromophores.

James H. Alstrum-Acevedo¹, Joseph M. DeSimone^{1,2}, Cynthia K. Schauer¹ and John M. Papanikolas¹; ¹Chemistry, University of North Carolina, Chapel Hill, North Carolina; ²Chemical Engineering, North Carolina State University, Raleigh, North Carolina.

We are interested in the synthesis, characterization, and performance evaluation of functional nanoscale materials comprised of a polymeric scaffold with appended cationic transition-metal lumiphores. We have developed a methodology to prepare, spectroscopically characterize, and evaluate a series of organic copolymers functionalized with inorganic chromophores. Preparation of these hybrid systems first involves the synthesis of a linear AB diblock copolymeric scaffold in which A is polystyrene (PS) and B is poly(p-tert-butoxycarbonyloxystyrene) (PStBOC), using Reversible Addition-Fragmentation chain-Transfer (RAFT) radical polymerization. The PStBOC block (B) was converted into poly(4-hydroxystyrene) by acid hydrolysis of the t-BOC moieties, and Ru(II) trisbipyridyl complexes were covalently appended using standard ester coupling reagents. These lumiphores were selected due to their strong absorbance in the visible spectrum, chemical/photochemical stability, useful redox properties, and long-lived excited state lifetimes. Attachment of the cationic transition-metal chromophores to block B of these linear AB diblock copolymeric arrays is expected to promote solid-state self-assembly into nanoscale structures. The metal-loaded macromolecular assemblies were characterized spectroscopically and the determination of the solid-state morphology of films of these materials was investigated using Transmission Electron Spectroscopy (TEM).

SESSION EE9: Poster Session: Organic/Inorganic Hybrid Materials I
Wednesday Evening, December 1, 2004
8:00 PM
Exhibition Hall D (Hynes)

EES.1

Organic Thin-Film Transistor Arrays Fabricated using Self-Aligned Self-Assembly Process. Masahiko Ando^{1,2}, Shuuji

Imazeki^{1,2}, Masahiro Kawasaki^{1,2}, Hiroshi Sasaki³ and Masaya Adachi³; ¹Advanced Research Laboratory, Hitachi, Ltd., Hitachi-shi, Ibaraki-ken, Japan; ²OITDA, Tsukuba-shi, Ibaraki-ken, Japan; ³Hitachi Research Laboratory, Hitachi, Ltd., Hitachi-shi, Ibaraki-ken, Japan.

Organic thin-film transistors (TFTs) can be manufactured using inexpensive solution processing and direct printing processes rather than expensive vacuum deposition and photolithographic patterning. Therefore they have potential as building blocks for electronic devices with low-cost, flexible and large-area to supply the huge number of electronic devices for new forms of ubiquitous and mobile communication. However, their practical application requires the development of novel printing techniques and device structures that provide accurate definition of device patterns with micrometer resolution without highly complex processing. For this purpose, we

have recently developed a new fabrication process for printable organic TFTs called "self-aligned self-assembly process (SALSA)", where soluble nanomaterials such as metallic nanoparticles and organic molecules are self-assembled into a device structure with micrometer resolution and the components of TFT such as semiconductor, source, drain and gate are substantially self-aligned to each other. Here, we show SALSA process to fabricate organic TFT arrays mainly used as an active-matrix backplane to drive liquid crystal displays. An ordinary bottom-gate and bottom-contact TFT structure is used in which the gate electrode, gate insulator, self-assembled monolayer (SAM), and source and drain electrodes are stacked on a transparent substrate, and finally semiconductor film is formed to complete the device. A key point of this process is patterning the hydrophobic SAM by a back-substrate exposure technique using the opaque gate metal as a photomask [1]. The optically patterned SAM not only defines the self-aligned positions of the solution-processed pixel electrode and drain lines, but it also selectively orders the structure of the semiconductor molecules deposited on it. Therefore, both the electrodes and semiconductor are substantially self-aligned to each other. In order to fabricate TFT arrays, where gate lines and drain lines are crossed and TFTs at the cross points are electrically isolated each other, we design a specific gate pattern which defines boundaries of these electrodes fabricated using solution materials. We demonstrated to fabricate 3 x 9 arrays using SALSA process and now are trying to fabricate 64 x 64 arrays. SALSA process with a specific design of TFT-array patterns will become one of the powerful methods fabricating high-resolution self-aligned electronic components manufactured using inexpensive solution processing and direct printing processes without using any physical photomask and with small amounts of solution materials. [1] M. Ando et al., Ext. Abst., 2003 Int. Conf. Sol. Stat. Dev. and Mat. (Tokyo, Sept. 16-18), p.222, Proc. MRS 2004 Spring Meeting (San Francisco, April 12-16), to be appeared in Appl. Phys. Lett..

EE9.2

Three-Dimensional Structure and Liquid Transport Behavior of Siloxane Gels with Co-continuous Macropores.

Haruko Saito¹, Kazuki Nakanishi^{1,4}, Kazuyuki Hirao¹, Hiroshi Jinnai², Kei Morisato³ and Hiroyoshi Minakuchi³; ¹Material Chemistry, Kyoto University, Graduate School of Engineering, Kyoto, Kyoto, Japan; ²Polymer Science and Engineering, Kyoto Institute of Technology, Kyoto, Kyoto, Japan; ³Kyoto Monotech Co., Kyoto, Kyoto, Japan; ⁴PRESTO, Japan Science and Technology Agency, Kawaguchi, Saitama, Japan.

Sol-gel process of alkoxy-derived silica accompanied by phase separation leads to macroporous silica with interconnected skeletons and well-defined cylindrical pores. Co-continuous macroporous silica thus obtained has been an attracting separation media for a decade because of its numbers of advantages over conventional packed beads column: improved liquid transportation behavior and higher efficiency, which have successfully matured into commercial high performance liquid chromatography (HPLC) column. In spite of numerous reports on the performance of the columns, the flow behavior in co-continuous silica gels is still poorly understood. Traditionally, the flow behavior has been described by pressure drop using Kozeny-Carman equation with porosity and pore diameter as principal geometrical parameters of the flow path structure. The equation is known to exhibit good agreement with experimental data for particle-packed structure. Kozeny-Carman equation, however, is established only in a limited porosity range around $\epsilon = 0.4$ and is not suitable for co-continuous structure, which has porosity over 0.6. In a general method, porosities and pore diameters have been measured by Hg- porosimetry, in which macropores are assumed to be a bundle of cylindrical pores which has very different geometry compared with co-continuous structure. Laser scanning confocal microscopy (LSCM), on the other hand, is a recent technique for structural analysis. Three dimensional images of co-continuous structure can be reconstructed by stacking series of sliced LSCM images and makes it possible to analyze geometry of co-continuous structure in detail. In this study, organic-inorganic hybridized co-continuous macroporous siloxane gels have been prepared with independently controlled pore diameters and porosities. Geometrical parameters, i.e. porosity, pore diameter, and specific surface area, have been investigated by scanning electron microscopy (SEM), Hg porosimetry, and LSCM. The obtained siloxane gels have been also shaped into liquid chromatography column and the pressure drops have been measured with varying flow rate in order to investigate liquid transport behavior. The flow behavior has been evaluated by the structural parameters obtained from Hg porosimetry and LSCM.

EE9.3

On the mechanism of formation of SBA-1, SBA-2 and SBA-3 mesostructured silicas as studied by in situ XRD. Niki Baccile¹, Andrew Riley², Heinz Amenitsch³, Sarah Tolbert², Mika Linden⁴ and Florence Babonneau¹; ¹Chimie de la Matière Condensée, University Pierre et Marie Curie, Paris, France; ²Dept of Chemistry

and Biochemistry, UCLA, Los Angeles, California; ³Institute of Biophysics and X-ray Structure Research, Austrian Academy of Sciences, Graz, Austria; ⁴Dept of Physical Chemistry, Abo Akademi University, Turku, Finland.

The mechanism of formation of ordered mesoporous silica synthesized in the presence of surfactant aggregates used as structure-directing agents has been already studied in some detail. It is now fairly well established that the formation process is co-operative in nature and is crucially dependent on the balance between the relative strengths of the surfactant-surfactant, silicate-surfactant, and silicate-silicate interactions. Furthermore, in many cases the reaction is under kinetic control and can be chemically frozen into non-equilibrium states as a consequence of inorganic condensation reactions. Most mechanistic studies cover the alkaline synthesis route, which usually involves negatively charged silicate species and a positively charged surfactant. The acidic synthesis route has attracted much less attention from a mechanistic point of view, despite the fact that morphology control can be much more readily achieved under acidic rather than alkaline conditions. Here, the silicate species carry a slight positive charge, and the interaction with the surfactant is thought to be mediated through counter-ions present in solution. In this communication we report on the in situ synchrotron X-ray diffraction, XRD, data obtained during the first stages of the formation of SBA-1 (cubic Pm3n), SBA-2 (hexagonal P63/mmc) and SBA-3 (hexagonal p6m) silicas. They have been prepared from TEOS in acidic medium (HCl) using respectively cetyltrimethylammonium bromide (CTEAB), cetyl(dimethylammonium)propyltrimethylammonium dibromide (MMG) and cetyltrimethylammonium bromide (CTAB), as surfactants. The three final phases form directly after an induction period of few minutes, with no intermediate mesophase. However one difference can be noticed: while sharp XRD peaks appear in the case of SBA-2 and SBA-3 phases, the presence of a diffuse scattering peak precedes the appearance of the XRD peaks due to the Cubic SBA-1 phase. This suggests different interaction mechanisms that will be discussed with respect to the nature of the surfactants.

EE9.4

Silica Monoliths Hierarchically Textured via Concentrated Direct Emulsion and Micellar Templates.

Renal Backov¹, Florent Carn¹ and Annie Colin²; ¹Chemistry, CRPP-CNRS UPR8641, Pessac, Gironde, France; ²Physical-Chemistry, LOF-UMR-CNRS Rhodia FRE2771, Pessac, 33607, France.

In a general context of bio-inspired materials researches aim to generate highly organized materials with emphasis toward obtained a certain degree of hierarchy and complexity. Generating this class of materials is not such an easy task to reach. One way is to promote inorganic condensation at macroscopic metastable thermodynamic interfaces. In this route we make the use of concentrated direct emulsion to tune silica macroscopic void spaces while micellar templates is used at the mesoscale to create mesoporosity. In order to control the size of the monolith macropores we varied the starting emulsion viscosity by increasing the oil volumic fraction. By increasing the emulsion viscosity we increase the shear stress applied to the oil droplets during the oil phase emulsification process minimizing thus both the droplet sizes and the sizes of the windows that connect two adjacent cells. Beyond the oil volumic fraction we used the pH conditions to tune the wall textures that connect two adjacent cells providing either only internal cell junctions (windows that connect two adjacent cells) or both internal and external cell junctions (knots connecting four adjacent cells). Those materials show interconnected macroporosity associated to vermicular-type mesostructure. They possess and average mesoporosity of around 800 m²g⁻¹ associated to bulk density as low as 0.08 g cm⁻³ which is comparable to values obtained for silica aerogel. 1- Inorganic monoliths hierarchically textured via concentrated direct emulsion and micellar templates. Florent Carn, Annie Colin, Marie-France Achard, Elisabeth Sellier, Marc Birot, Herve deleuze And Renal Backov. J. Mater. Chem. 2004, 14, 1370.

EE9.5

Rational Design of Macocellular Metal Oxide Monoliths Obtained by Combining Soft Chemistry and Air-Liquid Foams.

Renal Backov¹, Florent Carn¹ and Annie Colin²; ¹Chemistry, CRPP-CNRS UPR8641, Pessac, Gironde, France; ²Physical-Chemistry, UMR-CNRS Rhodia FRE2771, Pessac, 33607 Gironde, France.

Recently new concepts of "chemistry of shapes" or synthesis over "all length scales" have enhanced the generation of hierarchically organized materials associated to complex textures. To achieve such high organization, patterns or templates at different length scales have to be used while processing growth of inorganic scaffolds or particles. One way of shaping solid state materials is to combine soft matter and soft chemistry. In this general context, we aim to present the synthesis and characterization of mesoporous macrocellular scaffolds

of different metal oxide scaffolds with emphasis toward rational design over the macroscopic void space sizes and shapes. By using air-liquid foams as macroscale pattern we were able to prepare macrocellular mesoporous metal oxide scaffolds where both Plateau-border lengths and widths as cell morphologies (i.e. spherical or polygonal shapes) can be tuned on demand while offering vermicular mesoporosity. This dynamic approach based on the control of foam's liquid fraction during the mineralization process has been first applied to the synthesis of SiO₂ amorphous macrocellular foams that depicts internal porosity of 1400 m²g⁻¹. In a second approach we succeed in extending this strategy to the generation of crystalline anatase or rutile TiO₂ monolith-type materials reached upon thermal treatment. For the TiO₂ macrocellular foams, beyond the control over the macroscopic void space sizes and morphologies we can change the Plateau-border topologies from smooth tubular to fibrous or flat-like ones by varying the surfactant and the aging time in use. 1- Rational design of macrocellular silica scaffolds obtaining by a tunable sol-gel foaming process. Florent Carn, Annie Colin, Marie-France Achard, Herve deleuze, Zoubida Saadi and Renal Backov. Adv. Mater. 2004, 16, 140.

EE9.6

Monolithic Periodic Mesoporous Silica with Well-defined Macropores. Tomohiko Amatani¹, Kazuki Nakanishi^{1,3}, Kazuyuki Hirao¹ and Tetsuya Kodaira^{2,3}; ¹Material Chemistry, Kyoto University, Graduate School of Engineering, Kyoto, Kyoto, Japan; ²Nanoarchitectonics Research Center, National Institute of Science and Technology, Tsukuba, Ibaraki, Japan; ³PRESTO, Japan Science and Technology Agency, Kawaguchi, Saitama, Japan.

The first synthesis of oxides with highly ordered mesopores templated by structure-directing agent was reported in the early 1990s. They have attracted considerable attention due to their fascinating structures and wide potential applications in the fields of separation, photonics, optics, drug delivery and supports for catalysts. Mesoporous materials are now available in the forms of fine powder, rods, thin film and controlled-size particles, and even in monolith. In spite of a drastic progress in the synthesis of mesoporous materials, the preparation of materials with a simultaneous control of morphology and pore size on different length scales still remains as a challenging task. In particular, the synthesis of well-defined macroporous monoliths with highly ordered mesopores is difficult to achieve. If these monoliths with well-defined pore structures on different scales can be synthesized, a lot of benefits arise from the integrated pore systems. Here, we present the successful preparation and characterization of pure silica monoliths having hierarchical pore structure (macroporous and mesoporous). Monolithic silica gels with spontaneous hierarchical pore structure have been synthesized via sol-gel process from silicon alkoxide in the presence of structure-directing agent and micelle-swelling agent. Monolithic bodies with well-defined co-continuous macropores are results of concurrent phase separation and sol-gel transition induced by the polymerization reaction, whereas the mesopores are templated by the supramolecular-assembly of the structure-directing agent. These bimodal pore systems are formed simultaneously and spontaneously in a closed condition at a constant temperature. The following removal of surfactants by calcination gives silica gels with hierarchical and fully accessible pores in discrete size ranges of micrometer and nanometer. The highly ordered 2D-hexagonal arrays of mesopores have been confirmed by XRD measurements and FE-SEM images. Furthermore, by additions of larger amounts of micelle-swelling agent, the mesostructural transition from well-ordered 2D-hexagonal arrays to mesostructured cellular foams (MCF) have been induced without effectively influencing the micrometer-range structure. Due to the interconnected nature of large pores, monolithic macroporous MCF is a promising candidate for supports for catalysts and in separations involving large molecules. The silica materials have been characterized in detail by SEM, FE-SEM, Hg porosimetry, N₂ adsorption, and XRD measurements.

EE9.7

Alkylene- and Arylene-Bridged Co-polysilsesquioxane Xerogels: A Fundamental Study Examining the Origins of Porosity in Sol-Gel Derived Hybrid Organic-Inorganic Systems. James Howard Small and Douglas Anson Loy; Polymers and Coatings Group, Los Alamos National Laboratory, Los Alamos, New Mexico.

We wish to present here a systematic study of the fundamental interactions associated with the formation of co-polysilsesquioxane xerogels, a unique family of hybrid organic-inorganic materials. These materials were prepared by the sol-gel polymerization of the corresponding hexylene- or phenylene-bridged hexaethoxysilane under relatively mild conditions (0.1 N NaOH or HCl catalyst, THF, and 6 equiv H₂O) either as a homopolymer or as a copolymer. Gas sorption porosimetry, in conjunction with electron microscopy, will be used to graphically display the dramatic effect that may manifest by alteration of the sol-gel catalyst. The focus of this presentation,

however, will showcase the use of various solid-state NMR techniques to investigate the hydrocarbon spacer homogeneity, the structural identity of primary and secondary particulates, and how these building blocks assemble to ultimately afford macromolecular porosity. One-dimensional ¹H, ¹³C, and ²⁹Si CP MAS experiments were instrumental in the elucidation of both the structure and dynamics of the hydrocarbon spacer and silicate framework of the xerogels. Two-dimensional Frequency-Switch Lee-Goldburg (¹³C-¹H and ²⁹Si-¹H) heteronuclear (FSLG-HETCOR) experiments were used to correlate all nuclei via the magic angle spinning chemical shift information in the direct dimension (¹³C or ²⁹Si) and the ¹H isotropic CRAMPS information in the indirect dimension. Systematic variation of the contact time gave both temporal and spatial information concerning both spacer homogeneity and mobility. These results will be presented using Lee-Goldburg build-up curves and subsequent comparison with expected cross-polarization distance values. Cross-polarization correlation times will be discussed as pertinent to the differences in morphology of the gels. Two-dimensional ¹H-¹H Lee-Goldburg Combined Rotation and Multiple Pulse Spectroscopy (LG-CRAMPS) experiments were used to correlate ¹H isotropic chemical shift information and ¹H magic angle spinning information. And finally, selective deuterium incorporation into one spacer and subsequent analysis by the techniques just discussed will afford further insight into spacer homogeneity and overall spatial information of the hydrocarbon and silicate functionalities present within the xerogel.

EE9.8

Polyfunctional phenyloctasilsesquioxane by modification of bromoderivatives. Novel Nanoconstruction Sites. Mark Roll², Richard M. Laine^{1,2}, Chad Brick³ and Michael Asuncion²; ¹MSE, University of Michigan, Ann Arbor, Michigan; ²Macromolecular Science and Engineering Center, University of Michigan, Ann Arbor, Michigan; ³Chemistry, University of Michigan, Ann Arbor, Michigan.

Mark Roll, R.M. Laine, C. Brick, M. Asuncion, Depts. of Materials Science and Engineering, Chemistry, and Macromolecular Science and Eng. University of Michigan Ann Arbor, MI. 48109-2136, U.S.A. Palladium catalyzed coupling reactions are used widely to replace aryl halide bonds with new functional groups. Well known coupling reactions include the Heck and Suzuki catalysts. The use of brominated octaphenylsilsesquioxanes as the aryl halide source allows the development of novel polyfunctional functional nanosized components with novel electronic properties. Specifically cyanation and arylation reactions were explored and are reported. The arylation reaction provides complete conversion of the halide to a diaryl moiety, while cyanation provides moderate-to-good conversion of the halide to nitrile. Up to 16 groups of the same type can be incorporated onto octaphenylsilsesquioxane. Selected photo-physical properties of these materials will be described.

EE9.9

Collapse of Porosity during Drying of Alkylene-Bridged Polysilsesquioxane Gels. Influence of the Bridging Group Length. Douglas Anson Loy¹, James H. Small¹, Kimberly A.

Defriend¹, McKenzie Minke², Colleen R. Baugher², Brigitta M. Baugher², Duane A. Schneider² and Kenneth J. Shea³; ¹Polymers and Coatings Department, Los Alamos National Laboratory, Los Alamos, New Mexico; ²Sandia National Laboratories, Albuquerque, New Mexico; ³Department of Chemistry, University of California, Irvine, California.

The introduction of organic substituents into sol-gel materials can often result in the networks that collapse during drying to afford non-porous xerogels. This can be useful if non-porous coatings or membranes are the ultimate objective. Collapse of porosity is also manifested in bridged polysilsesquioxanes with flexible bridging groups. Alkylene-bridged polysilsesquioxanes are hybrid xerogels whose organic bridging group is an integral constituent of the network polymer that can be systematically varied in length to probe its influence on the xerogels porosity and morphology. Our previous studies have shown that hexylene-bridged polysilsesquioxane xerogels prepared from 1,6-bis(trimethoxysilyl)hexane under acidic conditions are non-porous while the pentylene-bridged polysilsesquioxane xerogels, prepared under the same conditions, are porous. We also discovered that the more reactive 1,6-bis(trimethoxysilyl)hexane could polymerize under acidic conditions to afford porous xerogels. In this study we have extended our study of bis(trimethoxysilyl)alkanes to include the heptylene, octylene, nonylene, and decylene-bridges so as to ascertain at what bridging group length the porosity collapses. The morphology of the resulting xerogels was characterized by nitrogen sorption porosimetry and electron microscopy. Solid state NMR was utilized to structurally characterize the materials.

EE9.10

Alkylene and Arylene Bridged Polysilsesquioxane Aerogels. Kimberly Ann DeFriend, Douglas A. Loy and James H. Small; Los Alamos National Laboratory, Los Alamos, New Mexico.

Bridged polysilsesquioxanes are an organic-inorganic hybrid silica-based materials. The organic component allows the silica-based gel to possess inorganic and organic characteristics. The composition of the bridging group, an arylene or alkylene group, affects the physical structure of the gel, whether the gel behaves more elastically or more robust, respectively. Super critically drying the gels with CO₂, afford organically bridged polysilsesquioxane aerogels. We will describe our efforts to synthesize alkylene and arylene bridged polysilsesquioxane aerogels. The aerogels will be synthesized through sol-gel polymerizations of the bridged polysilsesquioxane monomer using acid and base catalysts, various water concentrations, and solvents, followed by super-critical CO₂ drying to afford the hybrid monolithic aerogels. Properties and characteristics of the resulting aerogels will be investigated.

EE9.11

CVD Modification of Low-Density Silica and Bridged Polysilsesquioxane Aerogels. Kimberly Ann DeFriend, Douglas A. Loy and James H. Small; Los Alamos National Laboratory, Los Alamos, New Mexico.

Silica and bridged polysilsesquioxane aerogels are transparent, low-density materials used in a wide range of applications, such as thermal insulation, porous separation media or catalyst supports, adsorbents, and cometary dust capture agents. Silica aerogels can be composed a second metal, forming a mixed-metal oxide. Forming the mixed-metal oxide enhances the characteristics of the aerogels and broadens their ability to be used in additional applications. Here, we will describe our efforts to chemically modify and enhance the characteristics of silica-based aerogels using chemical vapor techniques without sacrificing their characteristic low densities. Monolithic silica and organic-bridged polysilsesquioxane aerogels were prepared by sol-gel polymerization of the respective methoxysilane monomers followed by supercritical carbon dioxide drying of the gels. The gels were reactively modified with silylating agents or transition metal compounds to demonstrate the viability of CVD modification of aerogels, and to investigate the morphology, surface area, and mechanical properties of the modified aerogels.

EE9.12

Functional Layer by Layer Self Directed Assemblies Containing Inorganic. Nicole Zacharia¹ and Paula Hammond²; ¹Department of Materials Science and Engineering, MIT, Cambridge, Massachusetts; ²Chemical Engineering, MIT, Cambridge, Massachusetts.

Layer by layer (LbL) directed self-assembly has been proven to be a reproducible method of forming thin polymer films for a variety of applications, including for photovoltaics, solid state electrolytes, photoluminescent devices, photonic band gap structures, electrochromic devices, and sensors. LbL films can also be made containing inorganic, charged nanoparticles. Specific examples from our group's work include LbL inorganic/organic systems for electrochromism, drug delivery, and gas sensing. Here we report both structures combining multiple types of nanoparticles as well as the results of further characterization of the nanoparticle/polymer composites. We have previously reported electrochromic films constructed from nanoparticles of prussian blue and some of its other transition metal ion analogues. These films had high contrast and good switching speeds compared to other reported electrochromic films, and through recent work we have been able to further increase switching speeds. Addition of conducting nanoparticles improves electrical conduction through the polymer/nanoparticle composite. Characterization of these films by confocal microscopy, TEM, AFM, electrochemical testing and have led to increased understanding of the assembly process. We hope to be able to improve ion mobility through these composites by changing assembly conditions (ionic crosslink density throughout the film). We also have seen that nanoparticles can stop interdiffusion of layers within the LbL structure, in the same way that chemically crosslinked or tightly ionically crosslinked layers can do. This opens the possibility of using our nanocomposites to compartmentalize LbL films, which could be important for such applications as complex device construction or delivery of a schedule of multiple drugs.

EE9.13

Metal Oxide Doped Mesostructured Silica Films. Nicola Karola Huesing and Ralf Supplitt; Institute of Materials Chemistry, Vienna University of Technology, Vienna, Austria.

Since the discovery of the first mesostructured materials of the MCM-type, the development of novel porous materials with various pore-sizes and periodic structures has become an important field of today's research. Possible applications as sensors, catalysts, membranes, optical coatings and encapsulation materials yield in industrial interest. For many applications not only simultaneous

control over morphology e.g. monoliths, fibres or thin films and pore architecture (hexagonal versus cubic, pore sizes) is indispensable, but also the deliberate compositional design of the material. Especially thin film morphologies containing transition metal oxides (titanium, zirconium, iron) in an inert silica matrix are of interest as chemical sensors, membranes or catalysts. Achievements of high loadings with the transition metal oxide and good dispersion within the silica matrix by maintaining the mesoscopically organized film structure are the major concerns in this area. The focus of this work is on the preparation of mesostructured mixed oxide films relying on a combination of ligand-assisted templating and evaporation-induced self-assembly. By this approach, the surfactant not only serves as structure directing agent, but also acts as an agent to control and slow down the hydrolysis and condensation rate of the transition metal alkoxide and to position the latter at the template-silica interface to achieve a high homogeneity and dispersion within the silica matrix. We extended our previous work to different surfactant systems and various transition metal alkoxides. The first step in the synthesis of mesostructured, mixed metal oxide thin films is the synthesis of the surfactant/metal alkoxide complex. Polyether containing surfactants such as the poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock copolymer Pluronic P123 or polyether-based Brij 56, were reacted with metal alkoxides such as titanium isopropoxide, zirconium isopropoxide, iron ethoxides, etc. By using these modified surfactants as template, well ordered mesostructured silica/metal oxide films were prepared. The ratio of block copolymer to silica precursor and the acid concentration in the dip coating solution were varied and the influence on the mesostructure studied. For the characterization of the final films, X-ray diffraction and small angle X-ray scattering, transmission electron microscopy, X-ray photoelectron spectroscopy, EXAFS and sorption techniques were applied. N. Huesing, B. Launay, G. Kickelbick, S. Gross, L. Armelao, G. Bottaro, M. Feth, H. Bertagnolli, F. Hofer, G. Kothleitner, Appl. Catal. 2003, 254, 297. N. Huesing, B. Launay, F. Hofer, G. Kickelbick, J. Sol-Gel Sci. Technol. 2003, 26, 615.

EE9.14

Hierarchically Structured Silica Monoliths Carrying Organic Functions. Nicola Karola Huesing and Doris Brandhuber; Institute of Materials Chemistry, Vienna University of Technology, Vienna, Austria.

In the synthesis of mesostructured monoliths, diol- or polyol-modified silanes, such as tetrakis(2-hydroxyethyl)silane, have some distinct advantages compared to commercially available tetraalkoxysilanes, (e.g. tetraethoxysilane), since they can be condensed without a co-solvent, under neutral conditions (no catalyst is required to start the sol-gel reactions), and the diols/polyols released upon hydrolysis show a very good compatibility with lyotropic phases of surfactant molecules. The materials obtained from polyol-modified silanes are characterized by a distinct ordering in the mesoscopic regime and a very unique macrostructure. In this work, we present three different approaches towards the modification of the material prepared from polyol-modified silanes with organic groups: a) co-condensation reactions of polyol-modified tetraalkoxysilanes with the corresponding polyol-modified trialkoxysilanes e.g. phenyl- or methylsilanes, b) reaction of polyol-modified bridged silanes, e.g. bis(tri-2-hydroxyethyl)silylthane, and c) the posttreatment of materials prepared from polyol-modified silanes with organofunctional silanes, e.g. trimethylchloro-, methacryloxymethyl-, aminopropyltrimethoxysilane, etc.. For route a) the main focus is on investigations of the reaction rates of the different precursors and the differences in the structure compared to an unmodified material. With respect to route b) the structural features of the material will be compared to one prepared from the corresponding ethoxy- or methoxyderivative. Pathway c) not only allows to modify the monoliths with functional units, but in addition, offers an alternative to supercritical drying. The material is not only silylated, but the template is extracted simultaneously from the monolith and drying can be performed easily by heating. The final material is characterized with respect to its organic functions by elemental analyses, spectroscopic techniques such as IR and solid state NMR spectroscopy, and thermal analyses (TGA, DSC). Structural characterization is carried out by small angle X-ray scattering, electron microscopy (SEM, TEM), sorption techniques, and mercury porosimetry.

EE9.15

Fabrication of Bio-inspired Silica Composites. Christina Fritscher^{1,2}, Helga C. Lichtenegger¹, Juergen Stampfl¹, Nicola Huesing², Robert Liska³ and Sabine Seidler¹; ¹Institute of Materials Science and Testing, Vienna University of Technology, Vienna, Austria; ²Institute of Materials Chemistry, Vienna University of Technology, Vienna, Austria; ³Institute of Applied Synthetic Chemistry, Vienna University of Technology, Vienna, Austria.

Nature uses basic materials that exhibit a sophisticated architecture on different length scales. Based on the cellular structure found in

tissues like wood or bone, artificial "bio-inspired" ceramic composites were fabricated. The goal of this work was to merge different approaches to obtain controlled structures on the particular hierarchical levels (nanometer to micrometer range). On the one hand nanostructured silica was synthesized using the sol-gel-method with different precursors, such as tetraethyl orthosilicate (TEOS), tetramethyl orthosilicate (TMOS), ethyleneglycol modified silane (EGMS) and spherosilicates (QS), and surfactants (Brij56, P123, CTAB) leading to mesoporous materials with or without implemented organic network. External fields were applied to influence the orientation of these precursor/surfactant systems while still in the liquid crystalline state. The macroscopic structure of the material was designed using organic moulds built by rapid prototyping (RP). This method provides enormous flexibility in realizing different macroscopic shapes. The precursor/surfactant mixture was infiltrated into these sacrificial cellular RP moulds and polycondensation of silica was allowed to take place inside the template. Position resolved small-angle X-ray scattering (scanning SAXS) was used to investigate the nanostructure. Mechanical properties of the cellular nanocomposite ceramics were tested and compared to those of cellular ceramics with different structures on the nanometer scale.

EE9.16

A Novel Method for Rapid Formation of High-ordered Self-Assembled Monolayer. Yoshitaka Fujita¹, Norifumi

Nakamoto¹, Hiroyuki Takeda¹, Tomoya Hidaka¹, Nobuo Kimura¹, Hiroshi Suzuki¹, Noriyuki Yoshimoto² and Satoshi Ogawa³; ¹R. & D. Laboratory for High-Performance Materials, Nippon Soda Co., Ltd, Ichihara, Japan; ²Graduate School of Engineering, Iwate University, Morioka, Japan; ³Faculty of Engineering, Iwate University, Morioka, Japan.

Self-assembled monolayers (SAMs) spontaneously form molecular films on certain materials surface and homogeneously covered a wide area. On the other hand, SAMs are able to be easily decomposed, therefore they are expected for use as a resist. We have studied a fast and simple formation process of the high-ordered SAMs. We report a novel chemisorption method with octadecyltrimethoxysilane (ODMS) under normal temperature and pressure. The SAMs are rapidly and homogeneously formed on various inorganic surfaces with a high-order. ODMS was dissolved in toluene (10mM/kg) and the solution was saturated with water at about 500 ppm. One wt% toluene solution of the initiator was dropped into the solution (The initiator for the formation of the SAM was introduced in some metal oxides, M(Ti, Zr, Si . . . , /ODMS = 0.1 mol/mol) with stirring. Two hours later, the solution was filtered (1 μ m glass filter) and saturated with water, then a clear ODMS-SAM solution was prepared. The washed Si substrate was cleaned with UV/ozone irradiation, and immersed in the solution. After immersion, the substrate was washed by super-sonic waves in toluene and then dried. The process was done on other substrates such as, alkaline glass, non-alkaline glass, quartz and indium-tin oxide (ITO). All processes were done in air at room temperature. The water contact angle of all the substrate surfaces in the experiments were up to $105\pm^\circ$ after a minute immersion. The thickness estimated by ellipsometry and X-ray reflectometry (XRR) were 2.1 ± 0.2 nm, suggesting that a moderate length of the octadecyl chain stood vertically against the substrate. The 0.42 ± 0.02 nm spacing calculated by grazing incidence X-ray diffraction (GIXD) showed a crystalline order for the ODMS-SAM. AFM images of the Si substrate showed the formation process of the SAM. For short of immersion time, there were 2D aggregates (2 nm height and 80 nm diameter), then 30 seconds later, it seemed to have a dendritic crystal growth. After 5 minutes, the surface was flat and had no defects. Namely the solution, which had been clear for 2 months or more after preparation, covered all of the substrates with ODMS-SAM in 5 minutes. We would like to discuss about the mechanism of rapid formation of the SAM. Reference: N. Nakamoto et al., the 51st Annual Meeting of Applied Physics, No.3, 30a-ZF-6 (2004) 1356

EE9.17

Layer-by-Layer Surface Modification and Patterned Electrostatic Deposition of Quantum Dots. Saeeda Jaffar¹, Ki

Tae Nam³, Ali Khademhosseini², Jia Xing¹, Robert S. Langer¹ and Angela M. Belcher³; ¹Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; ²Bio Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; ³Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Modification of quantum dot (QD) surfaces with polyelectrolyte coatings, and subsequent layer-by-layer deposition to build hierarchical structures is presented. Mercaptoacetic acid (MAA) treated QDs were sequentially coated with polyallyl amine (PAA) and polyvinylsulfonic acid (PVSA), and their properties were analyzed using zeta potentials, absorbance spectra and transmission electron microscopy. The modified QDs were deposited on patterned hyaluronic acid (HA) glass substrates to produce self assembled

heterostructures (QDs-MAA/QDs-PAA/HA/glass), as revealed by fluorescence and atomic force microscopy.

EE9.18

LDH-DNA Nanohybrids: A Complete Biophysical

Characterization. Fabrice Leroux¹, M. Benbelkacem¹, G. Guyot², C. Taviot-Gueho¹, P. Leone³, L. Cario³, L. Desigieux⁴ and B. Pitard⁴; ¹Materials Chemistry, Université Blaise Pascal, Aubiere, France; ²Laboratoire des Matériaux Inorganiques UMR 6002, Université Blaise Pascal (Clermont-Ferrand II), Aubiere, France; ³Institut des Matériaux Jean Rouxel, Nantes, France; ⁴U533, Inserm, Nantes, France.

The successful intercalation of biological and drug molecules such as DNA, ATP or ibuprofen into layered double hydroxides (LDH) has led to consider their potential as drug or gene delivery carriers (1,2,3). In one approach developed by Choy(3), DNA-LDH hybrid can be obtained by simple ion-exchange upon substituting NO₃- anions incorporated between hydroxide layers. Alternatively, and to be demonstrated here, immobilization of DNA within LDH can be achieved by coprecipitation reaction in which the layered inorganic lattice and the intercalate of DNA are simultaneously formed. Well defined LDH-DNA nanohybrids were obtained by the coprecipitation method which allows to fine-tune the design of this new kind of inorganic delivery vector. In this work, we report a complete biophysical characterization of DNA-LDH hybrids obtained from magnesium-aluminium, magnesium-iron and magnesium-gallium LDH with double-stranded DNA fragments of various length and plasmid. The effect of LDH physico-chemical properties i.e. hydroxide layer composition and charge density on the DNA/LDH interaction was examined at the molecular level in terms of DNA stability, conformation, size and binding affinity. Many experiments have been performed to this end: ethidium bromide exclusion and gel retardation experiments, x-potential measurements, dynamic light scattering, circular dichroism, X-ray diffraction, 31P MAS NMR, FTIR spectroscopy and transmission electron microscopy. The main results of this study are that the colloidal stability and the morphology of DNA-LDH nanohybrids depend on the DNA/M3+molar ratio (M3+ : Al3+, Fe3+, Ga3+) initially introduced into the reactor, also the temperature of synthesis and DNA length. As already reported elsewhere, beside the intercalation, it appears that DNA acts as a template enhancing the building of nanostructured system. For syntheses carried out with long DNA fragments and low DNA/M3+molar ratios, size and x-potential measurements revealed the formation of electroneutral hybrid particles with a mean diameter ranging from 200 to 300 nm. The lamellar spacing of the structure indicates intercalation with DNA helix orientated parallel to LDH hydroxide layers. Thus, d-spacing does not depend on DNA length, on the other hand, it is strongly affected by the synthesis temperature as well as Mg2+ /M3+ molar ratio leading to values ranging from 16 to 24 angstroms. FTIR and NMR spectroscopies suggest that DNA binding is mainly through the phosphate group, yet small spectral changes in the region of 1700-1500 cm⁻¹ may also indicate a participation of the nitrogenous bases of DNA or partial helix destabilization. References : (1) J.-H. CHOY, S.Y. KWAK, J.S. PARK, Y.J. JEONG, J. PORTIER J. Am. Chem Soc 121 (1999), 1399-1400 (2) V. AMBROGI, G. FARDELLA, G. GRANDOLINI, L. PERIOLI Int. J. Pharm. 220 (2001) 23-32 (3) J.-H. CHOY J Phys Chem Solids 65 (2004) 373-383 and references therein

EE9.19

Constrainment Effects of Interleaved Organic Molecules into Layered Double Hydroxides. M. Dubois, El M. Moujahid, J.-P. Besse and Fabrice Leroux; Materials Chemistry, Université Blaise Pascal, Aubiere, France.

Functionalized organic molecules have been incorporated between the sheets of layered double hydroxides. Two commercialized dye molecules, tropaeolin (acid Orange 6) (I) and acid Green 25 (II), which are mono- and di-functional macromolecules and two aniline-based monomers, m- amino-4-benzenesulfonic (III) and 3-aniline-1-propanesulfonic (IV) acids were chosen according to our criteria, i.e. possibility of in-situ polymerization for the aniline-based monomers and tunable optical properties for the dye molecules. The inorganic - organic hybrid materials obtained by coprecipitation method are characterized by means of X-ray diffraction, FTIR and 13C CP-MAS NMR spectroscopies. In each case, the organic molecule is propping apart the lamellar structure. From calculations based on the molecular size, the arrangement of the organic moiety will be discussed. The effect of the confinement evidenced by a shift in the UV-visible curve is not similar between the two dye molecules, of weak amplitude for (I), the spectrum is largely shifted to lower wavelength for (II). For the aniline-based monomers, a combination of techniques was used to better understand the process of polymerization. In-situ electron spin resonance (ESR) spectroscopy was found to be useful to address whether the polymerization process was occurring in temperature. A narrow signal is observed for (III), characteristic of

organic radicals, whereas a contribution composed of several lines is present for (IV), which was refined by the presence of super hyperfine interaction between localized spins and two neighboring nitrogen nuclei. For the former, it is explained by a polymerization, for the latter by a dimerization occurring between monomer molecules. Additionally, electrochemical measurements were performed under potentiostatic mode in aprotic medium. The correlation between the different findings (electrochemistry vs ESR) will be presented. The thermal behavior of the hybrid materials are studied. Organic molecules are found to provide a clear enhancement of the structural stability in temperature, therefore from both sides (organic and inorganic), the assembly may appear as a mutual benefit.

EE9.20

Influence of TiO₂ on the Pore Structure and Texture of SiO₂-PDMS Hybrid Materials. Lucia Tellez², Juan Rubio³, Miguel Valenzuela¹, F. Rubio³, E. Morales³ and Jose Luis Oteo³;

¹Lab. Catalisis y Materiales, Instituto Politecnico Nacional, Mexico City, Mexico; ²Dpt. Ing. Metalurgica y Materiales, Instituto Politecnico Nacional, Mexico City, Mexico; ³Instituto de Ceramica y Vidrio, CSIC, Madrid, Spain.

SiO₂-PDMS-TiO₂ hybrid materials have been prepared by the Sol-Gel method using tetraethylortosilicate (TEOS), silanol terminated (PDMS) and tetrabutylortotitanate (TBT) as precursors. In this work, the influence of the TBT concentration in the final pore structure and texture of SiO₂-PDMS-TiO₂ hybrid materials was studied. These materials were characterized by means of nitrogen adsorption, mercury porosimetry and helium pycnometry. All samples show micro, meso and macroporosity. The microporosity is constituted by both ultra and supermicropores. Meso and microporosity are predominant in all studied samples. The increase in TBT concentration decreases the pore volume of micropores, mesopores and macropores and promotes the decreasing of specific surface area of the samples. However it is also observed that at the specific surface area of meso and macropores decreases but increasing of specific surface of micropores. This is attributed to the formation of ultramicropores. Surface roughness increases with the increase of TBT concentration and is attributed to the formation of oxide-based nanoparticles. The presence of TBT also changes the connectivity between porous and their average linear dimensions.

EE9.21

Wear Properties of Carbon Nanotube-Filled Ultra High Molecular Weight Polyethylene Prepared by *in-situ* Ziegler-Natta Polymerization. Hong-Jo Park¹, Seung-Yeop Kwak¹ and Soonjong Kwak²; ¹Material Science & Engineering, Seoul National University, Seoul, South Korea; ²Polymer Hybrid Research Center, Korea Institute of Science and Technology, Seoul, South Korea.

Ultra high molecular weight polyethylene (UHMWPE) has been recognized as a most suitable bearing material for artificial joints implanted in human body. Chief operation of artificial joints is a sliding action between soft UHMWPE and hard femoral material that is metal or ceramic. Therefore, wear behavior of UHMWPE is one of the most important factors determining the durability of artificial joints. UHMWPE filled with ceramic or metal filler has displayed improved wear properties where a dispersion state of the filler in the UHMWPE matrix is of great importance for proper wear performance of the composites. In this study, we have polymerized UHMWPE/carbon nanotube(CNT) composites through *in-situ* Ziegler-Natta polymerization method and investigated their wear behaviors. Fixation of catalyst on the surface of CNT and polymerization of ethylene were consecutively carried out in a pressure reactor. When compared at the same CNT content, polymerized composite displayed higher tensile modulus and yield strength than mechanically blended composite. Wear test was performed on a ring-on-block type apparatus without lubrication. Wear rate of the polymerized composites was significantly lower than unfilled UHMWPE and mechanically blended composites. Scanning electron microscopy (SEM) observations of frictional surfaces of wear specimens showed that the wear mechanisms of the polymerized composites are totally different from those of unfilled UHMWPE. The neat UHMWPE showed a ploughing wear, which is well known to result from the abrasive removal of soft UHMWPE. The ploughing was greatly suppressed for the CNT-filled composites, which is supposed to result from the increase in surface hardness and subsequent suppression in abrasive wear. It is believed that uniform dispersion of CNT and improved interfacial properties produced in the *in-situ* polymerization are the main factors leading to the superior mechanical and tribological properties of the polymerized composites.

EE9.22

Two-step De-intercalation and Intercalation Induced by Polymer Crystallization and Melting in Poly(ethylene oxide)/Organoclay Nanocomposites. Lu Sun¹, Lei Zhu¹, Jianjun

Miao¹, Carlos A. Avila-Orta², Igors Sics² and Benjamin S. Hsiao²;

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²Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York.

Polymer/clay nanocomposites are of interest to both industry and academia, because these materials often have superior properties and are ideal systems for understanding polymer dynamics in nanometer-confined spaces. In this work, phase morphology and its relationship with polymer crystallization in semicrystalline polymer/clay nanocomposites were studied. A poly(ethylene oxide) (PEO) with a number-average molecular weight of 4,800 g/mol was intercalated into an organo-modified natural montmorillonite, Cloisite10A (C10A, Southern Clay Product, TX), through a solution-casting process. The organoclay content was determined by thermogravimetric analysis (TGA) to be 48.7 wt.%. Time-resolved synchrotron one-dimensional (1D) small-angle X-ray scattering (SAXS) and wide-angle X-ray diffraction (WAXD) were used to correlate the intercalation morphology of the nanocomposite to the PEO crystallization and melting behaviors. Two-step de-intercalation and intercalation were observed in a range of -30 °C to 70 °C. During cooling at 2 °C/min, two-step decreases in clay gallery spacing (3.35 nm at 70 °C, 3.00 nm at 30 °C, and 2.60 nm at -30 °C) occurred at 40.3 °C and -9.3 °C, respectively. Coincidentally, the PEO crystallinity increased from 0 wt.% at 70 °C to 68 wt.% at 30 °C, and finally to 0.81 wt.% at -30 °C. During heating at 2 °C/min, the gallery spacing also increased in two steps, e.g., 2.60 nm at -30 °C to 2.97 nm at 25 °C, and finally 3.35 nm at 60 °C. The PEO crystallinity decreased from 81 wt.% to 62 wt.%, as the temperature increased to 25 °C. Above 60 °C, the PEO crystals completely melted. The organoclay and PEO crystal orientations were studied by two-dimensional (2D) WAXD on oriented samples. It was observed that PEO chains were perpendicular to the organoclay layers. Based on the 2D WAXD results, a tentative model/morphology was proposed. Some PEO lamellar crystals might interface with the opening of an organoclay tactoid, the PEO crystallization at the lamellar front would exhaust the crystallizable materials outside the clay tactoid. In order to maximize the PEO crystallinity to lower the system free energy, the PEO intercalated in the clay gallery were pulled out and the clay gallery spacing thus decreased. The two-step de-intercalation processes were associated with heterogeneously and homogeneously nucleated PEO crystallizations, which occurred at 40.3 °C and -9.3 °C, respectively. The heating process was a reverse process (i.e., two-step intercalation), after the PEO crystals melted. Acknowledgements. This work was supported by the University of Connecticut Research Foundation, ACS Petroleum Research Fund, and NSF CAREER award (DMR-0348724). The synchrotron X-ray experiments were carried out at Advanced Polymer Beamline X27C in the National Synchrotron Light Source, Brookhaven National Laboratory, which is supported by the Department of Energy.

EE9.23

Coordination Compound Molecular Sieve Membranes.

Jongok Won, of Applied Chemistry, Sejong University, Seoul, South Korea.

Highly selective coordination compound molecular sieve composite membranes have been prepared using well dispersions of porous transition metal complexes confined within amorphous glassy polysulfone. The new approach reported here is a promising method for fabricating organic molecular sieve composite membranes with tailor-made structure and pore size. In contrast to the inorganic molecular sieve membrane counterparts, the organic molecular sieves exhibited enhanced selectivities for H₂ over CH₄ (ca. 200 at 5 wt% loading), which is the highest selectivity reported for the molecular sieve composite membranes. Therefore this membrane has a high potential to contribute to produce a renewable energy source, hydrogen from the hydrogen plant, in which hydrogen is produced by reforming hydrocarbon feedstock, such as CH₄.

EE9.24

Vanadium oxide nanotubes: new synthesis routes and mechanisms of formation. Maguy Jaber, Nathalie Steunou, Sophie Cassaignon, Thierry Azais, Jean-Pierre Jolivet and Jacques Livage; Chimie de la Matière Condensée, University Paris 6, Paris, Ile de France, France.

Vanadium oxide based materials have been extensively studied during the past decades due to their electrical, magnetic, catalytic and electrochemical properties. Hybrid organic-inorganic vanadium oxides have been synthesized by the sol-gel process at low temperature or under mild hydrothermal conditions. Depending on the nature of the species present in the reaction medium, they may exhibit a wide range of structures and morphologies that are crucial to the performance of the materials in applications. In particular, vanadium phosphates phases are interesting materials for the mild oxidation of light alkanes.

Recently, mesostructured vanadium oxides with a tubular morphology have been synthesized in the presence of long alkyl chain amines.[1] These vanadium oxide nanotubes are made of multilayer scrolls with thick walls composed of sheet packs of several vanadium oxide layers.[1] The anisotropic tubular shape is expected to lead to unusual physical and chemical properties. This communication deals with the synthesis of vanadium oxide nanotubes from $V_2O_5 \cdot nH_2O$ gels and hexadecylamine. $V_2O_5 \cdot nH_2O$ gels are synthesized via the reaction of crystalline V_2O_5 with H_2O_2 . Another synthesis route is also proposed and is based on the incorporation of phosphate groups into the network of the vanadium oxide nanotube. The different VO_x nanotubes were characterized by X-ray diffraction, scanning and transmission electron microscopy and ^{51}V (or ^{31}P) solid state NMR. In-situ experiments were performed in order to get a better understanding of the mechanism of these nanotubes formation. References [1] Krumeich, F., Muhr, H.-J., Niederberger, M., Bieri, F., Schnyder, B., Nesper, R. J. Am. Chem. Soc., 121 (1999) 8324 Niederberger, M., Muhr, H.-J., Krumeich, F., Bieri, F., Gunther, D., Nesper, R. Chem. Mater., 12 (2000) 1995 Muhr, H.-J., Krumeich, F., Schronholzer, U.P., Bieri, F., Niederberger, M., Gauckler, L.J., Nesper, R. Adv. Mater.12 (2000) 231

EE9.25

Interlamellar Incorporation of a Functionalized Hydrophobic Polymer Nanoparticle into the Pristine Sodium Montmorillonite. Svetlana V. Khvan, Sang-Soo Lee and Junkyung Kim; Polymer Hybrid Research Center, Korea Institute of Science and Technology, Seoul, South Korea.

A majority of the properties of polymer-clay nanocomposites (PCNs) are a function of the extent of dispersion of the individual clay platelets into a continuous polymer matrix as well as of the compatibility of the two intrinsically non-miscible phases. In so far, a solution intercalation of either a hydrophilic polymer into pristine clay or a hydrophobic polymer into the organically modified clay has been known to obtain polymer-clay nanocomposites (PCNs) via an exfoliation-adsorption or exfoliation-exchange mechanisms. In the present work an alternative exfoliation-adsorption of a hydrophobic polymer (polystyrene) latex directly into the gallery of pristine clay has been proposed. The approach involves an incorporation of a functionalized polystyrene latex with particle size of few tens nm into interlamellar gallery of a pristine sodium montmorillonite to provide a desired degree of dispersion of clay sheets. A particular emphasis has been put on the study of a nature and a contribution of the interactions between hydrophobic polymer molecules and a virgin silicate surface into the issue of the compatibility between the two phases. Surface characterization, performed with XPS and ToF SIMS, provided the results on the existence and the nature of the functional groups on the latex surface, which have been found to be in a good compliance. Estimation of recovery of the latex from clay gallery with TGA data has revealed that the amount of the firmly attached polymer particles is equivalent to that of the organic surfactant when the latter is bound to the silicate surface by replacement of the quaternary alkyl ammonium cations with sodium ions of clay. Further, the suggestion that the hydrophilic nature of the silicate surface was not rendered hydrophobic by incorporation of the latex was implied from TGA results. It was stated that the cationic exchange between an onium ion and the intergallery cation of clay, which is true for the organic modification of clay, is not a dominant intercalation mechanism responsible for adsorption of the polymer latex on the clay surface. Rather, the ion dipole and hydrogen bonding as well as π -bonding due to the presence of the polar functional groups with partially negative charge on the surface of the functionalized polymer latex have been suggested to make a dominant contribution into the interaction net. Thus it is believed that the adjusting the interaction enthalpy between functionalized hydrophobic polymer and hydrophilic clay surface can be achieved without assistance of special compatibilizing agents.

EE9.26

Synthesis of molecular building blocks containing 2,6-dicarboxypyridine units for the design of porous crystalline solids. Kasim Biyikli, Joseph C. Bush and John C. MacDonald; Chemistry & Biochemistry, Worcester Polytechnic Institute, Worcester, Massachusetts.

We are investigating a family of supramolecular building blocks to construct solids with nanoporous properties. We have shown previously that complexes between mono- and bis-2,6-dicarboxypyridines and transition or lanthanide metals assemble through metal-ligand coordination and hydrogen bonding into two-dimensional or three-dimensional scaffolds several of which show modest porosity. Current efforts in our laboratory focus on the synthesis of large tetrahedral building blocks that self-assemble via metal-ligand coordination. Molecular building blocks that we are pursuing consist of organic molecules with four 2,6-dicarboxypyridine units linked covalently to acetylene units in a symmetrical

arrangement around a tetrahedral core. We currently are using several different approaches to synthesize tetrahedral molecules that utilize Sonogashira coupling to join the aryl units to acetylene. All compounds are characterized by NMR and IR spectroscopies. These compounds will provide large tetrahedral building blocks that bind transition metals at each of the four 2,6-dicarboxypyridine units. Metal-ligand coordination in this manner will promote molecular assembly in three dimensions. We expect the resulting metal-organic frameworks to have a diamondoid structure that features large channels.

EE9.27

Poly(L-lactic acid)-based nanocomposite fibers. Vahik Krikorian^{1,2}, Cheryl Casper^{1,2}, John F. Rabolt^{1,2} and Darrin J. Pochan^{1,2}; ¹Materials Science and Engineering, University of Delaware, Newark, Delaware; ²Delaware Biotechnology Institute, University of Delaware, Newark, Delaware.

The possibility of organoclay incorporation in fiber electrospinning processes is explored. Two types of commercially available montmorillonite-based clays with different extent of miscibility with the polymer matrix were employed to study the effect of organic modifier/matrix interactions. The nanocomposites were fabricated by electrospinning a suspension of organoclay/dichloromethane with Poly(L-lactic acid), PLLA, a widely used biodegradable synthetic polyester. A high degree of birefringence in polarized light microscopy suggested that the polymer chains in as-spun fibers are highly aligned. However, Wide Angle X-ray Scattering (WAXS) data revealed no crystalline peaks in as-spun fibers. Annealed samples show a high degree of crystallinity-while the polymer chains in spun fibers are not in perfect crystalline registry, annealing the samples above the glass transition temperature induces high degree of crystallinity. Based on Scanning electron microscopy (SEM), spun fibers are highly porous, which may be beneficial in biomedical applications, membranes, and reinforcement matrices. Transmission electron microscopy (TEM) data shows the ordering of silicate platelets along the fiber axis, consistent with the d-spacings obtained from WAXS.

EE9.28

Electrospinning: A Novel System for Nanoscale Particle Alignment. Vahik Krikorian^{1,2}, Vikram Daga³, Norman J. Wagner³ and Darrin J. Pochan^{1,2}; ¹Materials Science and Engineering, University of Delaware, Newark, Delaware; ²Delaware Biotechnology Institute, University of Delaware, Newark, Delaware; ³Chemical Engineering, University of Delaware, Newark, Delaware.

Fiber electrospinning was employed to observe the feasibility of inorganic nanoparticles alignment. A variety of nanoparticles with different aspect ratios were used to fabricate one-dimensionally aligned nanoparticle/polymer fibers. Silica nanospheres synthesized by the Stober method, Laponite-type clay, and maghemite spindle-shaped nanoparticles were suspended in PEO/water solution and electrospun at different conditions. The nanoparticles were successfully aligned along the fiber axis by fine tuning the electrospinning and solution conditions, respectively. In addition, the effect of particle aspect ratio, size, concentration, and applied voltages were studied on the nanofiber formation, morphology and diameter. To characterize the nanoparticles and their dispersion within the PEO fiber matrix, dynamic light scattering, small angle x-ray scattering, and transmission and scanning electron microscopy techniques were utilized.

EE9.29

Abstract Withdrawn

EE9.30

Comparison of the Electrical and Mechanical and Morphological Properties of Polymer Nanocomposites Made from Multiwall Carbon Nanotubes (MWNT) and Nickel Nanostrands (NS). Max D. Alexander¹, George Hansen², Heather J. Dowty¹, Brandon Black¹, Matt Pettit² and Hilmar Koerner³; ¹Polymer Branch, Air Force Research Laboratory, Dayton, Ohio; ²Metal Matrix Composites, Heber City, Utah; ³Polymer Branch, University of Dayton Research Institute, Dayton, Ohio.

Here we explore polymer / inorganic nanocomposites based on a new high aspect ratio nano-material, nickel Nanostrands and compare the electrical, and mechanical behavior to that of multiwall nanotube composites. The nanostrands have the same dimension as the nanotubes but are made of solid nickel and can be readily produced in large quantities. The volume content of the nanostrands in a polyurethane matrix was varied from 0.1% to 20% to characterize the percolation behavior of the system. DC electrical characterization was performed at room and elevated temperatures as a function of polymer elongation. Identical loadings and dispersion technique were used for the multiwall nanotubes allowing for one to one performance characterization. The nanostrands were found to produce

conductivities substantially higher than the corresponding carbon nanotube composites and had the added advantage easily imparting a tailored orientation of the nano-element by the use of magnetically assisted processing.

EE9.31

Layered Tungsten Oxide-Based Hybrid Materials Incorporating Transition Metal Ions. B. Ingham¹, Shen Vun

Chong² and J. L. Tallon^{2,1}, ¹Victoria University of Wellington, Wellington, New Zealand; ²Industrial Research Limited, Lower Hutt, New Zealand.

A number of transition metal tungstates, $M^{2+}WO_4$, are known to exist; many of which occur naturally as pure or mixed tungstate ores (e.g. wolframite, ferberite, stolzite). The $M^{2+}WO_4$ species primarily form either in the wolframite or the scheelite structure, depending on the size of the M^{2+} ion. Recent work by our group on tungsten oxide based hybrid materials - consisting of layers of corner-shared WO_6 -octahedra separated by organic amine/ammonium 'spacer' molecules - has led us to explore the possible incorporation of transition metal ions within the hybrid structure, and/or the formation of new layered structures altogether. The materials were produced by a solution-based method and characterised by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), infrared and Raman spectroscopy, and magnetisation measurements. Preliminary results of manganese tungsten oxide-diaminoalkane hybrids show that this system has interesting properties. XRD and SEM of these new hybrids strongly indicate the presence of a layered structure, and magnetisation results show an antiferromagnetic transition at low temperatures. The transition temperature decreases with increasing alkyl chain length, which corresponds to the inter-inorganic layer spacing. This indicates a crossover from 2-dimensional to 3-dimensional magnetic behaviour, which is frustrated as the distance between the layers is increased.

EE9.32

Intercalation of n-Alkylamines in the Vapor Phase into Vanadium Pentoxide Xerogel Dispersed into Silica Matrix.

Herenilton Paulino Oliveira and Marisa Alves Figueiredo; Quimica, Universidade de Sao Paulo/FFCLRP, Ribeirao Preto, Sao Paulo, Brazil.

Over the past twenty years, the interest in the host-guest chemistry has mushroomed, mainly due to the large number of applications in energy storage, catalysts, adsorbents, optical devices, etc. In this work, we report a new intercalation reaction: three different n-alkylamines (n-butylamine, n-hexylamine and n-octylamine), in vapor phase, were intercalated into free vanadium pentoxide xerogel and into this lamellar material homogeneously dispersed into Si-O-Si network (obtained by polycondensation of the silicon alkoxide) interpenetrated with V-O-V and V-OH-V polymeric chains previously formed by oxolation and ololation reactions. The reaction with non-dispersed xerogel leads to increase of interlamellar distance for low time of reaction (up to 2 hours) and after 24 hours we observed a new phase. In contrast, for the reaction with xerogel dispersed in silica, it was observed only the increase of the basal distance retaining the original bi-dimensional structure (001 diffractions lines were observed); suggesting that the silica matrix stabilizes the vanadium pentoxide structure as the result of a mutual "solubility" due to cross-linking and entanglement of both components. The reactions were monitored using powder X-ray diffraction, infrared and electronic spectroscopy, electron paramagnetic resonance and scanning electron microscopy. Electrochemical properties were also investigated. Acknowledgement: Fundaco de Amparo a Pesquisa do Estado de Sao Paulo (fellowship no 02/12378-3 and grant no 01/01527-5).

EE9.33

Control of the Morphology of the Layered-Silicate Epoxy Nanocomposite. Chenggang Chen^{1,2} and Tia BensonTolle²;

¹University of Dayton Research Institute, Dayton, Ohio; ²Air Force Research laboratory, Wright-Patterson Air Force Base, Ohio.

Polymer layered-silicate nanocomposite has attracted great attention due to its unique nanostructure and properties. The property of the nanocomposite is determined by the morphology of the nanocomposite. The typical morphologies of the nanocomposite are the intercalated and exfoliated nanostructure. In this study, the layered-silicate epoxy nanocomposite with different morphology can be controlled and achieved. The different morphology could include the intercalated nanostructure with the 15 Å-increase of the interplanar spacing, the intercalated one with 150 Å-increase of the gallery and fully exfoliated nanostructure.

EE9.34

The Structure of a Molybdenum Disulfide Intercalation Compound. Ralf Bruening¹, Kristopher Bulmer¹, Rabin Bissessur²,

Pravin Varma¹ and Stephen Emeneau¹; ¹Physics Department, Mount Allison University, Sackville, New Brunswick, Canada; ²Department of Chemistry, University of Prince Edward Island, Charlottetown, Prince Edward Island, Canada.

The x-ray powder diffraction spectrum of molybdenum disulfide with intercalated tetraazamacrocyclic molecules was simulated. The measured spectrum shows well-defined peaks and broad scattering. Model crystallites were generated using a computer program, and the x-ray spectra corresponding to these trial structures were calculated by evaluating the Debye sum. The match between the measured and simulated spectra was improved by a trial-and-error procedure. Matching the peak widths shows that the crystallites contain typically 6500 MoS_2 units in about nine layers. While the layers in the best model structure are oriented in the same direction (not turbostratic), they are translated randomly in the plane perpendicular to the stacking direction. In contrast to prior work on intercalation compounds, which suggests various types of periodic reconstruction within the MoS_2 layer, we obtain the best match with a non-periodic reconstruction. It involves triangular and hexagonal groupings of the molybdenum atoms with a random choice of centers. This type of reconstruction reproduces the experimentally observed broad scattering in detail.

EE9.35

Effects of Surface Modification of Mg(OH)2 with Polysiloxane Oil and Silica Additive on the Flame Retardancy and Mechanical Properties of LDPE-Mg(OH)2 Composites.

Koji Kodama^{1,2}, Makoto Egashira¹, Yasuhiro Shimizu¹ and Takeo Hyodo¹; ¹Faculty of Engineering, Nagasaki University, Nagasaki, Nagasaki, Japan; ²Material R&D Center, Yazaki Parts Co.,Ltd, Susono, Shizuoka, Japan.

Magnesium hydroxide is considered to be a promising filler for polymer-based composites from the viewpoints of no generation of corrosive and toxic gases upon firing. To achieve sufficient flame retardancy, however, a high loading level of Mg(OH)2 is requested, and this results in degradation of mechanical properties of the composites, such as elongation and impact strength, due to poor affinity between nonpolar polymeric matrix and Mg(OH)2 powder. Therefore, special attention is being paid on the surface modification of Mg(OH)2 powder which enables us to realize a high loading level along with sufficient mechanical properties. Our recent studies have revealed that the addition of anhydrous silica treated with methyl group (M-silica) to the composites of low-density polyethylene (LDPE) and commercial magnesium hydroxide powder treated with stearic acid (Magnifin H5C, Albemarle Corporation) could improve flame retardancy, and that the surface treatment of Mg(OH)2 with methylhydrogen polysiloxane (MHS) was effective for improving flame retardancy without any degradation of mechanical properties of LDPE-Mg(OH)2 composites. In the present study, therefore, synergistic effects of the surface modification with MHS and the M-silica addition on the properties of LDPE-based composites have been investigated. For comparative purpose, another series of composites with similar composition was also prepared by Magnifin H5C. When comparison was made at the addition of 40 wt% Mg(OH)2 only, the composite with MHS-treated Mg(OH)2 was superior to that with Magnifin H5C from the viewpoints of oxygen index and large elongation, while yield strength was comparable to each other. With increasing the additive amount of M-silica at a fixed total filler content of 40 wt%, oxygen index and yield strength increased accordingly in both the composite series. However, elongation tended to decrease beyond 3 wt% M-silica in the case of the MHS-treated Mg(OH)2 composite, whereas it increased up to 2 wt% M-silica and beyond that reached a saturated value for the Magnifin H5C composite. As a result, the MHS-treated Mg(OH)2 composite showed a smaller elongation value than the Magnifin H5C composite at 5 wt% M-silica. In the next step, therefore, the effect of the total filler content on the composite properties was tested, while maintaining the additive amount of M-silica to be 12.5 wt% of the total filler content. Elongation could be improved, while maintaining a high oxygen index value of 24.6%, by the decrease in the total filler content from 40 to 35 wt% in the case of the MHS-treated Mg(OH)2 composite. Thus, the MHS-treated Mg(OH)2 composite showed higher oxygen index than the Magnifin H5C composite and comparative elongation and yield strength at the total filler content of 35 wt%. This result enabled us to reduce the total filler content with maintaining improved oxygen index and suppressing the degradation of elongation by the synergistic effect.

EE9.36

Responsive Polymer/Clay Aerogel Composites.

Suneel A. Bandi and David A. Schiraldi; Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, Ohio.

Responsive polymer/clay aerogel hybrid materials are synthesized by in-situ polymerization of Poly (N- isopropylacrylamide), PNIPAAm,

in a sodium exchanged Montmorillonite clay aerogel. Encapsulation of the aerogel with polymer leads to a slight change in the d-spacing from 12.5 to 13.5 Å. The composite shows reversible swelling behavior in water and demonstrates thermo-responsive properties of the polymer which undergoes a phase change at LCST (30-32°C). The interpenetrating structure of the polymer network through the low density aerogel retains the aerogel monoliths, even when submerged under water for extended periods; without the polymer, the aerogel loses its structure in water. Composites of various copolymer compositions are reported. Such aerogels-hydrogel composites may be used as absorbent of fluoride impurity, for trapping slow neutrons with the use of Cd clay, as insulating materials and for chromatography.

EE9.37

Self-Directed Assembly of Mesoscopically Ordered Polydiacetylene/Silica Nanocomposites from Bridged Silsesquioxanes. Huisheng Peng, Jiebin Pang and Yunfeng Lu; Chemical and Biomolecular Engineering, Tulane University, New Orleans, Louisiana.

Sol-gel chemistry opens new routes for designing hybrid organic-inorganic materials with novel properties. Recently, in an effort to better control structure and function, surfactant-directed co-assembly or self-directed assembly has been used to synthesize hierarchical organo-bridged polysilsesquioxanes that exhibit order over multiple length scale. In this work, we report the preparation of highly ordered polydiacetylene/silica nanocomposites with reversible or irreversible color changes by self-assembly of diacetylenic bridged silsesquioxanes without or using surfactants. The bridged silsesquioxanes were prepared by the reaction of diacetylenic diol (or acids) with γ -isocyanatopropyltriethoxysilane. After the bridged silsesquioxanes were subjected to acid hydrolysis with HCl in a 3:2 volume mixture of THF and water, the self-assembled supramolecular products were obtained by casting the resulting solutions on glass slides followed by very slow evaporation of solvent. The polymerization of diacetylenic units was carried out under ultraviolet irradiation, which was demonstrated by a color change from white to blue. Subsequent heating of the samples caused a reversible or irreversible blue to red thermochromatic transition. The PDA/silica nanocomposites were characterized by powder X-ray diffraction (XRD), transmission electron microscope (TEM) and ultraviolet-visible (UV-vis) spectrophotometer. The XRD patterns exhibit sharp peaks that indicate the materials with highly ordered lamellar or hexagonal structures. TEM analysis further confirms the lamellar or hexagonal structure of the diacetylene/silica nanocomposites. The reversible or irreversible thermochromatic transition were investigated by UV spectroscopy. The results showed the adsorption maximum at about 652 nm for the films with blue color and 541 nm for those with red color. In conclusion, this work demonstrates a powerful and clean way of producing highly ordered and mechanically robust conducting polymer-based optoelectronic materials with applications ranging from light-emitting diodes to biomolecular sensors.

EE9.38

Control on the Morphology and Polymorph Selectivity in Calcium Carbonate Mineralization. Suresh Valiyaveetil^{1,2,3}, Sindhu Swaminathan² and Parayil Kumaran Ajikumar³; ¹Chemistry, National University of Singapore, Singapore, Singapore; ²NUS Nanoscience and Nanotechnology Initiatives (NUSNNI), National University of Singapore, Singapore, Singapore; ³Singapore - MIT Alliance (SMA), National University of Singapore, Singapore, Singapore.

Understanding the process of biomineralization of calcium salts is an interesting theme owing to its perceived importance in restorative surgeries. Recently, we have investigated a few systems involving both soluble and insoluble templates for the nucleation of calcium salt crystals. In this presentation, we will describe our recent results from our lab in which polypeptides are used for the mineralization and morphology control by using temperature as an additional factor. The present talk will focus on detailed account of the crystallization conditions and the influence of various additives on morphology as well as full characterization of the crystals nucleated.

EE9.39

Pyridine on Si(100) and H-Si(100) - STM observation of dative bonded adducts. Jill Miwa¹, Brian Eves², Federico Rosei¹ and Gregory Lopinski²; ¹INRS-EMT, University of Quebec, Varennes, Quebec, Canada; ²Stecie Institute of Molecular Sciences, National Research Council of Canada, Ottawa, Ontario, Canada.

The potential of fabricating nanoscale hybrid organic/silicon molecular devices has stimulated considerable interest in understanding the interaction of organic molecules with silicon surfaces [1]. Unsaturated species react readily with the dimers of the Si(100)-2x1 surface, forming Si-C bonds. Nitrogen containing species

can additionally form dative bonded adducts, which involve donation of the N lone pair electrons to the silicon surface [2,3]. In this work we present scanning tunneling microscopy studies of the chemisorption of pyridine on Si(100). On the clean surface, low coverage images clearly show that pyridine binds primarily via formation of a dative bond. The resulting charge transfer complex, imaged as paired protrusions on a single dimer, gradually converts to a species similar to the 'tight-bridge' binding motif, reported previously for benzene adsorption on this surface [4]. The bridge structure is distinguished by its characteristic two dimer footprint. Back conversions to the dative species are observed and it is proposed that this mechanism is actually tip induced. To restrict binding to the dative bonding configuration, dosing of pyridine on an H-terminated Si(100) surface with a small density of isolated reactive sites has been explored. While pyridine readily datively bonds to individual clean dimers, isolated single dangling bonds remain unreacted. This observation can be explained in terms of the ability of the clean dimers to act as electron acceptor sites that can stabilize the dative bonded adduct. References 1. F. Rosei, J. Phys.-Condens. Mat. 16, S1373 (2004). 2. F. Tao, M. H. Qiao, Z. H. Wang, G. Q. Xu, J. Phys. Chem. B 107, 6384 (2004). 3. H.-J. Kim, J.-H. Cho, J. Chem. Phys. 120, 8222 (2004). 4. G.P. Lopinski, T.M. Fortier, D.J. Moffatt, R.A. Wolkow, JVST A 16, 1037 (1998).

EE9.40

Structure and Nanomechanical Properties of Electrospun Polystyrene/Clay Nanofibers. Yuan Ji¹, Shouren Ge¹, Bingquan Li¹, Tohru Araki², Harald Ade², Jonathan Sokolov¹ and Miriam Rafailovich¹; ¹Materials Science and Engineering, SUNY at Stony Brook, Stony Brook, New York; ²Physics, North Carolina State University, Raleigh, North Carolina.

Polystyrene/clay nanofibers can be fabricated successfully using electrospinning technique. Polystyrene/clay nanocomposites with different clay concentrations (0, 1%, 4%, 8%) were dissolved in a mixing solvent of tetrahydrofuran and N, N-dimethylformamide and then electrospun to form fibers with diameters ranging from 150nm to 10um by sensitively controlling the solution concentration and solvent composition. The structure and morphology of electrospun PS/clay fibers were investigated by scanning electron microscopy (SEM), transmission electron microscopy (TEM), scanning transmission x-ray microscopy (STXM) and atomic force microscopy (AFM). SEM and AFM pictures showed that the surface morphology of electrospun fibers changed from a typical porous structure (without clay) to a ridge like structure (with clay). STXM and TEM pictures showed that electrospinning can induce chain orientation in electrospun fibers and clay exfoliation can be found in electrospun fibers at a concentration of 4%. Shear modulation force microscopy (SMFM) was used to investigate the relative modulus of electrospun fibers as a function of fiber diameter and temperature. Results indicated that modulus of fibers increases relative to bulk films with decreasing fiber diameter when temperature is lower than glass transition temperature (Tg). modulus of fibers can be restored to bulk value when temperature is higher than Tg due to the chain relaxation above Tg. This result was consistent with STXM results. Tg measurement by SMFM showed that electrospun fibers had a higher Tg than the bulk film when clay exfoliated at a concentration of 4%. Supported by NSF MRSEC

EE9.41

Synthesis and Characterization of Mesoscopic Silica/Hydrogel Composites. Donghai Wang, Nurettin Sahiner, Lynn Rice, Vijay John and Yunfeng Lu; Chemical Engineering, Tulane University, New Orleans, Louisiana.

It is known that organic/inorganic hybrid nanomaterials can be synthesized by incorporating the polymer into a performed nano-structured material or vice versa, which possess synergetic properties for wide applications. Hydrogel can respond to some external stimuli such as temperature, pH, electric field, etc. For example, hydrogels can swell to form superporous networks with the response of pH changes. Co-assembly of silicate/surfactant spontaneously constructs highly-ordered mesostructured liquid crystal phase and thus form ordered mesoporous silica after removal of surfactants. Here we present synthesis and characterization of mesoscopic silica/hydrogel hybrid nanocomposites. Hydrogel have been prepared via redox and/or UV irradiation polymerization from cationic, anionic, and neutral monomers. Mesoscopic silica can be incorporated into hydrogel superporous networks when the hydrogel swell at the appropriate conditions such as pH, solvent, and hydrogel types. Cooperative assembly of silicate/surfactant nucleates at the liquid/polymer interface within hydrogel superporous networks and form hybrid nanocomposites after hydrogel shrinks. For mesoscopic silica/hydrogel nanocomposite characterization, swelling and pH responses behaviors were investigated, and SEM, TEM and BET measurement were employed to elucidate the mesoscopic silica/hydrogel nanocomposite structure. The nanocomposite morphology can be controlled from nanogels, films, to monoliths

depending on morphology of the hydrogel templates. This work provides a novel route to synthesize mesoscopic silica/hydrogel nanocomposites which can be used in drug release, encapsulation, template synthesis, and other applications.

EE9.42

Characterization of Carboxyl Functionalized SAMs and Surface-Attached Interlocking Molecules Using NEXAFS.

Louis J. Terminello³, T. M. Willey^{1,2}, L. Vance¹, T. van Buuren¹, C. Bostedt¹, Bradley R. Hart¹, R. W. Meulenberg¹, A. J. Nelson¹, L. J. Terminello¹ and C. S. Fadley^{2,3}; ¹CMS, LLNL, Livermore, California; ²University of California-Davis, Davis, California; ³Lawrence Berkeley National Laboratory, Berkeley, California.

Self-assembled Monolayers (SAMs) and other organo-thiol compounds on u(111) have become the basis for surface attachment of complex molecules. In order to produce useful films, one needs to understand the orientation, order, and substrate bonding of the molecules. Carboxyl and amino terminated SAMs are useful in functionalizing surfaces for surface attachment and immobilization of proteins, DNA, viruses, and for using the charged state of the endgroups in switchable surfaces. We are also using similar functionalization in surface-attached interlocking molecules to attempt to induce and measure reorientation and switching within monolayers. However, functionalization often (adversely!) affects the synthesis, order, packing, and formation of these films. With proper synthetic protocol, many of these issues can be overcome. Here, NEXAFS results probe the orientation of molecules while XPS is used to determine the attachment and chemical nature of the films. We present NEXAFS spectra to compare and contrast the ordering and between SAMs from mercaptohexadecanoic acid (HS(CH₂)₁₅COOH) a long-chain molecule with strong chain-chain interactions and thioctic acid (S₂(CH₂)₂CH(CH₂)₄COOH) with a large base hindering strong interactions between its short chains. Stark conformational differences occur in these films of the endgroups with deprotonation (COO⁻-vs. COOH.) We will also present preliminary results of direct measurement of conformational changes using functional groups for switching in monolayers of simple, surface-attached interlocking molecules. This work is supported by the U.S. Department of Energy, BES Materials Sciences under contract W-7405-ENG-48, LLNL; also W-DE-AC03-76SF00098 at the ALS at LBNL, DE-AC03-76SF00515 at the SSRL at SLAC.

EE9.43

Abstract Withdrawn

EE9.44

Synthesis of Poly(methyl methacrylate)/clay nanocomposites by pseudo-dispersion polymerization in Supercritical carbon dioxide. Qian Zhao¹ and Edward T. Samulski^{1,2}; ¹Curriculum in Applied Materials Sciences, University of North Carolina, Chapel Hill, North Carolina; ²Chemistry, University of North Carolina, Chapel Hill, North Carolina.

A novel route to synthesize PMMA/clay nanocomposites were presented by a pseudo-dispersion polymerization of MMA in presence of fluorinated surfactant modified clay (10F-clay) in supercritical carbon dioxide. The nanocomposites were characterized by SEM, TEM, X-ray Diffraction (XRD), TGA, and DMA, and showed partially exfoliated/intercalated structures as well as enhanced thermal stability, glass transition temperature and mechanical properties. It was also found that 10F-clay served not only as inorganic filler, but also an effective stabilizer for PMMA growth in CO₂. More stabilizing mechanisms were suggested by FTIR studies. This general route allows for clean synthesis of nanocomposites with high yields in supercritical CO₂, without the need for adding extra surfactant to stabilize the polymerizing system.

EE9.45

Strengthening of Silica Aerogels by Organic Chemical Vapor Deposition (CVD) Modification. Kennard Virden Wilson, Douglas A. Loy, Kimberly A. DeFriend and Jonathan M. Stoddard; MST-7 Polymers and Coatings Group, Los Alamos National Laboratory, Los Alamos, New Mexico.

Silica aerogels are prepared by the supercritical drying of gels obtained from the sol-gel polymerization of alkoxysilane monomers under either acidic or basic conditions. These materials, which possess surface areas over 1000 meters-squared per gram and densities as low as 3 milligrams per cubic centimeter, have been used as insulation, radiation detectors and as a component in targets used in inertially confined fusion experiments. The low density of silica aerogels also makes these materials fragile and difficult to handle, with shapes having to be molded in place rather than machined. We have been exploring the use of CVD treatments of silica aerogels with polymerizable organic monomers to create nanocomposite structures with improved mechanical properties. Surface area (nitrogen

porosimetry), density, and compression strength measurements were performed on the samples to determine before and after properties. Proton and carbon NMR studies were used to characterize the structure of the coating as well as serve to compare treated and untreated materials. Changes to the samples were also observed by optical microscopy. The ultimate aim of this research is to produce machinable, low density aerogels.

EE9.46

Molybdenum and Tungsten Oxide Nanowires Prepared by Electrospinning. Katarzyna Magdalena Sawicka¹, Pelagia Irene Gouma² and Mallikarjun B. Karadge²; ¹Chemistry, Stony Brook University, Stony Brook, New York; ²Materials Science and Engineering, Stony Brook University, Stony Brook, New York.

Molybdenum and Tungsten Oxide nanowires were obtained through the process of electrospinning. The materials have potential to be advanced chemical sensors. The versatile design and a much greater surface area to volume ratio indicate improvement over prior technology. Nanoparticles of Molybdenum and Tungsten Trioxide achieved through the sol gel method have been previously studied and utilized in metal oxide semiconductor gas sensor arrays. Depending on their crystal structure they proved to be selective to such gaseous analytes as ammonia, methanol, isoprene, and carbon monoxide. The metal oxide semiconductor gas sensor arrays offered efficiency in terms of sensitivity, and operation in diverse pressure environments. The emerging technique of electrospinning offers a relatively simple and versatile method of achieving composite nanofibers. In this process a polymer solution is injected from a small nozzle under the influence of an electric field as high as 30kV. The build up of electrostatic charges on the surface of a liquid droplet induces the formation of a jet. The jet is subsequently stretched to form a continuous fiber. Before it reaches the collecting screen the solvent evaporates or solidifies, and the fibers are collected on a conductor surface. They form nonwoven mats characterized by high surface areas and relatively small pore sizes. This method has been utilized in creating metal oxide semiconductor, and biological composite nanofibers. Differently proportioned mixtures of metal oxide sol gel solutions (MoO₃, WO₃) with Polyvinylpyrrolidone (PVP) solution were electrospun. Metal oxide composite nanowires of both molybdenum and tungsten were created. The process of electrospinning can be controlled through different parameters such as solution composition, flow rate, voltage, and needle to collector distance. The as received samples obtained were compared in terms of average diameter when concentration, and flow rate were varied, while other parameters kept constant. The Scanning Electron Microscopy and Transmission Electron Microscopy studies proved the diameter of as received composite samples is inversely proportional to the metal oxide concentration. It was also concluded that it is directly proportional to the flow rate. Self-supported one-dimensional metal oxide nanomaterials were obtained through heat treatment of as received samples deposited on Silicon Nitride grids. The TEM images of post heat treatment samples confirmed both Tungsten and Molybdenum Oxide one-dimensional nanowires were achieved through this process.

EE9.47

Attaching Aromatic Molecules to the Si(111) Surfaces via Si-N=CH- Linkages. Hideyuki Murata^{1,2} and Atsushi Itabashi¹;

¹Japan Advanced Institute of Science and Technology, Tatsunokuchi, Ishikawa, Japan; ²PRESTO, Japan Science and Technology Agency, Kawaguchi, Saitama, Japan.

Attaching functional organic layers to semiconductor surfaces may have applications in a number of areas, including molecular and biomolecular electronics, sensors and lithography. Here, we present a novel, two-step strategy for the covalent bond formation between aromatic molecules and silicon surfaces. In the first step, a H-terminated Si(111) surface reacts with amino radicals to give a NH₂-terminated Si(111) surface at room temperature. The amino radicals were generated by the thermal decomposition of ammonia gas with Tungsten filament heated at 1000°C. In the second step, the NH₂-terminated silicon substrate was immersed in a terephthalaldehyde/toluene solution for the formation of monolayer via Si-N=CH- linkages. The formation of NH₂-terminated surface and the monolayers is confirmed by X-ray photoelectron spectroscopy and Fourier Transfer Infrared Spectroscopy (FTIR). After the reaction of NH₂-terminated Si(111) with terephthalaldehyde, the Si(111) surface was covered by aldehyde groups and hence serve as a the functional surface for layer-by-layer growth of a conjugated polymer, Polyazomethine.

EE9.48

Morphology, Thermal, Tensile and Fracture Properties of Vinyl Ester/Clay Nanocomposites. Hongyu Chen¹, Michael Mullins², Larry Blankenship² and Ulrich Herold²; ¹Material Science, Dow Chemical Company, Freeport, Texas; ²Epoxy Products &

Intermediates, Dow Chemical Company, Freeport, Texas.

Vinyl ester resins are used as a thermoset matrix for glass fiber reinforced composites. These composites are used for a variety of uses, especially in civil engineering and for industrial applications. In this presentation we will describe the modification of vinyl ester resins with nanoclays. We have investigated the effects of clay type, synthesis routes and the type of vinyl ester on the morphology, thermal, tensile and fracture properties of vinyl ester/clay nanocomposites. We obtained an intercalated morphology with *d*-spacings expanded to twice that of the original clay. The nanocomposites made by adding clay after the esterification step during vinyl ester synthesis had slightly better intercalation than those made by adding clay before esterification. However, the difference did not lead to a significant impact on the properties. All nanocomposites had a higher glassy and plateau modulus than the unmodified resin. The nanocomposites had a similar *T_g* and higher fracture toughness compared to the unmodified resin. The analysis of the fracture surface also suggested that nanocomposites had a higher fracture toughness. However, all nanocomposites had a lower elongation to break than the unmodified resin. The clay clusters found in the nanocomposites may act as stress concentrators and may be responsible for the low elongation to break.

EE9.49

Abstract Withdrawn

SESSION EE10: Organosilicon-based Polymers
Chairs: Clement Sanchez and Ulrich Wiesner
Thursday Morning, December 2, 2004
Room 302 (Hynes)

8:30 AM *EE10.1

Photo-induced Optical and Chemical Properties of Polysilane/Inorganic Nano-Hybrids. Kimihiro Matsukawa and Yukihito Matsuura; Department of Electronic Materials, Osaka Municipal Technical Research Institute, Osaka, Japan.

Polysilane is a well-known functional organosilicon polymer with a high quantum efficiency of photoluminescence (PL), a high hole drift mobility, a significant photobleaching property, etc., which are associated with σ -conjugation along the Si-Si main chain. On the other, polysilane/inorganic hybrids, which polymethylphenylsilane (PMPS) is molecularly dispersed in inorganic matrix, might be an attractive material. For the preparation of polysilane/inorganic hybrid materials, a chemical modification of PMPS is essential to interaction or reaction with metal alkoxides in a sol-gel reaction. Polysilane block copolymers with reactive groups were synthesized by the photoradical polymerization of functional vinyl monomers using PMPS as a macro-photo-initiator. The polysilane/silica hybrid thin films were prepared from the PMPS-trialkoxysilylpropylmethacrylate copolymer and tetraethoxysilane via sol-gel reaction, in which PMPS segments homogeneously embedded in silica matrix. These exhibited unique and interesting photoelectric properties; refractive indices and the energy migration could be controlled by the PMPS concentration in the hybrid thin films. The photo-decomposition of PMPS segments in polysilane/inorganic hybrid caused the significant changes for the optical, chemical, and morphological characteristics. It was found that a refractive index in the hybrid thin films changed due to the photo-decomposition of PMPS segments. The fixation of high refractive index difference (ca. 3.5%) on the polysilane/silica hybrid thin films was also investigated. This reactive index change seems to be effective for important applications, such as periodic optical waveguides, distributed feedback lasers, so on. Furthermore, as the PMPS copolymers had a photo-reducing characteristics, Au (III) ions in hydrogen chloraurate were reduced to gold nano particles (5nm diameter) by using PMPS-acrylamide copolymer under UV irradiation. In this reaction, polyacrylamide segments acted as the protecting groups for gold nano-particles. The color changed to reddish purple resulted from the plasmon resonance of gold nanoparticles. During photo-reduction of Au ions, the silanols derived from photolysis of PMPS segments functioned as reactive components in the sol-gel reaction and provided the gold nano particles thin films. And, the negative pattern of gold nano particles was successfully fabricated by UV irradiation through a photomask.

9:00 AM EE10.2

Crystallization of POSS in a PEO-Based Multiblock Polyurethane Architecture. Jian Wu¹, Qing Ge², Kelly A. Burke¹ and Patrick T. Mather^{2,1}; ¹Chemical Engineering Department, University of Connecticut, Storrs, Connecticut; ²Institute of Materials Science, University of Connecticut, Storrs, Connecticut.

To date, polyhedral oligosilsesquioxanes (POSS) have been incorporated into a wide range of polymeric systems, either as a molecular-level filler or as a comonomer, but usually without ordering

of the POSS moieties as evidenced by x-ray diffraction analysis. Building upon earlier success in forming materials with crystalline ordering of POSS via the telechelic architecture with POSS end-capping polyethylene glycols, here we report similar ordering in PEO-POSS thermoplastic polyurethanes. Thus, a unique series of thermoplastic polyurethanes (TPU) were synthesized using poly(ethylene glycol) (PEG) as soft segment and incorporating an isobutyl-functionalized POSS diol (TMP POSS diol) in the hard segment. The molecular weight of PEG was systematically varied to include 10, 20, and 35 kDa while the mole ratio of PEG to POSS diol (as chain extender) was also varied. The diisocyanate employed for TPU polymerization was 4,4'-methylenebis(phenyl-isocyanate) (MDI). Wide-angle x-ray diffraction (WAXD) studies revealed that both the hydrophilic soft segments (PEG) and hydrophobic hard segments (POSS) can form crystalline structures driven by micro-phase separation, itself due to thermodynamic incompatibility. As molecular reinforcements, the presence of nanoscale POSS crystals remarkably improves the mechanical properties of the new TPUs. To be contrasted with common TPUs, the characteristic stress-strain curves of the new POSS-based TPUs show a clear necking-based yield and large strain-to-failure. During deformation, reflection peaks attributed to POSS crystals surprisingly features two kinds of orientation of POSS crystalline planes, parallel and perpendicular, with respect to stretching direction. Differential scanning calorimetry (DSC) revealed that the PEG block molecular weight and thermal history are both important parameters in controlling the crystallization of POSS-rich nanophase. In particular, increasing the PEG block length, inhibits the crystallization of POSS moiety. Meanwhile, increasing the cooling rate monotonically decreases the crystallinity of the same POSS-rich phase. Rheological study of the POSS nanophase crystallization further showed that faster cooling rates result in a decrease in the ultimate dynamic storage modulus following POSS crystallization and an increase of the loss angle for temperatures above *T_m* of PEG and below *T_m* of POSS. Following a detailing of these results, our presentation will offer suggestions for the origin of each influence on POSS crystallization and postulate other polymeric architectures that might favor POSS organization.

9:15 AM *EE10.3

Evolution of Porosity and Morphology in Alkylene-Bridged Polysilsesquioxane Xerogels as a Function of Gel Aging Time. Douglas Anson Loy¹, James H. Small¹, Kimberly A. Defriend¹, McKenzie Minke², Colleen R. Baugher², Brigitta M. Baugher², Duane A. Schneider² and Kenneth J. Shea³; ¹Polymers and Coatings Department, Los Alamos National Laboratory, Los Alamos, New Mexico; ²Sandia National Laboratories, Albuquerque, New Mexico; ³Department of Chemistry, University of California, Irvine, California.

Aging of silica gels before drying is known to result in significant changes in xerogel morphology, porosity and properties. In this study, the influence of aging gels on the porosity and morphology of alkylene-bridged polysilsesquioxane xerogels was examined. Gels of hexylene-, heptylene, octylene, nonylene, and decylene-bridged polysilsesquioxanes were prepared by the sol-gel polymerization of the respective bis(trimethoxysilyl)alkane monomers under acidic or basic conditions in methanol and in tetrahydrofuran. The gels were aged 3,7,14, 21, 28, 35, 42, 49, and 56 days before drying to afford xerogels. The xerogels were characterized by nitrogen sorption porosimetry and scanning electron microscopy. Xerogels prepared in THF were non-porous. Those prepared and aged under basic conditions in methanol or tetrahydrofuran exhibited coarsening of porosity with aging time. With the exception of the hexylene-bridged gels, those prepared and aged in acidic methanol showed little change with aging. The surface area of the hexylene-bridged xerogels nearly tripled with aging times of up to several weeks, then decreased, for the gels aged for more than two weeks, to around 100 meters squared per gram.

10:15 AM *EE10.4

Structure, Properties, and Assembly of Silsesquioxanes by Molecular Simulation. John Kieffer, Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan.

Polyhedral oligomeric silsesquioxane (POSS) consist of an inorganic core that can be functionalized with various organic or inorganic groups to produce a wide gamut of nano-sized building blocks. Today, such POSS-based building blocks can be synthesized reliably and cost-effectively. A great variety of molecular designs have already been realized and possibilities for the creation of new entities seem endless. However, a systematic knowledge of how to control the self-assembly behavior of these building blocks, how to manipulate these molecules at the nano-scale, and how to achieve specific properties in the resulting nano-structured hybrid inorganic-polymer materials is still lacking. To advance this knowledge, we are developing a computational framework for the simulation of structural assembly in POSS nanocomposites by combining computational techniques ranging from ab initio quantum mechanical calculations to molecular dynamics simulations to coarse-grained mesoscale modeling methods.

Using ab initio calculations we can predict the inherent properties of molecular building blocks. Using large-scale molecular dynamics simulations we can reproduce the transport, reaction, and microphase evolution processes that occur during nano-assembly, and thereby generate realistic models that serve to establish structure-property-processing relationships for these materials. In this presentation the general approach taken with our computational framework will be outlined and results from two representative materials simulation studies will be discussed. One example details the strategies pursued for the design of materials with photonic applications. The other one describes the peculiar amphiphilic behavior of mono-tethered POSS that causes nano-phase separation and can be exploited for pattern formation at this scale. This work is supported by the National Science Foundation (DMR-0103399).

10:45 AM **EE10.5**

Effect of Precursor Functionalization on Sol-Gel Derived Silica Network Structure. Sudin Bhattacharya^{1,2}, Feng Qi²,

Jinhua Zhou² and John Kieffer²; ¹Mechanical Engineering, The University of Michigan, Ann Arbor, Michigan; ²Materials Science and Engineering, The University of Michigan, Ann Arbor, Michigan.

Reactive molecular dynamics based on a three-body potential with dynamic charge transfer is used to study the effect of precursor functionalization on the nature of nanoporous silica structures produced by sol-gel condensation reactions. We have simulated different precursor molecules - pure silicic acid monomers and dimers, dimers functionalized with hydrogen atoms, and dimers functionalized with cyclohexyl groups - covering a range of functional groups from pure silanols to silanol-organic hybrids. With monomer precursors, the sol-gel aggregation process produces fractal 3-D network structures. As we alter the precursor from silanol-functionalized dimers to hybrids - we observe closed cage-like structures in the network, followed by the emergence of isolated silica clusters. In this presentation we discuss the mechanisms that control structural developments in these systems, as well as the structure-property relationships of the resulting configurations.

11:00 AM **EE10.6**

Affinity Control of Aminopropylsiloxane-based Organic/Inorganic Hybrids for Optical Sensors. Shingo Katayama¹,

Noriko Yamada² and Masanobu Awano³; ¹Fine Ceramics Research Association, Nagoya, Japan; ²Nippon Steel Corporation, Chiba, Japan; ³Advanced Manufacturing Research Institute, AIST, Nagoya, Japan.

The Aminopropylsiloxane-based inorganic/organic hybrids have known as a sensitive material for optical sensing systems such as Mach-Zehnder interferometer[1] and composite optical waveguide-based polarimetric interferometer[2]. For sensing toward nitrogen dioxide gas, the aminopropylsiloxane-based inorganic/organic hybrids have a high sensitivity but irreversible detection. We investigated the affinity control of the aminopropylsiloxane-based inorganic/organic hybrid toward nitrogen dioxide gas. The inorganic component derived from Nb(OC₂H₅)₅ was incorporated into the aminopropylsiloxane-based inorganic/organic hybrid to weaken the strong basicity resulting from amino groups. The aminopropylsiloxane-based inorganic/organic hybrid containing an Nb inorganic component resulted in a detectable change in the optical properties and acted as a reversible sensitive material toward nitrogen dioxide gas. 1) A. Barndenburg, et al., *Sensors and Actuators B*, 11, 361(1193). 2) Y. Xu, et al., *Chemical Sensors* 18, 145(2002).

11:15 AM **EE10.7**

Photoluminescence study of organic/inorganic hybrids for integrated optic devices. Luis Dias Carlos¹, Rute Sa Ferreira¹,

Veronica de Zea Bermudez², Silvia Nunes², Celso Molina¹, Sidney Ribeiro³, Joanna Cybinska^{1,4} and Janina Legendziewicz⁴; ¹Physics, University of Aveiro, Aveiro, Portugal; ²Chemistry, University of Trás-os-Montes e Alto Douro, Vila Real, Portugal; ³Chemistry, UNESP, Araraquara; ⁴Chemistry, University of Wrocław, Wrocław, Poland.

Sol-gel processing offers a low temperature route for the development of organic-inorganic hybrid materials potentially suitable for the production of optical waveguides and functional integrated optic devices at low cost. Urea cross-linked poly(oxyethylene)/siloxane and new amido cross-linked poly(ethylene)/siloxane nano-hybrids, classed as di-ureasils and di-amidosils, respectively, have been shown to simultaneously present acceptable transparency and mechanical flexibility leading to easier processing of thick films. These hybrids are also versatile hosts able to incorporate high concentrations of lanthanide ions (up to 15 % w/w) and, therefore, to achieve high luminescence efficiency (desirable for optical amplifiers and lasers). Another type of attractive hybrid matrix is that derived from methacryloxypropyltrimethoxysilane (MAPTMS) which contains a photopolymerizable organic group and thus can be easily patterned

using ultraviolet light radiation and lithographic techniques. Control over the refractive index of the films produced with this hybrid precursor can be achieved through the use of a stable sol containing nanoparticles of zirconium oxide. The hybrid hosts are room-temperature (RT) efficient white light emitters lacking metal activator ions with RT emission quantum yields as high as 20 % [1,2]. In spite of the potential technological relevance of such materials, the origin of their efficient white-light intrinsic photoluminescence (PL) is not yet completely clarified. With the goal of investigating further the nature of such emission and to develop innovative hybrid systems with a wide range of useful and tailored properties, the influence of the incorporation of nanoparticles of zirconium oxide (ZrO) and MAPTMS into the di-ureasils and di-amidosils was studied by photoluminescence in steady state and time-resolved modes. Preliminary results indicate that the di-ureasils and di-amidosils incorporating nanoparticles of ZrO and MAPTMS are efficient RT white-light emitters due to the convolution of donor acceptor pairs recombination that occur in the NH groups of the urea/amido linkages and in the siliceous nanodomains, similarly to the situation found in the undoped di-ureasil [1,2]. However, changes are observed in the peak energy of zirconium and MAPTMS-based hybrids. Moreover, these new hybrids present smaller recombination time-scale mechanisms than the undoped di-ureasils, for instance for a zirconium doping concentration around 25 % lifetime values of ca. 75 and 2-3 ms were detected for the NH and siliceous nanodomains related emissions, respectively. These values are smaller than those previously reported for di-ureasils, ca. 160 and 3.5 ms, respectively [2]. [1] L. Fu, R. A. Sa Ferreira, N. J. O. Silva, L. D. Carlos, V. de Zea Bermudez, J. Rocha, *Chem. Mater.* 16, 1507 (2004). [2] L. D. Carlos, R. A. Sa Ferreira, V. de Zea Bermudez, S. J. L. Ribeiro, *Adv. Funct. Mater.* 11, 111 (2000).

11:30 AM **EE10.8**

Polybromophenylsiloxanes. Highly Polyfunctional Nanoconstruction Sites. Richard M. Laine^{1,2,3}, Chad Brick²,

Michael Asuncion³ and Mark Roll³; ¹MSE, University of Michigan, Ann Arbor, Michigan; ²Chemistry, University of Michigan, Ann Arbor, Michigan; ³Macromolecular Science and Engineering Center, University of Michigan, Ann Arbor, Michigan.

Richard M. Laine, C. Brick, M. Asuncion, M. Roll Depts. of Materials Science and Engineering, Chemistry, and Macromolecular Science and Eng. University of Michigan Ann Arbor, MI. 48109-2136, U.S.A. Organic/inorganic hybrids represent a new frontier in materials chemistry, science, and engineering because they offer the potential to develop and tailor composite materials with control at the finest length scales. The potential exists to create new materials with novel properties by synergistic combinations of organic/inorganic components through intimate mixing of components. Intimate mixing, especially at nanometer length scales, creates extensive interfacial interactions that engender nanocomposite properties nonlinearly related to the bulk properties of the component phases. Indeed, nanocomposite properties do not comply with the rule of mixture, used to estimate the properties of macroscopic composites, because of these extensive interfacial interactions. The development of both general use and highly property targeted nanocomposite materials, all constructed using the same rules, requires a comprehensive library of nano-building blocks. The key to such a library is to have a diverse set of the smallest components (blocks) that exhibit distinct properties, readily available. Motivation for this approach is that control of molecular structure and properties at the smallest scales offers optimal control of macroscale properties. However, this approach requires an excellent understanding of the relationships of the components, their organization during and after processing, and resulting macroscopic properties in order to select the best components and processing conditions to realize target properties. This presentation will focus on the development of libraries of multifunctional octasilsesquioxanes from Polybromoocta-phenyloctasilsesquioxanes, [BrxPhSiO_{1.5}]₈, BrxOPS (x = 4-16 and higher).

SESSION EE11: Chemical Strategies for the Design of
New Hybrid Materials
Chair: Francois Fajula
Thursday Afternoon, December 2, 2004
Room 302 (Hynes)

1:30 PM ***EE11.1**

Synthesis of nanomaterials in Highly Swollen Liquid Crystals.

Miriam Tokumoto¹, Eduardo Pena dos Santos¹, Geetarani Surendran^{1,2}, Hynd Remita², Laurence Ramos³ and Eric P. Prouzet¹; ¹I.E.M., C.N.R.S., Montpellier Cedex 05, France; ²L.C.P., C.N.R.S., Orsay Cedex, France; ³G.D.P.C., C.N.R.S., Montpellier Cedex, France.

Highly Swollen Liquid Crystals (SLC) that exhibit hexagonal, cubic

or lamellar symmetry have been demonstrated to form a new type of soft nanoreactors. These mesophases are formed by a quaternary mixture combining a surfactant, an aqueous solution of inorganic salt, cyclohexane as a hydrophobic swelling solvent and pentanol-1 as a co-surfactant. Unlike previous works that used a "nanocasting" approach in a binary liquid crystal, the composition of these SLC allows syntheses to be proceeded inside the aqueous and/or the organic phase. Therefore inorganic, metallic or organic materials can be prepared and the geometry of the SLC controls the final shape of the prepared by this approach. We will describe various materials that were obtained by different processes in these SLCs: rod-like nanoaggregates of metal nanoparticles were synthesized by chemical reduction in the aqueous part of the hexagonal mesophase, microrods of zirconia were obtained by slow crystallogenesis from hydrated zirconium oxychloride, mesoporous zirconia was prepared by a faster hydrolysis and polymer micro- and nano-fibers were obtained in the organic phase by photopolymerization or radiolysis. We will show how the changes in the SLC structure can modify the structure of the compounds synthesized inside and that this system constitutes a quite universal medium for the preparation of nanomaterials or nanostructured systems.

2:00 PM **EE11.2**

Ionogels: Ionic Liquids Confined in Silica Membranes, a new Class of Solid State Electrolytes. Marie-Alexandra Neouze¹, Jean Le Bideau¹, Fabrice Leroux² and Andre Vioux¹; ¹CMOS UMR CNRS 5637, Université Montpellier, Montpellier CEDEX 5, France; ²LMI UMR CNRS 6002, Université Blaise Pascal - CNRS, Clermont-Ferrand, France.

In the course of our studies on hydrolytic and non-hydrolytic sol-gel processes, the use of ionic liquids for their own properties as well as reactant medium appeared to be a promising field. Indeed, ionic liquids have been studied for some time as alternative solvents for series of chemical reactions, as liquid electrolytes, as extractant liquids. Their potential is enhanced by their very low volatility, their recyclable and reusable feature. Moreover their chemical and physical properties may be tune by the choice of cation / anion content. We have carried out a typical one-pot sol-gel reaction (tetramethoxysilane with formic acid) in some ionic liquids among which the 1-butyl-3-methylimidazolium [BMI] bis(trifluoromethylsulfonide)imide [TFSI]. This results in a transparent solid material that we have named Ionogel. This material exhibits high ionic conductivity, up to 2.10⁻² S.cm⁻¹ around 470 K. Mechanical characterization of this solid shows a Young modulus at 63 MPa. For characterization necessity, the ionic liquid can be washed off: the resulting compound is the inorganic skeleton alone and presents an adsorption isotherm which permits to deduce a BET area at 900 m².g⁻¹ with a quasi-monodisperse pore size around 120Å. In Ionogels, the ionic liquid is nanoconfined in a highly stable oxide framework. The confinement of ionic liquid within the pores of the inorganic skeleton is expressed by several specific behaviour, like for instance that seen on 1H NMR spectra. The spectrum of the solid state Ionogel recorded without spinning shows very poor resolution, resolution which is recovered even with a low spinning (400 Hz). This evidences the peculiar state of the ionic liquid within the Ionogel. Studies are in progress in order to identify the origin of the ionic liquid conductivity in such a level of confinement. It is noteworthy that we have obtained here ionic conductivities for our solid state material in the order of magnitude of the ionic liquid itself. Moreover, this one-pot process yield a material which is still a gel, the reactant medium, bringing also the desired property, being preserved in the final compound.

2:15 PM ***EE11.3**

Hybrid Materials Based on Organophosphorus and Organosilane Coupling Molecules : what is the Difference. P. Hubert Mutin¹ and Gilles Guerrero²; ¹Chemistry, CNRS, Montpellier, France; ²Chemistry, University Montpellier 2, Montpellier, France.

Organophosphorus [1] and organosilane [2] coupling molecules can both be used to tether organic groups to an oxide network through the formation of M-O-P and M-O-Si bonds, respectively (M = Ti, Al, Zr, Si, etc.). Thus, phosphonic acids (RP(O)OH)₂ or phosphonic esters (RP(O)(OEt)₂) as well as trialkoxysilanes (RSi(OMe)₃, RSi(OEt)₃) or trichlorosilanes (RSiCl₃) have been used to prepare ionic-covalent organic-inorganic hybrid solids, either by sol-gel processing or by surface modification of an oxide support.[3-5] However, the reactivity of organophosphorus and organosilane coupling molecules are quite different. For instance, the hydrolysis of P-O-Et groups and the condensation of P-OH groups require harsh conditions, contrary to Si-O-Et and Si-OH groups. This behavior leads to different structures for the hybrid materials based on organophosphorus molecules. The stabilities of the M-O-P or M-O-Si interfacial bonds can also be quite different, depending on the nature of M. Thus, Si-O-P bonds are easily hydrolyzed whereas Ti-O-P bonds show exceptional hydrolytic stability, particularly under basic conditions.[3] Here, we wish to

illustrate the differences between organophosphorus and organosilane coupling molecules with several recent results and examples of application in our group, including: - study of the bonding mode of phosphonate units in titania/phosphonate hybrid solids by 17O MAS-NMR spectroscopy; [6] - simultaneous phase transfer and surface modification of titania nanoparticles - selective surface modification of patterned silica-titania supports and mixed oxides - alkylphosphonic acid self-assembled monolayers on titania for applications under strongly basic conditions: extraction of heavy metals using thiol-terminated SAMs and octadecylphosphonic acid SAMs as anti-scratching coatings. (1)Vioux, A.; le Bideau, J.; Mutin, P. H.; Leclercq, D. Topics in Current Chemistry 2004, 232, 145. (2)Judeinstein, P.; Sanchez, C. J. Mater. Chem. 1996, 6, 511. (3)Guerrero, G.; Mutin, P. H.; Vioux, A. Chem. Mater. 2000, 12, 1268. (4)Guerrero, G.; Mutin, P.; Vioux, A. Chem. Mater. 2001, 13, 4367. (5)Helmy, R.; Fadeev, A. Y. Langmuir 2002, 18, 8924. (6)Lafond, V.; Gervais, C.; Maquet, J.; Prochnow, D.; Babonneau, F.; Mutin, P. H. Chem. Mater. 2003, 15, 4098.

SESSION EE12: Applications I

Chair: John Kieffer

Thursday Afternoon, December 2, 2004

Room 302 (Hynes)

3:00 PM **EE12.1**

Bioactive Aerogels. Luis Maria Esquivias¹, Manuel Pinero², Nicolas Daniel De la Rosa-Fox¹, Jose Gonzalez-Calbet⁴, Antonio Salinas³ and Maria Vallet-Regi³; ¹Fisica de la Materia Condensada, Universidad de Cadiz, Puerto Real, Cadix, Spain; ²Fisica Aplicada, Universidad de Cadiz, Puerto Real, Cadix, Spain; ³Quimica Inorganica, Facultad de Farmacia, Universidad Complutense, Madrid, Madrid, Spain; ⁴Quimica Inorganica, Facultad de Quimica, Universidad Complutense, Madrid, Madrid, Spain.

One of the sol-gel routes to organic-inorganic hybrid materials (OIHM), incorporates an organic phase in the inorganic precursor sol in combination with the assisted high power ultrasounds. When both phases are chemically bonded a sono-ormosil, also called hard ormosil, results after gelation. These hybrid materials combine the advantages of the sol-gel process regarding the use of metallo-organic precursors, organic solvents and low processing temperature, with the specific characteristics of the organic polymers as hydrophobic/hydrophilic parts. These materials are being used for implants since they are tolerated by the human organism that creates a fibrous tissue when they are embedded in the body. However, they do not become bonded to the bone unless they are bioactive. In such case, a layer of hydroxycarbonateapatite (HCA) grows wrapping the material when it is immersed in blood plasma. HCA layer is also formed when bioactive materials are soaked in solutions mimicking the features of plasma. These are so-called in vitro assays of bioactivity, a common tool in the development of new biomaterials, where HCA formation is monitored. In addition, for their complete performance, these materials require to approach their mechanical behavior to that of the bones. Two actuations on the biologically tolerant hard ormosil have been undertaken. Recently, several mixtures obtained by ultrasonic agitation of colloidal silica with a sol solution containing tetraethoxysilane (TEOS) were used to form crack-free monoliths. The addition of colloid silica particles to TEOS-based aerogels has enabled network porous volume and pore radius to be tailored. The porous structure also features the performance and applications of these materials because it permits the specimens to get infiltrated and vascularized. Specimens of these hybrid colloid-polymer gels exhibited elastic strain, followed by yield and plastic hardening. Bulk modulus was significantly reduced as the content of silica particles in the gel was increased. We have used this combination colloid-polymer as precursor of the inorganic part of the OIHM with the aim of tailoring the porosity to control the density and mechanical strength in the range of those of human bones. Finally, in vitro bioactivity of this material has been promoted by adding calcium to the initial sol. In ormosils, it has been shown that Ca cations together with unreacted silanol form the bioactive hydroxyapatite layer in a simulated body fluid. The effect of calcium addition in the microstructure of the OIHM was studied by High Resolution Transmission Electron Microscopy (HRTEM). An increase in the distances between [SiO₄]- units as a consequence of the presence of calcium ions was shown. In this paper we also present some results on the structure on this composite as related to their mechanical properties.

3:15 PM **EE12.2**

Recent Developments in the Synthesis and Use of Highly Spherical Porous Hybrid Organic/Inorganic Particles as Reversed-Phase HPLC Packing Materials.

Kevin Daniel Wyndham, John O'Gara, Ken Glöse, Nicole Lawrence, Bonnie Alden, Cheryl Boissel, Tom Walter and Pamela Iraneta; Waters Corporation, Milford, Massachusetts.

A wide-variety of applications for hybrid organic/inorganic materials have emerged over the last ten years including their use as polymer additives, catalyst supports, monolithic materials, bioconjugates, and photonics materials. Siloxane-based hybrid organic/inorganic materials are a unique group of hybrid materials that are comprised of organofunctionalized siloxane networks. As part of our ongoing exploration into the new field of hybrid organic/inorganic particles as chromatographic packing materials, we have recently evaluated the preparation of porous, highly spherical ethyl-bridged and methyl hybrid particles for use in reversed-phase high performance liquid chromatography (RP-HPLC). The reversed-phase chromatographic properties of these hybrid materials proved to be a combination of properties that are often observed for both silica-based materials (i.e., high separation efficiencies, mechanical stability) and organic polymeric materials (i.e., a large usable pH range of 1-12). In this report, we will compare mechanical and physical properties of hybrid particles with conventional silica particles, and describe the implications of hybrid particle technology for improved RP-HPLC applications - having a focus on the material attributes of porous hybrid particles before and after surface modification. For example, the presence of surface organofunctional groups of most hybrid particles results in less surface silanol groups in comparison with silica particles. This decrease in surface silanol groups results in a lower concentration of unreacted silanol groups after surface bonding reactions, and drastically reduced peak tailing of basic analytes that are caused by residual silanol groups in Reversed-Phase HPLC applications.

3:30 PM *EE12.3

Hierarchical Porous Silicas for Chromatographic Applications Obtained by Pseudomorphic Synthesis. Anne Galarneau, Julien Iapichella, Carolina Petitto, Francesco Di Renzo and Francois Fajula; UMR 5618, ENSCM/CNRS, Montpellier, France.

Pseudomorphic transformation of pre-shaped silica beads into MCM-41 and MCM-48 is introduced as a new versatile procedure to independently control and finely tune the textural characteristics of advanced high-performance chromatographic supports at nano- and micro- meter scale. The reaction takes place in the intergranular porosity of the parent silica-gel particle which acts as a nanoreactor. Because the resulting hybrid mesophase is metastable in its synthesis medium, the kinetics of each of the elementary steps (diffusion of hydroxide and surfactant, dissolution of parent silica, self assembly, condensation of the new silica network) must be precisely controlled. In the lecture examples will be given of the preparation of discrete homodisperse spherical particles of MCM-48 and MCM-41, with mesopore sizes in the range 4 to 9 nm, from different silica sources.

4:00 PM *EE12.4

Hybrid Materials Approach in the Design of Electrodes and Electrolytes for Energy Storage and Conversion. Pedro Gomez-Romero, Materials Science Institute of Barcelona, CSIC, Bellaterra, Spain.

The integration of electrochemically active inorganic species in polymer matrices allows for the design of either electrode or electrolyte materials depending on the conducting or insulating properties of the polymer used. Conducting polymers can be used as the basis for a variety of hybrid electrode systems, whereas other polymers such as polybenzimidazoles have been used as electrolyte membranes by themselves or in combination with inorganic solid acids. We will discuss the general approach of hybrid design with this in mind and specifically we will describe our recent results on the use of polyoxometalate-containing hybrids in energy storage and conversion devices. In this respect we have worked in our laboratory on electrochemical supercapacitors and fuel cells but emphasis should be made on the broader potential fields of application of this type of materials.

4:30 PM EE12.5

Electrochemical Characterization of Phosphosilicate-modified Nafion Membranes. Lisa C. Klein¹ and Mario Aparicio²; ¹Rutgers University, Piscataway, New Jersey; ²CSIC, Instituto de Ceramica y Vidrio, Cantoblanco (Madrid), Spain.

Hybrid membranes containing Nafion and phosphosilicate gels were prepared using infiltration and recasting methods. Nafion is a perfluorosulfonate ionomer commonly used in proton exchange membrane fuel cells (PEMFC) and direct methanol fuel cells (DMFC). The reason for introducing a hygroscopic gel is to increase water retention in the membranes when operating above the 1 atmosphere pressure boiling point of water. The hybrid membranes were investigated using complex impedance spectroscopy. Conductivities were determined as a function of temperature and relative humidity. Infiltrated membranes, which contained gel in more or less discrete particles, were compared with recast membranes where

the gel was more evenly distributed. Both of the modified membranes were compared to unmodified Nafion. The impedance spectra were analyzed to distinguish electrode interface effects from bulk transport phenomena. Assuming that Nafion conducts protons by a combination of hopping mechanisms and transport in a continuous liquid-like phase, the influence of the hygroscopic inorganic phase can be evaluated, with respect to its presence in the heterogeneous structure of Nafion.

4:45 PM EE12.6

Proton Conducting Organic/Inorganic Hybrids for Polymer Electrolytes Fuel Cells. Itaru Honma and Je-Doek Kim; EEI, AIST, Tsukuba, Ibaraki, Japan.

Polymer electrolyte membrane fuel cells (PEFC) using hydrated perfluorosulfonic polymers such as NAFION have been developed in the past years. However, the high materials cost and complicated water managements are major obstacles for practical applications of PEFC. Also, CO poisoning of Pt alloy electrodes requires the complicated reforming system, which purify the hydrogen rich gas down to the CO contamination level of few ppm. One of the technological challenges is to develop an electrolyte membrane that can be operated at higher temperatures (100-200C) and lower humidity level, which drastically improve the Cell electrode performance and the cell efficiency. In this paper, we have investigated the structure and proton conductivities of organic/inorganic hybrid membranes synthesized by sol-gel processing with polydimethylsiloxane (PDMS) or polytetramethylene oxide (PTMO) and metal (zirconium, titanium) alkoxides. The hybrid membranes have been found to be temperature tolerant and stable even at higher temperature with acidic condition. The membranes become a proton conducting electrolytes by the soaking of phosphoric solution or adding heteropolyacids such as 12-phosphotungstic acid (PWA). Various polymer membranes by incorporated acids afford the conductivity of the membrane. The hybrid membranes showed good protonic conductivities at intermediate temperatures up to 150C.

SESSION EE13: Poster Session: Organic/Inorganic Hybrid Materials II
Thursday Evening, December 2, 2004
8:00 PM
Exhibition Hall D (Hynes)

EE13.1

Di-Urethane Cross-Linked Poly(Oxyethylene)/Siloxane Nanohybrids Doped with Eu(Cf3so3)3.

Maria Cristina Alvares Pereira Goncalves¹, V. De Zea Bermudez¹, D. Ostrovskii², R. A. Sa Ferreira³ and L. D. Carlos³; ¹Departamento de Quimica and CQ-VR, Universidade de Tras-os-Montes e Alto Douro, 5000-911 Vila Real, Portugal; ²Department of Applied Physics, Chalmers University of Technology, 41296 Goteborg, Sweden; ³Departamento de Fisica and CICECO, Universidade de Aveiro, 3810-193 Aveiro, Portugal.

In many scientific areas the sol-gel method is considered to be one of the best ways of synthesizing organic/inorganic hybrid systems with tuneable design and a wide scope of technological applications. In particular, the hybrid concept has been extensively used to produce room-temperature efficient white-light photoluminescent materials [1]. With the goal of developing materials with high quantum efficiency for application in optics, sol-gel derived poly(oxyethylene) (POE)/siloxane frameworks, designated as di-urethanesils, containing POE chains with 6 OCH2CH2 repeat units (average molecular weight, MW = 300 g/mol) and incorporating a wide concentration range of europium triflate (Eu(CF3SO3)3) were investigated [2-5]. In these materials the organic and inorganic components are bonded through urethane linkages (-NHC(=O)O-). In the present work Eu(CF3SO3)3-doped di-urethanesil analog xerogels including longer POE chains (13 OCH2CH2 repeat units (MW = 600 g/mol)) were analyzed. Fourier Transform mid-infrared and Raman spectroscopies and Photoluminescence (PL) were used to determine the local cationic and anionic environments as a function of salt concentration. The Eu3+ coordination in these materials depends markedly on the amount of Eu3+ incorporated, inducing changes in the PL features of the xerogels, namely in the emission color coordinates (determined according to the Commission Internationale d'Eclairage procedure). [1] L. D. Carlos, R. A. Sa Ferreira, V. de Zea Bermudez, S. J. L. Ribeiro, Adv. Funct. Mater. 11(2) (2001) 111 [2] M. C. Goncalves, V. de Zea Bermudez, D. Ostrovskii and L. D. Carlos, Ionics, 8(1&2) (2002) 62 [3] K. Dahmouche, M. C. Goncalves, C. V. Santilli, V. de Zea Bermudez, L. D. Carlos, a. F. Craievich, Nucl. Instr. Met. Phys. Res. B, 199 (2003) 117 [4] L. D. Carlos, R. A. Sa Ferreira, M. C. Goncalves and V. de Zea Bermudez, J. Alloys & Comps., 374 (2004) 50 [5] M. C. Goncalves, V. de Zea Bermudez, R. A. Sa Ferreira, L. D. Carlos, D. Ostrovskii, J. Rocha, Chem. Mater., in press

EE13.2

Study of Relationship between Morphology and Mechanical Properties of SiO₂-Polyacrylate Hybrid Nanocomposite.

Yi-Hsiao Kao¹, Wei-Fang Su^{1,2} and KengChing Kathy Lin³;

¹Institute of Materials Science and Engineering, National Taiwan University, Taipei, Taiwan; ²Institute of Polymer Science and Engineering, National Taiwan University, Taipei, Taiwan;

³Department of Physics, FuJen Catholic University, HsinChuang, Taiwan.

The atomic force microscopic technique is utilized to study the spatial distribution of silica nanoparticles embedded in poly(tetraethylene glycol diacrylate) matrix. The casting samples of these hybrid materials show distinct mechanical property change as the weight ratio (SiO₂/polyacrylate) reaches 40%. The morphological observation from spin-coated films on silicon substrates shows pronounced nanoparticle network formation correlated to the elasticity transition. The percolating particles reduce the local strain field, i.e. inhibit the deformation of the stratum, and cause the dramatic increase in the Young's modulus. Our experimental result is consistent with recent theoretical prediction[1]. [1] Gavin A. Buxton and Anna C. Balazs, *Phy. Rev. E* 67, 031802 (2003). Funding source: Department of Industrial Technology in the Ministry of Economic Affairs, R.O.C, contract number 92-EC-17-A-08-S1-0015

EE13.3

Comparison of Different Reversed-Phase Packing Materials Based on Ethyl Bridged Hybrid Particles.

Nicole Lawrence, Kevin Daniel Wyndham, John O'Gara, Ken Glose, Pamela Iraneta, Bonnie Alden, Cheryl Boissel and Tom Walter; Waters Corporation, Milford, Massachusetts.

As part of our ongoing exploration into the new field of hybrid organic/inorganic particles as HPLC packing materials, we have recently evaluated the use of ethyl bridged alkoxy silanes as particle precursors. By employing a 4:1 molar ratio of inorganic (SiO₂) to organic substituent groups (SiO_{1.5}CH₂CH₂SiO_{1.5}), novel hybrid materials have been shown to be excellent base particles for the preparation of efficient and resilient reversed-phase (C₁₈, C₈, phenyl, embedded polars) packing materials. In this report, we take a close look at the synthesis and characterization of different reversed-phase bondings on these ethyl bridged particles. We will also evaluate the reversed-phase chromatographic performance of these new packing materials, and compare these results with conventional silica-based materials under similar chromatographic conditions.

EE13.4

Synthesis of Daisy-Shaped and Multipod-Like Silica/Polystyrene Nanocomposites.

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Colloidal nanocomposites have attracted a great attention in recent years as new multifunctional materials with unusual properties that originate from both their organic and inorganic counterparts. Among their important features are the interface characteristics between both components. In that work, we report the synthesis and morphology characterization of original multipod-like and daisy-shaped hybrid nanoparticles consisting of spherical silica beads (in the diameter range of 100 nm) supporting smaller polystyrene ones. Their synthesis was derived from the seeded heterophase styrene polymerization. In a first step, silica particles of various sizes were synthesized according to procedures inspired from the literature. In a second step, they were functionalized by adding organotrialkoxysilane molecules. Finally, they were used as seeds during the polymerization of styrene in water using a non-ionic surfactant as emulsifying agent and sodium persulfate as initiator. Scanning and transmission electron microscopy experiments showed that nanocomposite morphologies are strongly dependent on (i) the organosilane nature, (ii) its surface density onto silica beads and (iii) the styrene conversion.

EE13.5

Tailoring the Surface of Organically Substituted Zirconium Oxide Clusters Used as Precursors for Inorganic-Organic Hybrid Materials.

Myhedine Jupa, Franz Rene Kogler, Michael Puchberger and Ulrich Schubert; Institute of Materials Chemistry, Vienna University of Technology, Vienna, Austria.

Reaction of zirconium butoxide with methacrylic acid in different molar ratios results in the formation of Zr₄O₂(methacrylate)₁₂ or Zr₆O₄(OH)₄(methacrylate)₁₂. These clusters are structurally well defined nanosized building blocks and can be used as co-monomers in

polymerization reactions. Adding carboxylic acids, like propionic acid or iso-butyric acid, to a cluster-containing solution results in exchange reactions between the methacrylate ligands bonded to the cluster surface and the carboxylic acids. Hence it is possible to partially or completely exchange methacrylate ligands to other carboxylate ligands. By changing the chemical properties of the cluster surface it is possible to lower the density of functional groups on the cluster surface, to adjust solubilities, as well as bringing in new functionalities.

EE13.6

Electro-Spraying of Polymer-Inorganic Mixture Solution for Microparticles in Electrophoretic Display.

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The present work focuses on the preparation of polymer-inorganic composite particle by electro-spraying and the characterization of resultant composite particles. These composite particles were utilized for Electrophoretic Display (EPD). EPD is a reflective type display using the electrophoretic phenomena of charged particles suspended in a liquid medium and displayed with the migration of charged particles as Electric Field [1]. The basic requirements for EPD microparticle materials are high refractive index, high surface charge and specific-gravity-match to the liquid medium [2]. To obtain suitable microparticles, the feasibility of electro-spraying method was investigated. Rutile TiO₂ (mean size: 0.2 μm) and polyethylene (Mn: 7,700) were used to prepare composite reaction medium. The homogeneity of stock solution prepared by dissolving TiO₂, polyethylene and polyisobutene succinimide (OLOA 1200) in tetrachloroethylene was maintained with rod type sonificator. OLOA 1200 was utilized as a dispersant and the charge control agent. The electro-spraying was performed with the range of 0.5-2.0 ml/hr in flow rates and 6-10 kV DC voltage for applied electric field. The counter electrode was located in insulator bottle filled with nonpolar-nonsolvent oil (halocarbon 0.8 cst, polychlorotrifluoroethylene), such that resultant composite particles were retrieved from this oil. The analyses of sprayed particles were performed with electrophoretic light scattering spectrophotometer, SEM and thermogravimetric analyzer. The mean size of produced particles was maintained from 0.8 to 3.0 μm by controlling the solution concentration, OLOA 1200 concentration, the flow rate and the electric field. The zeta potential of produced particles was controlled from 50 to 90 mV with the OLOA 1200 concentration. Density of particle was controlled from 1.3 to 1.7 g/cm³ with the polyethylene concentration. The actual electrophoretic driving test of microparticles was proceeded in a device formed by two patterned ITO cell with 70 μm spacer at 100 V external field. The result proved that electro-sprayed composite particles were suitable for EPD in the requirements of the size, high surface charge and density. [1] S. Inoue et al., *IBEETrans.ElectronDevices* 49, 1532(2002). [2] B. Comiskey et al., *Nature* 394, 253(1998).

EE13.7

Abstract Withdrawn

EE13.8

Dielectric Properties of Poly(Vinyl Butyral)/Titanium Oxide Nanocomposite Thin Films Formed by Sol-Gel Process.

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There has been a growing research effort in organic electronics to improve the semiconducting, conducting, and gate insulating properties of organics (polymer and oligomers) and hybrids (organic-inorganic composites) through novel synthesis and self-assembly techniques. In these organic electronics, the polymeric insulator has been an essential component to provide the performance and reliability of semiconductor devices such as the organic field effect transistor (OFET). Capacitance and breakdown voltage are two important parameters for the organic insulators to be applied. Consequently, the use of high dielectric constant (k) gate insulators in OFETs might be expected to enable devices to operate at low drive voltages with good current-voltage characteristics. High k (41) titanium oxide is one of the good candidates as the gate insulator in FET. In this study, we have prepared nanocomposites of poly(vinyl butyral) and titanium oxide by sol-gel process and examined the physical and electrical properties of thin films, which were fabricated through spin coating process. Because poly(vinyl butyral) is flexible

and has adhesive properties with glass, metals, and other plastics, organic/inorganic nanocomposites are shown to have both process advantages of the polymeric material and excellent dielectric characteristics of the inorganic materials.

EE13.9

Photoresponsive Hybrid Organic-Inorganic Polysilsesquioxane Materials Containing Functionalized Coumarin Dimer.

Lihua Zhao¹, Douglas A. Loy² and Kenneth J. Shea¹; ¹Department of Chemistry, University of California, Irvine, Irvine, California; ²Polymers and Coatings Group, Los Alamos National Laboratories, Los Alamos, New Mexico.

Creation of siloxane networks by sol-gel polymerization has been widely used to prepare thermally and chemically robust, hybrid organic-inorganic materials for numerous applications including membranes for gas separations, electro-optic systems and catalyst supports. Detailed structure information of these macromolecular architectures would be valuable for designing and synthesizing nanoscale structures with improved properties. The focus of our research is to develop a "photochemical" dissection process that would render the intractable, hybrid organic-inorganic networks into more readily characterizable, soluble fragments. We describe the synthesis and characterization of monomers containing coumarins and their dimers. The sol-gel derived polysilsesquioxane networks or co-polymer networks are built from the coumarin containing monomer and bis-trialkoxysilane co-monomers. The photochemical dissection has been used in both solution and in thin films to provide detailed structural information on the developing bridged polysilsesquioxane network.

EE13.10

Oligoacetylenephenyloctasilsesquioxanes. Highly Polyfunctional Nanoconstruction Sites.

Michael Asuncion³, Richard M. Laine^{1,2}, Chad Brick² and Mark Roll²; ¹MSE, University of Michigan, Ann Arbor, Michigan; ²Macromolecular Science and Engineering Center, University of Michigan, Ann Arbor, Michigan; ³Chemistry, University of Michigan, Ann Arbor, Michigan.

M. Asuncion, R. M. Laine, C. Brick, M. Roll Depts. of Materials Science and Engineering, Chemistry, and Macromolecular Science and Eng. University of Michigan Ann Arbor, MI. 48109-2136, U.S.A. Polybromooctaphenyloctasilsesquioxanes, [BrxPhSiO_{1.5}]₈, BrxOPS (x = 4-16 and higher) can be readily transformed using a variety of simple catalytic coupling reactions to introduce 8, 16 or even more functional groups to octaphenylsilsesquioxane (OPS). OPS is an unusual molecule because each phenyl group is positioned in a different octant in Cartesian space. Consequently, the functional groups are organized nearly spherically about the silica core, which offers the rigidity and heat capacity of silica. This leads to thermally robust compounds that offer high degrees of functionality that can be used as starting points to construct materials in one, two or three dimensions one nanometer at a time. We discuss here the synthesis of acetylene functionalized cubic silsesquioxanes by simple catalytic coupling of BrxOPS with a variety of acetylene compounds. Selected products offer very unexpected photoluminescence properties.

EE13.11

Highly Luminescent Stilbeneoctasilsesquioxanes.

Chad Brick¹, Michael Asuncion³, Mark Roll³, Ryo Tamaki¹, Richard Laine^{2,3}, Matthew Neurock⁴ and Jean-Sebastien Filhol⁴; ¹Chemistry, University of Michigan, Ann Arbor, Michigan; ²Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan; ³Macromolecular Science and Engineering, University of Michigan, Ann Arbor, Michigan; ⁴Chemical Engineering and Chemistry, University of Virginia, Charlotte, Virginia.

The field of molecular electronics now covers diverse subject areas perhaps best epitomized by work directed towards the development of organic light emitting diodes (OLEDs). Despite extensive efforts to optimize materials for light emitting devices many synthesis and processing problems remain to be resolved. Among these are the need for simple synthetic routes to easily purified and processed materials whose photo- and electroluminescent properties are readily tailored. Still other needs include methods of avoiding aggregate and exciplex formation which introduce extraneous emissions, promote self-absorption and radiationless decay of excited states. High thermal and oxidative stability without crystallization (high T_g) are also desirable. Recent work by many researchers has demonstrated that dendrimeric materials offer a means to minimize many of the above problems. However, dendrimer syntheses are typically multistep and can require extensive purification. Thus, our recent discovery of a room temperature method of multiply brominating octaphenylsilsesquioxane [C₆H₅SiO_{1.5}]₈ (OPS) coupled with the fact that bromoaromatics are easily modified at ambient via Heck or other coupling catalysts, suggested simple two step routes to nano-meter size dendrimer-like cores. In such cores, it is possible to introduce

eight (or more) functional groups each pointing in a different octant in Cartesian space thereby isolating the individual functional groups from each other. Such cores may serve as building blocks for the facile synthesis of new nanoscale dendrimer-like components for molecular electronics and photonics applications. We now find that stilbeneoctasilsesquioxanes (RStilxOPS, x = 5-6) synthesized in two steps from OPS are strongly photoluminescent (PL) compared to stilbene with unexpectedly large red shifts (60-100 nm, 0.60-0.80 eV, and order of magnitude increases in quantum efficiencies (35-60 % vs. 5%) that may result from some form of 3-D excited state conjugation involving the silica core. This contrasts with the traditional view of silsesquioxanes as insulators of sufficient quality to be used extensively as low-k dielectrics in microelectronics

EE13.12

Simulation of Organic-tethered Silsesquioxane Nanocube Assemblies.

Xi Zhang¹, Elaine R. Chan², Lin Ho² and Sharon C. Glotzer^{2,1}; ¹Department of Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan; ²Department of Chemical Engineering, University of Michigan, Ann Arbor, Michigan.

Polyhedral oligomeric silsesquioxane (POSS) based materials are a class of organic/inorganic hybrid nanomaterials with superior properties. Recent experiments have demonstrated that the self-assembly of tethered POSS nanocubes is a promising route to synthesis of novel materials with highly ordered complex nanostructures. Using a coarse-grained model developed for tethered POSS [1], we present the results of molecular simulations of organic-tethered POSS molecules, to investigate how the novel architecture of these hybrid building blocks can be exploited to achieve useful structures via self-assembly [2-4]. We systematically explore the parameters that control the assembly process and the resulting equilibrium structures, including concentration, temperature, tethered POSS molecule topology, and solvent conditions. We report conventional lamellar and cylindrical structures as typically found in block copolymer and surfactant systems, but with interesting modifications of the phase diagram caused by the bulkiness and cubic geometry of the POSS molecules. [1] T. Ionescu, X. Zhang, E.R. Chan, C-Y Lee, H.C. Li, P. Cummings, J. Kieffer, C. McCabe, M. Neurock and S.C. Glotzer, preprint. [2] X. Zhang and S.C. Glotzer, preprint. [3] E.R. Chan, X. Zhang, A.S. Keyes, C-Y Lee, M. Neurock and S.C. Glotzer, preprint. [4] L. Ho, E.R. Chan, X. Zhang and S.C. Glotzer, preprint. This work is supported by the National Science Foundation under grant no. DMR-0103399.

EE13.13

Abstract Withdrawn

EE13.14

Two Synthetic Routes to the Formation of Tungsten Oxide Hybrid Compounds.

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Self-assembling systems have been a popular topic of investigation in the past few decades due to their relevance to both fundamental and applied sciences. While self-assembled monolayers of silanes, thiols, etc. on surfaces have been more extensively investigated in recent years, the self-assembling of molecules from solution to form two-dimensional layered compounds still plays an important part in the development of novel materials. Tungsten oxide has been a much-studied compound due to its rich electronic and structural properties. An example of the former is the amazing colour range displayed in the various tungsten bronze series; while the latter can be seen in the complex arrangement of tungsten oxide octahedra (WO₆) through a combination of edge or corner sharing to form 1-, 2-, or 3-dimensional network structures. In this paper we report the syntheses of two-dimensional layered hybrid compounds with alternating organic amines and tungsten oxide layers. The syntheses of these tungsten oxide hybrids via homogenous and heterogeneous routes were explored and compared. In the former case, tungstic acid (H₂WO₄) and an appropriate diamine were dissolved in ammonia solution under nitrogen atmosphere, and the product was precipitated out via evaporation of the solvent. In heterogeneous synthesis, a non-aqueous approach was employed in which H₂WO₄ powder was aged in a solution consisting of the diamine dissolved in an appropriate organic solvent (for example hexamethylene-diamine in toluene). XRD and FTIR showed that the hybrid materials obtained from the two different methods are identical. This has enabled us to prepare films/coatings of the hybrid materials by dip-coating tungstic acid films prepared by sol-gel technique, in a non-aqueous diamine solution. The XRD spectra of these films exhibit a series of harmonic peaks, indexed as [00k], which correspond to the Bragg peaks for the hybrid compounds. SEM shows the morphology of the platelets changes from the irregularly shaped ("cornflakes"-like) tungstic acid to a needle-like structure of the hybrids and resulted in a loosely

packed (more open structure) coating.

EE13.15

Abstract Withdrawn

EE13.16

Refractive index measurements of thin films using both Brewster and m-line technique: a combined experimental setup. Mauro Casalboni¹, Fabio De Matteis², Paolo Proposito¹ and Stefano Schutzmann³; ¹Dipartimento di Fisica e Istituto Nazionale per la Fisica della Materia (Coherentia), University of Rome Tor Vergata, Rome, Italy; ²Dipartimento di Fisica e Istituto Nazionale per la Fisica della Materia, University of Rome Tor Vergata, Rome, Italy; ³Dipartimento di Scienze e Tecnologie Chimiche e Istituto Nazionale per la Fisica della Materia, University of Rome Tor Vergata, Rome, Italy.

We report on the refractive index measurements of guiding and non-guiding films synthesized by sol-gel technique. An experimental setup has been developed in our laboratory based on both m-line and Brewster angle methods. The main feature of the setup is the possibility to perform both m-line and Brewster angle measurements on the same sample. This allows a more careful evaluation of the refractive index. The combined method, based on the application of both m-line and Brewster angle techniques, represents a completely non-destructive, inexpensive (compared to traditional ellipsometric techniques) and, in addition, very simple method. Moreover, using different laser sources at different wavelengths, we are able to measure refractive index as a function of wavelengths in the visible and near infrared spectral range. We have tested our experimental setup performing measurements on many guiding and non-guiding sol-gel films deposited by spin-coating technique on glass substrate. We have synthesized both purely inorganic and hybrid organic/inorganic solgel-based films. The purely inorganic samples were based on zirconium(IV)-propoxyde, while the hybrid ones were based on 3-glycidioxypropyltrimethoxysilane as organic modifier and tetramethylorthosilicate and zirconium(IV)-propoxyde as inorganic components. Estimation of refractive index values for non absorbing thin films with an accuracy of about $1 \frac{0}{100}$ and with good reproducibility in a wide spectral region have been achieved.

EE13.17

Electrochromic Hybrid Materials. Mariya Khiterer and Kenneth J. Shea; Chemistry, University of California, Irvine, Irvine, California.

Electrochromism is defined as the ability of redox active species to develop new electronic absorption bands upon oxidation or reduction. Typical electrochromic devices can function as self-darkening or "smart" windows and mirrors and have the potential to be used in large area displays. Sol gel matrices are often used to immobilize electrochromophores on electrode surfaces to afford air stable devices with fast response times. There have also been reports, where bridged polysilsesquioxanes were utilized to afford solid electrochromic films. Boraadamantane is a caged trialkylborane, where the boron atom is forced into a tetrahedral geometry, resulting in a strong Lewis acid that forms stable complexes with σ -donors. The neutral 4,4''-(dipyridyl)-1,1''-bisboraadamantane exhibits redox activity similar to that of cationic viologens. The radical anion product of the first reduction is very stable and can remain in solution for periods of time. In the present work electrochromic behavior of 4,4''-(dipyridyl)-1,1''-bisboraadamantane is explored by cyclic voltammetry and bulk electrolysis, where absorption changes are monitored by UV/Vis spectroscopy. Thus, the boraadamantane complex can be incorporated into a polysilsesquioxane network via a trialkoxy-bridged monomer to yield a novel electrochromic system with an unprecedented reduction potential.

EE13.18

Fabrication of Organic/Inorganic Nanocomposites using Pulsed Laser Ablation of Zinc in Aqueous Solutions. Takeshi Sasaki, Changhao Liang, Hiroyuki Usui, Yoshiki Shimizu and Naoto Koshizaki; Nanoarchitectonics Research Center, National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki, Japan.

Pulsed laser ablation in gas phase has been widely used for the preparation of variety of nanostructures such as nanoparticles, nanotubes, and nanocomposites. Recently noble metal nanoparticles of gold, silver and platinum, and oxide nanoparticles of TiO₂ and SnO₂ have been prepared by the pulsed laser ablation of the metallic target in water. This technique can be also apply for the preparation of organic/inorganic nanocomposites, because ablated metallic species with high energy can be easily oxidized with water to form oxides and/or hydroxides, and these nuclei can react with the organic molecules in aqueous solution. In this paper we report that the fabrication of organic/inorganic nanocomposites via pulsed laser ablation of Zinc in aqueous solutions of various surfactants. Zn plate

was ablated by a pulsed Nd:YAG laser in four types of surfactant solutions (cationic, anionic, amphoteric and nonionic) with different concentrations. Zinc oxide nanoparticles with average diameter of 10-40 nm were obtained in cationic, amphoteric and nonionic surfactant solutions. In contrast unique organic/inorganic nanocomposites with the thickness of 20-30 nm were obtained in anionic surfactant solutions. The nanocomposite platelets with octagonal shape formed in the solution of the anionic surfactant, sodium dodecyl sulfate: SDS, have a layered structure composed of zinc hydroxide layer and surfactant molecules. In this presentation, the detailed structure and the formation process of the layered organic/inorganic nanocomposite will be also discussed.

EE13.19

Femtosecond Fluorescence Studies of Auramine O in Hybrid Sol-Gel Derived Films. Paolo Proposito¹, Hong Zhang² and Max Glasbeek²; ¹Physics Department and Istituto Nazionale per la Fisica della Materia (INFM), University of Rome Tor Vergata, Rome, Italy; ²Laboratory for Physical Chemistry, University of Amsterdam, Amsterdam, Netherlands.

Femtosecond fluorescence upconversion experiments have been performed on Auramine O (a diphenylmethane dye) in polymethylmethacrylate (PMMA) and in hybrid organic/inorganic sol-gel based films. Tetramethyl orthosilicate (TMOS) and 3-(trimethoxysilyl)propyl methacrylate (TMSPM) were used as inorganic and organic modifier, respectively. Different films were studied with relative molar concentration of TMOS/TMSPM from 70/30 to 30/70. Two experimental set-ups have been employed for the optical characterization of the samples. The first one is a picosecond time-correlated single photon counting fluorescence set-up (for characterization in time windows up to 10 ns) and the second one is a femtosecond fluorescence upconversion equipment (for characterization in time windows up to 13 ps). Fluorescence transients of Auramine O were measured for a series of different detection wavelengths within the emission band in order to trace the excited state dynamics. The averaged decay time was found to be dependent on the detection wavelengths: the longer the detection wavelength the slower the kinetics. All the investigated samples showed an instantaneous rise followed by a fast decay (few picoseconds) and long decay (hundreds of picoseconds). The fast components are representative of the rapid cooling of the excitation energy excess to the matrices. We found a weak dependence of the fast components on the matrix composition. The long components are representative of the excited-state lifetime of the probed molecules. Auramine O in solid matrices showed lifetimes longer than in liquid solutions [1,2,3]. Torsional diffusion motions of the two phenyl rings of the molecule are held responsible for the excited-state dynamics. Longer decay times have been found for more viscous liquids since the torsional movements are then slowed down [2]. For all film samples, the excited-state lifetime of Auramine O was found to be long when compared to that in liquid solution. The longest lifetime was for samples with the highest concentration of TMSPM (70%). This behaviour indicates a higher hindering of the torsional motions of the phenyl groups in films characterized by a higher organic content and a lower solvent content. A dynamic Stokes shift has been observed for all samples. The lack of a rise time when detection was on the red side is explained in terms of an adiabatic coupling between emissive and nonemissive excited states, as is the case of liquid solutions [1]. Different spectral shifts have been measured for PMMA and hybrid glasses. This is attributed to a different coupling between the emissive and nonemissive excited states for the two types of matrices considered. [1] M. J. van der Meer, H. Zhang and M. Glasbeek J. Chem. Phys. 112, 2878 (2000). [2] P. Changenet, H. Zhang, M. J. van der Meer, M. Glasbeek P. Plaza and M. M. Martin J. Phys. Chem. A 102, 6716 (1998). [3] M. Glasbeek and H. Zhang, Chemical Reviews 104, 1929(2004).

EE13.20

Thermally stable organic/inorganic hybrid materials for waveguiding applications. Shane O'Brien, Richard Winfield, Andrew Connell and Gabriel Crean; NMRC, Cork, Ireland.

In the context of materials development for optical applications, such as waveguides, inorganic-organic hybrid materials offer new and exiting opportunities. The development of multi-functional organo-silanes, such as acrylate and methacrylate alkoxysilanes, has enabled increased control over chemical composition, cross-linking and phase stability. This has resulted in the production of new materials that have the optical transparency of polymers, but also have inorganic characteristics, such as the thermo-mechanical properties of a glass or ceramic. Such tunability of properties is of particular interest in the area of optical waveguide materials. These hybrid material systems cannot be produced by conventional material processing methods, such as CVD or sputtering and therefore new processing routes are required. In this work, a novel preparation method for epoxy functionalised silica material is described. This materials system was chosen, because of the enhanced mechanical and

thermal stability imparted by epoxy functionality, in comparison to other organic functional groups, such as methacrylate or acrylate. These cationic photo-curable silicones have the advantage of being compatible with onium salts, which are efficient as photo-initiator species, and also are not sensitive to oxygen-inhibition of cure. The sol-gel material can be easily formulated and deposited by spin or dip coating to form layers of up to 25 μm in thickness. The resulting film were selectively cross-linked using photo-lithography, as part of a UV-thermal curing process. The basic refractive index of untreated layers can be adjusted between 1.48 and 1.515 by modifying the concentration of DPDMS present. The refractive index of treated layers then ranges from 1.49 to 1.52. The onset of purely thermal cross-linking was found to occur at 260°C, as determined by DSC analysis. Consequently, the change in refractive index (Δn) between the core and cladding material established by UV-thermal curing should be thermally stable at temperatures that do not exceed 260°C. This represents a significant improvement in thermal stability over other inorganic-organic hybrid waveguide materials systems which generally contain acrylate or methacrylate groups that are easily cured by thermal processes. Waveguide structures were fabricated; the near-field image of transmitted radiation (633nm) showed waveguiding and efficient light confinement within the UV-thermally produced core regions. It is therefore concluded that this materials system has the potential for use in waveguiding applications in environments where enhanced thermo-mechanical stability is required.

EE13.21

Effects of Nanoparticle Morphology and Composition on the Physical and Barrier Properties of Natural Rubber Nanocomposites. Michael Sennett, Elizabeth Welsh, Walter Zukas, Axel Rodriguez and David Ziegler; US Army RDECOM Natick Soldier Center, Natick, Massachusetts.

Nanocomposites made by adding nanoparticle reinforcement to polymers have been demonstrated to have significantly enhanced properties at relatively low levels of added reinforcement. The observed properties have in some cases been attributed to the shape of the reinforcing particle. Nanoparticle additives with a variety of particle morphologies and compositions have become commercially available in recent years. A study was carried out to examine the effects of varying nanoparticle morphology and composition on the mechanical and barrier properties of polymer nanocomposites made with natural rubber (NR). NR compounds were prepared containing different nanoparticles including smectite clays, exfoliated graphite nanoparticles, carbon nanotubes and conventional carbon black. Barrier testing included permeation of selected organic compounds utilizing different vapor and liquid permeation methods. The relationship between the observed properties of the nanocomposites and the nanoparticle composition and morphology will be discussed.

EE13.22

Nanocomposites of Semiconducting CdS Nanoparticles and Polymers: Structural Characterization by WAXS and SAXS Analyses. Tiziana Di Luccio^{1,2}, Bert Nickel², Marzia Pentimalli¹, Francesco Antolini¹ and Leander Tapfer¹; ¹UTS MAT, ENEA, Brindisi, Italy; ²Department fuer Physik, Ludwig-Maximilians-Universitaet, Muenchen, Germany.

The structural properties of nanocomposite films of CdS nanoparticles and polymeric compounds are investigated by small and wide angle x-ray scattering (SAXS and WAXS, respectively). A simple dependence of the nanoparticle dimensions on the annealing temperature was found. Cadmium sulphide (CdS) nanoparticles are synthesised within polymeric matrices by a thermolytic process. A thiolate precursor is dispersed in the polymer solution and a film is obtained by casting. Thermal annealing of the precursor/polymer film leads to the formation of a nanocomposite of nanometer-sized CdS dispersed in the polymer. Different polymers were used in particular we employed a cyclo-olefin copolymer (COC) for its good optical properties and extremely low water absorption. Upon annealing with a temperature between 230 and 250 Celsius degrees in vacuum (pressure of about 6x10⁻² mbar) the nanoparticles are found to be crystalline with diameter of about 1nm, as evaluated from WAXS data. The nanoparticle size can be increased up to 8nm by annealing at higher temperatures (300 Celsius degrees). SAXS measurements on the CdS/polymeric films show a strong peak due to packing of the nanoparticles embedded in the polymeric matrix. Here, the separation between the nanoparticles compares with their diameter determined by WAXS.

EE13.23

Magnetotransport Properties of Compression Molded CrO₂-Polyimide Composite. Sanjay R. Mishra¹, Kartik Ghosh², Joe Losby¹ and Ted Kehl²; ¹Department of Physics, The University of Memphis, Memphis, Tennessee; ²Department of Physics, Astronomy and Materials Science, Southwest Missouri State University, Springfield, Missouri.

Recently, many studies have been focused on extrinsic magnetotransport effects in ferromagnetic oxides with half metallicity, because there is an intensive demand of highly spin-polarized ferromagnetic materials for spintronics devices. The nearly perfect spin polarization of CrO₂ suggests that it would be ideal for applications in ferromagnetic tunneling junctions, where large magnetoresistance (MR) ratio is expected. More recently, therefore, much effort has been made to obtain large extrinsic MR, and understanding the physical properties of polycrystalline ceramics, films and pressed powders. The display of low field MR in these samples is believed to be due to spinpolarized tunneling mechanism. In this study, we attempt to introduce an insulating polymer as a barrier between CrO₂ particles, and study phenomenally the influence of polymer on low and high field MR. Magnetoresistive granular composite of CrO₂/polyimide were prepared by compression molding various weight percent of CrO₂ coarse particles with polyimide powder. Systematic magnetotransport study was performed as a function of weight percent of CrO₂ in the composites at 5 and 75K up to 15T magnetic field. The microstructures and thermal behaviors of the composite are analyzed by SEM, TGA and DSC. The temperature dependence of the electrical resistance is studied at the temperature range 10 to 298 K. It is observed that the maximum in %MR change is temperature dependent reaching at maximum, 20% in 35 Wt. % CrO₂ and 22% in 50 Wt% CrO₂ at temperature 5 and 75 K, respectively. Thus, a significant enhancement in %MR in CrO₂-polymer composite compared to pressed CrO₂ powder (6%MR without polymer) has been observed. Further a rapid increase in %MR is observed in the field < 2 kOe for all samples. The temperature dependence of the resistance is in good agreement with Mott's law in a three dimension system. The origin of enhanced MR is most likely from intergranular tunneling electrons, aligned at a low field.

EE13.24

Preparation of Intercalative Organic/MoO₃ Nanohybrid Thin Films and their VOC gas sensing properties. Ichiro Matsubara, Norimitsu Murayama, Woosuck Shin and Noriya Izu; National Institute of Advanced Industrial Science & Technology, Nagoya, Japan.

We have proposed intercalative type organic-inorganic hybrid materials as the chemical sensors for selective detection of volatile organic compounds (VOCs). The organic and inorganic components take part in molecular recognition and transduction of chemical signals to measurable resistance changes, respectively. In this paper, we have prepared intercalative organic/MoO₃ hybrid thin films by an ex-situ intercalation process. The host MoO₃ films were first deposited on LaAlO₃ (LAO) single crystal substrates using CVD method followed by the intercalation of polypyrrole (PPy) or n-butylammonium ions (BuNH₃) into the MoO₃ films. A semiconducting-like transport is observed for both the (PPy)_xMoO₃ and (BuNH₃)_xMoO₃ hybrid thin films. These thin films exhibit a distinct response to VOCs by increasing in their electrical resistivity, which could be induced by the incorporation of VOC molecules into the interlayers. The two types of hybrid films show different gas selectivity to VOCs, indicating that the VOC gas selectivity can be controlled by the organic component.

EE13.25

Ligand Control of Semiconductor Nanocrystals for Efficient Carrier Injection. Tomohide Murase, Harumi Asami and Itaru Kamiya; Nanomaterials Lab., Mitsubishi Chemical Group Science and Technology Research Center, Inc., Yokohama, Japan.

Recently, electronic interaction between colloidal semiconductor nanocrystals (NCs) and their organic ligands has been extensively investigated to integrate the NCs into organic/inorganic hybrid devices such as photo-voltaic cells and light-emitting diodes (LEDs).[1,2] For LED application, the ligands require several functions: 1) prevention of NC aggregation and quenching fluorescence, 2) no fluorescence from ligands, and 3) efficient carrier injection through ligands. In order to realize the functions above, we investigated CdSe/ZnS core/shell NCs covered with two kinds of organic ligands. One is for dispersibility, and the other is for carrier injection. The carrier injection ligand itself shows no fluorescence, and its highest occupied and lowest unoccupied molecular orbitals were adjusted to energy levels of the NCs for the purpose of efficient carrier injection from ligands to the NCs. The NCs were prepared by ligand exchange from NCs capped with trioctylphosphine oxide (TOPO). The prepared NCs can be dispersed in organic solvent, and photoluminescence spectra show fluorescence only from NCs. These NCs were spun-coat on ITO/glass substrates to form thin films that are 20 nm thick without any matrix. The conductivity of these thin films was extremely improved in comparison with that of TOPO-capped NCs. [1] O. Schmelz, A. Mews, T. Basche, A. Herrmann, K. Mullen, Langmuir 17, 2861 (2001). [2] D. J. Milliron, A. P. Alivisatos, C. Pitois, C. Edder, J. M. J. Frechet, Adv. Mater. 15,

EE13.26

Modification and Characterization of Si-Based Nanobuilding Blocks to Design Hybrid Oxide-Polymer Materials. Najiba Douja¹, Fayna Mammari¹, Christian Bonhomme², Florence

Babonneau² and Sandra Dire¹; ¹Dipartimento di Ingegneria dei Materiali e Tecnologie Industriali, Università di Trento, Trento, Italy; ²Laboratoire de Chimie de la Matière Condensée, Université Pierre et Marie Curie, Paris, France.

Mild synthetic conditions provided by sol-gel chemistry allows to incorporate organic components into an inorganic network, leading to organic-inorganic materials. The inorganic component is commonly prepared by hydrolysis-condensation of metal alkoxides precursors and the degree of interpenetration of organic and inorganic components ranges between the sub-micro and the nano scale level. Consequently, the sol-gel route provides an easy method to synthesize nanocomposites with promising applications in different fields (optics, electronics, mechanics, protective coatings. . .). However, the sol-gel process usually leads to an infinity of microstructures, generally polydispersed in size. Since few years, well-defined nanobuilding blocks (NBB) have been used to assure the control of stereochemistry, reactivity, functionality and properties of hybrid materials. This work presents the modification and the characterization of Si-based nanobuilding blocks composed of cyclic Si oligomers and polyhedral oligomeric silsesquioxanes (POSS) holding functionalizable organic moieties. Three precursors (tetramethylcyclotetrasiloxane, isobutyl-dimethylsilane-POSS and octasilane-POSS) were modified by hydrosilylation to introduce a polymerizable vinylic group. ATR-FTIR and multinuclear NMR spectroscopies have been used to describe the reaction mechanisms and to determine the structure of the modified NBB obtained by hydrosilylation of the available Si-H bonds with allyl alcohol or 4-penten-1-ol. Firstly, the competition between C and O-silylation was shown to be governed by the nature of the solvent; when C-silylation occurred, the methacrylate group was grafted to the modified NBB by addition of methacryloylchloride. The comparison between reactivities exhibited by cyclic oligomers and POSS will be discussed. The European Community is acknowledged for the financial support (contract Nr. HPRN-CT-2002-00306).

EE13.27

Kinetics of Anatase-to-Rutile Phase Transformation in PEO-TiO₂ Hybrids. Yun-Mo Sung, Kyung-Soo Park, Jin-Kyung Lee, Yong-Ji Lee, Jung-Jun Na and Kyung-Woo Kim; Materials Sci. & Eng., Daejin University, Pochun-si, Kyunggi-do, South Korea.

TiO₂ is an oxide semiconductor, showing wide range of applications including high-refractive optics, oxide semiconductors, oxygen sensors, photovoltaics, photocatalysts, etc. It shows formation of three different crystalline phases such as brookite, anatase, and rutile, among which anatase shows the highest photocatalytic properties. Poly(ethylene oxide)-TiO₂ hybrid films were synthesized using sol-gel chemistry and spin coating. Acetylacetone (AcAc) was added to enhance the strong bonding between TiO₂ and PEO components and aging time was varied during hybrid synthesis. Hybrid films were heated to fully crystallize to anatase phase and further heated to transform anatase phase to rutile at different temperatures for different time periods. The volume fraction values (x) of anatase-to-rutile phase transformation were obtained using a multi-peak separation program for x-ray diffraction (XRD) patterns and an XRD quantitative analysis method. Hybrids, containing AcAc and aged for long time, showed the lowest phase transformation kinetics, while pure TiO₂ films showed the highest phase transformation kinetics. Also, PEO-TiO₂ hybrids without AcAc showed intermediate phase transformation kinetics. The volume fraction values were used for Johnson-Mehl-Avrami (JMA) isothermal kinetic analyses and JMA plots were produced for each system with temperature variation. Avrami exponent (n) was determined for each hybrid film using the slopes of the JMA plots. Also Arrhenius plots were produced using the y-intercept values of JMA plots and activation energy values for phase transformation were determined from the slopes of the curves. The hybrids having AcAc and aged for long time period showed the highest activation energy, while the pure TiO₂ film showed the lowest one. Long-term aging would result in the strong hydrogen bonds between PEO and AcAc, and thus strong molecular networks of (Ti-O-Ti)-AcAc-PEO-AcAc-(Ti-O-Ti) would form, which hinders the fast phase transformation of anatase to rutile. Heat treatment of PEO-TiO₂ hybrids created nanoporous films, and AcAc addition into the hybrids efficiently delayed phase transformation of anatase to rutile at a high temperature. Thus, this hybrid approach suggests an effective way for the fabrication of nanoporous anatase films with high functionality.

EE13.28

Organic-Inorganic Hybrid Materials Based on Organophosphorus Coupling Molecules : Octadecylphosphonic Acid

Self-assembled Monolayers as Lubricant Coatings Stable in Alkaline Media. Jeremie Soullier^{1,2}, P. Hubert Mutin¹ and Philippe Tordjeman²; ¹Chimie Moléculaire et Organisation du Solide, CNRS-University Montpellier, Montpellier, France; ²Laboratoire d'Analyse des Interfaces et de Nanophysique, CNRS-University Montpellier 2, Montpellier, France.

Organophosphorus coupling molecules such as phosphonic acids (RP(O)OH)₂ can be used to prepare organic-inorganic hybrid solids, either by sol-gel processing[1] or by surface modification of an oxide support.[2, 3] Formation of Self-assembled Monolayers (SAMs) occurs in the case of long-chain alkylphosphonic acids [4,5] There has recently been much interest in SAMs as boundary layer lubricants for micro-electro-mechanical devices (MEMS).[6,7] However, most examples concern SAMs of alkane thiols (on gold or silver), alkyltrichlorosilanes or trialkoxysilanes (on oxidized silicon or glass).[8,9] Here, we report the formation, tribological properties, and chemical stability of octadecylphosphonic acid SAMs on glass substrates coated by a 100 nm layer of titanium, deposited by cathodic sputtering. Friction coefficients were measured with a home-made tribometer equipped with a non-rolling metal ball (hardness: 260 HV, diameter: 2 mm, rugosity 0.06 micrometer), using normal forces up to 50 N. The kinetics of SAM formation from solutions of octadecylphosphonic acid in water was investigated using water contact angle measurements, friction coefficient measurements, optical and atomic force microscopies. Octadecylphosphonic acid bound strongly to the native oxide layer of the titanium coating. However, the formation of dense, hydrophobic SAMs required several days. Octadecylphosphonic acid SAMs efficiently decreased the friction coefficient, preventing the formation of cracks even at high normal forces. Moreover, the friction coefficient did not increase even after treatment in a NaOH solution (pH 14) at 338 K for 100 minutes. This excellent stability was ascribed to the high chemical stability of titania and of the interfacial Ti-O-P bonds. (1) Guerrero, G.; Mutin, P. H.; Vioux, A. Chem. Mater. 2000, 12, 1268. (2) Randon, J.; Blanc, P.; Paterson, R. J. Membrane Sci. 1995, 98, 119. (3) Guerrero, G.; Mutin, P.; Vioux, A. Chem. Mater. 2001, 13, 4367. (4) Gao, W.; Dickinson, L.; Grozinger, C.; Morin, F. G.; Reven, L. Langmuir 1996, 12, 6429. (5) Helmy, R.; Fadeev, A. Y. Langmuir 2002, 18, 8924. (6) McDermott, M.T.; Green, J.-B.D.; Porter, M.D. Langmuir 1997, 13, 2504. (7) Zhou, Y. H.; Fan, H.; Fong, T.; Lopez, G.P. Langmuir 1998, 14, 660. (8) Laibinis, P. E.; Hickman, J. J.; Wrighton, M. S.; Whitesides, G. M. Science 1989, 245, 845. (9) Ulman, A. An Introduction to Ultrathin Films; Academic Press: San Diego, CA, 1991.

EE13.29

Use of 12-Mercaptododecylphosphonic Acid Modified Titania for the Extraction of Heavy Metals. P. Hubert Mutin¹, Gilles Guerrero², Florence Brodard-Severac² and Sébastien Antherieu²; ¹Chemistry, CNRS, Montpellier, France; ²Chimie Moléculaire et Organisation du Solide, University Montpellier 2, Montpellier, France.

Organophosphonate coupling agents are an excellent alternative to organosilylated derivatives for the preparation of organic-inorganic hybrid materials based on titania either by sol-gel processing¹ or surface modification². An important potential advantage of such materials is their high stability in basic media in comparison with silica based materials. The formation of self-assembled monolayers (SAMs) with long-chain alkylphosphonic acids has already been reported^{3,4}. Self-assembly leads to dense monolayers with high grafting densities. In this work, our objective was to prepare hybrid materials functionalized by thiol groups with a large number of reactive functions. The strategy of SAMs formation with 12-mercaptododecylphosphonic acid on titanium dioxide allowed us to introduce the maximum amount of terminal functional groups on the surface of the inorganic support. Investigation of the grafting by ³¹P MAS NMR indicated the covalent bonding of the organophosphorus derivative on the oxide surface. Infrared spectroscopy and elemental analysis informed us respectively on SAMs formation, long chains organization degree and on surface coverage. Similar results as in the case of SAMs formation with octadecylphosphonic acid on titania⁵ have been obtained. As thiol groups have a high affinity for binding heavy metals^{6,7}, extraction experiments have been realized on 10 ppm mercury(II) alkaline aqueous solutions. Atomic absorption measurements of remaining metal concentrations indicated a nearly quantitative removal of mercury from solutions. 1- Guerrero, G.; Mutin, P. H.; Vioux, A., s. Chem. Mater. 2000, 12, (5), 1268. 2- Guerrero, G.; Mutin, P. H.; Vioux, A., Chem. Mater. 2001, 13, 4367. 3- Gao, W.; Dickinson, L.; Grozinger, C.; Morin, F. G.; Reven, L., Langmuir 1996, 12, (26), 6429. 4- Pawsey, S.; Yach, K.; Reven, L., Langmuir 2002, 18, (13), 5205. 5- Helmy, R.; Fadeev, A. Y., Langmuir 2002, 18, (23), 8924. 6- Bove, C. A.; Benson, R. F.; Martin, D. F., J. Env. Sci. Health. Part A 2002, A37, (8), 1391. 7- Feng, X.; Fryxell, G. E.; L.-Q., W.; Kim, A. Y.; Liu, J.; Kemner, K. M., Science 1997, 276, 923.

EE13.30

Investigation of Li+-Doped Di-Urethanesil Poe/Siloxane Hybrid Materials. Maria Cristina Alvares Pereira Goncalves¹, V. De Zea Bermudez¹, M. M. Silva², M. J. Smith², R. A. Sa Ferreira³, L. D. Carlos³ and J. Rocha⁴; ¹Departamento de Quimica e CQ-VR, Universidade de Tras-os-Montes e Alto Douro, 5000-911 Vila Real, Portugal; ²Departamento de Quimica, Universidade do Minho, Gualtar, 4710-057 Braga, Portugal; ³Departamento de Fisica e CICECO, Universidade de Aveiro, 3810-193 Aveiro, Portugal; ⁴Departamento de Quimica e CICECO, Universidade de Aveiro, 3810-193 Aveiro, Portugal.

Li+-based solid polymer electrolytes, produced by the dissolution of a lithium salt in high molecular weight polymers containing suitable coordinating sites, have been the subject of intense study because of their important technological applications as electrolytes in electrochemical devices, such as high energy-density batteries and fuel cells [1]. To serve as components in commercial lithium batteries these electrolytes must exhibit high ionic conductivity and good mechanical and electrochemical stability. With the goal of developing highly conducting ormolytes (organically modified silicate electrolytes) for primary and secondary batteries, we used the sol-gel process to prepare a new family of lithium triflate-doped poly(oxyethylene) (POE)/siloxane hybrids (di-urethanesils [2-3]) containing a wide range of salt concentration. In these materials the organic and inorganic components (POE chains with approximately 13 OCH₂CH₂ repeat units and a siliceous backbone, respectively) are bonded through urethane linkages (-NHC(=O)O-). The morphology, structure, thermal stability and ionic conductivity of the xerogels produced were characterized by X-ray diffraction, thermogravimetric analysis, differential scanning calorimetry and complex impedance measurements. [1] F. M. Gray, RSC Materials Monographs, Royal Society of Chemistry, London, 1997 [2] M. C. Goncalves, V. de Zea Bermudez, D. Ostrovskii and L. D. Carlos, *Ionics*, 8(1&2) (2002) 62 [3] M. C. Goncalves, V. de Zea Bermudez, R. A. Sá Ferreira, L. D. Carlos, D. Ostrovskii and J. Rocha, *Chem. Mater.*, in press

EE13.31

Novel Er3+-Doped Polyether/Siloxane Hybrid Materials for Optoelectronics. S. C. Nunes¹, V. de Zea Bermudez¹, R. A. Sa Ferreira², L. D. Carlos², D. Ostrovskii³ and J. Rocha⁴; ¹Departamento de Quimica, Universidade de Tras-os-Montes e Alto Douro, Vila Real, Portugal; ²Departamento de Fisica, Universidade de Aveiro, Aveiro, Portugal; ³Department of Applied Physics, Chalmers University of Technology, Goteborg, Sweden; ⁴Departamento de Quimica, Universidade de Aveiro, Aveiro, Portugal.

The versatility of the sol-gel chemistry (low-temperature processing and shaping, high sample homogeneity and purity, availability of precursors and possibility of preparation of nanocomposites) has motivated the development of rare earth (RE)-doped organic/inorganic hybrids for optics. One of the drawbacks of this strategy is the fact that the luminescence efficiency of RE ions in most sol-gel-derived structures is limited by quenching processes associated with hydroxyl groups (from residual water and silanol groups of the hybrid matrix itself) which markedly reduce the RE emission intensity, due to non-radiative decay pathways of the RE ions. In this context the di-ureasils (urea cross-linked polyether/siloxane networks) appear to be extremely promising for several reasons: (1) they are essentially hydrophobic; (2) they act as effective protecting cages capable of encapsulating the luminescent centers, virtually eliminating quenching effects; (3) they may withstand extremely high concentrations of photoactive species. The present work was focused on a family of Er3+-doped di-ureasils. Previous studies [1] allowed us to suggest that these materials have potential application in the domain of optical amplification, especially for the fabrication of wave guides. The di-ureasil framework employed (d-U(2000)) comprises polyether chains containing approximately 40.5 oxyethylene repeat units. The active centres were introduced as erbium triflate (Er(CF₃SO₃)₃). Xerogel samples containing a wide range of Er(CF₃SO₃)₃ concentration were studied by means of X-Ray Diffraction, Differential Scanning Calorimetry, and Fourier Transform Infrared and Photoluminescence Spectroscopies. [1] S. M. Gomes Correia, V. de Zea Bermudez, R. A. Sa Ferreira, L. D. Carlos, M. M. Silva, S. Barros and M. J. Smith, *Ionics*, 8(1&2) (2002) 73

EE13.32

Study of Novel Poly(ϵ -Caprolactone)/Siloxane Biohybrids Doped with a Calcein-Europium Complex and Europium Triflate. S. C. Nunes¹, V. de Zea Bermudez¹, L. D. Carlos², R. A. Sa Ferreira², D. Ostrovskii³ and J. Rocha⁴; ¹Departamento de Quimica, Universidade de Tras-os-Montes e Alto Douro, Vila Real, Portugal; ²Departamento de Fisica, Universidade de Aveiro, Aveiro, Portugal; ³Department of Experimental Physics, Chalmers University of Technology, Goteborg, Sweden; ⁴Departamento de Quimica, Universidade de Aveiro, Aveiro, Portugal.

The biocompatibility, biodegradability and permeability of poly(ϵ -caprolactone) (PCL) have been extensively explored in the last few years in the medical field for the production of biodegradable sutures, artificial skin, resorbable prostheses and containers for drug delivery. Recently the suitability of sol-gel derived Class II PCL(MW = 2000 g mol⁻¹)/siloxane hybrid systems as degradable bioglasses, non-toxic for living organisms was demonstrated [1,2]. Applications of these hybrids as coating materials for bone implants, prosthetic devices and as supports for enzyme immobilisation were also suggested [1,2]. In the present work we propose that Class II PCL(MW = 530 g mol⁻¹)/siloxane biohybrid structures are adequate host cages for the entrapment of Eu3+ ions and the development of technologically attractive materials for optical devices, as they efficiently protect the cations from quenching effects, leading to high quantum yields. The lanthanide ions were introduced as a calcein/europium (CC)-Eu complex and as europium triflate, Eu(CF₃SO₃)₃. The use of the CC ligand is advantageous, since it, not only shields the lanthanide ions from deactivating groups, but it also gives rise to the antenna effect. Class I poly(ethylene glycol)/siloxane hybrids doped with lanthanide complexes of CC with intense near-infrared luminescence were recently prepared [3]. 1. D. Tian, Ph. Dubois and R. Jerome, *Polymer*, 37(17) (1996) 3983 2. S-H. Rhee, J-Y. Choi, H-M. Kim, *Biomaterials*, 23 (2002) 4915 3. K. Driessen, R. V. Leuven, C. Gorller-Walrand and K. Binnenmans, *Chem. Mater.*, 16(8) (2004), 1531

EE13.33

Characterization of Dendrimer-Gold Nanocomposite Materials. Lajos P. Balogh^{1,2,4}, Thelma Rosie Ganser³ and Xiangyang Shi²; ¹Dept. of Internal Medicine & Dept. of Biomedical Engineering, University of Michigan, Ann Arbor, Michigan; ²Center for Biologic Nanotechnology, University of Michigan, Ann Arbor, Michigan; ³UROP Program, University of Michigan, Ann Arbor, Michigan; ⁴MACRO, University of Michigan, Ann Arbor, Michigan.

Dendrimer-gold nanocomposite ({Au} DNC) materials have many applications in catalysis, optics, biological sensing, cancer treatments, and they can be used as building blocks to assemble functional films. Primary amine-terminated poly(amidoamine) (PAMAM) dendrimers of different generations (generation 2 through 6) were used as templates to synthesize gold-dendrimer hybrid nanocomposites. These nanocomposite materials have been extensively characterized by UV-vis spectrometry, fluorescence, transmission electron microscope (TEM), dynamic light scattering (zeta-potential, particle size distribution), polyacrylamide gel electrophoresis (PAGE), and capillary electrophoresis. Results show that the size and structure of {Au} nanocomposites are highly dependent on the generation number of dendrimer templates. These nanocomposites have a stronger emission intensity (458 nm) than commercially available Au nanoparticles do. PAGE analysis shows that the dendrimer-gold nanocomposites have an electrophoretic migration pattern, which is similar to the dendrimer template. Three components of the {Au} migration peak can be differentiated in capillary electrophoresis. The combination of different techniques provides new insights into the structure and properties of dendrimer-gold nanocomposite materials.

EE13.34

Evaluation of Polypyrrole Coating on Fe3O4 and its Effect on Nanocomposite Properties. Silvia Liong¹, Alexa W. Harter², Rick L. Moore² and William S. Rees^{1,3}; ¹School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia; ²Signatures Technology Laboratory, Georgia Tech Research Institute, Atlanta, Georgia; ³School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia.

Since the discovery of doped polyacetylene by MacDiarmid and his group, it has created new possibilities for novel materials. With the appropriate dopant, polymers like polyacetylene and polypyrrole may become alternative conductive materials because their resistivity approaches that of metals. Magnetic nanocomposites have also been the focus of much research work because they have applications in biosensors, recording media, and electromagnetic (EM) shields. Incorporating conducting polymers into magnetic nanocomposites would produce a novel hybrid material with multifunctional properties and could extend the applications to batteries and non-linear optics. Magnetite (Fe₃O₄) nanoparticles (average diameter is 10nm) will be coated with polypyrrole, and then embedded in a polymer matrix. The polypyrrole coating can impart surface conductivity on these particles. In addition to having magnetic properties, Fe₃O₄ nanoparticles also can act as a reinforcing material. By incorporating polypyrrole-coated magnetite nanoparticles in a polymer matrix, such as epoxy, a hybrid material with controllable magnetic, electrical, and mechanical properties will be fabricated. Two processes will be investigated to coat polypyrrole on the surface of magnetite nanoparticles. The first process is surface polymerization, adapted from coating conductive polymer on textiles. Polymerization of pyrrole takes place on the surface of particles by controlling the ratio of monomer to surface area (of nanoparticles). The second process is based on admicellar

polymerization, which uses surfactant to promote polymerization of pyrrole on the surface of the particles. The morphology of the coating will vary with each process, and it will ultimately affect the properties of the nanocomposite. For example, surface polymerization is expected to form a thicker coating than admicellar polymerization, producing particles with higher surface conductivity. However, the thicker coating may interfere with the interfacial strength between the particles and the matrix, causing a reduction in mechanical properties. The scope of this work is to compare the two coating processes in terms of the overall properties of the composite. Firstly, the magnetite nanoparticles will be characterized. Qualitative analysis of the surface of nanoparticles will be conducted using FTIR and SEM. XPS will be used for quantitative chemical analysis of polypyrrole coating, while TGA will be used to analyze its thermal stability. Conductivity of the particles will be measured using 4-point probe method. Secondly, composite samples at different levels of particle loading will be studied. The mechanical properties of the composite will be measured using 3-point bending test. Microstructures of the composites will be studied using SEM, TEM, and MFM. Electromagnetic properties of the nanocomposites will be measured as functions of temperature, DC magnetic field, and frequency.

EE13.35

Self-assembled Monolayers of High Silica Zeolites. Wanda Lew, Aleksander Shornikov and Andrew S. Ichimura; Chemistry and Biochemistry, San Francisco State University, San Francisco, California.

Zeolites are microporous materials that have traditionally found use in catalysis, separations, and exchange processes. However, zeolites with conducting or semiconducting properties might find use in the development of chemical or optical sensors and detectors. One class of materials that have the potential for such applications are inorganic electrides, which are formed from the gas phase addition of alkali metals to pure silica zeolites (M@SZ; M=Na-Cs).[1] Inorganic electrides are similar to their organic complexant based cousins in that the added alkali metal ionizes to yield a stoichiometric number of trapped electrons, as shown by optical spectroscopy and nuclear magnetic resonance studies.[1] In addition, density functional calculations show that the band structure of the silica lattice is significantly altered by alkali metal addition to silica zeolites and suggests that inorganic electrides may be good conductors.[2] While much work remains to be done on these materials at a fundamental level, in order to develop applications they must be interfaced with conducting or semi-conducting substrates. To this end, we are pursuing a strategy of self-assembly in which the silica zeolite is tethered to a gold or indium tin oxide (ITO) surface by suitable linker molecules. For example, a zeolite may be functionalized by condensation of the surface hydroxyl groups with 3-chloropropanethiol, which leaves the thiol group available for binding to gold. Zeolite monolayers can be formed by mixing a suspension of the linker-coated zeolite in the presence of gold-coated silicon wafers. Relatively uniform zeolite monolayers can be formed by this strategy. These monolayers are stable to short sonication times and stable to desorption at 120 degrees celsius for upto 5 minutes. Scanning electron microscopy and FTIR specular reflectance measurements are used to monitor zeolite assembly. We will report on our efforts to self-assemble silica zeolites on gold and ITO surfaces and compare the quality and stability of the resulting monolayers as a function of molecular linker and conditions. 1. Wernette, D.P.; Ichimura, A.S.; Urbin, S.A.; Dye, J.L. Chem. Mater, 2003, 15, 1441-1448. 2. Li, Z.; Yang, J.; Hou, J. G.; Zhu, Q.; J. Am. Chem. Soc., 2003, 125, 1170-1171.

EE13.36

Preparation of Metal Organic Framework Films and the Synthesis of a Novel Metal Organic Framework Utilizing the Zinc Complex of 1,7-Di(aniline)cyclen as a Pillar Ligand. Thomas J. Pisklak and Kenneth J. Balkus, Jr.; Chemistry, The University of Texas at Dallas, Richardson, Texas.

The metal organic framework $\{Cu(OOC-C_6H_4-C_6H_4-COO)_{1/2} C_6H_{12}N_2\}_n$ has been shown to have a higher methane adsorption capacity than the theoretical maximum for activated carbon. This polymer would be ideal for use in the separation of methane from natural gas. In its as-synthesized form the MOF is a powder, which is impractical for use in separations. Two techniques were investigated for the production of $\{Cu(OOC-C_6H_4-C_6H_4-COO)_{1/2} C_6H_{12}N_2\}_n$ membranes. The first method was to utilize the pulsed-laser deposition method to produce thin films, and the second was to grow MOF films connected to a substrate via aminosilane tethers. To introduce functionality into the MOF, a new MOF was synthesized in which the zinc complex of 1,7-di(aniline)cyclen is the pillar ligand instead of 1,4-diazabicyclo[2.2.2]octane.

EE13.37

Active Photonic Structures from Fluorescent Silica Nanoparticles. Andrew A. Burns, Christopher A. Coenjarts,

Christopher K. Ober and Ulrich Wiesner; Materials Science & Engineering, Cornell University, Ithaca, New York.

We have developed a novel class of radiative organic/inorganic hybrid nanoparticles referred to as CU dots and investigate their applications to photonic structures and devices. The aim of this work is to develop enabling technologies through fundamental research to allow for suitable control of light in a variety of different fields and applications. CU dots are silica nanoparticles synthesized from a dye-rich silicate core coated in a silicate shell. This architecture introduces a variety of interesting photophysical effects including enhanced fluorescence efficiency and photostability versus free dye in solution. In addition to the synthesis of novel particle architectures and studies of the fundamental photonic properties of individual dots, these optical elements are incorporated into waveguiding structures prepared by a variety of advanced 2D and 3D lithographic methods. Specifically, two photon lithography offers three-dimensional structure control by localized two photon excitation of a radical initiator at the focal point of a near-IR laser. This facilitates the creation of free-standing three dimensional structures for applications in photonics. This is the first demonstration of an integrated materials platform for three-dimensional structural control of encapsulated fluorophores in a hybrid organic/inorganic matrix.

EE13.38

Organic-Organosilicon Polymer Hybrid Matrix Composites. Bizhong Zhu¹, Yuhong Wu², Dimitris E. Katsoulis¹, Herschel H. Reese¹ and Frederick J. McGarry²; ¹Advanced Technologies and Ventures Business R&D, Dow Corning Corp, Midland, Michigan; ²Department of Materials Science and Engineering, M.I.T., Cambridge, Massachusetts.

Organo-silicon polymers are substantially inorganic in nature and are known for their excellent thermal stability, low flammability, good oxidation/radiation resistance, low dielectric constant and dissipation factor, almost negligible water absorption, and low surface energy, yet they are still easily processable. Most organic polymers, however, do not perform well in applications demanding a combination of these properties. But organic polymers usually are much more robust mechanically than organosilicon polymers which have not found wide use for load bearing applications. In this paper an effective approach to combine the strengths of both types of polymers will be presented. Emphasis will be given to glass and quartz fabric reinforced organosilicon/organic polymer laminates. It is shown that by constructing a hybrid composite of organosilicon resins with some common organic resins, the attractive characteristics of silicone resins are retained, and the mechanical properties can be better than composites of any single type of resins due to a synergistic effect. The effect of composite construction geometry, processing methods and conditions, and compatibilizing co-polymers will be discussed. Meanwhile the mechanisms for the synergistic effect will be elucidated.

EE13.39

Femtosecond Laser Direct Writing of Sol-gel Optical Waveguides. Santosh Kumar Pani^{1,2}, Chee Cheong Wong¹, David Kuang Yong Low² and Xiao Zhang²; ¹School of Materials Engineering, Nanyang Technological University, Singapore, Singapore; ²Singapore Institute of Manufacturing Technology, Singapore, Singapore.

Femtosecond laser (FSL) direct writing offers the attractive potential of one-step processing of optical structures. In this study, thick films were prepared on the glass wafers by organic-inorganic hybrid sol-gel materials, in which 3-methacryloxypropyltrimethoxysilane (MEMO) and zirconium n-propoxide were used as precursors, following a modified sol-gel fabrication process. Optical waveguides were directly written into the bulk of this film by using FSL at the wavelength of 775 nm and pulse width of 150 fs at various laser power ranges. Other writing variables such as writing speeds and focus depths were also considered for controlling the dimensions and locations of the waveguides. We shall report on the refractive index changes and waveguide propagation loss characteristics along with the resolution and dimensional control of waveguide structures and their dependences on FSL processing conditions. *Corresponding author: pb2563001@ntu.edu.sg

EE13.40

Organic Transistors with High Mobility on Silica Fiber Substrates with Dip-coated Dielectrics. Jimmy Erik Granstrom and Howard Edan Katz; Materials Research, Bell Labs, Lucent Technologies, Murray Hill, New Jersey.

It is difficult to deposit a very thin polymer layer onto a fiber-shaped substrate from solution because the high interfacial energy can lead to dewetting. This difficulty presents itself when attempting to apply a gate dielectric to conductive fiber substrates during the fabrication of fiber transistors for use in applications such as "electrotextiles" and

optical switches. We present a dip coating process that applies a gate dielectric to metal-coated optical fibers with high uniformity and reproducibility, resulting in pentacene field-effect transistors (FETs) with excellent transistor characteristics including mobilities up to 0.3 cm²/Vs and on/off ratios up to 7000. In one case, a memory effect was demonstrated. Several gate dielectrics were successfully applied to the optical fibers, suggesting a baseline set of suitable materials for this purpose. A thorough study of the dip coating conditions is presented, including proposed explanations of the effects of different coating procedures and solution physical properties. Finally, alternative architectures that would provide much higher W/L ratios and on-currents will be described.

EE13.41

Ce³⁺ Doped Borophosphosilicate Glasses Obtained by Sol-Gel Procedure. Roberto Scotti¹, Carmen Canevali¹, Mariachiara Mattoni¹, Franca Morazzoni¹, Stefano Polizzi², Radenka Krsmanovic², Marco Bettinelli³ and Adolfo Speghini³; ¹Scienza dei Materiali, Univ. Milano-Bicocca, Milano, Italy; ²Chimica Fisica, Univ. Ca'Foscari - Venezia, Venezia, Italy; ³Scientifico e Tecnologico, Univ. Verona, Verona, Italy.

Trivalent cerium is one of the most widely used rare earth (RE) ions in luminescent materials, but its luminescence efficiency is limited by the Ce³⁺ attitude to clusterize and/or oxidize in the solid state. In order to obtain the highest possible concentration of homogeneously dispersed luminescent activators, RE doped glasses seemed to be a very suitable alternative to crystalline materials. To this purpose dispersion of Ce³⁺ in silica glasses was attempted by sol-gel method, but clustering and CeO₂ segregation occurred for Ce:Si molar ratio > 5·10⁻⁴ RE^{1,2}. In order to make the glass matrix more suitable to embed RE ions by avoiding clustering and segregation of oxidized phase, silica was modified with B and P glass formers. The presence of B and P should induce local distortions in the silica network, resulting in a less compact glass texture, and should increase the relative distance between cerium centers. Besides, B and P related defects could arise and stabilize the RE trivalent oxidation state. Phospho-(PSG), boro-(BSG) and borophosphosilicate (BPSG) monolithic glasses doped with Ce³⁺ were prepared by a sol-gel procedure from Si, B and P methoxides and cerium nitrate. HRTEM investigation showed that Ce-doped BSG, PSG and BPSG, unlike Ce-doped SiO₂ glasses, were amorphous up to Ce:Si = 5·10⁻³ molar ratio and CeO₂ nanoparticles segregated only at the highest investigated RE content, Ce:Si = 1·10⁻² molar ratio. Ce³⁺ photoluminescence emission yields in PSG and BPSG were greater than in BSG and SiO₂ glasses. BSG and SiO₂ showed emission band at 2.9 and 2.65 eV, respectively, whereas the PSG and BPSG ones were in the range 3.9–3.7 eV, depending on the P:Ce ratio. The range is very similar to that of Ce³⁺ in phosphate glasses prepared by melting. The phosphate interaction with Ce³⁺ was supported also by EPR. Spectra of Ce-doped SiO₂ and BSG glasses, recorded at 4.2 K, showed the resonance lines of isolated Ce³⁺ centers; their amount suggested that CeO₂ segregation and/or spin coupling effects occurred. PSG and BPSG glasses showed two different paramagnetic Ce³⁺ centers: one as in SiO₂ and a second one related to RE interaction with P=O groups in the silica network. These results demonstrated that the inclusion of P and B in silica network favoured the RE dispersion, lowering the tendency of Ce to segregate as CeO₂, and assessed that the presence of P modifies the coordination environment of the RE with respect to SiO₂ and BSG. This interaction of Ce³⁺ ions further hindered RE clustering and CeO₂ oxidative segregation, both effects responsible for luminescence quenching. 1) A. Vedda, A. Baraldi, C. Canevali, R. Capelletti, N. Chiodini, R. Francini, M. Martini, F. Morazzoni, M. Nikl, R. Scotti, G. Spinolo, Nucl. Instr. and Meth. A, **486**, 408 (2002) 2) D. Di Martino, A. Vedda, G. Angella, M. Catti, E. Cazzini, N. Chiodini, F. Morazzoni, R. Scotti, G. Spinolo, Chem. Mat., submitted (2004)

EE13.42 TRANSFERRED TO EE7.2

EE13.43

Nucleation, aggregation and stabilization of metal and metal oxide nanoparticles. Rina Tannenbaum, Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia.

Reactive metallic fragments that are formed by the decomposition of organometallic complexes undergo a nucleation and growth process resulting in the formation of nanocrystals. In the absence of stabilizing molecules, the aggregation process is self-restricting mainly due to the decreasing mobility of the particles and their declining diffusional rates as a function of their increasing size. On the other hand, in the presence of a polymer, the growing metallic fragments are stabilized by the surface adsorption of the polymer chains, thus lowering their surface energy and creating a barrier to further aggregation. Studies of the nucleation and growth kinetics of the metallic particles formed in this way have been used to shed light on the mechanism of their formation. In this study, we attempt to decouple the kinetic characteristics of the various steps that comprise

the overall nucleation and growth process for cobalt oxide nanoparticles. A combination of infrared and x-ray photoelectron spectroscopies, transmission electron microscopy and dynamic light scattering is used to identify the individual contribution of each step to the overall mechanism of metal nanocluster formation.

EE13.44

Abrasion Resistant Coatings with Ultraviolet Absorption, via Sol-Gel Dipping Method. Nanning Arfsten, Manuel A. Alvarez, Brandon Steel, Frank Rodriguez, Ian Peek and Hayes Rainier; Denglas Technologies LLC, Moorestown, New Jersey.

Multi-epoxy functional - glycidyl ether is used as a cross-linking epoxy compound between catalytically modified 2244tetrahydroxybenzophenone and silicone molecules. The adduct reaction products, as effective abrasion resistant coatings and yet reactive in the sol gel process, are formulated into the colloidal based polysiloxane resin as an essential part of the solution for dip coating sheets. Such coatings incorporate ultraviolet radiation selection or absorbing compounds with superb chemical stability and mechanical strength for coatings on substrates such as glass. The hardness of these coatings was measured at 6H following ASTM (D-3363) film hardness by pencil test. The resulting coatings were exposed to UV-A radiation during a time greater than 600 hours. The exposed samples still maintain excellent absorption in the UV range, superior to other coatings available in the market.

EE13.45

Two-Dimensional Crystalline Lattice Templating: A New Method for the Preparation of Polymer-Covered Metal and Alloyed Metal Nanorods by a Simple Redox Reaction.

Alexandru Cezar Pavel¹, Dwight K. Romanovitz¹, Miguel J. Yacamán⁴ and John T. McDevitt^{1,3,2}; ¹Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas; ²The Texas Materials Institute, Austin, Texas; ³Center for Nano- and Molecular Science and Technology, Austin, Texas; ⁴Chemical Engineering, The University of Texas at Austin, Austin, Texas.

The crystal lattice can be used as a template for the preparation of 1-D metal/alloyed metal nanostructures due to its intrinsic ordering of the constituent metal cations. The method shows great potential towards producing custom-made, compositionally tailored metal or alloyed metal nanorods by choosing the appropriate 2-D layered oxide and reacting it with pyrrole at moderate temperatures. Crystal lattice engineering by appropriate substitution/doping of some of the original metal cations can be used to create the appropriate precursor for the compositionally targeted final nanostructure.

EE13.46

Molybdenum Dioxide and Vanadium-Doped Molybdenum Dioxide Microcrystals in a Polymer Container.

Alexandru Cezar Pavel¹, Dwight K. Romanovitz¹ and John T. McDevitt^{1,3,2}; ¹Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas; ²Texas Materials Institute, The University of Texas at Austin, Austin, Texas; ³Center for Nano- and Molecular Science and Technology, The University of Texas at Austin, Austin, Texas.

Pyrrole can be used as a suitable reducing agent for the formation of novel organic polymer-inorganic metal oxide microstructures with potential applications in areas like selective catalysis and chemical sensing. Orthorhombic and hexagonal molybdenum trioxide and hexagonal vanadium-doped molybdenum trioxide with different grain sizes were used to produce polymer-contained monoclinic molybdenum- and vanadium-doped molybdenum dioxide crystals by a two-step redox process. By reducing the size of the precursor's grain it is possible to obtain polymer-contained nanocrystals of the final oxide. The method can be applied to other binary or ternary transitional metal oxides which contain the cation(s) in their highest oxidation state in order to obtain nano- or microcrystals of lower oxidation state metal oxide.

EE13.47

Single-step Microstructure Patterning in Titania-doped Sol-Gel Glassy Films with Electron Beams. Xinshi Luo, Congji Zha and Barry Luther-Davies; Laser Physics Centre, The Australian National University, Canberra, Australian Capital Territory, Australia.

Microstructure patterning technologies for fabrication of integrated optical components such as planar optical waveguides and devices have received great attention in recent years. Conventionally microstructure patterning is achieved by lithographic technologies, which involve two main steps: structure patterning with UV-light or E-beam and structure developing by wet chemical etching or plasma etching. These processes are rather complex and are difficult to control the surface profile in the etching process. To achieve a low cost

and simple fabrication process, we explore a TiO₂-doped hybrid sol-gel glassy material that enables the fabrication of microstructure on film surface in a single step with focused electron beams. In this paper, we firstly describe an anhydrous sol-gel process based on hydrolysis and condensation of metal alkoxides with boric acid under non-hydrous conditions, and show that this anhydrous sol-gel process is useful for homogeneously incorporating TiO₂ into silica network, which is difficult for the conventional aqueous sol-gel process because of the great hydrolysis reactivity difference between titanium alkoxide and silicon precursor. 3-methacryloxypropyltrimethoxysilane (MPS) was hydrolysed by mixing with boric acid at a molar ratio of MPS : boric acid = 1:0.5 : 1:1. The reaction was performed under reflux conditions for 2 hours with methanol as mutual solvent. Titanium ethoxide was then dripwise added to the hydrolysed MPS solution at molar ratios of Ti : Si = 0.1 : 0.7. After reflux for another hour, the solvent in the reaction mixture was removed under vacuum evaporation, giving clear transparent viscous resins. The TiO₂-doped hybrid polymer resins with varied TiO₂ concentrations (up to 40 mol%) were spin coated onto fused silica substrates and silicon wafers. Thin films were UV cross-linked with a mercury lamp (350-380nm) irradiation, and then thermally cured (160 °C for 10 h under vacuum conditions). Optical characterisations for the TiO₂-doped hybrid glassy thin films were performed. The TiO₂-doped hybrid material showed a low OH absorption, low optical losses at telecommunication windows (<0.40 dB/cm at 1550 nm and <0.20 dB/cm at 1310 nm respectively), good thermo-optical linearity and good thermal stability up to 200 °C. In the second part of this paper, we examined single-step direct surface patterning in the TiO₂-doped hybrid glassy films with focused electron beams. Results show that fine structure with resolution higher than 0.4 micron can be fabricated in the films. As the process does not need a developing (etching) process, the profiles of the lines fabricated by the E-beam direct writing showed few distortion. The high precise patterning microstructure with submicron feature sizes in the TiO₂-doped hybrid glassy thin films may provide potentials for fabrication of sub-micron period gratings with E-beam direct writing technology.

EE13.48

Improvement of Polymer Electret Characteristics by Inclusion of Au Colloids. Myongseob Kim, Yumin N. Shen, Chunguo Lee and Edwin C. Kan; School of Electrical and Computer Engineering, Cornell University, Ithaca, New York.

Polymer electrets have seen a rapid development in their micro-device applications, such as electro-acoustic and piezoelectric transducers, integrated microphones, nonvolatile storage, and electrographic devices [1-2]. We propose a hybrid material of mixing insulating polymers and gold colloids to improve the charge retention and programming characteristics with convenient liquid-phase processing and tunable colloidal density. The enhancement on the effective charge density and poling response results from the colloids as effective charge retention sites. In comparison with the single-atom metal ionomers, the metal macro-molecules embedded in insulating polymer chains can form stable energy bands that can store large number of charges with only minute shifts in the Fermi level. The colloidal size determines the self capacitance and energy level shifts in progressive charging, while the spacing determines both the available charge retention site and the leakage current. The colloidal parameters are hence designed to have best trade-offs between self capacitance and charge leakage. There are various methods for forming space-charge and dipolar electrets including carrier injection by particle beam and plasma discharging [2], high-voltage poling [3], photopoling [1], and piezoelectric poling [4]. By using an EEPROM device with a large extended floating gate in contact with the polymer electrets [5], we present experimental characterization for effective charge density and poling response of the hybrid materials. Higher colloidal density in the polymer can improve electret characteristics under fixed photopoling and piezoelectric poling conditions up to a limit where either colloid clustering or insulator leakage starts dominating. With the enhanced charging properties, the hybrid electret materials can be effectively used for low-power sensing and large-area nonvolatile storage. References: [1] G. M. Sessler, *Electrets*, Topics in Applied Physics, Vol. 33, Springer-Verlag, 1980. [2] R. Kressmann, G. M. Sessler, and P. Gunther, "Space-charge electrets," *IEEE Trans. on Dielectrics and Electrical Insulation*, vol. 3, no. 5, pp. 607-623, 1996. [3] P. D. Southgate, "Room-temperature poling and morphology changes in pyroelectric polyvinylidene fluoride," *Appl. Phys. Lett.*, vol. 28, no. 5, pp. 250-252, 1976. [4] G. Eberle, H. Schmidt, and W. Eisenmenger, "Piezoelectric polymer electrets," *IEEE Trans. on Dielectrics and Electrical Insulation*, vol. 3, no. 5, pp. 624-646, 1996. [5] Y. N. Shen, Z. Liu, C. Lee, B. A. Minch and E. C. Kan, "Charge-based chemical sensors: a neuromorphic approach by the chemoreceptive neuron MOS transistors (C_vMOS)," *IEEE Trans. Electron Devices*, vol. 50, no. 10, pp. 2171-2178, Oct. 2003.

EE13.49

Improvement in Performance of an Organic Field Effect

Transistor by Controlling the Molecular Alignment.

Takuya Kambayashi¹, Hideo Takezoe¹, Ken Ishikawa¹, Hiromichi Ohta², Kenji Nomura² and Hideo Hosono²; ¹Organic and Polymeric Materials, Tokyo Institute of Technology, Tokyo, Japan; ²Hosono Transparent ElectroActive Materials Project, Japan Science and Technology Corporation, Kawasaki, Japan.

Organic molecules have attracted much attention toward electronic devices such as thin film transistors, light emitting diodes, photo conductors for xerography, and so on. Performances of these devices are, however, not so good as those of inorganic semiconductors, since the mobility of organic materials is quite low particularly in amorphous and randomly oriented polycrystalline films. Therefore, controlling molecular alignment in active layers is important. In this presentation, we will report on bottom contact field effect transistors (FET) using metallophthalocyanines (MPc) as active layers. To control molecular alignment in the active layer, we applied molecular beam epitaxy (MBE) growth of MPc on an atomically flat transparent conducting and insulating films. These films were grown on Yttrium stabilized Zirconia substrates by pulsed laser deposition. MPc were epitaxially grown on atomically flat Indium-Tin oxide (ITO) conducting films. [1, 2] The stacking axis of MPc is parallel to the surface both in vanadylphthalocyanin (VOPc) and copperphthalocyanine (CuPc). The charge carrier mobility of MPc is higher along the stacking axis, so that this orientation is favorable for applying them to the active layers of an FET with a lateral channel. To fabricate the bottom contact FET device we had to deposit MPc not on the conducting layer but on an insulating layer deposited on the conducting layer. We selected Scandium Yttrium Oxide (ScYO) as an insulating layer; the lattice parameter of (Sc_{0.7}Y_{0.3})₂O₃ is 1.0073 nm, which is almost the same as that of ITO. The (Sc_{0.7}Y_{0.3})₂O₃ dielectric layer was fabricated on the single crystalline ITO film by pulsed laser deposition technique. From analysis of (Sc_{0.7}Y_{0.3})₂O₃ by high resolution X ray diffraction, (Sc_{0.7}Y_{0.3})₂O₃ was heteroepitaxially grown on the ITO film. Root mean square roughness of the (Sc_{0.7}Y_{0.3})₂O₃ layer was approximately 1 nm. Then VOPc and CuPc layers were deposited on the bi layered film of (Sc_{0.7}Y_{0.3})₂O₃ / ITO as active layer. From the analysis of the active layer by atomic-force microscopy and X ray diffraction, active layers (MPc) had the same molecular alignment of MPc layers grown on ITO films. These MPc transistors have rather large field effect mobility, VOPc: ~10⁻³cm²(Vs)⁻¹ and CuPc: ~10⁻²cm²(Vs)⁻¹, and the on / off ratios ~10³ were obtained. In conclusion, FET characteristics were well improved, by controlling molecular alignment in the MPc layers [3], as compared with the values reported on MPc. [1] H.Ohta et al., *AdvancedMaterials*. 16, 312(2004) [2] T.Kambayashi et al., *Cryst.GrowthDes.* submitted [3] H. Ohta et al., *AdvancedMaterials*. 15, 1258(2003)

EE13.50

Design, Synthesis and Characterization of Functional Metallopolymers. Abdiaziz A. Farah¹ and William J. Pietro²; ¹National Research Council of Canada, Institute of Microstructural Sciences, Ottawa, Ontario, Canada; ²Department of Chemistry, York University, Toronto, Ontario, Canada.

Multifunctional polymers with covalently attached luminophores promise potential applications for useful and interesting optical materials. In our group, the molecular design, synthesis and characterization of a single component bifunctional macromolecules was successfully achieved through facile incorporation of Ru tris(bipyridine) chromophore initiators into poly(N-(?-alkylcarbazolyl) methacrylates) chains via atom transfer radical polymerization. With these metalloinitiators, multifunctional linear and star type polymers and blocks containing well-defined domains for the chromophores were obtained with predetermined molecular weight and low molecular distribution. Heteroleptic ruthenium-centered poly(*ε*-caprolactones) of various dimensionality were also obtained via ring-opening polymerization of *ε*-caprolactone by using bpy or quinoline ligand initiators followed by chelation to metal ions. Electronic absorption and emission spectra of the resultant functional polymers provided evidence of the presence of both chromophores within a single polymeric chain. Their high thermal properties were also investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

EE13.51

Abstract Withdrawn

EE13.52

Self-Extinguishing Polymer Nanocomposites. Mayu Si¹, Hsinchou Chu¹, Miriam Rafailovich¹, Jonathan Sokolov¹, Daniel Heffer³, Jonathan Heffer² and Aryeh Sokolov⁴; ¹Materials Science and Engineering, Stony Brook University, Stony Brook, New York; ²University of Pennsylvania, Philadelphia, Pennsylvania; ³DRS High School, Woodmere, New York; ⁴HAFTR High School, Cedarhurst,

New York.

Very few polymers are currently self-extinguishing when exposed to a flame. Since polymers ignite easily, the combustion process can be retarded through compounding with conventional flame retardant agents such as decabromodiphenyl oxide (DB) and antimony trioxide (AO). The efficacy of these compounds depends on the ability to disperse them within the polymer. Since they are generally immiscible with most materials, very few polymers can be rendered self-extinguishing according to the stringent UL-V0 designation. The addition of functionalized clays to polymers is known to improve their rheological properties and in some cases to improve flame retardance. Here we show that when the clays are mixed with the retardant agents excellent dispersion within polymer can be achieved. We have investigated three different polymers; highly combustible acrylics? Elvacite resins and PMMA as well as EPDM rubber and polypropylene. The combustion behavior was first investigated by subjecting slabs of the polymer to UL-94 V0 testing. We found that the polymers with only the retardant agents or the clay could not pass. On the other hand all polymers with both components were self-extinguishing. TEM images indicated that the clay was instrumental in dispersing the DB and AO components. DMA results show that the introduction of clay improved PMMA bending modulus by 28 % and increased T_g by 8 C. Similar behavior has also been found in EPDM/clay system and the addition of clay can effectively avoid dripping during burning test. Addition of the DB and AO did not have a significant effect on the mechanical properties. Hence the quantities used here were not sufficient to embrittle the polymers. Based on TEM and combustion test, the general mechanism is proposed that the introduction of clay can improve the compatibility between polymer and fire-retardant agent, the synergy between the char formed by the clay and gas phase isolation due to the conventional flame-retardant agents make the material become fire-retardant. Supported by NSF funded MRSEC at Stony Brook

EE13.53

Electrical Transport in Multilayers of Au/Ag Nanoparticles Films. Claudiu Hapenciu¹, Ashavani Kumar², G. Ramanath² and Theodorian Borca-Tasciuc¹; ¹Mechanical Aerospace and Nuclear Engineering, Rensselaer Polytechnic Institute, Troy, New York; ²Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York.

Nanoparticles based nanostructured films are of high interest since they offer the potential for applications in various fields such as semiconductors, molecular electronics, photovoltaic, thermoelectric, chemical and biological sensing and catalysis. This work reports electrical transport measurements of Au/Ag multilayers of nanoparticles films. An aqueous solution containing 100nm size nanoparticles capped with 4-Aminothiophenol was used to deposit thin-films on glass substrates pre-patterned with microelectrode arrays. DC electrical transport measurements are performed in the 80-300K temperature range for individual monolayers of Au and Ag nanoparticles films and for an Au/Ag bilayer film. The experimental results are discussed in the context of existing models for electrical charge transport in nanostructures.

EE13.54

New Methods for Synthesis of Mesoporous Carbons Through Inverse Replication and Self-assembly. Michal Kruk¹, Bruno Dufour¹, Ewa B. Celer², Krzysztof Matyjaszewski¹, Tomasz Kowalewski¹ and Mietek Jaroniec²; ¹Chemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania; ²Chemistry, Kent State University, Kent, Ohio.

Mesoporous carbons have recently attracted much attention, because of their usefulness as adsorbents for large molecules, components of electrochemical double-layer capacitors, catalyst supports and so forth. One of important recent achievements in this field was the synthesis of ordered mesoporous carbons through inverse replication of ordered mesoporous silica templates. Herein we describe the combination of this approach with another novel route to nanostructured carbons based on the pyrolysis of nanoscale phase-separated block copolymers. In the latter route, one block, e.g., polyacrylonitrile, serves as carbon precursor whereas the other block, immiscible with the first one, induces self-assembly into a variety of nanostructures and is sacrificed upon pyrolysis. Use of an organic sacrificial block, which is volatilized before carbonization of the carbon precursor block, poses the challenge in replicating and preserving of bulk nanostructure, in particular in maintaining the connectivity of mesopores. In order to overcome this difficulty, we have now designed a new system, in which sacrificial block is water soluble and is used as a template for formation of silica. Silicious phase acts as a scaffolding supporting the evolving carbon phase during pyrolysis and is subsequently etched away, leaving behind mesoporous carbon. Appropriate copolymers were synthesized using atom transfer radical polymerization (ATRP) which provides

necessary control over the polymer composition and molecular weight. Mesoporous carbons obtained from these novel precursors exhibited high specific surface area (typically 750-1000 m² g⁻¹), large pore volumes (up to 2.8 cm³ g⁻¹) and pore diameters ranging from about 4 to 25 nm. In contrast with most mesoporous carbons reported to date, they exhibited very low microporosity. The templates, precursors and carbons were extensively characterized using nitrogen adsorption, thermogravimetry, transmission electron microscopy and powder X-ray diffraction.

EE13.55

Order-Order Transition in a Block Copolymer Induced by Polymer-Coated Gold Nanoparticles. Bumjoon Kim¹, Julia J. Chiu¹, Gi-Ra Yi¹, David J. Pine^{1,2} and Edward J. Kramer^{1,2}; ¹Chemical Engineering, University of California at Santa Barbara, Santa Barbara, California; ²Materials, University of California at Santa Barbara, Santa Barbara, California.

Self assembly of inorganic nanoparticles within a block copolymer offers a way to produce materials with unique optical, electronic and magnetic properties. To reveal some of the fundamentals of this self assembly we have investigated symmetric diblock copolymers consisting of various polystyrene-poly(2-vinylpyridine) (PS-P2VP) with total molecular weight (Mn) ranging from 59 to 115 kg/mol and 4 nm diameter Au nanoparticles whose surfaces are modified by PS chains (Mn= 1.5 kg/mol) terminated with thiol groups. Thick (100 μm) films of PS-P2VP with various concentrations of PS coated Au nanoparticles are cast by slow evaporation from toluene and THF. The morphology of these films is determined from cross-sectional transmission electron microscopy. At all concentrations the PS coated Au particles are preferentially located near the center of the PS domains. While at low particle concentrations the block copolymer morphology is lamellar, it changes to a morphology of hexagonal P2VP cylinders in a PS/ PS coated Au particles mixture at higher concentrations. At intermediate concentrations a two-phase macrostructure is observed with the surface layers of the film being lamellar with low particle concentration and the substrate layers being hexagonal with high particle concentration. The PS-coated Au particle additives thus appear to behave like PS homopolymer, inducing an order-order transition between block copolymer phases as the concentration is increased.

EE13.56

Core-shell Titanium Dioxide-Polystyrene Nanoparticles, an Organic-Inorganic Nanocomposite Which Forms Smooth and Flexible High K Dielectric Films. Ashok Joseph Maliakal¹,

Howard Katz¹ and Pat Cotts²; ¹Materials Research, Bell Laboratories, Murray Hill, New Jersey; ²Dupont Central Research, Wilmington, Delaware.

In the field of plastic or flexible electronics, a gate dielectric material that exhibits a high dielectric constant and is also capable of forming smooth and flexible films would be valuable. In pursuit of this goal, it would be desirable to combine the ease of processing of organic polymers with the high dielectric constant of inorganic oxides such as titanium dioxide. To this end, organic/inorganic core shell nanoparticles have been synthesized using high K TiO₂ as the core nanoparticle, and polystyrene as the shell. These materials form transparent, continuous thin films which exhibit a dielectric constant enhancement of more than double that of bulk polystyrene.

EE13.57

A Unifying Analogy Between Polymer Nanocomposites and Planar Polymer Films. Amitabh Bansal¹, Hoichang Yang³, Kilwon Cho³, Sanat Kumar² and Linda S. Schadler¹; ¹Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York; ²Chemical and Biological Engineering, Rensselaer Polytechnic Institute, Troy, New York; ³Department of Chemical Engineering, Pohang Institute of Science and Technology, Pohang, Kyungbuk, South Korea.

We unequivocally show that the thermodynamic and dynamic properties of polymers filled with nanoparticles are quantitatively equivalent to the behavior of thin polymer films between two parallel impenetrable planar walls. To provide the underpinnings for this unifying picture we have measured the glass transition temperature (T_g) of polystyrene (PS) when it is blended with 15 nm diameter SiO₂ particles over a range of silica loadings. For PS filled with untreated SiO₂, the T_g of the polymer is found to decrease with increases in silica loading - qualitatively consistent with depression in glass transition found with decreasing thickness of polymer films sandwiched between planar silica walls. Conversely, the T_g of PS filled with surface modified SiO₂ particles shows an increase with increasing silica loading - consistent with increases in glass transition found with decreasing thickness of polymer films coated on substrates with attractive interfaces. The glass transition is controlled by the relative

lengths of grafted vs. matrix PS chains. This analogy is quantified using electron micrograph images of the nanocomposites which yield an appropriate average ligament thickness, the nanocomposite analog for the wall-to-wall distance in thin films. In combination with recent results on polymer blend phase transitions, where both filled systems and thin films provide similar results, we conclude that the proposed analogy between nanofilled polymers and thin polymer films helps to provide a unified quantitative understanding of these two apparently disparate physical situations

EE13.58

New High-Dielectric-Constant Polymer-Ceramic Composites.
Milind Arbatti, Lisa L. Orona and Z.-Y. Cheng; Materials Engineering, Auburn University, Auburn, Alabama.

Capacitors are widely used to store energy and/or to perform specific functions. The development of electronic devices and circuit of reduced size led to a need for significantly smaller capacitors having increased performance. The electronic industry utilizes materials that have high dielectric constants and that also flexible, strong, and easy to process. Finding single component materials possessing all these properties is different. Therefore, a great deal of efforts has gone in to developing polymer-ceramic composites that are flexible and easy to process and are of relative high dielectric constant and high breakdown strength. Ferroelectric and relaxor ferroelectric materials are widely used as ceramic filler in the composites. However, these materials exhibit a strong electromechanical effect which is not desirable for developing high performance capacitors. Additionally, the dielectric property of these materials is strongly dependent on the temperature. Recently, it was found that $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) has a dielectric constant in a range of 10,000 to 100,000. More importantly, the CCTO does have the electromechanical effect and its dielectric constant is almost independent of temperature over 100 K to 600 K. Therefore, it is very interesting to develop CCTO-based composites for high-dielectric-constant applications. The dielectric property of the composites of CCTO particles and P(VDF-TrFE) copolymer was studied and reported in this presentation. The influence of morphology on the property of composites was studied experimentally. The flexible polymer-CCTO composites are developed. It is found that the electric breakdown field (>10 MV/m) of the composites is much higher than the CCTO ceramics and many ceramics. At room temperature, the dielectric constant at 1 kHz reaches more than 250, which presents a new record for the highest reported dielectric constant. At about 70 °C, the dielectric constant of the composites can reach about 600 due to the high dielectric constant of polymer matrix at the temperature.

SESSION EE14: Applications II
Chair: Pedro Gomez-Romero
Friday Morning, December 3, 2004
Room 302 (Hynes)

8:30 AM *EE14.1

Functional Mesostructured Hybrid Materials for Energy Transfer, Electron Transfer and Molecular Machines.

Jeffrey I. Zink, Payam Minoofar, Raquel Hernandez, Paul Sierocki, Thoi Nguyen, Bruce Dunn and Fraser Stoddart; Chemistry and Biochemistry, UCLA, Los Angeles, California.

Functional nanostructured hybrid films are synthesized by incorporating molecules designed to carry out the desired function. A dip-coating method that allows one or more molecules to be deliberately placed in specified spatially separated regions of nanostructured silicate materials in a one step synthesis has been developed. The nanostructured thin films contain three distinct regions: the silica framework, the organic non-polar region in the interior of the micelle, and the ionic interface between the charged surfactant head groups and the silica pore surface. Three strategies, succinctly termed "philicity", "bonding", and "bifunctionality" have been developed for directing molecules to any one of the regions. Simultaneous placement of two different molecules in two different regions has also been demonstrated. Such placement and the maintenance of long range order requires a delicate balance among film preparation methodology, design of the molecules, and concentrations of all of the species. Details and examples of the induced functionality will be discussed. Energy or electron transfer properties are designed by choosing pairs of molecules (one a donor and the other and appropriate acceptor) that are spatially separated in the different regions of the films. Detailed studies of energy transfer use a chelated lanthanide as the donor and a rhodamine derivative as the acceptor. Electron transfer is studied using trisbipyridylruthenium derivative as the electron donor and a substituted viologen as the acceptor. Functional materials involving motion (reciprocating motion, rotary motion, and action as a molecular valve) are described. The design, activation and operation of the first two types will be

described briefly. The most developed is a functioning nano-machine in the form of a supramolecular nanovalve that opens and closes the orifices to molecular-sized pores in nanostructured silicate and releases molecules on demand. The nanovalve is a pseudorotaxane composed of two components - a long thread containing a 1,5-dioxaphthalene donor unit that is attached to the solid support, and the moving part, the tetracationic cyclophane acceptor/receptor, cyclobis(paraquat-p-phenylene), which controls access to the interior of the nanopore. Operating the nanovalve involves three steps: (i) filling the container, (ii) closing the valve, and (iii) opening the valve to release the contents of the container on demand. The tubular pores, which are approximately 2 nm wide, are filled with stable luminescent $\text{Ir}(\text{ppy})_3$ molecules by allowing them to diffuse into the open pores. The orifices are then closed by pseudorotaxane formation. An external reducing reagent or light is used to effect the dethreading of the pseudorotaxane that unlocks the tubes and allows the guest molecules to be released. This nanovalve is a supramolecular machine consisting of a solid framework with moving parts capable of doing useful work.

9:00 AM *EE14.2

Solution processable nanocomposites based on silsesquioxane cores for use in organic light emitting diodes (OLEDs).

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Organic light emitting diodes (OLEDs) have been a highly targeted area of technology since the early 1990's for their application in flat panel displays. Over the years there has been much debate over which family of materials - small-molecules or polymers - is best suited for OLEDs. Small-molecules can be highly purified and vacuum deposited in multi-layer stacks, both important for display lifetime and efficiency. However, vacuum deposition techniques require costly equipment and a limitation to practical display size. Polymers are generally of lower purity but can access larger display sizes at much lower costs using solution-based deposition techniques. Here we report nanocomposite materials based on polyhedral oligomeric silsesquioxane (POSS) architectures that combine the advantages of both small-molecule and polymer approaches to OLEDs. The materials contain a spherical "silica" core with eight functional sites that can be easily decorated with a plethora of OLED functional groups. The resulting materials offer numerous advantages for OLEDs including: high glass-transition temperatures (T_g), high solubility, and high-purity via column chromatography. Initial OLED device performance data is presented that shows a 30% improvement over their molecular counterparts. For example, simple undoped Alq3-based devices prepared using the nanocomposite material as a hole transport layer have high brightness ($>35,000\text{cd/m}^2$), and relatively high quantum efficiency (1.25%).

9:30 AM EE14.3

Hybrid Materials for Optical Limiting. Stephane Parola¹, Marcus

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Optical Power Limiting (OPL) materials were developed for the protection of optical sensors against intense laser aggressions. We have investigated thiacalixarenes for optical limiting purposes on the basis that they display delocalised electrons, they can be selectively functionalised either on the upper rims or the lower rims and are interesting species for the formation of metal complexes. Moreover, the presence of electron donating sulphur bridges can play an important role regarding non-linear optical properties. Alkynylthiacalixarene derivatives have shown very good nonlinear absorption, with low clamping values, at visible wavelengths and high linear transmission. Our intention was also to incorporate the molecules into an inorganic matrix and study the behaviour of the molecules in contact with the matrix. It is well known that the sol-gel route allows easy inclusion of organic dyes into an oxide network because of the low temperature of the process. Both dispersed and grafted hybrids were considered. Hybrid materials incorporating Pt acetylde groups and similar thiacalixarenes were elaborated and characterized. Class I materials were found to be inhomogeneous and only low concentrations of dye could be reached in the material. Class II grafted hybrids were thus considered to permit the elaboration of highly concentrated and stable hybrids. A second functionalisation

(lower rims of the thiacalixarenes) with silane groups was therefore investigated in order to prepare class II hybrid materials incorporating the optically active molecule. Both molecular engineering and preparation of solid-state materials will be presented. Interactions between the matrix and the dye will be discussed.

9:45 AM *EE14.4

ORMOCER[®]s (Organic-Inorganic Hybrid Polymers) for Telecom Applications: Structure/Property Correlations. Frank Kahlenberg and Michael Popall; Fraunhofer - ISC, Wuerzburg, Germany.

The development and characterization of fluoroaryl functionalized inorganic-organic hybrid polymers for optical waveguide applications is presented. The materials are prepared from organoalkoxysilanes in a two-step process. The first step is the establishment of the inorganic polysiloxane network by hydrolysis and polycondensation in order to obtain a soluble resin. This can be mixed with a photo initiator and applied onto a substrate as a photo-sensitive film. Micro patterns (waveguides with core and cladding) are then manufactured in a second step by exposure to UV-light through a mask. The polymers are characterized with respect to application in the fabrication of telecom optical waveguide devices. Thus, special attention is turned to optical losses in the telecom wavelengths at 1310 nm and 1550 nm as well as to refractive indices. During all stages of ORMOCER[®] preparation, structure-property relations are deduced from presented characterization data. Various spectroscopic tools give an insight into network structures of polycondensate resins and cured hybrid polymer samples. ²⁹Si NMR in particular is used for the quantitative analysis of siloxane species. With the aid of molecular modeling, structural characteristics of oligomeric intermediates as determined by experiment are visualized. ORMOCER[®] resins with low optical losses of 0.28 dB/cm at 1310 nm and 0.42 dB/cm at 1550 nm, respectively, are prepared. Subsequent micropatterning by means of photolithography results in waveguide and other test patterns. A low optical loss of 0.51 dB/cm at 1550 nm is measured on a waveguide manufactured from a photopatternable fluoroaryl functionalized ORMOCER[®]. The presentation will include an overview on ORMOCER[®] based prototypes and demonstrators for in telecom applications. [®] Registered Trademark of Fraunhofer Gesellschaft zur Foerderung der angewandten Forschung e.V. in German